Texture Control in Lead Zirconate Titanate Multilayer Thin Films

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Abstract—Multilayer actuators (MLAs) offer an increase of force per unit area, a reduction in power consumption, and a reduction in required driving voltages compared with single-layer actuators. For example, switching from a single 0.5- or 1.0-μm layer of PZT to multiple 250-nm-thick layers would enable a 2.3 to 3/4 reduction in actuation voltage and an increase of 2 to 3 times in actuation force per area for a PZT MEMS switches and robotics. Efforts have been focused on developing actuators using four 250-nm-thick layers of PZT with a 1.5/48% ratio of 52/48 (i.e., the morphotropic phase boundary). The PZT films used a previously established method of achieving greater than 98% (001/100) oriented PZT by chemical solution deposition (CSD). By performing X-ray diffraction measurements between each layer, the texture within the films could be monitored during the growth process. To electrically measure the quality of the PZT multilayer stack, a series of six-sided capacitors were fabricated. The devices were connected in parallel with an average dielectric constant of 1150 for each PZT layer and an average total capacitance of 45 nF. In addition to capacitors, cantilever actuators were fabricated to measure the piezoelectric induced deformation. Comparisons with 100-μm-long cantilever between a single 1-μm-thick PZT and four 250-nm-thick layer PZT stack have shown comparable displacements of 3.7 μm and 4.0 μm, respectively, with an applied electric field of 10 V/μm across the film. These measurements on MLA PZT films demonstrate high piezoelectric coefficients that are suitable for tactile radio and millimeter-scale robotic devices.

I. INTRODUCTION

Piezoelectric ceramics have been studied extensively since the 1880s, when the Curie brothers first proved the existence of the piezoelectric effect. Since then, the properties of crystals exhibiting this effect have been used in a wide range of applications from timekeeping in watches to the first sonar system during World War I [1]. In the last decade, piezoelectric based microelectromechanical systems (MEMS) have been investigated for numerous military applications [2], [3] and are now commercialized in products such as ink jet printers [4] and gyroscopes [5].

Lead-based piezoelectric materials have exhibited the highest piezoelectric constants [6], [7], particularly the well-studied material lead zirconate titanate [Pb(Zr,Ti)O₃, PZT]. For thin films, the piezoelectric properties of PZT reach a maxima in highly (001)-oriented thin films with compositions at the morphotropic phase boundary (MPB), x = 0.52 [8]–[11]. Efforts toward (001)-orientation control through the use of PbTiO₃ (PTO) seed layers, optimization of the platinum bottom electrode, and annealing conditions have been discussed in [12] and [13].

To date, a large amount of research has focused on multilayer capacitors, including studies on different designs, different active materials, and an emphasis on various deposition techniques. Higher capacitance values can be obtained by increasing the active electrode area or by decreasing the film thickness as shown in the equation for the capacitance of a parallel plate capacitor,

\[ C = \frac{k \varepsilon_o A}{t}, \]

where \( C \) = capacitance, \( k \) = permittivity of material, \( \varepsilon_o \) = permittivity of free space, \( A \) = area of parallel plates, and \( t \) = material thickness between plates. Thinner and denser dielectric films for multilayer capacitors have been reported using chemical solution deposition [14]. These films ranged from 50 to 250 nm in thickness. More recently, reported research on multilayer actuators has increased, showing an improvement in capacitor density, smaller packaging, and faster response times with lower power consumption [15]–[17]. A very thorough publication on piezoelectric multilayer capacitors can be found in [18] and [19], and a brief theoretical understanding of multilayer actuators can be found in [20]. However, these previous efforts fail to provide information on the texture of each individual piezoelectric thin film. Because the material properties are highly dependent on the texture of the film, a controlled method of maintaining high (001) texture within each of the piezoelectric thin film layers is desirable.

