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Processing Method for Creating Ultra-Thin Lead Zirconate Titanate (PZT) Films Via Chemical Solution Deposition

by Richard Piekarz and Ronald G. Polcawich

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT

This report summarizes the effort to use modifications to a lead zirconate titanate (PZT) chemical solution process to create high performance ferroelectric, dielectric, and piezoelectric thin films with reduced film thicknesses.

15. SUBJECT TERMS

PZT, thin film, chemical solution deposition

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1. Introduction

The increasing demand on performance in everything from computers to sophisticated radar systems has resulted in a wealth of research in alternative materials and device architectures to meet these demands. One example is the investments in electrostatic switches to replace high insertion loss pin diode and field effect transistor (FET) switches that have been in the several tens of millions of dollars just over the past decade. Furthermore, research into piezoelectric actuation as a replacement to high voltage electrostatic designs has become of interest in the past few years. The piezoelectric material of most interest is lead zirconate titanate (PZT) because of its high piezoelectricity, large dielectric constant, and large scale use in mesoscale systems. It should be mentioned that aluminum nitride has also been studied heavily because of its relative use of integration with complementary metal-oxide semiconductor (CMOS) processing. However, its material properties are significantly less than that of PZT thin films.

To create high quality PZT thin films, there exist two primary methods of deposition: sputtering and chemical solution deposition (CSD). In the past few years, CSD (a.k.a., sol-gel) has exhibited significantly higher material properties than other methods with effective transverse piezoelectric coefficients, $e_{31,f}$, values of –15 C/N-m, nearly twice that of sputtering.[1] The common CSD methods for depositing PZT include multiple deposition, spin coating, and crystallization procedures to achieve the desired film thickness. Prior work on CSD films of PZT have been published throughout the past several decades but the focus of this technical note will be on our previous work outlined in ARL Technical Report 02-02.[2] A limitation of this procedure is the minimum achievable thickness was 0.25 microns, assuming a standard four layer spin, pyrolyze, and then crystallize procedure. Thinner films, especially below 0.12 micron, created by reducing the number spins were unable to create high performance capacitors and possessed poor material properties. This technical note addresses these limitations in an attempt to create a more stable, reproducible fabrication process for creating ultra-thin PZT films by modifying a standard CSD solution.

2. Experimental Procedure

The test procedure started with the preparation of the substrates used for the PZT deposition. The wafers used were four single side polished (SSP), (100)-oriented silicon (Si) wafers with a resistivity in the range of 1 to 30 Ohm-cm. Next, the wafers were coated with plasma enhanced

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[1] Calame, F.; Muralt, P. Growth and properties of gradient free sol-gel lead zirconate titanate thin films. *App. Phys. Lett.* **2007**, *90*, 062907-1–062907-3.

[2] Piekarz, R. *Sol-gel PZT Process*; ARL-02-02; U.S. Army Research Laboratory: Adelphi, MD, 2002.

chemical vapor deposition (PECVD) silicon dioxide (SiO_2) thin film (approximately 200 nm) using a Plasma Therm 790 deposition system. Following the deposition, the SiO_2 is annealed in an A.G. Associates rapid thermal anneal (RTA) system at 700 °C for 60 s in flowing nitrogen (N_2). This anneal procedure was used to remove trapped hydrogen from the thin film. Following the anneal, a bi-layer of titanium (Ti) and platinum (Pt) was sputter deposited using a Unaxis Clusterline 200 Sputter System. The Ti/Pt layer was deposited at 500 °C and was comprised of 20 nm of Ti and 85 nm of Pt. Two wafers were cleaved into approximately 1 in. square samples. These test samples were then used to deposit various PZT solutions.

The PZT solution is prepared using a chemical solution deposition method described previously[2]. The key steps of this process and any changes will be described in the following. The process begins by measuring the proper amount of the lead (Pb) precursor, lead acetate tri-hydrate (table 1). The lead precursor was combined with 150 mL of 2-methoxyethanol (2-MOE) in a 1000 mL flask inside a negative pressure humidity controlled glove box with a relative humidity of 0.00214 (dew point of –80 °C). The lead solution mixed in a rotary evaporator (Heidolph Labarota 4000) inside a laminar flow hood for 20 min. The solution rotated at 120 rpm in a silicone oil bath set at 120 °C with N_2 flowing. The Zr/Ti precursors, zirconium n-propoxide and titanium isopropoxide, were measured with a graduated auto pipet and combined with 45 mL of 2-MOE in a 125 mL flask. The solution mixed on a stir plate inside the glove box until needed.

