The Pennsylvania State University

The Graduate School

# PIEZOELECTRIC MICROMACHINED ULTRASOUND TRANSDUCERS USING LEAD ZIRCONATE TITANATE FILMS

A Dissertation in

Materials Science and Engineering

by

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Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

December 2021

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#### Abstract

The goal of this research was to fabricate Piezoelectric Micromachined Ultrasound Transducers (PMUTs) and a) evaluate their suitability for 1D deterministic particle manipulation, b) establish their potential for ultrasound and photoacoustic imaging, and c) develop ways to improve their acoustic properties. In addition, the crack propagation was evaluated as a function of the Zr/Ti ratio in the lead zirconate titanate (PZT) films, as well as the failure behavior of clamped versus released multilayer-actuator devices.

PMUT arrays were fabricated with high quality {001} oriented PZT that produced 9.5 kPa at 7.5 mm distance in water and 40 nm/V deflection in air at 6-8 MHz resonant frequency with a bandwidth of 62.5%. SiO<sub>2</sub> beads 4  $\mu$ m in diameter were successfully manipulated in 1D without the need of microfluidic control. In addition, multiple levitation planes were observed for driving frequencies greater than 30 MHz, well outside the operational bandwidth of 62.5%. The homogeneity between elements was high, with the permittivity variation between elements < 2%.

The PMUT arrays were also used for ultrasound and photoacoustic imaging. For ultrasound imaging, an 18 mm by 18 mm clay target was imaged. A compact handheld photoacoustic imaging device was fabricated by wirebonding the array to a printed circuit board integrated with a fiber optic light guide. Targets such as pencil leads, a single follicle of hair, and tubes filled with indocyanine green (ICG) or blood were successfully imaged with photoacoustics. Pencil lead targets and the tube filled with ICG tubes were imaged even under 5 mm thick chicken tissue. However, the tubes filled with blood under chicken tissue could not be imaged well. In addition, for ultrasound imaging, scanning metal needle targets of 0.5 mm – 0.7 mm in diameter was difficult,

even though 120  $\mu$ m resolution was expected. This may have been due to scattering from a cylindrical target using a single element for transmit and receive.

Three methods were investigated to increase the transmit and receive sensitivities of PZT based PMUTs. For transmit sensitivity, by increasing the effective area by 1.4 times and changing to a single rectangular diaphragm as opposed to a series of circular diaphragms, the pressure output increased by ~ 2 times. For receive sensitivity, two methods were investigated. Firstly, a DC bias was used to increase the receive sensitivity (or voltage coefficient) by approximately two times when 15 V (75 kV/cm) was applied to the PMUT with a PZT composition of 52/48. This increased the piezoelectric coefficient  $e_{31,f}$  and decreased the relative permittivity. 15 V DC bias applied to the 52/48 PMUT generated stronger photoacoustic signals and enabled images of targets at greater depths. Secondly, PZT films of different compositions (with Zr/Ti ratios of 52/48, 40/60, 30/70, and 20/80) were tested for suitability in receive. When 0 DC bias was applied, PZT 20/80 had the highest voltage coefficient compared to PZT 52/48, 40/60, and 30/70. When 15 V (75 kV/cm) DC bias was applied, PZT 52/48 matched the receive sensitivity of PZT 20/80.

The crack initiation stress and strength of the entire stack of 2  $\mu$ m-thick PZT 52/48, 40/60, and 30/70 on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates were tested. For PZT 52/48 films, it was found that the PZT films cracked prior to failure of the stack. As a result, the PZT film thickness served as the critical flaw size that drove failure. This produced a Weibull modulus of 17 (11 – 24 at 95% confidence interval) and a stack strength of 1137 MPa (1091 – 1183 at 95% confidence interval). As the PZT compositions moved towards PbTiO<sub>3</sub>, the characteristic strength increased while the Weibull modulus decreased to ~ 1580 MPa (1355 – 1807 MPa at 95% confidence interval) and 3.0 (2.5 – 3.6 at 95% confidence interval) respectively; these values are comparable to those of the substrate itself, suggesting a much broader distribution of critical flaw sizes. Two potential

contributions to the change in cracking behavior were investigated: ferroelastic toughening and residual thermal stresses associated with the thermal expansion coefficient between the film and substrate upon cooling from the crystallization temperature to the Curie Temperature. The residual thermal stresses did not vary significantly with Zr/Ti ratio. It was found, however, that the volume fraction of c-domains increased as compositions became more Ti-rich. This could increase ferroelastic toughening, as more c-domains can switch to a-domains when the sample is subjected to biaxial tensile stress. It was found that the PZT films had a mixture of a-domains, c-domains, and rhombohedral phases for all average compositions. A line scan via TEM indicated that Zr/Ti concentration gradients were present for all compositions, which may account for the observation of a rhombohedral phase for average compositions in the tetragonal phase field.

Finally, the breakdown behavior of multilayer actuator PZT based devices was investigated. Four main observations were made. First, released films showed two families of behaviors in the current versus time graphs: one in which the current exceeded two orders of magnitude higher than the base current along with various current spikes, and the other in which the diaphragm breaks before the current increases two orders of magnitude. Secondly, the lateral size of the thermal breakdown events for released films were much smaller (typically less than 5  $\mu$ m) compared to clamped films. Thirdly, breakdown events were not connected via cracks in released films, in contrast to observations on clamped films. Fourthly, the released films were more likely to experience immediate membrane breakage upon voltage application. Fifthly, the activation energy for failure was found to be  $1.02 \pm 0.17$  eV and  $0.46 \pm 0.20$  eV for clamped and released films, respectively. The t<sub>50</sub> lifetime between released and clamped devices were similar at temperatures  $\sim 150 \text{ °C} - 170 \text{ °C}$  but diverged at  $\sim 200 \text{ °C}$ , where the released films exhibited higher lifetimes. Thermal imaging of the electrode indicated no significant changes in the temperature profile over time under voltage, so the difference in apparent activation energy is not thermal in origin.

The thermal breakdown behavior for clamped films was also examined. It was found that these breakdown events were not randomly distributed in space, but were often within 50  $\mu$ m from each other. The characteristic time to reach 50% of the cumulative number of breakdown events decreased with increasing applied electric field. Moreover, at lower fields, breakdown events were spaced out over a longer period of time.

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#### Acknowledgements

Firstly, I would like to thank my advisor, Dr. Susan Trolier-McKinstry. I remember during my interview at the Penn State open house, I asked her that if I joined her lab, since she would be paying me for results, what would the yearly expectations be. She immediately said, "No, no. I am not paying you for results. I am paying you to become a good researcher." That was the line that brought me to Penn State. She is one of the best advisors, mentors, and scientists to ever exist, hands down. She believed in me when I did not believe in myself, and has provided invaluable guidance and advice during my Ph.D. If I can just be 1% of what Dr. McKinstry is, I would be set as a scientist for life. It was an honor and privilege to work for her.

Secondly, I would like to thank my committee members. Dr. Jackson's weekly advice on fabrication always gave me direction. I would go into our meetings thinking there was only one or two solutions to a processing challenge and come out with ten ways. Dr. Randall's class on the fundamentals of ferroelectrics strengthened my materials science foundation. Dr. Kothapalli laid the foundation for my ultrasound testing fundamentals.

I would also like to thank several collaborators on this work. In particular, Dr. Ajay Dangi was instrumental in helping me understand the practicalities as well as the fundamentals of ultrasound testing and integration. Without him, this thesis would not be possible. He is truly the king of all trades in his lab. I was also very fortunate to go work as a summer research fellow under Dr. Ronald Polcawich in the U.S. Army Research Lab in Adelphi, Maryland. As a then-first year graduate student, it helped me grow confidence in my processing skills and I will always be grateful for the patience and care he and his team were able to impart on me. I am also grateful for my time spent in Dr. Sandy Cochran's lab at the University of Glasgow, as his post-docs (particularly Dr. Holly Lay and Dr. Yongqiang Qiu) and graduate students were so welcoming and

patient when teaching me acoustic measurements. I am also grateful for Kilian Shambaugh and Mario Pineda of Polytec for teaching me the laser doppler vibrometry and their hospitality while I was at Irvine.

I am forever indebted to the Materials Research Institute (MRI) and Materials Characterization Lab community, particularly the MRI nanofabrication staff. They were instrumental in providing me cleanroom guidance as well as tips and tricks that otherwise would have cost me thousands of hours in the cleanroom reinventing the wheel. Thank you all for dealing with my constant barrage of questions during my first two years of graduate school, when I was still trying to figure things out. I would like to thank Shane Miller for teaching me the fundamentals of heating during an etch process. I would like to thank Mike Labella and Kathy Gehoski for teaching me all that lithography, cleaning processes, and all those photolithography masks at lightning speed. I would like to thank Bill Drawl for teaching me the sputter tools, Chad Eichfeld for teaching me the photolithography spray coater, Andy Fitzgerald for teaching me the wet bench processes, and Bangzhi for teaching me the FESEM, ALD, and parylene coater – I remember it took me an hour to try and focus on my sample on the FESEM, and with a flick of the wrist Bangzhi gave me a crisp image. I would also like to thank Bill Mahoney for teaching me the BCB, PDMS, and wirebonding processes, Guy Lavallee for teaching me so much about the wet and dry etches, Maria DiCola for teaching me the dicing saw, Gino and Nichole for teaching me the XRD, and Sarah Eichfeld, Jeff Long, and her team for taking such a proactive stance in keeping the MRI building safe. I also must thank Joanne Aller and Sandie Elder, whose organization skills and email response rate are absolutely unparalleled.

I am forever grateful to have been with the current and previous group members of Dr. McKinstry's lab. When I came into graduate school, I was the type of person who, when the exam

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has an intermediate step of 2+2, I would type 2+2 in my calculator just to be safe. I was able to find confidence in myself while in the group, but all were also invaluable in discussing research, fundamentals, quick sanity-checks, and just hanging out and having fun. I would like to give special thanks to Wanlin Zhu and Betul Akgun-Akkropu for helping me with processing and electrical measurements. I would like to thank Carl Morandi for teaching me processing techniques and putting up with my constant questions of fundamentals and sanity-checks, as well as Tianning Liu for teaching me processing techniques. I would also like to thank Kathleen Coleman for being a fantastic cubemate and friend. Apart from being a fantastic scientist and researcher, she is one of the most empathetic people I've ever met, organizing events for the McKinstry group and keeping the atmosphere fun and light. I would also like to thank Dixiong Wang, Julian Walker, Veronika Kovacova, Runar Dahl-Hansen, Juliette Cardoletti, Nicole Hall, Nathan Bishop, Shruti Gupta, Michael Hahn, Sanshiro Aman, Leonard Jacques, Song Won Ko, Smitha Shetty, Jung In Yang, Travis Peters, Daisuke Hama, Gavin Hennessey, Quyen Tran, and Pannawit Tipsawat.

There are also those who were not directly involved in my current research but were instrumental in my growth as a material scientist, researcher, and person. I would like to thank my undergraduate research professors (Dr. Bharat Jalan, Dr. Eray Aydil, and Dr. Robert Tranquillo) for trusting an undergrad with equipment that costs hundreds of thousands of dollars and giving me the foundation of how to work in a lab setting. I also would like to thank 3M; I worked under three different managers in three different divisions there and they broadened my horizons and gave me experience before I even had experience: thank you to Dr. Myles Brostrom, Dr. Marian Appelt, and Dr. Jessica Voss-Kehl. I must also thank the teachers even further back. In particular, thank you to Ms. Foley from Eden Prairie High School. I remember I had to work very hard for her 10<sup>th</sup> grade enriched biology class just to survive, as that was the first class in which I shockingly

learned that homework isn't graded on completion. Thank you to Ms. Foley and Ms. Gabel for sparking my interest in biology. Thank you to Ms. Snyder for sparking my interest in chemistry. Thank you to Mr. Maas for sparking my interest in physics. Thank you to Mr. Thomas for teaching me not be afraid of calculus. I must also thank Ms. Erin Webster from Central Middle School and the Eden Prairie High School Speech Team. Without them, I would have never found my voice or built up my confidence in public speaking.

Finally, I would like to thank my parents, Chi-June Ko and Thim Cheng. I was not always the best son, but you were and are always the best parents I could ever ask for. Looking back, I can see why you said, "one Chris is enough." I promise not to move back into your house upon finishing this Ph.D. program.

Thank you all: all the good that people see in me has come from all of you.

This manuscript is based on work supported by three funding sources: the National Science Foundation Material Research Science and Engineering Center (MRSEC) supported by the National Science Foundation under grant DMR-1420620, the MTEC Global Co., Ltd., and the National Defense Science and Engineering Graduate Fellowship.

Note: The findings and conclusions in this thesis do not necessarily reflect the view of the funding agency.

#### **Chapter I: General Background and Thesis Organization**

*Portions of this chapter have been reproduced from:* **C. Cheng**, A. Dangi, L. Ren, S. Tiwari, R. R. Benoit, Y. Qiu, H. S. Lay, S. Agrawal, R. Pratap, S. Kothapalli, T. Mallouk, S. Cochran, and S. Trolier-McKinstry, "Thin Film PZT-Based PMUT Arrays for Deterministic Particle Manipulation," *IEEE TUFFC*, vol. 66, no. 10, pp. 1605-1615, July 2019.