Incorporating a multilayer configuration in PZT thin-film-based MEMS actuators can overcome one of the principle limitations of traditional MEMS unimorph actuators; namely, the inability to achieve bi-directional displacements at electric fields larger than the coercive field. In contrast, multilayer actuators can independently control PZT layers both above and below the neutral axis, enabling true bi-directional displacements for the same strain state in the piezoelectric. Moreover, multilayer MEMS actuators offer several additional advantages including lower power, lower drive voltages, higher forces,
and increased actuator work per unit areas. As shown in Fig. 1, for a cantilever actuator comprised of a SiO₂ elastic layer and Pt/PZT/Pt actuator layers (with a PZT thickness of 0.25 μm), the predicted blocking force and maximum work per unit area increases for each additional PZT actuator layer added to the overall structure. The blocking force is the force exerted by a piezoelectric actuator while fully mechanically clamped or equivalently the maximum force that can be generated by the actuator. For this model, the piezoelectric coefficient of the actuators is assumed to be the same for each additional actuator layer. To achieve the previously highlighted benefits, maintaining a high degree of (001) texture, and therefore a high piezoelectric coefficient for each actuator layer, is crucial. This article discusses a method of fabricating a highly (001) textured multilayer PZT thin film composite and reports on the experimental results from both multilayer capacitors and actuators.

II. Fabrication

100-mm-diameter (100) silicon wafers were coated with 500 nm of thermally grown silicon dioxide (SiO₂) thin film. Using an Oerlikon Clusterline 200 (CLC; Oerlikon Advanced Technologies AG, Balzers, Liechtenstein) sputtering system, 30 nm of titanium (Ti) was deposited and then annealed in a furnace in oxygen in a Bruce Technologies Inc. (North Billerica, MA) tube furnace at 750°C to convert the Ti to TiO₂. Using the CLC, 100 nm of platinum (Pt) was deposited at 500°C. Additional information on the TiO₂/Pt fabrication process can be found in [13]. Following the Pt deposition, PbTiO₃ (PTO) and/or PZT (52/48) were deposited on the wafers using chemical solution deposition (CSD), sol-gel. The solutions were prepared using a modified process similar to Budd et al. [21] that is described in [12].

The 0.15 molar PTO solution was deposited onto the entire surface of the wafer using a 10-mL syringe with a 0.1-μm PTFE membrane filter. Once the wafer surface was saturated with solution, it was spun using a Bibtec SP100 spin coater at a speed of 4000 rpm for 30 s. A pyrolysis was performed on a Wentworth Laboratories Inc. (Brookfield, CT) vacuum hot plate at 350°C for 2 min to remove some of the organic materials from the solution. The film was crystallized during a rapid thermal anneal (RTA) at 700°C with a temperature ramp of ~199°C/sec using an AG Associates Heatpulse 610 RTA (San Jose, CA). The resulting film thickness was about 17 nm. The 0.4 molar PZT (52/48) solution was deposited with a similar process, except multiple PZT (52/48) depositions were required at a spin coater speed of 2000 rpm to achieve a film thickness of 250 nm. The film thickness was determined using a J. A. Woollam variable angle spectroscopic ellipsometer (J.A. Woollam Co. Inc., Lincoln, NE).

Following the final crystallization anneal, the PZT layer was coated with 500 Å of Pt using the CLC at 500°C. After this coating, X-ray diffraction measurements were performed using a Rigaku Ultima III diffractometer (Rigaku Corp., Tokyo, Japan) with Bragg-Brentano optics. To create the multi-layer coatings, the samples were coated with another 250 nm of PZT with and without a PTO seed layer in subsequent layers as shown in Fig. 2. Again, a 500-Å Pt layer was deposited and X-ray diffraction measurements were performed. This sequence was repeated until a 4-layer Pt/PZT multilayer structure was created (Fig. 2).

To investigate the texture control within the multilayers, two samples were prepared. Sample A used the PbTiO₃ seed layer on only the first Pt interface (i.e., the one closest to the Si substrate). Sample B included a PbTiO₃ on all Pt/PZT interfaces for orientation control. The purpose was to determine if the texture obtained on the initial PZT layer could be maintained throughout the entire multilayer stack. In addition to X-ray diffraction measurements, the ferroelectric, dielectric, and piezoelec-
The capacitors and cantilever arrays were fabricated using a five ion-mill process to pattern the PZT and Pt layers. The wafers were coated with Clariant AZ5214E photoresist (Clariant Corp., Somerville, NJ) using an EVG 120 automated resist processing system (EV Group, St. Florian am Inn, Austria). A Karl Suss MA/BA6 contact aligner (Suss Microtec, Garching, Germany) was used for photolithography. After the exposure, the image was developed in AZ300MIF (AZ Electronic Materials USA Corp., Somerville, NJ). A 5 min descum with an oxygen plasma was performed using the Metroline/IPC plasma photoresist stripper (Metroline, Corona, CA) to remove any unpatterned resist that remained on the surface. In preparation for ion milling, the wafer was then UV cured using an Axcels UV photosensitizer (Axcels Technologies Inc., Beverly, MA), which further hardens the resist. A 4wave Inc. (Sterling, VA) 4W-PSIBE ion beam etch system is used for ion milling. Using a secondary ion-mass spectrometer endpoint detection system during the etch, the ion-milling process was terminated after exposing and removing a Pt layer. Subsequently, the resist was removed and this process was repeated with a different photomask area until all electrodes are exposed (Fig. 3).