Table 1. PZT solution precursor weights and volumes.

Solution	**Pb Acetate Tri-Hydrate (g)**	**Zr n-Propoxide (mL)**	**Ti Iso-Propoxide (mL)**
45/55 (8%)	36.05	17.75	14.61
52/48 (8%)	36.05	20.5	12.75

After the Pb solution mixed, the N_2 was shut off and the vacuum was turned on to start the vacuum distillation. During the distillation, all of the moisture and a large percentage of 2-MOE were separated from the lead acetate. The endpoint of distillation was the formation of a white paste within the flask at which time the vacuum pressure was increased and the N_2 was reopened. The flask was then removed from the oil bath and the excess oil was allowed to drip from the flask. After a bulk of the excess oil had been removed, the flask was separated from the rotary evaporator and cooled in a tub of water.

Inside the glove box, the Zr/Ti precursor was added to the flask containing the distilled Pb lead solution along with 120 ml of 2-MOE. After placing the Pb/Zr/Ti solution back onto the rotary evaporator, refluxing of the solution began and lasted for 3.5 h. The refluxing was followed by a 5 min (low vacuum) distillation to remove any by-products, including any excess water vapor. After cooling, the PZT solution volume was measured and a 4 volume percent of formamide (a drying control agent) was added to the mixture. The solution was then left on a magnetic stir plate overnight. To assess the ferroelectric quality of the solution, a 0.5 micron layer of PZT was deposited (process described below) on a 1 in. test sample.

The PZT solution deposition and crystallization procedure is schematically described in figure 1. For these tests, approximately 1 in. square samples comprised of Si/SiO_2/Ti/Pt were used for the PZT deposition (figure 2). Multiple spin, pyrolysis, and crystallization steps are used to achieve the desired film thickness of 0.25 or 0.5 µm. An image of a PZT-coated test specimen is illustrated in figure 3. A total of four specimens were tested and included the following:

A. PZT(45/55) – 0.4 M

B. PZT(52/48) – 0.4 M

C. PZT(45/55) – 0.1 M

D. PZT(52/48) – 0.1 M

The reduced molarity solutions were prepared by mixing 20 mL of a 0.4 M solution into a small jar with stir bar. An additional 60 mL of 2-MOE is added to the 20 mL of PZT. The jar was sealed and stirred for 1 h prior to depositing onto the test specimen.

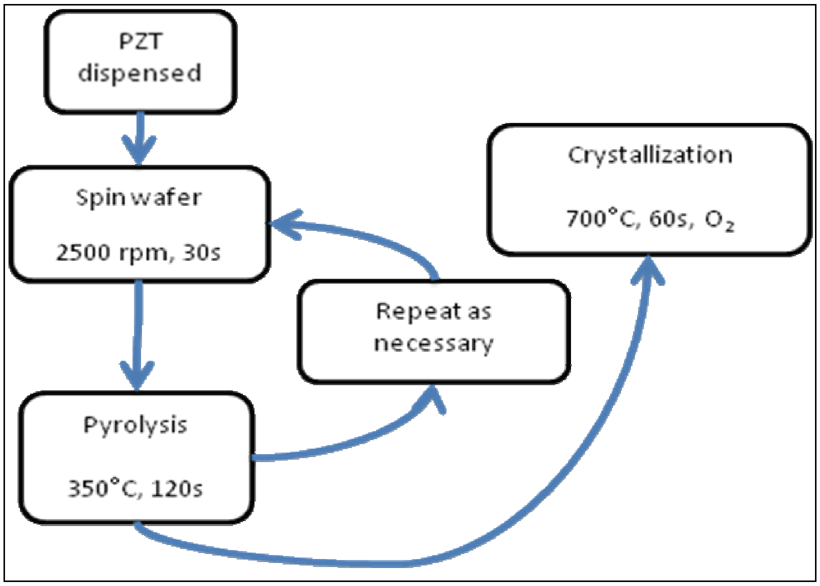

Figure 1. Schematic flow chart describing the deposition and crystallization process for CSD PZT thin films.

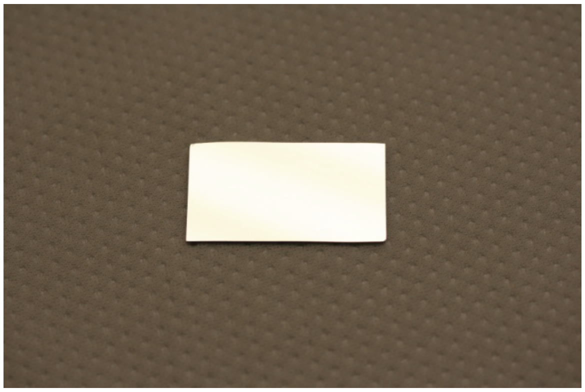

Figure 2. Optical image of a test specimen (~1 in.^{2}) consisting of a (100) Si substrate with the following thin films: SiO_2 (200 nm)/Ti (20 nm)/Pt (82 nm).