#### 1.1 Background in ferroelectrics and piezoelectrics

Ferroelectrics are a class of materials that possess a spontaneous polarization that can be reoriented between crystallographically-defined directions by applying an electric field. Ferroelectrics are a subset of piezoelectrics. Piezoelectrics are materials in which polarization can be induced via an applied stress, or a strain can be induced via an applied electric field. These are known as the direct and converse piezoelectric effects, respectively, and can be expressed as

$$D_i = d_{ijk}\sigma_{jk} \tag{1-1}$$

$$x_{ij} = d_{kij} E_k \tag{1-2}$$

where *i*, *j*, and k = 1, 2 and 3, *D* is the charge per unit area (dielectric displacement),  $\sigma$  is the stress, *x* is the strain, *E* is the electric field, and *d* is the piezoelectric charge coefficient [1-3]. To exhibit piezoelectricity, a material must be non-centrosymmetric. Of the 32 crystallographic point groups, 20-point groups are potentially piezoelectric [4, 5].

Piezoelectric materials are utilized in various devices, such as sensors, actuators, transducers, energy harvesters, and memory devices [3, 6 - 13]. Lead zirconate titanate (PZT), Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PMN-PT), zinc oxide (ZnO), aluminum nitride (AlN), scandium-doped aluminum nitride (Sc<sub>x</sub>Al<sub>1-x</sub>N), sodium potassium niobate (KNN), and bismuth ferrite (BFO) have been researched for use in such applications. Their material properties of relative permittivity ( $\varepsilon_r$ ), piezoelectric coefficient ( $e_{31,f}$ ), voltage coefficient ( $h_{31,f}$ ), and loss tangent (tan $\delta$ ) are given in Table 1.1.

Property	PZT	ZnO	PMN-PT	Sc <sub>x</sub> Al <sub>1-x</sub> N	AlN	KNN	BFO
	[14-16]	[15-18]	[19, 20]	[21, 22]	[15, 23-25]	[26-30]	[31-34]
- $e_{3l,f}$ (C/m <sup>2</sup> )	12 – 16	1	27	3	1	2-5.6	3.5
Relative	1200	10	1500	14	10	500 -	~100
permittivity						1000	
$-h_{3l,f}(C/m^2)$	0.01	0.1	0.018	0.21	0.1	0.01	0.035
tanδ	< 0.05	0.01 - 0.1	0.07	< 0.1	0.003	< 0.07	< 0.1

Table 1.1. Properties of Select Thin Film Piezoelectric Materials

In recent years, interest in lead-free piezoceramics has grown considerably as concerns about lead toxicity led the European Union to institute the Restriction of Hazardous Substances Directive, limiting lead containing components. While lead was granted an exemption for piezoelectric ceramic devices, this exemption is time limited and must be reviewed periodically for continued exemption [35]. Great progress has been made on lead-free materials, with some lead-free piezoceramics being introduced into commercial products [36-39]. However, these materials present challenges. For example, it is relatively difficult to control the stoichiometry in KNN-based films due to the volatilization of two alkaline elements (sodium and potassium); these films are susceptible to moisture and often show high leakage current density [40-42]. BiFeO<sub>3</sub> based films also often demonstrate high leakage currents, presumably due to the presence of Fe<sup>2+</sup> ions, oxygen vacancies, and sometimes second phases [43, 44]. ZnO is challenging to grow as a highly resistive film, and is not as compatible with silicon semiconductor technological processes (as Zn is a fast-diffusing ion) [15]. Both ZnO and AlN have low piezoelectric coefficients that necessitate higher voltages to achieve large displacements in actuators [15]. Processing optimization is still needed for  $Sc_xAl_{1-x}N_x$  as abnormally oriented grains can occur with increasing Sc-doping concentrations and increasing thicknesses [46]. Even with significant progress in the

development of these materials, lead-free piezoceramics have not reached the overall performance of lead-based piezoceramics.

In the family of lead-based piezoelectric ceramics, PZT and PMN-PT are of particular interest due to their high piezoelectric coefficients and permittivity. PMN-PT has higher piezoelectric coefficients and shows high deflections in cantilevers; however, it is difficult to process to large thicknesses on Si substrates [47-49]. PMN-PT is susceptible to property degradation from secondary phases such as pyrochlore and is more susceptible to stresses and cracking at larger thin film thicknesses. Furthermore, its low coercive voltage can interfere with poling stability [47-49]. Thus, lead zirconate titanate is more commonly used due to its processability and its high piezoelectric coefficients at the morphotropic phase boundary of Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub>. PZT will be the material of choice in this dissertation.

PZT has a perovskite crystal structure with ABO<sub>3</sub> stoichiometry, where the  $Zr^{4+}$  and  $Ti^{4+}$  are located at the center of the unit cell, the oxygens are located near the face centers, and the Pb<sup>2+</sup> ions are in the corners, as shown in Fig. 1.1.



Fig 1.1. (a) The cubic prototype phase of PZT (perovskite structure ABO<sub>3</sub>). (b) shows the center atom (Ti) moving towards an oxygen site, causing the unit to cell to elongate parallel to the displacement direction.

When the material is cooled through the Curie Temperature ( $T_c$ ), the cubic structure elongates along the axis parallel to the Ti displacement, as the Ti ion moves closer to one of the oxygens in the tetragonal distortion; it should be noted there are also lead displacements [50-52]. These displacements cause spontaneous polarization. The morphotropic phase boundary of PZT allows the following possible polarization directions: 8 polarization directions via the rhombohedral phase, 6 along the tetragonal phase, and possibly more with the monoclinic phase [53-55]. In addition, studies have shown that the morphotropic phase boundary composition allows for domains to align with the electric field readily during poling, as the relative energy barriers separating polarization states are lowered. Likewise, the polarizability at smaller field is also high. Thus, polarizability and piezoelectric properties peak at the MPB, as it is on the brink of structural instability between the rhombohedral, tetragonal, and monoclinic phases [4, 53-55]. Additionally, the Pb<sup>2+</sup> ion has a lone pair electron configuration and large polarizabilities [4], resulting in asymmetric coordination geometries. Fig 1.2. shows the phase diagram.



A key characteristic of ferroelectric materials like PZT is the polarization vs. electric field hysteresis loop, as shown in Fig 1.3. When a ferroelectric is cooled below  $T_c$ , domains form so as to minimize the electrostatic and ferroelastic energy. Since there are multiple possibilities for the spontaneous polarization directions, different regions of the ferroelectric material can have different orientations. Each region with the same spontaneous polarization direction is called a domain. Separating different domains are the domain walls, often described by the angle between the polar axis of the different domains. They are typically categorized as 180° and non-180° domain walls. The former can only be activated with an electric field, while the latter can be activated via an electric field as well as a mechanical force [58-61].



Fig. 1.3. Typical polarization-electric field hysteresis loop for ferroelectrics [62]. Schematic domain structures are shown for different positions on the hysteresis loop for a uniaxial ferroelectric.

The directions of the domains are often random immediately following processing of a polycrystalline film and thus the sample has a net polarization of zero (point 1). When an electric field is applied, the domains can be reoriented to align more nearly with the applied electric field.

At small electric fields (well below that of the coercive field  $E_c$ ), the polarization increases linearly. At higher fields, the polarization increases non-linearly as new domains nucleate and expand in the direction of the applied electric field. Once the spontaneous polarization is aligned as well as possible at high electric fields, the polarization starts to saturate ( $P_{max}$ ) at point (2). When the electric field is removed, local strains and electric fields cause back switching, which reduces the remanent polarization at point (3). As an electric field is applied with the opposite polarity and increasing magnitude, domains in the direction of this opposite polarity will nucleate and grow. As the domains change sign and reorient, the net polarization becomes zero at the coercive field at point (4). Eventually, the domains saturate at  $-P_{max}$  at point (5).

The piezoelectric properties of ferroelectrics and piezoelectrics can be enhanced in several ways; to understand how these properties can be improved, it is important to understand the contributions to the dielectric and piezoelectric properties, which can be split into two categories: intrinsic and extrinsic. Intrinsic contributions arise from changes of a single domain lattice response. Extrinsic contributions are mainly due to motion of boundaries in the materials, such as domain walls and phase boundaries [63].

To achieve a net piezoelectric coefficient, the domains must be oriented by creating a net polarization. To this end, the domain can be oriented by poling at high DC fields, often at least 3 times the coercive field for extended periods of time (i.e., 15 minutes). Poling at high temperatures (i.e., 100 - 150 °C) has also been shown to enhance the piezoelectric properties, increasing the  $e_{31,f}$  by 20 - 60% and resulting in improved stability of the net polarization compared to room temperature poling [64, 65].

Another way to enhance the piezoelectric properties is by doping. It is known that donor dopants such as niobium can create lead vacancies that correlate with improved domain wall motion, while acceptor dopants can lower the dielectric constant and loss via an internal bias field [66-69]. The films studied in this dissertation are niobium doped PZT.

## 1.2 Background in Micromachined Ultrasound Transducers (MUTs)

There is an on-going need to improve medical imaging technology, especially for non-ideal patients. For example, obesity rates have risen significantly in the past decade; as of 2020, the U.S. adult obesity rate is ~ 40% [70]. According to the World Health Organization, ~40% of adults greater than 18 years of age are overweight [71]. Consequently, conventional medical imaging technology can no longer be used to generate acceptable quality images for accurate medical diagnostics. For example, a study found that in obese patients, 94% of the ultrasound waves are attenuated before they even reach the target organs [72]. Consequently, many methods have been used to improve imaging technology, including different modes of imaging (such as photoacoustics and ultrasound) and introducing atypical architecture to increase the device bandwidth and vibration amplitude. Ultrasound waves can be used for imaging and for the manipulation of micro and nano-scale particles. For instance, Huang et al. showed that using acoustic-based microfluidic devices can separate circulating tumor cells from regular red blood cells with high efficacy [73].

Many ultrasonic transducer designs have been explored for these two applications, as shown in Fig. 1.2.1. Conventional transducers are based on electroded bulk piezoelectric materials or piezocomposites, often with a matching layer to enhance energy transfer between the high acoustic impedance of the device and the low acoustic impedance of the medium. A backing layer may be used to dampen ringing [74]. Bulk piezoelectric transducers also exhibit much larger pressure outputs (and larger piezoelectric coefficients) than their thin film counterparts. This is due to two

factors: (1) substrate clamping effects, which inhibit the film from expanding/contracting in-plane and thus reduce the mechanical strain, and (2) the limited mobility of non-180° domain wall pinning in thin films [75-82]. However, conventional bulk transducer structures are constrained in the geometry due to dicing blade limits and difficulties inherent in electrical impedance matching of the small elements in two- dimensional arrays for particle manipulation applications [83]. Hence, some particle manipulation applications utilize micromachined ultrasound transducers, allowing for ultrasonic arrays to be configured flexibly, with high spatial resolution, from many small diaphragms. In addition, by using Microelectromechanical Systems (MEMS), transducers can be aggressively miniaturized. In this way, it is possible to introduce many elements per device unit area, and as the number of elements per device increases, more agile beam steering and acoustic tweezing via time delays can be achieved. Such minimization can lead to placing the device directly on the tips of surgical needles or catheters, or even the manufacturing of a "Sonopill" in which the entire transducer device can be swallowed, and ultrahigh resolution images can be taken within the body for more accurate medical diagnoses and imaging of areas previously inaccessible via ultrasound in vitro [84-86]. Furthermore, unlike in bulk piezoelectric transducers, the resonant frequency of MUTs is not dependent solely on the thickness of the piezoelectric layer but is defined by a range of parameters including density, flexural rigidity, diaphragm radius and shape of the membrane [74, 87-89]. Thus, MUTs will be the focus of this dissertation.

MUTs offer intrinsically good acoustic matching and operating bandwidth and the potential for excellent electrical impedance matching. In the realm of micromachined ultrasound transducers, two distinct platform technologies have emerged: capacitive micromachined ultrasonic transducers (CMUTs) and piezoelectric micromachined ultrasonic transducers (PMUTs). Both types of transducers have been used for ultrasound imaging. Micromachined transducers have been commercialized by companies such as Qualcomm, TDK Chirp, EXO Imaging, and Butterfly Network, Inc.



Fig. 1.4. Typical architectures of (a) a bulk piezoelectric transducer, (b) a capacitive micromachined ultrasonic transducer and (c) a piezoelectric micromachined ultrasonic transducer (adapted from [71]).

CMUTs are based on flexural vibrations of a membrane caused by varying electrostatic attraction to a substrate. In the transmit mode, both a direct current (DC) and an alternating current (AC) is applied; the DC brings the two electrodes in close proximity to each other, while the AC causes the membrane to vibrate. In the receive mode, the DC brings the two electrodes close together, and the gap indicated in Fig. 1.4 can change (and thus the capacitance can also change) based on the incoming pressure waves. CMUTs can generate ample acoustic pressures for medical imaging and particle trapping [90, 91]. They also integrate well with silicon electronics for voltage amplification and detection. However, they typically need high DC bias voltages (30 - 100 V) to operate, often near the collapse voltage [92, 93]. This has led to interest in devices that do not require biasing. PMUTs, which accomplish membrane deflection through lateral strain induced by the piezoelectric effect, meet this need. Generally, they have higher capacitances than CMUTs and thus lower electrical impedance, facilitating impedance matching to electrical circuitry. Therefore,

PMUTs offer significant freedom in their design, and will be the device architecture of focus in this dissertation.