### III. Results and Discussion

The samples were analyzed using X-ray diffraction (XRD) after every PZT/Pt layer to determine the effects of each additional layer on film orientation. The XRD data shows a contribution of all deposited layers to the overall film orientation at the time the data was collected. Fig. 4(a) shows the (001) and (100) orientation as a function of deposition layer for sample A. The first layer consisted of the bottom Pt/PTO/PZT stack and showed a strong {100} orientation. Peak broadening is noted in subsequent layers and peak intensity diminishes in the overall stack by the final layer. Using the Lotgering factor to quantify the percentage of orientation in the {100} family, a significant decrease in orientation is observed. The first PZT layer is nearly 100% oriented along the (001) and (100) directions. By the second, third, and fourth layers, the orientation across the deposited film has dropped by 7%, 17%, and 44%, respectively [insert in Fig. 4(a)]. By the top-most PZT layer deposition, orientation across the entire stack resembles a randomly oriented PZT without any film optimization on Ti/Pt electrodes instead of highly (111)-optimized TiO₂/Pt electrodes [22]. Sample B [Fig. 2(b)] using the PTO seed layer in between every Pt and PZT layer exhibited a significantly improved orientation compared with Sample A. High degrees of {001} orientations with {100} Lotgering factors values of 90% and greater were maintained in all four layers of the multilayer stack, as shown in the insert in Fig. 4(b), leading to a high degree of orientation across the entire stack.

Parallel plate capacitors were fabricated as described in Fig. 3(b), with all 5 platinum electrodes exposed to allow access for electrical contact [insert in Fig. 5(a)]. After the device was fabricated, a series of electrical measurements were performed. There is a small variation in the capacitor electrode area [see Fig. 5(b) table insert] to prevent shorting between layers with the top most electrode, PZT layer 4, consisting of the smallest area and the bottom-
most, PZT layer 1, with the largest area. As shown in Fig. 5(a), individual capacitors within the multilayer stack were electrically active. It should be noted that overall yield for these capacitors was limited to 20% to 25% of the devices because of fabrication related defects, electrical shorting between electrode layers, and inadvertent high electric field application during initial testing. These issues will be addressed in future research. It has been reported that during the fabrication of multilayer capacitors, pinhole defects in the PZT and small electrode areas lead to electrical shorts in between the different electrode layers [14]. Individual layer capacitance values at 0 V varied between 6 and 14 nF, with the corresponding relative dielectric constants varying between 822 and 1423; see Fig. 6. The variability in relative dielectric constant observed in the individual layers can possibly be attributed to the changes in texture between the layers, and will also be investigated in future work.

In addition to testing individual PZT layers, alternating electrodes were connected to create a parallel connection with the capacitors. In this configuration, Pt layers 2 and 4 and Pt layers 1, 3, and 5 were electrically coupled, respectively. Using the HP 4192A LCR impedance analyzer, a capacitance versus voltage sweep was performed twice, the first measurement looked at electrically grounded Pt layers 2 and 4; the second measurement electrically grounded Pt layers 1, 3, and 5. At 0 V, the device capacitance areal density was 3.77 × 10^3 nF/cm^2. This corresponds to the summation of the individual capacitance, 44.1 nF, of each of the 4 layers summarized in the insert of Fig. 5(b) at 0 V. In the parallel configuration, the capacitor exhibited a tuning ratio of 3.4 from 0 V to 8 V as compared with a tuning ratio of 2.1 for a single-layer
A second set of samples was prepared to evaluate the piezoelectric induced deformation in cantilevers. For this set of experiments, three wafers were fabricated with a total PZT thickness target of 1 μm with either a single layer, two 500-nm layers, or four 250-nm layers of PZT, as depicted in Fig. 7(a)–7(c). Similar to the earlier samples, XRD measurements were performed after each Pt deposition. Unfortunately, technical problems with RTA temperature ramp rate limited this new set of wafers to a ramp rate of ~40°C/sec instead of the optimized ~199°C/sec. The issues with the RTA led to reduced [001] orientations in the films, particularly noticeable in layer 2 of the 2-layer stack and layers 3 and 4 in the 4-layer stack, as observed in the {100} Lotgering factors [Fig. 7(d)].