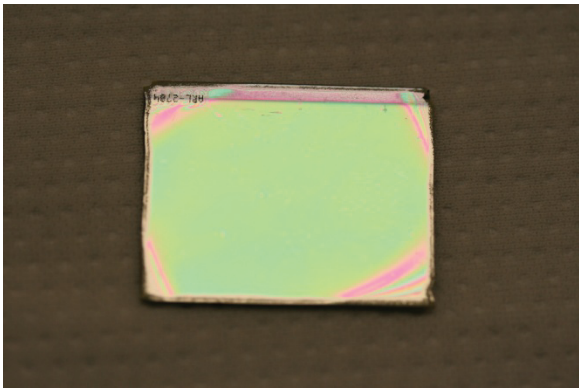

Figure 3. Optical image of the test specimen after CSD of PZT.

After the PZT deposition, the sample was patterned with photoresist. A photomask consisting of 500 µm x 500 µm squares was used to pattern a 2.0 µm layer of Clariant AZ5214-E photoresist. The photoresist was spin deposited at 2000 rpm for 40 s and heat treated on a hotplate at 110 °C for 60 s. Using a Karl-Suss MA/BA-6 photolithography tool, the resist was exposed for 2.1 s at 20 mW/cm^2. A post-exposure hotplate bake at 120 °C for 30 s was performed to convert the resist into a negative resist. Following the bake, the sample was flood exposed for 3.5 s at 20 mW/cm^2. After the flood exposure, the resist was developed in Clariant AZ 300 for 90 s. After resist patterning, the sample was exposed to oxygen plasma to remove any remaining monolayers of resist using a Metroline ML4 ash system. The resist coated sample was then coated with 1050 Å of Pt using the Varian 3190 DC magnetron sputtering system. After deposition, the Pt was patterned using a lift-off technique with acetone to remove the photoresist and any unwanted Pt. To ensure clean edges on the sample, the sample was immersed in de-ionized water (H_2O) and subjected to ultrasonic cleaning for 30 s. The ultrasonic cleaning ensured that any unwanted Pt at the edge of the 500 µm squares was removed (figure 4).

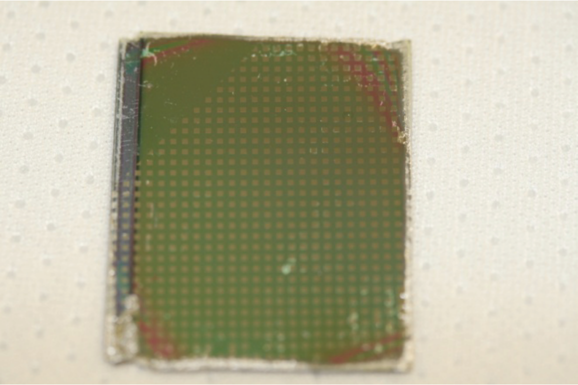

Figure 4. Optical image of the test specimen after deposition and patterning of the Pt top electrodes (500 µm x 500 µm) via sputtering and lift-off.

To open access to the bottom Pt electrode, the sample was manually coated with AZ5214-E resist using a clean room swab. The entire sample except one corner was coated with resist. Then, the sample baked on a hotplate at 110 °C for 60 s. The exposed PZT at the corner of the sample was removed using a wet etch comprised of 120 mL of hydrochloric acid (HCl), 1 mL of hydrogen fluoride acid (HF), and 240 mL of de-ionized H_2O. The etching process was completed in approximately 12 s. After etching, the photoresist was removed using an acetone for 5 min followed by rinsing the sample with liberal amounts of methanol, isopropyl alcohol, and de-ionized H_2O. The final step was to anneal the sample at 350 °C for 120 s to ensure intimate contact between the Pt top electrode and the PZT. An image of the sample in its completed state is illustrated in figure 5.