## 1.3. Fundamental equations and relations for transducer properties

The equation for the resonant frequency  $f_r$  of a circular thin plate diaphragm in MUTs is given as [87-94]

$$f_r = \alpha^2 / \frac{D_e}{\sum_k \rho_k t_k}$$
(1-3)

where *E*, *t*,  $\rho$ , *R*,  $\alpha$ , *a*, *D<sub>e</sub>*, are Young's modulus, thickness, density, radius of diaphragm, the frequency parameter constant (equal to ~ 3.196 for a clamped circular diaphragm), and the flexural rigidity of the diaphragm, respectively. The subscripts *total*, *avg*, and *k* denote the properties of the total stack, average value, and material *k*, respectively. It should be noted that this equation holds true only for circular-shaped diaphragms and the thin plate approximation, where the ratio  $t_{total}/(2R)$  is less than 0.1 [95]. It should also be noted that during fabrication, intrinsic stresses develop. If the intrinsic stress is large, it can dominate over the flexural rigidity and lead to deviations from the targeted resonant frequency.

For the applications of particle manipulation and imaging, one of the key parameters of assessment is the pressure output generated by the MUT diaphragm. The general pressure output P for an oscillating harmonic w can be expressed via

$$P_w(x, y, z) = j \cdot k \cdot \rho_m \cdot c_m \iint u_w(x_o \cdot y_o) G_w(x, y, z | x_o \cdot y_o \cdot 0) dx_o dy_o$$
(1-4)

where k,  $\rho_m$ ,  $c_m$ ,  $u_w$ , and  $G_w$ , are the wave number, density of medium, speed of sound in the medium, displacement velocity of the diaphragm, and Green's function of the three-dimensional wave equation, which varies for different thin plate boundary conditions and shapes [96, 97].

The pressure output of an MUT can be simplified to relate with the acoustic impedance  $Z_a$ , the velocity at the center of the vibrating membrane v, and the effective surface area  $A_{effective}$  of vibration via [10]

$$P = Z_a \cdot v \cdot A_{effective} \tag{1-5}$$

Equation (1-5) can be further expanded to include the fundamental frequency  $f_r$  and the oscillating displacement d via

$$P = (2 \cdot \pi \cdot f_o \cdot d) \cdot Z_a \cdot A_{effective}$$
(1-6)

Jiang et al. and Lu et al. derived the relations between  $v_p$ , d, and bandwidth *BW* with the physical properties of the MUT, such as the radius and thickness of the diaphragm stack. The relations are given as [10, 21]

$$v_p = 2 \cdot \pi \cdot f_r \cdot d \propto \frac{1}{t^3} \tag{1-7}$$

$$d = Q \cdot d_s \propto \frac{e_{31,f} \cdot n \cdot BW}{D \cdot f_r} \propto \frac{R^2}{t^4}$$
(1-8)

$$BW \propto A_{eff} \tag{1-9}$$

$$BW \propto \frac{1}{(A_{eff} \cdot t)} \propto \frac{1}{M}$$
(1-10)

where  $d_s$  is the static displacement of the membrane, Q is the quality factor, n is the distance between the middle of the material plane to the bottom laminate, and M is the mass of the membrane [10]. Based on equation (1-6) through (1-8), a thinner diaphragm thickness is desired to increase pressure output and widen bandwidth. However, based on equation (1-3), a thicker or smaller diaphragm is needed for higher frequencies. Thus, finite-element modeling is needed to ascertain the balance in achieving high frequencies via thicker and laterally smaller membranes but also maintaining high velocities and deflections.

Another variable to be considered is that of the impedance mismatch between the actuating device and the fluid media. In many ways, acoustic impedance mismatching is the acoustic analog to refractive index mismatches; if there is too great of a value difference between one object (the device) to the other (the fluid medium), the sound pressure would not be transferred efficiently from one medium to the next. Bulk transducers typically utilize one or more matching layers to increase the energy transmission efficiency, as there is a large acoustic impedance mismatch (i.e. PZT has an acoustic impedance ~ 35 MRayl, while the acoustic impedance of water, tissue, and air are ~1.5 MRayl, 1.6 MRayl, and ~400 Rayl, respectively) [74, 98]. With MUTs, the diaphragm has a mass that is significantly lower compared to the loaded mass of the fluid, as well as having a tunable stiffness. This theoretically would allow MEMS-based diaphragms to have much better coupling with the fluid media [99].

The general equation for the acoustic impedance can be given as

$$Z_a = \frac{F_a}{v} \tag{1-11}$$

where  $F_a$  is the acoustic force generated in the medium and *v* is the average velocity [100, 101]. For a clamped radiator (which is often the case for PMUT and CMUT diaphragms), the electrical equivalent circuit model introduced by Mason et al. describes the acoustic impedance in more detail via

$$Z_{a} = \frac{j \cdot \omega \cdot \rho \cdot d_{m} \cdot a \cdot k_{1} \cdot k_{2} \cdot [k_{2} \cdot J_{0} \cdot (k_{1} \cdot a) \cdot I_{1} \cdot (k_{2} \cdot a) + k_{1} \cdot J_{1}(k_{1} \cdot a) \cdot I_{0} \cdot (k_{2} \cdot a)]}{a \cdot k_{1} \cdot k_{2} \cdot [k_{2} \cdot J_{0} \cdot (k_{1} \cdot a) \cdot I_{1} \cdot (k_{2} \cdot a) + k_{1} \cdot J_{1}(k_{1} \cdot a) \cdot I_{0} \cdot (k_{2} \cdot a)] - 2 \cdot (k_{1}^{2} + k_{2}^{2}) \cdot J_{1} \cdot (k_{1} \cdot a) \cdot I_{1} \cdot (k_{2} \cdot a)}$$
(1-12)

$$k_{1} = \sqrt{\frac{\sqrt{d^{2} + 4 \cdot c \cdot \omega^{2} - d}}{2 \cdot c}}$$
(1-13)

$$k_2 = \sqrt{\frac{\sqrt{d^2 + 4 \cdot c \cdot \omega^2} + d}{2 \cdot c}} \tag{1-14}$$

$$c = \frac{(E+T) \cdot d_m^2}{12 \cdot \rho \cdot (1-\nu^2)}$$
(1-15)

$$d = \frac{T}{\rho} \tag{1-16}$$

where  $J_0$  and  $J_1$  are Bessel Functions,  $I_0$  and  $I_1$  are modified Bessel functions,  $\omega$  is the radial frequency,  $\rho$  is the density of the membrane material, *E* is the Young's Modulus, *T* is the residual stress,  $d_m$  is the membrane thickness, , and *v* is the Poisson's ratio [103, 104].

Dangi et al. simplified the acoustic impedance term in Equation (1-5) and (1-6) to be

$$Z_a = \frac{\rho_m * \omega^2}{\pi \cdot v_s} \tag{1-17}$$

where  $\omega$  is the angular frequency [88, 102]. This holds true if the product of the wave number of the acoustic signal and the radius of the membrane is less than 1.

Thus, the acoustic impedance is governed by a variety of factors, such as the characteristics of the medium, the dimensions of the diaphragm, and the frequency of operation.

#### 1.4. Thesis organization

This dissertation discusses the fabrication and processing of PMUTs, their use in two applications (particle manipulation and imaging), as well as routes to improve their properties. Chapter II discusses the suitability of the fabricated PMUTs in particle manipulation applications. Chapter III discusses the suitability of the fabricated PMUTs in photoacoustic applications. Chapter IV discusses two different ways to improve the receive sensitivity of the PMUTs, using DC bias as well as different PZT compositions. Chapter V discusses the crack propagation characteristics versus composition of the PZT films. Chapter VI compares the DC lifetime of released and non-released states of multilayer thin film actuators. Chapter VII discusses future experiments to be

done, such as novel device architectures to potentially improve PMUT properties in imaging and particle manipulation applications.

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#### **Chapter II: Piezoelectric Micromachined Ultrasound Transducers for Particle**

#### **Manipulation Applications**

*Portions of this chapter have been reproduced from:* C. Cheng, A. Dangi, L. Ren, S. Tiwari, R. R. Benoit, Y. Qiu, H. S. Lay, S. Agrawal, R. Pratap, S. Kothapalli, T. Mallouk, S. Cochran, and S. Trolier-McKinstry, "Thin Film PZT-Based PMUT Arrays for Deterministic Particle Manipulation," IEEE TUFFC, vol. 66, no. 10, pp. 1605-1615, July 2019.

## 2.1 Introduction

There is a growing interest in devices that are able to manipulate microscale objects independently and deterministically; this is of particular interest in the biological sciences in applications such as drug delivery, bioanalysis, and self-cleaning surfaces [1-3]. Microfluidic Lab-On-Chip based devices, in which fluids are manipulated via microchannels, have been explored throughout the past two decades. Their reduced reagent consumption (thus less waste and cost), precise handling and control of small volumes of fragile samples (such as DNA or proteins), and increased efficiency in separation methods compare favorably to their bulk counterparts [1-3]. Thus, a myriad of particle manipulation technologies has been developed for lab-on-chip based devices including contact and non-contact methods. Non-contact methods are strongly preferred in biological applications as they maintain the integrity of cells and minimize interference with intercellular and intracellular processes [4, 5]. Such methods include hydrodynamic methods, electrophoresis, dielectrophoresis, thermophoresis, optical tweezing, magnetic methods, and acoustophoresis [6-16]. In this chapter, the focus will be on acoustophoresis.

Acoustophoresis is particularly attractive for biological applications as it does not require labelling, has no known toxic effects, manipulates objects from the millimeter to the nanometer scale successfully, and maintains cell integrity during operation [17-21]. Acoustophoresis-based devices have also been shown to effectively trap cells, pattern, levitate, and sort particles/cells [22-

31]. In acoustophoresis, the differences in acoustic impedance between the particle and the fluid media and the variations in the generated pressure field are exploited to maneuver particles. Different types of devices can be used to generate these acoustic forces, such as bulk transducers, interdigitated transducers, and micromachined ultrasound transducers. The generated waves can also vary, i.e., standing waves, surface acoustic waves, and traveling waves. Thus, acoustophoresis-based devices can be used for a variety of functions and applications.

To describe how particles should move in a pressure field, the acoustic potential is related to the acoustic radiation force,  $F_{rad}$ . The acoustic radiation force is caused by the scattering of the acoustic wave by the particle, and can be expressed via Gor'kov's model,

$$F_{rad} = -V^* \left[\frac{f_1}{2}\beta_m \nabla < p_s^2 > -\frac{3f_2}{4}\rho_m \nabla < v_s^2 > \right],$$
(2-1)

where *V* is the volume of the particle and the terms in the brackets relate to the acoustic potential,  $\beta_m$  is the compressibility of the medium in which the particle is suspended,  $\rho_m$  is the density of the medium,  $v_s$  is the acoustic velocity, and  $p_s$  is the pressure on the particle [32-39]. The terms  $f_1$  and  $f_2$  are coefficients given by

$$f_I = 1 - \frac{\beta_s}{\beta_m},\tag{2-2}$$

$$f_2 = \frac{2(\rho_s - \rho_m)}{2\rho_s + \rho_m},$$
(2-3)

where  $\beta_s$  and  $\rho_s$  are the compressibility and density of the particle, respectively [32-39]. Most commonly, the particles move towards the pressure nodes or antinodes. This depends on the acoustic contrast factor  $\phi$ , where if  $\phi > 0$ , the particles will be trapped in the nodes, while if  $\phi < 0$ , the particles will be trapped in the antinode. The acoustic contrast factor is expressed as:

$$\phi = \frac{5\rho_s - 2\rho_m}{2\rho_s + \rho_m} - \frac{\beta_s}{\beta_m},\tag{2-4}$$

It should also be noted that in fluids, in addition to acoustic radiation forces, there is also a contribution from acoustic streaming. The acoustic streaming velocity field manipulates the particles through the Stokes Drag Force,  $F_D$ . This streaming-induced drag force can be expressed as [40-42]

$$F_D = 6 \cdot \pi \cdot \eta \cdot r \cdot (v - u) \tag{2-5}$$

where  $\eta$ , *r*, *v*, and *u* are the dynamic viscosity, radius of the particle, the flow velocity, and the particle velocity, respectively. The force direction is in the same direction as the local flow around the particle. Based on equations (2-1) and (2-5), the acoustic radiation force is proportional to the cube of the particle radius. Thus, this force tends to dominate the manipulation of large particles, while smaller particles are dominated by acoustic streaming. It is also noteworthy that at higher operating frequencies, the acoustic streaming increases [40-45].