The cantilever devices followed the same fabrication procedure outlined in Fig. 3 with the addition of a reactive ion etch of the 500-nm SiO2 elastic layer to expose the Si substrate to a XeF2 release etch at the end of processing to release the cantilevers (Fig. 8). A Polytec MSV laser Doppler vibrometer (LDV) system was used for noncontact displacement measurements using a frequency of 1 Hz and a poling voltage of 10 V. Displacement data presented in Fig. 8(b) shows piezoelectric induced displacement using both positive and negative unipolar drive pulses for the 1-layer stack, the 2-layer stack, and PZT layers 1 and 2 in the 4-layer stack of a cantilever with a length of 180 μm. LDV data was limited to the smaller length cantilevers as a result of the large positive residual stress-induced curvature in the cantilevers which steers the reflected laser signal away from the optics.

Upon initial examination of the displacement, the choice of the elastic layer thickness and the location of the neutral axis of the cantilevers determine the displacement direction and amplitude for the different multilayer configurations [Fig. 8(b)]. For the single-layer case, the neutral axis resides roughly in the bottom third of the PZT layer [Fig. 9(a)]. As a result, the PZT section above and below the neutral axis effectively work against one another, limiting the amplitude of the bending deflection. For the 2-layer case, the neutral axis resides just below the middle Pt electrode [Fig. 9(b)]. As a result, the cantilevers deform in the negative z-direction (into the wafer) when PZT layer 1 is actuated and deform in the positive z-direction (out of the wafer) when PZT layer 2 is actuated. Similarly for the 4-layer case, the neutral axis resides close to the Pt layer between PZT layer 1 and 2 [Fig. 9(c)]. As a result, the cantilevers deform in the negative direction when PZT layer 1 is actuated and positive direction when actuated with PZT layer 2, 3, or 4. Note, data for layers 3 and 4 of the 4-layer stack was unavailable because of both device yield and aforementioned inadvertent overdriving of these layers during testing.

Cantilevers that can actuate at large electric fields with either positive or negative vertical displacements will allow for the creation of large bi-directional actuation in multi-layer actuators compared with vertical-direction unimorph actuators. Additionally, Fig. 8(b) compares the displacement of the different multilayer configurations as
a function of the electric field experienced by the different layer thicknesses. The results in Fig. 8(b) illustrate how the multilayer actuators leverage higher electric field actuation using significantly lower voltages than a single layer of the same total thickness.

IV. Conclusion

Several multilayer PZT stacks were fabricated using sol-gel PZT deposition techniques. It was shown that more than 90% (001) and (100) orientations was maintained both 2-layer and 4-layer composites when a 17-nm PbTiO3 seed layer was used between every Pt/PZT interface. Simple capacitors and cantilever actuators were processed using a 5-step ion-mill procedure, which allowed access to all 5 Pt electrodes for electrical testing. Testing of the individual PZT layers in a 4-layer stack at 0 V showed capacitance values between 6 and 14 nF with relative dielectric constants between 822 and 1423. Additionally, this research has demonstrated that proper choice of the elastic layer combined with a multilayer PZT actuator enables large, displacement bi-directional control of the actuation.

Future work involves optimizing a unique fabrication process to minimize the number of ion mills required for device fabrication. This will significantly reduce the time, masks, and fabrication steps required to process devices as well as lessen the damage to the PZT films. Additional electrical testing is required in all 4 layers of the 4-layer PZT stack to gain further insight on control of cantilever deflection in these devices.

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