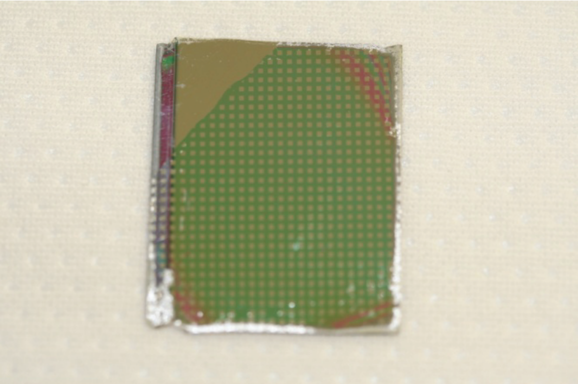

Figure 5. Optical image of the test specimen in its final form after one of the corners has been patterned to remove the PZT and expose the underlying Ti/Pt electrode.

The electrical properties of the PZT thin films were tested using a manual probe station (figure 6), a Radiant Technologies RT-66A Ferroelectric Test System for the ferroelectric properties and a HP 4192A Impedance Analyzer for the dielectric properties. The sample was placed onto the probe station and a pair of probes was used to contact one of the 500 µm squares (top Pt) and the wet etched corner of the test sample (bottom Pt). The ferroelectric measurements were recorded at 19 V with 248 data points while the dielectric measurements were recorded using at 10 kHz with a 100 mV excitation.

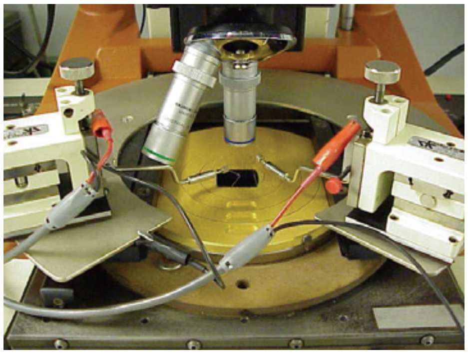

Figure 6. Optical image of the probe station arrangement for measuring the dielectric and ferroelectric properties of the PZT thin films.

3. Results and Discussion

The test results from all four specimens are summarized in tables 2–5. Each table consists of five data points from each specimen and lists the remnant polarization (P_{rem}), dielectric constant, and dielectric loss tangent. A comparison between tables 2 and 3 and between tables 4 and 5 highlights that very little difference is observed between the 0.4 M and 0.1 M solutions for both PZT (45/55) and PZT (52/48). In either case, the dielectric constant and loss tangent remain relatively similar with a slight increase in dielectric constant observed in the 0.1 M PZT (52/48) solution relative to its 0.4 M case. Additionally, a slight increase in the positive P_{rem} was observed in the 0.1 M PZT (45/55). In both these cases, the relative changes are minor and can be attributed normal statistical variations observed, which are similar to those observed with the standard PZT device processing. For completeness, the ferroelectric hysteresis loops for each of the four samples can be seen in figures 7 and 8. Similar to the data listed in the tables, each of the hysteresis loops overlap one another highlighting the consistency between the 0.1 M and 0.4 M solution processing.

Table 2. Dielectric and ferroelectric data for a 0.4 M PZT (45/55) solution measured on a 0.25 μm thin film capacitor.

PZT (45/55) → 0.4 M Solution			
Sample #	**P_{rem} (μC/cm^2)**	**Dielectric Constant**	**tan δ**
01	+10.4/–16.1	947	.0713
02	+10.7/–16.5	885	.0558
03	+10.6/–16.4	881	.0553
04	+10.2/–15.5	881	.0554
05	+10.4/–15.9	798	.0408

Table 3. Dielectric and ferroelectric data for a modified, reduced molarity, 0.1 M, PZT (45/55) solution measured on a 0.25 μm thin film capacitor.

PZT (45/55) → Modified Solution with 60 mL 2-MOE			
Sample #	**P_{rem} (μC/cm^2)**	**Dielectric Constant**	**tan δ**
01	+12.0/–16.9	956	.0765
02	+12.0/–16.8	897	.0772
03	+11.4/–15.8	850	.0686
04	+12.1/–16.8	890	.0700
05	+12.0/–16.8	896	.0712

Table 4. Dielectric and ferroelectric data for a 0.4 M PZT (52/48) solution measured on a 0.25 μm thin film capacitor.

PZT (52/48) → 0.4 M Solution			
Sample #	**P_{rem} (μC/cm^2)**	**Dielectric Constant**	**tan δ**
01	+5.3/–9.4	600	.0312
02	+5.1/–9.4	594	.0478
03	+5.2/–9.6	591	.0483
04	+4.7/–9.4	599	.0468
05	+5.1/–9.3	597	.0474

Table 5. Dielectric and ferroelectric data for a modified, reduced molarity, 0.1 M, PZT (52/48) solution measured on a 0.25 μm thin film capacitor.