Particle manipulation and trapping via acoustophoresis has been achieved in a variety of platforms, including transducers with interdigitated electrodes that use surface acoustic waves (SAW) to trap particles in the pressure wave antinodes [32, 46, 47], transducers that use standing bulk acoustic waves in a channel for droplet sorting [48], and single beam acoustic transducers (SBAT) for particle and cell manipulation [49, 50]. These techniques have demonstrated high efficiency in particle sorting and trapping. SAW-based devices and SBAT often require higher voltage input or a power amplifier during operation (> 10  $V_{pp}$  operation) [50, 51], and the manipulation is generally confined to a few wavelengths away from the substrate. While particle trapping has been shown to be possible with CMUTs [32, 33], to date it has not been extensively demonstrated with PMUTs. In addition, manipulation of particles from element to element in an array has been reported using microfluidic flow with either bulk or thick film transducers [35, 52-55]. Further, particles have been reported to agglomerate towards the center of MUT diaphragms

when the MUT is excited at the fundamental resonant frequency [32-33]. While this fundamental mode thus enables particle trapping, use of higher frequencies has not been extensively explored. If adequate pressures can be generated at higher modes, particles may be systematically manipulated in correspondence with the vibration mode of the diaphragm, allowing dynamic patterning with a single element.

In this chapter, 1D and 2D PMUT arrays of multiple elements, each comprising many diaphragms connected electrically in parallel, are demonstrated through their manipulation of 4  $\mu$ m SiO<sub>2</sub> particles via acoustophoresis without the assistance of microfluidic flow. It is shown that bead patterns can form outside of the device operating bandwidths and can take place over a wide frequency range.

## 2.2 Design

The design of the PMUT was based on equation (1-3) in Chapter 1 and the material stack described in Section 2.3. A diaphragm diameter of 60  $\mu$ m was chosen to achieve a fundamental resonant frequency,  $f_{fr} = 10$  MHz. At 10 MHz, the half wavelength in water,  $f_{fr}/2 \approx 75 \mu$ m, is at least on the order of or larger than the dimensions of most cells, bacteria, and enzymes [56-58]. This increases the possibility of successful acoustophoretic manipulation. The diaphragms were separated by a 15  $\mu$ m gap with a pitch of 75  $\mu$ m, corresponding to  $f_{fr}/2$ . The top electrode diameter was set to 65% of the diaphragm diameter to increase deflection [59-61].

#### 2.3 Fabrication

The full fabrication process for a PMUT is shown in Fig. 2.1. The base substrate was a silicon on insulator (SOI) wafer with a 2  $\mu$ m Si thickness and a 2  $\mu$ m buried thermal oxide layer

(Ultrasil Corporation, Hayward, California, USA). An SiO<sub>2</sub> passive elastic layer ~0.16  $\mu$ m thick was grown on both sides of the wafer by wet oxidation. Then, 30 nm of Ti was sputtered on the device side, followed by rapid thermal annealing with 10 sccm of oxygen flow for 15 minutes at 700 °C to form TiO<sub>2</sub>. This generates a well oriented 100 nm bottom electrode layer when Pt is sputtered at > 500 °C [11].

To achieve the highly oriented (001) PZT films needed for optimal functional performance in applications, a thin Pb( $Zr_{0.52}Ti_{0.48}$ )O<sub>3</sub> sol-gel solution with 2% Nb and 20 mol% excess Pb (Mitsubishi Materials Corporation, Hyogo, Japan) was first spun on the wafer at 6000 rpm for 30 s as the seed layer [62, 63]. The seed layer was then pyrolyzed at 200°C for 150 s before crystallization via rapid thermal annealing in a Pb-rich environment at 700°C for 1 min. For the functional thin film PZT layer, 14 mol% lead excess Pb( $Zr_{0.52}Ti_{0.48}$ )O<sub>3</sub> solution doped with 2% Nb (Mitsubishi Materials Corporation, Hyogo, Japan) was spun on at 2750 rpm for 45 sec. The film was then pyrolyzed at 100°C for 1 min and 300°C for 4 min, followed by crystallization in a leadrich rapid thermal annealer for 1 min at 700°C. This process was repeated until a total thickness of 1.9 µm was achieved. Typically, 20 repeats were needed. Afterwards, a thin PbO capping layer was deposited at 6000 rpm for 45 s, with the same pyrolysis and crystallization steps as the PZT layers, to remove pyrochlore from the surface of the film.

The top electrode was formed by sputtering 2 nm Ti as an adhesion layer followed by 50 nm of Pt without breaking vacuum. The top electrode was annealed at 600 °C for 1 min before an additional 500 nm of Au was deposited and patterned to complete the top electrode. Access to the bottom electrode in areas not covered by the top electrode was gained by ion milling. An insulation layer was created by spinning and curing 0.9  $\mu$ m thick bis(benzocyclobutene) to reduce parasitic capacitance over the areas defining the fan out and bonding pads. These were subsequently

patterned via liftoff and ~30 nm Ti and 500 nm Au was sputtered without breaking vacuum. The devices were then released via silicon deep reactive ion etching (DRIE). Details of many of the processing steps are provided in the Appendix.

The wafer was diced into individual PMUT dies. These were mounted in the cavity of a pin grid array (PGA) (Spectrum Semiconductor Materials, San Jose, California, USA) with silver paste to prevent water leakage from the backside. Electrical connections were made with wire bonding and the whole package was coated conformally with  $\sim$ 4 µm of parylene for waterproofing. An equipotential plane was formed to eliminate dielectrophoresis in the particle manipulation experiments by depositing a 100 nm thin film of Au with e-beam evaporation. A second protective layer of parylene ( $\sim$  2 µm) was then coated onto the device. Prior to characterization of the PMUT and the particle manipulation experiments, the array elements were poled at twice the coercive field of the PZT films for 15 min at room temperature.



Fig. 2.1. PMUT fabrication process, with cross-sectional and top view of the fabricated PMUT

## 2.4 Experimental Setup

For particle manipulation experiments, two linear types of PMUT arrays were tested: a 1D array in which each element comprised one single diaphragm (referred to here as E1) and a 1D array in which each element consisted of twenty diaphragms (referred to here as E20). In each case, the PGA cavity was filled with distilled water with varying concentrations of 4  $\mu$ m SiO<sub>2</sub> beads (Sigma Aldrich, St. Louis, Missouri, USA). The water/air interface at the top of the cavity served as an acoustic reflector to generate standing waves. The PMUT elements were driven with continuous sinusoidal waves of amplitude 5 V<sub>pp</sub> and a 2.5 V DC offset unless otherwise stated. A unipolar excitation was used to maintain the poling state of the PZT.

## 2.5 Simulations

It has been reported that acoustic tweezing with a single beam CMUT source is based on gradient forces arising from the fluctuation of the generated pressure field when the source is activated. The gradient forces move particles to local/global acoustic pressure maxima or minima, depending on the properties of the particle [32, 33]. When a PMUT diaphragm is excited at resonance, the first mode results in the highest diaphragm deflection and highest pressure in the acoustic medium at the center and the least deflection and pressure at the periphery of the diaphragm. Therefore, it is expected that the maximum acoustic potential gradient arises between the center and edge of the diaphragm. Equations (2-1) – (2-3) were defined in COMSOL Multiphysics (COMSOL Inc., Burlington, MA, USA) for a single PMUT diaphragm, with 4  $\mu$ m SiO<sub>2</sub> beads as the particles to be manipulated.

The results in Fig. 2.2 show that when a diaphragm is excited, particles agglomerate at the center and close to the surface of the diaphragm, in areas of high acoustic pressure. Similar

behavior is reported in the literature but with CMUTs as the ultrasound source [32, 33]. Fig. 2.3 shows the pressure fields generated by a pair of diaphragms, simulated with COMSOL.



Fig. 2.2. Pressure fields generated by a single 60  $\mu$ m diaphragm and particle movement for (b, c) fundamental mode and (d) second harmonic (0,2) mode. The arrows indicate the direction of SiO<sub>2</sub> beads particle movement. The colored arrows in (c, d) indicate the acoustophoretic force exerted on the particle. The length of the arrows corresponds to the relative force. The simulations were done for an axisymmetric model; only 1/2 of the diaphragm is shown, with the center at the origin as indicated by the black arrows. A point of reference is shown in (a). Note the model used was a planar simulation with mirror symmetry along the Z axis. This X-Z view is also used for Fig. 2.3. A physicallymatched layer was used at 200  $\mu$ m distance from the membrane surface to prevent excitation of standing waves.

The pressure fields generated by individual diaphragms overlap with adjacent diaphragms. Also, the particle movement caused by one diaphragm in Fig. 2.2 draws particles as far as 200  $\mu$ m from a diaphragm center. It was calculated from COMSOL that close to the PMUT surface, the acoustic force was approximately ~10 pN and the effect of gravity force is two orders of magnitude lower (~ 0.4 pN). At approximately 50  $\mu$ m away from the PMUT surface, the acoustic force is on the same order of magnitude as the gravity force. Thus, the particles were expected to move very close to the PMUT surface. In addition, if the pressure field is sufficiently large in extent and the

distance between elements is sufficiently close, beads can potentially move from one element to another without assistance from microfluidic flow. This possibility was deliberately increased by designing the PMUT elements with a pitch of 75  $\mu$ m, corresponding to  $f_{fr}/2$  at 10 MHz in water.



Fig. 2.3. (a) Individual pressure fields generated by two 60  $\mu$ m diaphragms with 75  $\mu$ m pitch, with each diaphragm excited individually and their individual pressure fields overlaid, (b) pressure field generated by two diaphragms excited in unison at resonance, (c) pressure field generated by two diaphragms excited in unison at 40% above the resonant frequency, and (d) pressure field generated by a single diaphragm excited at the second harmonic mode. The black arrows indicate the center of the diaphragms. The pressure fields overlapping in (a) and (b) indicate the potential for particles to move from one diaphragm to another. A physically-matched layer was used at 200  $\mu$ m distance from the membrane surface to prevent excitation of standing waves

In addition to those generated by the fundamental mode, patterns generated by different modes could potentially be useful. From the results shown in Fig. 2.3 and 2.4, different vibrational modes

should generate different bead patterns based on the resultant pressure field. For example, the (0, 2) mode would occur at a frequency approximately 3.89 times the fundamental (0, 1) mode frequency of a clamped circular plate [64]. For the (0, 2) mode, the pressure field is shown in Fig. 3(d) and 4(d). This suggests there would be two areas where the beads could agglomerate: at the center of the diaphragm and in a circular node around the center of the diaphragm.

Figs. 2.2 and 2.3 were produced with a physically matched layer to water positioned at 200  $\mu$ m vertically from the membrane surface to prevent excitation of standing waves. If this condition is removed, allowing reflection, and the distance between the PMUT and the reflecting surface is multiple half-wavelengths, large pressure fields can be generated and correspondingly higher acoustic field amplitudes that can cause particles to move to levitation planes at the acoustical nodes [65]. The positions of the levitation planes (LPs) normal to the acoustic source direction can be expressed as

$$LP = n \cdot \lambda/4,\tag{5}$$

where *n*, and  $\lambda$  are a whole integer and the acoustic wavelength, respectively. The depth of the water in the PGA cavity was not controlled systematically in this study; however, levitation planes can be more readily formed if the cavity height is a multiple of the driving wavelength. Such planes increase in number if the driving frequency is high, as the number of nodal planes in a fixed distance increases with driving frequency.

## 2.6 PMUT Characterization

For a high quality PMUT, the PZT quality needs to be high. X-ray diffraction (XRD) and field-

emission scanning electron microscopy (FESEM) were used to confirm that the PZT films were phase-pure perovskites and highly (001) oriented, as shown in Fig. 2.4. The relative permittivity,  $\varepsilon_r$ , and loss tangent, tan  $\delta$ , were measured for twenty different elements in an array to test for uniformity after the entire process was completed. Hysteresis loops were also measured to confirm the quality of the PZT. The electrical measurements are presented in Fig. 2.4. For a 95% confidence interval at 1 kHz,  $\varepsilon_r = 1487 \pm 8$  and tan  $\delta = 1.40 \pm 0.06$  %, respectively, indicates high uniformity between elements. The remanent polarization,  $P_r$  was  $\approx 24 \,\mu\text{C/cm}^2$ , and the coercive field,  $E_C$  was  $\approx 50 \,\text{kV/cm}$ .



Fig. 2.4. Results of structural analysis of PZT via (a) X-Ray Diffraction and (b) Field Emission Scanning Electron Microscopy. Phase-pure perovskite was achieved with chemical solution deposition. No visible pyrochlore or secondary phases were found. The asterisks (\*) denote substrate peaks. (c) shows the hysteresis loops of a single element with a remanent polarization of  $\approx 24 \ \mu\text{C/cm}^2$ . (d) and (e) show the permittivity and loss tangent of twenty diaphragms, respectively.

Laser doppler vibrometry (LDV) was used to evaluate  $f_{fr}$  and the field-induced deflection of the

fabricated device. The results are shown in Fig. 2.5. It was found that, for PMUTs on the same wafer,  $6 < f_{fr} < 8$  MHz, due primarily to the footing effect in the DRIE process which increases the diaphragm diameter. This was verified with a cross sectional image as shown in Fig. 2.6.



Fig. 2.5. LDV measurements in air showing center deflection spectra (a) over a wide frequency range at  $0.5 - 3.0 V_{pp}$  driving voltage via laser chirp measurement and (b) close to resonance via peak hold measurement. Higher frequency modes are seen in (a) at 13 MHz and 19.5 MHz. The measurements here were from the same batch of devices used in later experiments.



Fig. 2.6. Cross section of a diaphragm. The arrow indicates the etch direction. Footing, or lateral etching, is present, increasing the diaphragm width and thus decreasing the operating resonant frequency.

Within a given die, the values of  $f_{fr}$  were well-matched, with larger variations observed across the 4" wafer. Higher modes can also be seen at 13.0 MHz and 19.8 MHz, which correspond to the (1, 1) and (0, 2) modes, respectively [53]. The LDV instrument (Polytec GmbH, Walbronn, Germany) could record a maximum deflection signal of only 79 nm, hence, for higher driving voltages, the center deflections seen in Fig. 6(b) were extrapolated from the deflections near the diaphragm periphery, where motion is more strongly clamped. Using this technique, the deflection profiles indicate that in air, high deflections (~ 40 nm/V) can be achieved for low driving voltages for both the E1 and E20 array.

The pressure output, P, and bandwidth, BW, were evaluated for the E20 array. The array was placed in an acrylic water-tank and operated in transmit mode while a hydrophone (HGL-0085, Onda Inc., Sunnyvale, California, USA) acted as a receiver at 7.5 mm distance from the surface of

the transducer. One element was excited with a 5 V<sub>pp</sub> unipolar sinusoidal burst of 5 cycles to measure *P*. For *BW*, the same unipolar voltage excitation was used but with a single cycle sinusoid at the resonant frequency, and a total of 59 dB gain was used to amplify the signal. A Fourier transform was then used to calculate BW at -6 dB. The results are shown in Fig. 2.7. An element of 20 diaphragms (E20) yielded an output pressure of ~ 9.5 kPa at 7.5 mm and the bandwidth at -6 dB was approximately 62.5%. The underwater resonance frequency was found to be ~ 8 MHz.



Fig. 2.7. Acoustic characterization of E20 array. (a) Time and frequency characteristics with single cycle sinusoidal excitation (with 59 dB total gain), and (b) hydrophone output at  $f_{fr}$  with 5 cycle sinusoidal excitation. The response was ~0.46  $\mu$ V which corresponds to ~9.5 kPa at 5 V<sub>pp</sub> unipolar excitation at 7.5 mm distance from the PMUT. The bandwidth at -6dB was ~ 62.5% from the Fourier transformation of the signal response, with a center frequency of 8 MHz.

# 2.7 Particle Manipulation Experimental Results

The PMUT elements were excited below  $f_{fr}$  with a unipolar signal at 5 V<sub>pp</sub> with a function generator, with a low concentration of 4  $\mu$ m SiO<sub>2</sub> beads in the water medium. The setup for the particle manipulation experiments is shown in Fig. 2.8.



Fig. 2.8. (a) Sideview and (b) top view of experimental setup.

Particle manipulation experiments results are shown in Fig. 2.9. The lower frequency was used because, when an element is excited very close to the resonant frequency, as presented in Fig. 2.9 (a) and (b), cross-coupling excited neighboring elements. At driving frequencies ~ 18% below  $f_{fr}$ , the cross-coupling was much less severe.



Fig. 2.9. SiO<sub>2</sub> bead patterns generated when the E20 array was excited at (a) ~6 MHz, (b) ~ 4.9 MHz. Cross-coupling is less severe below resonance, indicated by the much heavier clustering of particles at the excited element. Generally, the beads agglomerated most effectively with *f* in the range 5 - 6 MHz. Higher density particle clustering was observed for (c) 5 V<sub>pp</sub> excitation than for (d) 1 V<sub>pp</sub> excitation.

It was observed that the bead clusters became more tightly packed, as seen in Fig. 2.9 (c) and (d), as the applied unipolar voltage increased from 1 V<sub>pp</sub> to 5 V<sub>pp</sub> with  $f \approx f_{fr}$ . Furthermore, the velocity of the beads towards the axis of the diaphragm increased as the excitation voltage increased and when  $f_{fr}$  was approached. This is reasonable [32, 33] as higher deflections result in larger pressure outputs, generating larger pressure gradients and thus larger acoustic forces. The phenomenon of bead agglomeration towards the center of the diaphragm as the driving frequency approaches the resonant frequency corresponds with what has been reported for CMUTs [32, 33]. PMUTs which were not released by back side etching yielded no movement of the particles,

showing that the particle manipulation arises from acoustophoresis.

To test control of particle motion in 1D, individual and adjacent elements of the E1 PMUT array were excited or turned off to facilitate particles moving to the generated local acoustic potential minimum. A similar excitation pattern was used on the E20 PMUT array to investigate whether particle trapping is possible over multiple diaphragms simultaneously when one array element was excited. The results are presented in Fig. 2.10.



Fig. 2.10. Manipulation of 4  $\mu$ m silica beads using two elements from the E1 (a) – (d) and E20 (e) – (h) PMUT designs. The images show the SiO<sub>2</sub> beads when (a) elements are off, (b) both elements are turned on, (c) when the left element is switched off and the right element remains on, and (d) when the right element is switched off and the left element is switched on. This technique was used when manipulating the beads with the E20 design, where beads were trapped and moved from element 1 to element 4. The white arrows indicate the direction of particle movement. Note the scalebars are consistent between (a) – (d) and (e) – (h).

When an element is turned on, nearby beads cluster over the center of the diaphragm and, when the element is turned off, the bead cluster disperses and moves toward neighboring elements that remain activated, due to the gradient in acoustic pressure, in agreement with the simulations presented in Figs. 2.2 and 2.3. This behavior was observed for both the E1 and E20 arrays. Because the pressure gradient increases between the center of a diaphragm and its periphery as *f* approaches  $f_{fr}$  [9, 10], the beads can be moved from one element to another by tuning the driving frequency.

The effects of different excitation frequencies on bead patterns and behavior over diaphragms in the E1 and E20 arrays are illustrated in Figs. 2.10 and 2.11, respectively. For the E1 array, again the beads agglomerate at the center of the diaphragm at  $f_{fr}$ . The beads remain at the center of the diaphragm until  $f \approx 17$  MHz, where they begin to form an annulus. As *f* approaches 23 MHz, two beads move towards the center of the diaphragm, while most stay in the nodal torus formed previously. The pattern in which the torus appears matches the simulated pressure field generated by the (0,2) mode shown in Fig. 4 (d). If the resonant frequency is taken to be ~ 6 MHz (at which frequency the beads tended to agglomerate most effectively), 23 MHz is approximately 3.9 times  $f_{fr}$ , again matching theory [38]. The (1,1) mode was not seen via bead excitation. The inplane stress in the piezoelectric layer induced by the electric field produces a uniform bending moment along the periphery of the top electrode. This favors radial modes instead of non-radial modes; hence, the amplitude of the (1,1) mode may be too low to cause acoustophoretic motion of beads [64, 66].



Fig. 2.11. Particle behavior stimulated by driving one element at frequencies (a) 5 MHz, (b) 13 MHz, (c) 17 MHz, and (d) 23 MHz. The scalebar applies to all of (a) - (d).

For the E20 device, similar patterns emerged; beads agglomerated at the center of each diaphragm when resonance was approached, and torus shapes were seen at approximately  $f \approx 3.9 f_{fr}$ . However, several unique behaviors were seen in elements with 20 diaphragms compared to elements with only 1 diaphragm, as shown in Fig. 2.12. Beads moved away from the excited diaphragm at 7 MHz and returned at 8 MHz. This behavior was also seen when transitioning from 9 MHz to 13 MHz. One possible explanation can be drawn from the simulation illustrated in Fig. 4 (c), where above  $f_{fr}$ , an acoustic potential well can encourage beads to move away from the diaphragm. When the elements are excited together, depending on the separation distance between elements and the excitation frequency, larger acoustic pressures may be generated between diaphragms, with the resulting gradient pushing the beads towards the higher-pressure regions.

Crosstalk from neighboring, non-electrically excited elements may thus be the cause of behaviors seen in Fig. 12 (c)-(d), (e)-(f), and (g)-(h).

At higher driving frequencies, even without precise control over the height of the chamber, levitation planes were also observed, as shown in Fig. 13, with the heights of the levitation planes indicated in Table 2.1.



Fig. 2.12. Silica bead patterns generated using E20 with driving frequencies at (a) 1 MHz, (b) 3 - 6 MHz, (c) 7 MHz, (d) 8 MHz, (e) 9 MHz, (f) 13 MHz, (g) 17 MHz, (h) 18 MHz, (i) 22 MHz. Arrows indicate directions of particle motion before the particles settle into their observed position. The scalebar applies to (a) – (i).



Fig. 2.13. Levitation plane of 4 µm SiO<sub>2</sub> beads when PMUTs E1 were excited at (a) 30 MHz and (b) 50 MHz. The levitation planes are identified in Table I. The levitation planes are evident due to the need to defocus the microscope from the PMUT surface and focus on areas above it. The scalebar applies to (a) and (b).

In some cases, multiple levitation planes were observed. The levitation planes form at heights that correspond approximately with  $n\lambda/4$  as predicted by Equation (5). While the beads are trapped in the levitation plane, they have little motion in the X and Y directions. It is noteworthy that these effects were observed far beyond the limits of the measured BW of 62.5%.

Driving Frequency (MHz)	Half wavelength value (µm)	Observed Levitation Plane Heights (from PMUT surface, µm)
30	25	56, 74
50	15	19, 38, 51
60	12.5	10, 20

TABLE 2.1: LEVITATION PLANE HEIGHTS AT DIFFERENT EXCITATION FREQUENCIES			
Driving	Ualfwavalanath	Observed Levitation Plane Heights (from	

# 2.8. Additional Experiments

# 2.8.1. Nanorod and cell manipulation

Micromanipulation with the E1 and E20 array was also tested with other particles: gold nanorods

(2-3  $\mu$ m in length and ~ 300 nm in diameter) and cancer cells (10  $\mu$ m). The nanorods were easily moved from one element to another, either by turning adjacent elements on and off, or by changing the phase delay between the elements (from 100° to 260°), as seen in Fig. 2.14.



Fig. 2.14. Manipulation of (a - b) SiO<sub>2</sub> beads and (c - d) gold nanorods utilizing different phase differences in excitation. The blue arrows indicate the excited elements in (a) and (b), while the highlighted elements are excited for moving nanorods between them in (c) and (d). The white arrow in (c) and (d) show the cluster of nanorods that move based on the phase differences between the two elements. The phase ranges used were 100° to 260°.

The results of cancer cell manipulation with the E20 array are shown in Fig. 2.14. While the cancer cells did show movement from one element to another, they moved at a much slower velocity than the silica beads. In addition to the cancer cells being much larger, the acoustic impedance of cancer cells is much closer to that of water compared to SiO<sub>2</sub> beads, which will decrease the driving force causing motion.



Fig. 2.15. Manipulation of cancer cells with the E20 array. The white arrows indicate movement of the cancer cells as the element the cancer cells are on top of in (a) is excited at different frequencies. (b) shows the cells moving away the excited element. The light blue arrow above indicates the excited element.

### 2.8.2. 2D Array Design

A 2D array design was also fabricated in the same batch of PMUTs as the E1 and E20 array, as shown in Fig. 2.16. The goal for this design was to see if 2D particle manipulation could be achieved. The results are shown in Fig. 2.17. Again, with a combination of changing the resonant frequency and phase delay between elements, 2D movement could be achieved. However, the spacing between each of these elements needs to be further optimized, as the beads did not easily move from one element to another. This is potentially because the pitch between each element of 9 diaphragms was 300 microns compared to 75  $\mu$ m with the E1/E20 devices. Moreover, as there are 9 diaphragms excited at once, the acoustic pressure field is probably more complicated than a single diaphragm source.



Fig. 2.16. Picture of 2D array



Fig. 2.17. Preliminary 2D particle manipulation of 4 micron  $SiO_2$  beads. The white arrow indicates the excited element and reference point. Only the white element is excited for (a - d). The cluster of  $SiO_2$  beads are excited at (b), move to the left at (c), and split into two clouds, moving to the bottom and right in (d).

## 2.9. Conclusions

PMUT arrays were successfully fabricated with high quality (001) oriented PZT that produced  $\sim$  9.5 kPa at 7.5 mm distance in water and 40 nm/V deflection in air at 6 – 8 MHz resonant frequency. In addition, the fabricated arrays showed high electrical and acoustic uniformity, as the permittivity varied less than 2 % for an array of 20 PMUT elements. The arrays were used to control the location of SiO<sub>2</sub> beads and bead agglomerations in 1D (laterally) by selecting which PMUTs were excited. At higher excitation frequencies, different bead patterns were observed. Even well above the -6 dB bandwidth of the fundamental resonant mode, levitation planes and bead patterning were observed, demonstrating generation of sufficient pressure to realize these effects at frequencies as
high as 60 MHz. This shows the potential for use for patterning cells and particles in ways other than the agglomeration at the diaphragm center, demonstrated previously with CMUTs [32, 33].