PZT (52/48) → Modified Solution with 60 mL 2-MOE			
Sample #	**P_{rem} (μC/cm^2)**	**Dielectric Constant**	**tan δ**
01	+5.5/–9.5	669	.0417
02	+5.6/–9.6	668	.0424
03	+5.7/–9.9	669	.0421
04	+5.8/–9.8	672	.0427
05	+5.8/–9.8	672	.0426

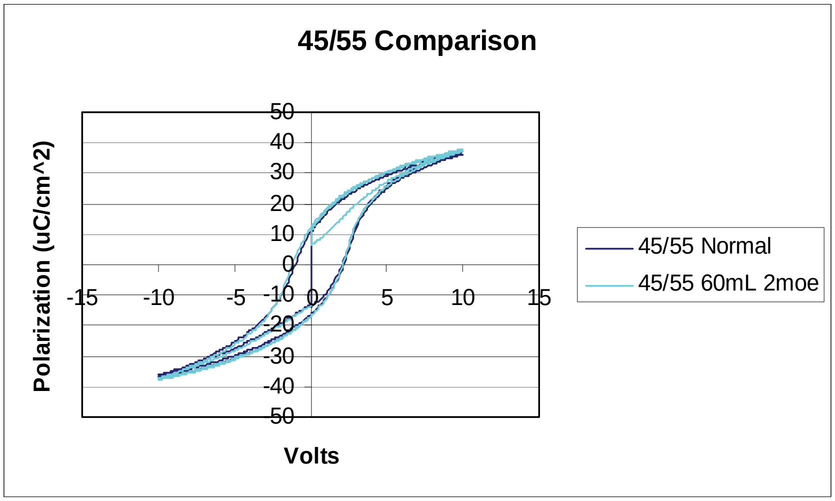

Figure 7. Comparative plots of a 0.4 M and a 0.1 M PZT (45/55) solutions.

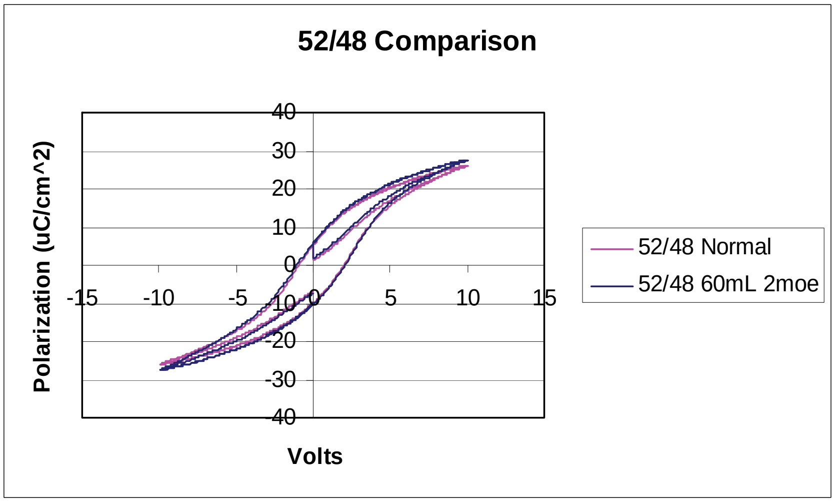

Figure 8. Comparative plots of a 0.4 M and a 0.1 M PZT (52/48) solutions.

4. Conclusion

This research has highlighted the ability of maintaining the material characteristics of a CSD PZT thin film with the reduction in solution molarity after the precursor solution has been prepared. The ability to maintain material properties is critical as this process enables the creation of ultra-thin film PZT layers with large polarization and dielectric constants. These layers are critical as the next generation of microdevices is scaled to smaller dimensions, which has been instrumental in the creation of the first working PZT-based nanoswitch.[3]

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[3] Polcawich, R.; Judy, D.; Pulskamp, J. U.S. Army Research Laboratory, unpublished research.

Acronyms

2-MOE	2-methoxyethanol
CMOS	complementary metal-oxide semiconductor
CSD	chemical solution deposition
FET	field effect transistor
H_2O	water
HCl	hydrochloric acid
HF	hydrogen fluoride acid
N_2	nitrogen
PECVD	plasma enhanced chemical vapor deposition
Pb	lead
P_{rem}	polarization
Pt	platinum
PZT	lead zirconate titanate
RTA	rapid thermal anneal
SSP	single side polished
Si	silicon
SiO_2	silicon dioxide
Ti	titanium

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