This work opens a pathway towards 2D manipulation of various microparticles via PMUT arrays; in this work, control of nanorods, cells, SiO<sub>2</sub> beads was demonstrated. It is anticipated that the PMUTs can be applied more generally to manipulate other microparticles such as tumor cells, bacteria, proteins, fullerene, and enzymes. Basic movement of cancer cells and nanorods were achieved with 1D and 2D devices, albeit further optimization in pressure output and diaphragm distances are needed. These acoustic waves will not only be useful for particle manipulation, but also for imaging applications, as will be discussed in the next chapter.

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#### Chapter III: Piezoelectric Micromachined Ultrasound Transducers for Imaging

#### Applications

*Portions of this chapter have been reproduced from:* 

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#### 3.1. Introduction

Different frequencies are used in medical ultrasound imaging depending on the area of the body under investigation. Table 3.1 shows a typical range of resonant frequency ultrasound transducers used in medical imaging and their targets; this frequency range is commonly 2 to 20 MHz. Low frequency ultrasound energy penetrates tissue effectively however, higher frequency ultrasound transducers yield better spatial resolution; the smaller the wavelength, the greater the resolution.

I III ICHE ICH (OL OI )										
Operating										
Frequency	Target/Application									
(MHz)										
1 – 10	Pregnancy/obstetric									
2 - 5	Abdomen, deep veins									
3 - 10	Intravaginal/gynecology									
7.5 – 13	Breast									
7 - 10	Retina (general)									
7.5 - 18	Thyroid									
8	Superficial Veins									
20 - 50	Retina (cystoid macular edema detection, central serous retinopathy, evaluation of ciliary body)									
30 – 50 MHz	Fingerprint									

 TABLE 3.1

 Typical Range of Operating Frequency vs Ultrasound Target [1-11]

In this thesis, three metrics were examined to produce an improved ultrasound transducer: pressure output, bandwidth, and receive sensitivity. This chapter discusses pressure output and bandwidth while Chapter 4 discusses receive sensitivity.

Multiple attempts to improve the pressure output and bandwidths of MUTs are reported in the literature; Table 3.2 provides a summary. In CMUTs, different operation modes have been developed to improve the electromechanical coupling coefficient and pressure output. For example, in the collapse-snapback mode, the bias is operated above the pull-in voltage, resulting in increased pressure output [12, 13]. Likewise, several studies have reported approaches to improve the acoustic attributes of PMUTs. Hajati et al. demonstrated an improvement in bandwidth and pressure output by fabricating dome-shaped PMUTs and connecting different dome sizes in one element to artificially increase the bandwidth per element [14, 15]. The curvature of the PMUT

diaphragms allows for an additional out-of-plane stress contribution compared to a 2D/flat PMUT diaphragm when a voltage is applied, enhancing deflection [14, 15]. Akhbari et al. and Sammoura et al. demonstrated similar increases in diaphragm displacement (and thus pressure output) when using curved PMUT membranes [16-18]. Another method shown by Wang et al. and Muralt et al. was to partially release the boundary of the PMUT diaphragm, resulting in a 61% displacement improvement; a partially clamped diaphragm allowed for larger volumetric displacement compared to a fully clamped structure [19, 20].

∞	20	10.3	9.3	4	50	40	0.345	0.291	0.291	0.291	20	17	1 - 20	1-5	4	5, 11	6	11	14	3.85	5.5	13.5	19	11	16	Frequency (MHz)
40	Х	Х	Х	Х	х	Х	452	188	104	86	10	25	х	х	Х	Х	Х	10	10	Х	500	18	25	316	100	Deflection (nm/V), in Air
1.900	х	26.400	12.700	8.571	х	х	х	х	Х	х	0.240	0.727	Х	Х	50.000	х	130.000	0.068	0.392	х	0.300	Х	х	х	2.000	Pressure Output (kPa)/V
1.900	х	25.067	12.059	9.344	х	х	х	х	х	х	0.196	0.595	х	х	45.864	х	119.246	0.053	0.305	х	0.243	х	х	х	1.612	Normalized to 7.5 mm by Hydrophone Receive Distance (kPa/V)
7.5	Х	6	6	10	4	7.4	Х	Х	х	Х	1.7	1.7	х	х	ъ	Х	υ	0.4	0.22	Х	1.4	Х	х	Х	1.25	from Device to Hydrophone (mm)
20	80	64	64	14	10	1	1	1	1	1	64	49	х	х	72	Х	58	56	56	20	1	4	х	Х	81	# of Diaphragms
3.36*10-5	Х	5.54*10-4	6.66*10 <sup>-5</sup>	1.33*10-12	х	х	Х	Х	Х	Х	1.56*10-6	6.19*10-6	Х	Х	1.33*10-4	Х	7.27*10-4	9.80*10-7	4.22*10-5	Х	4.05*10-5	Х	х	Х	1.58*10-5	(Normalized Pressure)/ (total active area) (kPa/V/µm <sup>2</sup> )
0.095	х	х	х	0.816	х	х	х	Х	Х	Х	0.001	0.003	Х	Х	0.463	Х	1.494	0.00006	0.00021	х	0.056	х	х	Х	0.004	(Pressure Output)/ (# of Diaphragms)
62.50%	85%	147%	124%	Х	56%	83%	х	Х	х	Х	х	х	165% (-20 dB)	170% (-20 dB)	Х	67%	х	37%	37%	43%	97%	Х	х	Х	32.70%	Bandwidth
PZT	CMUT	CMUT	CMUT	PZT	PZT	PZT	AIN	AIN	AIN	AIN	AIN	ScAIN	PNZT	PNZT	PNZT	PNZT	PNZT	AIN	AIN	PZT	PZT	AIN	AIN	PZT	PZT	Material Type
30.0	9.0	15.0	30.0	100 x ~4000	40.0	40.0	170.0	230.0	230.0	230.0	25.0	25.0	х	47 - 69.5	32 - 46	37 - 45	30.0	17.5	30x43	50.0	30 x 200	30.0	25.0	25.0	20.0	Diaphragm Radius or Dimension (µm)
PMUT, Current Work	CMUT	CMUT	CMUT	PMUT	PMUT	PMUT	Bimorph w/ dual electrode driven	Unimorph w/ dual electrode driven	Unimorph PMUT w/ central electrode	Unimorph PMUT w/ annular electrode (peripheral)	PMUT	PMUT	PMUT Semi-ellipsoid dome	PMUT uses 16 different dome sizes	PMUT uses different dome sizes	PMUT uses 5 different dome sizes	Dome-shaped PMUT	Circular PMUT	Rectangular PMUT	PMUT, metal bridge connections	Ribbon PMUTs	PMUT	PMUT	PMUT	PMUT	Notes
Current work	D. Yeh et al.	K. Park et al.	K. Park et al.	Klee et al.	Qiu et al.	Griggio et al.	Akhbari et al.	Akhbari et al.	Akhbari et al.	Akhbari et al	Wang et al.	Wang et al.	Hajati et al.	Hajati et al.	Hajati et al.	Hajati et al.	Hajati et al.	Jiang et al.	Jiang et al.	Jung et al.	Lu et al.	Wang et al.	Lu et al.	Lu et al.	Lu et al.	Source

Photoacoustic imaging has been explored to complement ultrasound-based imaging and improve medical diagnostics. Over the last decade, photoacoustic imaging (PAI) has emerged as a promising biomedical imaging modality. Continued improvements in instrumentation and image reconstruction and success in pre-clinical and translational levels [30-36] has spurred interest in PAI. In PAI, a pulsed light source illuminates a target, which expands due to transient thermoelastic expansion. These expansions generate pressure pulses in the media, which then can be detected by an ultrasound transducer placed at the surface of the tissue [37-39].

PAI offers several benefits over current non-invasive biomedical imaging modalities. Firstly, PAI uses non-ionizing radiation and is a safe and cost-effective alternative to standard whole-body imaging modalities such as Magnetic Resonance Imaging (MRI), Positron Emission Tomography (PET), and Computed Tomography (CT) [40]. Secondly, the photoacoustic contrast arises from the optical absorption of the tissue rather than the acoustic impedance mismatch in ultrasound imaging. Thus, photoacoustic imaging can supplement medical diagnostics for conditions where definitive medical diagnoses based on mechanical/anatomical differences alone are not possible. For example, photoacoustic imaging can supplement information on blood vessel structure (obtained through ultrasound) with information regarding oxygen saturation levels of hemoglobin [41]. Thirdly, since ultrasound and PAI share the same detection platform, conventional ultrasound imaging systems can be adapted to simultaneously display anatomical ultrasound and photoacoustic contrasts in real time. These capabilities have advanced the clinical translation of PAI in imaging of multiple organs including breast, prostate, ovary and thyroid systems, as well as in monitoring Crohn's disease activity [42 - 48].

Recent advances in semiconductor technologies have transformed the computational and electronics backend of ultrasound imaging systems. While these advances have enabled ultrasound

imaging devices in portable form, conventional ultrasound array transducers are not well-suited for portable and wearable devices due to their bulky size and high-voltage operation [49]. Micromachined Ultrasound Transducers (MUTs) fabricated on silicon have emerged as an alternative to conventional ultrasound arrays [50 - 58]. MUTs reduce device size and weight, are cost efficient (due to batch fabrication in foundries) and provide multi-frequency imaging capabilities using a single array [59]. By using packaging techniques such as flip-chip bonding with application specific integrated circuits (ASICs) spatially matched to the ultrasound array elements, the number of ultrasound channels can be increased dramatically, thus enhancing real-time volumetric imaging capabilities [60]. Consequently, MUTs have already been demonstrated for fingerprint sensing in smartphones and in handheld probes for B-mode ultrasound imaging [61 - 67].

MUTs are mainly of two types: capacitive MUTs (CMUTs) and piezoelectric MUTs (PMUTs) [68, 69]. Unlike CMUTs, PMUTs can operate at low voltages (<5V) and do not require a large bias voltage, making CMOS integration/close coupling much easier (though often at the expense of more difficult materials integration challenges). DC bias is not needed in photoacoustic applications as PMUTs function solely as a receiver. PMUTs can also be impedance matched with typical data acquisition systems designed for bulk ultrasound transducers; this is useful in preliminary testing situations when ASIC integration is not available [63, 64, 68]. CMUTs have already been widely explored for PAI, for example via tissue phantom experiments [50, 59, 70], as well as *in vivo* pre-clinical and clinical translation application for human prostate imaging [44 - 48]. While PMUTs have been utilized for ultrasound imaging applications, their potential for photoacoustic imaging has yet to be experimentally explored, particularly for deep-tissue imaging [63, 71]. Theoretical studies have shown that PMUTs are promising for PAI [72, 73]. A

preliminary experimental demonstration by Chen et al. using an AIN-PMUT array reported detection of weak photoacoustic signals from a black target placed less than a millimeter away from the PMUT in a clear (i.e. no optical or acoustic scattering) medium in a petri dish, when illuminated with a focused light spot [74]. This study pointed to a possibility of using PMUTs for photoacoustic imaging. In addition, AIN-PMUTs were utilized to detect photoacoustic images of targets up to 2-3 centimeters away in clear agar-gel phantoms [75]. PMUT technology shows great potential in multiple applications; understanding and demonstrating its capabilities for B-mode photoacoustic imaging in tissue at clinically relevant depths is critical.

In this chapter, the design, fabrication, packaging, and characterization of a Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (PZT) based PMUT array is reported, with a focus on photoacoustics and ultrasound imaging. The PMUT array was integrated into a PAI device with a custom designed printed circuit board (PCB) and an optical fiber bundle assembly; the resulting system was used to successfully demonstrate B-mode photoacoustic imaging on tissue phantoms for the first time with PMUTs.

# 3.2. PMUT Fabrication and Packaging



Fig. 3.1. Optical image of a linear 65-element PMUT array with each element consisting of 60 diaphragms. The inset shows the center-to-center distance between individual hexagonally packed PMUT diaphragms; the dashed circles denote the suspended membranes.

For imaging experiments, a PMUT device consisted of 60  $\mu$ m diaphragms arranged in a hexagonally-packed fashion with a 75  $\mu$ m center-to-center distance. The top electrodes consisted of three columns of 20 PMUT diaphragms which were shorted together to form one PMUT array element (60 diaphragms total per element), as shown in Fig. 3.1.

The PMUTs were made using a fabrication process similar to that described in Chapter 2. As shown in Fig. 3.2, a PAI device was developed by tightly integrating a custom-made fused silica-silica fiber bundle of 2 meter length (Fiberoptics Systems, Simi Valley, California, USA) and a custom-designed PCB bonded to a linear PMUT array. First, an individual PMUT array die was mounted on the PCB with silver paint. The PMUT array was then wire bonded to the PCB and conformally coated with ~4  $\mu$ m of parylene for waterproofing. The PCB-PMUT assembly was then fixed to the flat surface of the distal (light output) end of the fiber bundle; the distal end emitted light into the targeted imaging region from two rectangular optical windows 1.5 mm wide and 30 mm long, with a ~10 mm gap in between the windows to provide dark-field illumination. The distal end of the fiber bundle, consisting of a PCB-PMUT assembly at the center of the two



Fig. 3.2. (a) A schematic representation of the PMUT based photoacoustic imaging probe showing the integration of the linear PMUT array with the optical fiber bundles fused to produce two rectangular windows illuminating the imaging target. (b) A picture of the PMUT array wire-bonded to a PCB and integrated into the light guide apparatus.

optical windows, was integrated inside a semi-cylindrical acrylic housing to facilitate transrectal photoacoustic human prostate imaging applications in the future. The proximal (input) end of the fiber bundle assembly was connected directly to a wavelength tunable OPO laser (Phocus Mobile, Opotek Inc., Carlsbad, CA, USA), for photoacoustic imaging experiments.

### 3.3 PMUT characterization

The characterization of the PMUT device as an array of twenty elements is given in Fig. 3.3. Highly {100} oriented, phase-pure perovskite PZT was achieved. An average permittivity of 1490 and mean loss tangent of 1.3% were observed at 1 kHz, with element-to-element standard deviations of 18 and 0.1%, respectively. Hysteresis loops indicate a remanent polarization of ~21  $\mu$ m/cm<sup>2</sup> and a coercive field of ~50 kV/cm.



Fig. 3.3. Evaluation of the PZT via (a) XRD, and (b) hysteresis loops. Measurements of (c) permittivity and (d) loss tangent of the thin film PZT for multiple elements on the PMUT device. Permittivity and loss tangent showed less than 10% variation, respectively for 20 different elements on the same die. IQR stands for interquartile range.

The PMUT element was characterized for in-air resonance using a Laser Doppler Vibrometer (LDV) (MSA-500, Polytec GmbH, Waldbronn, Germany). When actuated in air, the first mode resonance was found to lie between 6.0 MHz and 8.0 MHz for PMUTs taken from across the wafer. These variations in the first mode resonant frequencies were attributed to variations in the diaphragm size caused by footing from the DRIE process. The frequency range within a die was narrow. A frequency sweep near the resonance for in-air vibrations gave a deflection sensitivity of ~55 nm/V at the center of a PMUT diaphragm. Higher harmonics were seen near 13.0 and 19.5 MHz, as shown in Fig. 3.4.



Fig. 3.4. In-air chirp excitation measurements using laser Doppler vibrometry from a PMUT array element show a first resonant peak between 6.0 MHz and 8.0 MHz. Higher modes can also be seen at ~13.0 MHz and ~19.5 MHz. The inset shows the peak-hold measurements around the first peak, giving ~55 nm/V deflection sensitivity for the PMUT at resonance.

For acoustic characterization of this specific device, pressure outputs were obtained from 12 different elements of a linear array, with each element having 60 diaphragms (3 rows of twenty

diaphragms in each element). The pressure output for each element was measured by placing the PMUT in an acrylic water-tank and operating the PMUT in transmit mode while a wideband hydrophone (HGL-0085, Onda Corp., Sunnyvale, CA, USA) acted as a receiver at 7.5 mm distance from the surface of the transducer. The elements were poled at 15 V for 15 minutes at room temperature prior to the experiments. One element was excited with a unipolar 5  $V_{pp}$  signal at resonance in a 5-cycle sinusoidal burst mode. Unipolar excitation was chosen so as to not depole the device during operation. The results are shown in Fig. 3.5. The output pressure recorded from 12 different elements shows on an average 16.2 kPa output with 0.96 kPa standard deviation, indicating good homogeneity amongst the elements.



Fig. 3.5. Pressure output for 12 different PMUT elements in the array at 7.5 mm from the PMUT surface, with each element containing 60 diaphragms excited using a 5  $V_{pp}$  unipolar input. The inset shows the experimental setup, with the hydrophone ~7.5 mm distance away from the PMUT.

Another critical figure-of-merit of ultrasound transducers for photoacoustic imaging

applications is the receive sensitivity. To characterize the receive sensitivity of the PMUT, a 0.5inch diameter single element bulk ultrasound transducer with 8 MHz center frequency was used as the acoustic source (transmitter). The bulk ultrasound transducer was excited using one cycle of 5 V<sub>pp</sub> sinusoidal pulse of 8 MHz frequency, generated by an arbitrary waveform generator (SDG6022X, Siglent Technologies, Solon, OH, USA). The ultrasound pressure at 26 mm distance from the transmitter was detected first by different elements of the PMUT array, then later by using the calibrated hydrophone. Both the PMUT array and the hydrophone were aligned along the longitudinal axis of the transmitter for these measurements. The output of the PMUT was amplified with 18 dB gain using a preamplifier (5073PR, Olympus NDT Inc, Waltham, MA, USA), and the resulting voltage signal was captured using an oscilloscope (MDO3024, Tektronix, Beaverton, OR, USA). Fig. 3.6 shows the voltage output of the PMUT averaged over eight acquisitions, giving ~65 mV peak-to-peak voltage output. Fig. 3.6 also shows the voltage output recorded by the hydrophone, which corresponds to ~17 kPa peak-to-peak pressure output. The receive sensitivity of the PMUT, estimated by dividing the peak-to-peak voltage output of the PMUT element by the peak-to-peak pressure measured by the hydrophone, was found to be ~0.48 mV/kPa with 0 dB gain.



Fig. 3.6. Receive sensitivity measurements: (a) Voltage output of a PMUT element when excited by the bulk ultrasound transducer transmitter placed 26 mm away actuated by single sinusoidal pulse input. (b) Voltage output of a calibrated hydrophone captured at the same location as that of the PMUT measurement.

### 3.4 Experimental setup for ultrasound imaging

The setup for ultrasound imaging via pitch catch mode is shown in Fig. 3.7. Here, the PMUT was mounted onto a stage that was connected to a 3-axis micromanipulator controlled by custom-made MATLAB code. One PMUT element was then excited at MHz using a 5  $V_{pp}$  unipolar sinusoidal burst wave at 7 MHz. A target was set 7.5 mm distance away from the device. Another element was set as the receiver and had 39 dB external gain. The target consisted of clay in the shape of a heart attached to a glass slide. The principle was the clay is acoustically attenuating, while the glass slide is acoustically reflective. The target was then raster scanned by the PMUT. The resultant

image is seen in Fig. 3.7 (c), where an 18 mm by 18 mm ultrasound image of the target is generated. The true lateral resolution and the effective coupling coefficient of the fabricated PMUTs should be investigated in future work.



Fig. 3.7. (a) Ultrasound setup for pitch-catch, (b) picture of the target, a clay in the shape of a heart on a glass slide, and (c) resultant 18 mm x 18 mm ultrasound image with dimensions.

# 3.5 Experimental setup and results for photoacoustic imaging

A 32 cm  $\times$  18 cm  $\times$  12 cm plastic tank, filled with de-ionized water, was used for the photoacoustic imaging experiments. Phantoms to be imaged were placed at the bottom of the tank; the entire PAI device was submerged with the PMUT array and light output facing the phantom. The distal end of the PAI device was fixed to a motorized 3-axis linear stage (NRT100, Thorlabs, Newton, NJ, USA) for alignment. The light pulses (from the laser) propagated through the imaging phantom and were absorbed by chromophores in the phantom, subsequently generating broadband photoacoustic pressure waves due to transient thermoelastic expansion. The generated photoacoustic pressure was sensed by the PMUT array. In the current experiments, the laser provided a maximum fluence of ~10 mJ/ cm<sup>2</sup> at 800 nm at the output end of the fiber bundle, which is well within the ANSI safety limits [78]. The voltage output from a single PMUT array element was connected to a commercial preamplifier (5073PR, Olympus NDT Inc, Waltham, MA, USA)

providing 39 dB gain. The pre-amplified output was digitized using a 16-bit data acquisition card (Gage RazorMax16, Dynamic Signals LLC, Lockport, IL, USA) at 1 GSPS in synchronization with each laser pulse.

B-mode photoacoustic imaging requires the ultrasound signals generated by the phantom to be captured by a linear array of ultrasonic receivers with typically 128 or 256 evenly spaced elements. The data acquisition system used for current experiments was limited to four channels. Thus, a linear array acquisition was emulated by linearly scanning the PAI device to 300 to 500 positions, depending on the size of the phantom, along the length of the device with a 100 µm step size, while the phantom was kept undisturbed. The raw photoacoustic A-line data captured at these positions mimics imaging with a linear array with a 100 µm element pitch. The position control of the device was achieved using the linear stage while Matlab (Mathworks Inc., Natick, MA, USA) based control software was used to control the data acquisition and the motion of the linear stage. 20 A-line signals were averaged at each spot to reduce the noise floor.

The device was tested for photoacoustic imaging capabilities using tissue-mimicking phantoms. First, an agar-gel phantom was prepared by mixing 1.5 grams of agarose in 100 ml of de-ionized water. The solution was heated for 2 minutes in a standard kitchen microwave. Before solidification, a portion of the solution was poured in a rectangular box, creating a 5-mm thick bed. The base agar-gel pad thus formed was allowed to settle by cooling in a refrigerator for 5 minutes. One pencil lead with 0.3 mm diameter was placed on the bed and another ~5 mm thick layer of agar-gel was poured on top. The process was repeated for 6 layers, resulting in an agar-gel phantom with six pencil-leads placed in diagonal pattern at depths between 4 mm to 20 mm depth, as seen in Fig. 3.9. The agar-gel phantom was then placed underwater along with the PMUT. The distance between the PAI device and the top surface of the agar-gel phantom was ~10 mm.

A single A-line signal captured from a pencil lead embedded in agar-gel and aligned for maximum photoacoustic output is shown in Fig. 3.8. The photoacoustic pulse, received ~23.5  $\mu$ s after the laser excitation, matched with the pencil lead at ~36 mm distance from the PMUT array element and showed ~350 mV<sub>pp</sub> pulse amplitude. Using this single A-line signal, the frequency response of the photoacoustic pulse was found to be ~6.75 MHz center frequency with ~89% bandwidth. It was noted that different devices sometimes had different bandwidths. Among the variables that could affect the bandwidth are poling, fabrication/processing quality, and alignment of the transducer and the hydrophone. Even at high poling fields at elevated temperature, variations in bandwidth were still seen. Little variation in process quality was expected on the fabricated PMUTs, as no significant variation was observed in the electrical measurements with elements on the same device as seen in Fig. 2.4 of Chapter 2. It is possible that some variation in the DRIE etch



Fig. 3.8. Photoacoustic signal captured from a pencil lead target shows  $\sim$ 320 mV peak-to-peak amplitude, after 39 dB gain at the preamplifier stage. The frequency response of the photoacoustic pulse shows a  $\sim$ 6.75 MHz center frequency with  $\sim$ 89% bandwidth.

may also change the boundaries of the diaphragm and thus may also change the frequency and

bandwidth. Alignment is a possible factor, albeit a 3-axis stage was used to fine tune acoustic measurements. Cross talk is also a factor that may affect bandwidth, particularly when adjacent vibrations are not in the same phase as the excited element. Cross talk was shown to occur in the fabricated PMUTs based on Fig. 2.9 of Chapter 2.

Using the PAI device, the agar-gel phantom with 6 embedded pencil leads was imaged. A Fourier transform based algorithm was used to reconstruct B-mode images from the raw voltagetime data [40]. Fig. 3.9 (b) shows the reconstructed B-mode photoacoustic image from the 500 signals captured by the PMUT array element while scanning the device over 5 cm with a 0.1 mm pitch. The first four pencil leads, identified as T<sub>1</sub> to T<sub>4</sub>, were clearly visible. The last two pencil leads T<sub>5</sub> and T<sub>6</sub> were barely visible in the reconstructed PAI image. No time gain compensation was used in the reconstruction algorithm; hence, the reconstructed image is expected to show a depth dependent decay in the photoacoustic contrast. As expected, a decrease in photoacoustic signal strength as a function of depth of the pencil lead can be seen from the plot in Fig. 3.9(c). Furthermore, the lateral and axial resolutions were estimated from the full width at half-maximum (FWHM) of the photoacoustic amplitude of a pencil lead target, T<sub>1</sub>, plotted along the horizontal and vertical axis, as shown in Fig. 3.9(d). The lateral and axial FWHM for  $T_1$  were found to be ~0.30 mm and ~0.15 mm respectively. The lateral FWHM was found to increase with depth, reaching up to 0.57 mm for the sixth pencil lead. It should be noted that for tomography measurements the operating frequency will dictate the device resolution, both in ultrasound and photoacoustic measurements. Theoretically, the resolution of this device was expected to be  $\sim 75$ µm. However, crosstalk, PMUT element spacing, alignment, and directivity of the device can affect the spatial resolution. In addition, it can be seen that the lateral distance is smaller than the size of the object imaged (pencil leads were 0.3 mm in diameter). This is because the shortest distance for the light to travel is a small area at the topmost surface of the pencil lead, and thus that area would have the highest intensity signal. The sides where the pencil lead doesn't have as much intensity. This creates arcs in the image that are filtered out via the reconstruction algorithm.



Fig. 3.9. B-mode photoacoustic imaging of six 0.3 mm diameter pencil-leads embedded inside agar-gel: (a) Experimental setup showing the agar-gel phantom with six pencil leads at various depths and the PAI device facing the phantom. (b) B-mode photoacoustic image obtained by frequency domain reconstruction over a 50 mm range with 0.1 mm pitch shows all six pencil leads. (c) The intensity of the photoacoustic signals from the pencil leads reduces as a function of depth inside the phantom. (d) Lateral imaging resolution estimated from the full width at half maximum (FWHM) of the peak intensity at the center of the pencil lead and the axial resolution determined from an envelope function fitted over the PA pulse from the pencil lead.

Additional photoacoustic imaging experiments were conducted for the four different conditions shown in Fig. 3.10. Firstly, Fig. 3.10(a) shows an agar-gel phantom with a polyethylene tube having 1.09 mm outer diameter and 0.38 mm inner diameter filled with a 200  $\mu$ M indocyanine green (ICG) solution, embedded inside the agar-gel. When the submerged PAI-PMUT probe was aligned directly above the ICG tube phantom, at a ~20 mm gap, a photoacoustic output of ~80 mV<sub>pp</sub> was captured.

Secondly, the agar-gel phantom with the ICG-filled tube was covered with ~3 mm of chicken tissue, as shown in Fig. 3.10(b), to induce scattering in the optical illumination. While the photoacoustic signal decreased (the amplitude of the photoacoustic pulse was reduced to ~30 mV<sub>pp</sub>), the ICG filled tube was imaged clearly at ~25 mm distance from the PMUT-PAI device, as seen in Fig. 3.10(f).

Thirdly, an imaging phantom consisting of two bovine blood (905-100, Quad Five Inc., Ryegate, MT, USA) filled polyethylene tubes, separated by a clear tube, all of which were embedded in agar-gel, as shown in Fig. 3.10(c), was investigated as a target. As shown in the reconstructed image in Fig. 3.10(g), the two blood-filled tubes were detected, while the tube without blood did not generate any above-noise photoacoustic signal due to the lack of absorption.



Fig. 3.10. B-mode photoacoustic imaging (PAI): (a) A clear agar-gel phantom with an ICG-filled tube as target. (b) Phantom shown in (a) is covered with 2 mm thick chicken tissue layer to introduce scattering of the light. (c) A clear agar-gel phantom with two blood filled polymer tubes embedded at 5 mm depth with an unfilled tube placed between the two tubes. (d) Pictures showing the preparation of chicken tissue-based phantom. Three 0.3 mm pencil leads were placed on the chicken bed and then an 8 mm thick chicken tissue layer was placed on top of the pencil leads. (e), (f), (g), (h), and (i) were the reconstructed B-mode (photoacoustic images from phantoms shown in (a), (b), (c), and (d) respectively. (i) signal from a single follicle of hair as the target. The color-bar for all the reconstructed images represents the photoacoustic intensity, normalized with respect to the maxima within each image, on log scale with 0 dB to -40 dB range. All images were acquired using linear scanning of single element PMUT with 0.1 mm step size

The fourth demonstration consisted of imaging pencil lead targets embedded under 8 mm of chicken tissue, as seen in Fig. 3.10 (d). An  $\sim$ 8 mm thick slice of chicken tissue was used as the bed on which three 0.3 mm pencil leads were placed with  $\sim$ 15 mm separation, and another  $\sim$ 8 mm thick chicken slice was placed on the top. Care was taken to minimize any air gap between the

layers of chicken tissues and the pencil leads. As shown in the reconstructed photoacoustic image in Fig. 3.10(h), the three pencil leads could be detected through 8 mm of chicken tissue. For the three pencil leads under chicken, the axial resolutions lie between 0.16 mm to 0.18 mm and the lateral resolutions lie between 0.30 mm to 0.50 mm, as estimated using the approach described for Fig 3.9(d).

The final demonstration consisted of a single follicle of hair as the target. The average follicle hair diameter was  $\sim 100 \,\mu\text{m}$ ; this was the smallest sample that was detected with the current acoustic setup.

Although the above photoacoustic imaging results with the PMUT arrays are encouraging, reducing the noise floor of the PMUTs will improve their photoacoustic sensitivity. Potential sources of noise include cross-coupling between neighboring elements, pressure induced surface and bulk acoustic waves in the PMUT substrate, the high capacitance of the PMUT element that increases the electrical noise, and the parasitic capacitance introduced by wires connecting the PMUT elements to the imaging system. These noise sources can be reduced by techniques such as introduction of trenches around the PMUT elements to attenuate substrate vibrations and cross-coupling or using lower permittivity materials. In addition, delamination was observed between the parylene layer and the top surface of the PMUT diaphragms for a few cases during the poling process or transmit mode operation after repeated uses. Such delamination was found to cause sudden degradation in the performance of the PMUT element and needs to be studied further.

# 3.6. Conclusions

Successful fabrication and characterization results of a ~7 MHz linear PMUT array with high acoustic/photoacoustic bandwidth with high uniformity (less than 5% variation in pressure output between elements) was presented. A compact handheld photoacoustic imaging device was

developed by wire-bonding the array to a printed circuit board and further integrating it with a fiber optic light guide. Photoacoustic imaging experiments on different tissue phantoms established the feasibility of imaging photoacoustic contrast from blood, ICG and pencil leads through scattering tissue using PMUT arrays. These results show, for the first time, the feasibility of a PMUT-based handheld photoacoustic imaging device for imaging targets inside optically and acoustically scattering tissue. Based on Table 3.2, the acoustic characteristics of bandwidth, frequency and pressure output is on par with what is reported in the literature. Future improvements can be achieved by using ASICs for pre-amplification and signal conditioning. Also, more complex architectures, such as PMUTs with curved or dome shaped membranes, can enable higher sensitivities [19, 79]. Low voltage (< 10 V) operation, high receive sensitivity, ease of impedance match with conventional ultrasound preamplifiers and ease of fabrication of miniaturized PMUTs of various shapes and sizes make them attractive for developing multi-scale and multimode photoacoustic imaging systems. Moreover, in this chapter, only a single element was used out of the array, and the device was raster scanned. It is imperative to exploit beam steering and focusing in the future. For the ultrasound imaging, as the resonant frequency was  $\sim 8$  MHz, 90  $\mu m$ resolution is expected. However, there was difficulty in scanning metal needle targets of 0.5 - 0.7mm in diameter. This is possibly due to the scattering of the cylindrical target (as opposed to a flat target such as a microscope slide). Thus, more elements will need to be connected to enable focusing and beam steering. Suggestions for improving the acoustic characteristics of micromachined ultrasound transducers will be discussed in Chapter 4.

# 3.7. Chapter References

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### **Chapter IV: Improving Transmit and Receive Sensitivity of PMUTs**

# 4.1 Introduction

Miniaturized ultrasound sensors capable of low voltage operation with high transmit and receive signals are desirable for many applications. Micromachined ultrasound transducers prepared via MEMS fabrication have been developed to meet this need; typically, the output acoustic signals of such devices are smaller than those from transducers built using bulk piezoelectrics [1]. In such devices, a variety of methodologies have been utilized to improve the acoustic characteristics of MUTs, such as operating in the collapse mode for capacitive micromachined ultrasound transducers or fabricating dome shaped membranes for piezoelectric micromachined ultrasound transducers [2, 3].

Lead zirconate titanate and aluminum nitride are commonly used materials for piezoelectric micromachined ultrasound transducers. PZT is valued for its high piezoelectric coefficient and thus high transmit pressures. The piezoelectric coefficient of AlN is about an order of magnitude lower than PZT; its dielectric constant is approximately two orders of magnitude lower than that of PZT [4, 5]. Although the receive sensitivity of AlN is desirable, it is important to be able to couple this with a higher transmit power for most ultrasonic imaging.

As stated in Chapter 3, several modifications to the PMUT architecture have been proposed to further improve the transmit power, such as partially etching the edges of the diaphragm to form a semi-clamped boundary condition, isolation trenches, and a curved PMUT diaphragm [3-8]. The transmit power is governed by equation (1-6). Thus, the factors that can be manipulated to improve transmit pressure output are resonant frequency, deflection, and the effective area. Based on equation (1-6), higher frequency would give higher pressure output. However, for PMUTs, higher

frequency also typically equates to a thicker device layer and thus a stiffer membrane, which lowers the deflection. These factors compete with one another in the thin plate and membrane regimes [9]. Thus, the transmit pressure can be more readily improved via the effective area. For example, the PMUTs indicated in Chapter 2 and 3 have elements that consist of a series of circular diaphragms shorted together. This type of MUT design is among the most common in literature [3-8, 10-13]. However, it should be noted that for PMUTs in which one element is  $\sim 1.5$  mm in length, the entire 1.5 mm length does not vibrate but rather individual circular diaphragms vibrate. Based on equation (1-6), increasing the area will linearly increase the transmit pressure. Thus, diaphragms of rectangular design are of interest. A single rectangular diaphragm is less prone to having the RC time constant impinge on the use frequency range, and it has a larger effective area. Jiang et al. calculated that an array of rectangular PMUTs can achieve twice the pressure output of a circular PMUT array due to a larger fill-factor. [14]. Balasigam et al. simulated higher ultrasound beam widths in rectangular PMUTS [15]. It is also seen that in equation (1-6), the pressure should increase with resonant frequency. However, in PMUTs, an increase in resonant frequency often results in either (1) increase in device thickness (and thus stiffness) or (2) a decrease in the width of the diaphragm (and thus decreases resonant frequency). It is also known that a stiffer diaphragm would vibrate more effectively in water loading conditions than a less stiff diaphragm. Therefore, this chapter studies the fabrication of rectangular PMUTs to test transmit pressure output versus effective area as well as stiffness of the device layer. Additionally, PZT compositions and their suitability for ultrasound receive sensitivity were explored.

Receive sensitivity is a function of the piezoelectric voltage coefficient,  $h_{31,f}$ , which is expressed via:

$$h_{3l,f} = \frac{e_{31,f}}{\varepsilon_r},\tag{4-1}$$

where  $e_{3l,f}$  and  $\varepsilon_r$  are the piezoelectric coefficient and permittivity, respectively. Thus, to improve receive sensitivity, the piezoelectric coefficient must be high and/or the permittivity must be low.

It is known that when sufficiently large electrical fields are applied to a ferroelectric such as PZT, the permittivity is lower than that at zero field value due to a reduction in the intrinsic and extrinsic contributions to the permittivity [16]. Moreover, the piezoelectric coefficient may also increase with large DC electric fields, as domains more readily remain aligned with the direction of the applied electric field (poling) [17-20]. Thus, if a DC electric field is applied while the PMUT functions as a receiver, the receive sensitivity should be higher than at zero applied bias. The trends in piezoelectric coefficient and permittivity have been observed previously for air coupled transducers [5] but have not been demonstrated in underwater ultrasonic and photoacoustic applications.

In addition, different PZT compositions and their suitability for ultrasound receive sensitivity will be explored. The morphotropic phase boundary (MPB) composition of PZT has a Zr/Ti ratio of 52/48, which is often utilized for its high permittivity and piezoelectric coefficients [21]. As the composition moves off the MPB, the piezoelectric coefficient and permittivity also decreases [21, 22]. However, the reduction in  $e_{3l,f}$  and  $\varepsilon_r$  may be at different rates. Thus, on changing the composition, the permittivity may decrease faster than that of the piezoelectric coefficient. Thus, it is hypothesized that for ultrasound applications, moving off the MPB may result in higher receive sensitivity while maintaining relatively high transmit power.

#### 4.2. PMUT Fabrication Process and Experimental Setup

The fabrication of the rectangular PMUTs to test transmit pressure output versus effective

area is similar to the fabrication of the aforementioned circular-diaphragm PMUTs, with two exceptions: the rectangular diaphragm features (which had a dimension of 46  $\mu$ m by 1710  $\mu$ m) and inverting the common electrode as the top electrode and patterning the bottom electrode. Here, an SOI wafer with a 5  $\mu$ m Si device and 1  $\mu$ m buried oxide layer was utilized (Ultrasil Corporation, Hayward, California, USA). An SiO<sub>2</sub> passive elastic layer ~0.5  $\mu$ m thick was grown on both sides of the wafer by wet oxidation. Afterwards, 60 nm of hafnium oxide was deposited via atomic layer deposition (ALD) at 200°C as a diffusion barrier to prevent PZT from reacting with SiO<sub>2</sub>. Then 30 nm of Ti was sputtered on the device side, followed by rapid thermal annealing with 10 sccm of oxygen flow for 15 minutes at 700°C to form TiO<sub>2</sub>. Then, 100 nm of Pt was sputtered at > 500°C [23].

To achieve the highly oriented (001) PZT films needed for optimal functional performance in applications, a thin Pb(Zr<sub>0.44</sub>Ti<sub>0.56</sub>)O<sub>3</sub> sol-gel solution with 2% Nb and 20 mol% excess Pb (Mitsubishi Materials Corporation, Hyogo, Japan) was first spun on the wafer at 6000 rpm for 30 s as the seed layer [23, 24]. The seed layer was then pyrolyzed at 200°C for 150 s before crystallization via rapid thermal annealing in a Pb-rich environment at 700°C for 1 min. Afterwards, the bottom electrode was patterned via reactive ion etching. For the functional thin film PZT layer, 14 mol% lead excess Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> solution doped with 2% Nb (Mitsubishi Materials Corporation, Hyogo, Japan) was blanket-coated via spinning at 2750 rpm for 45 sec. The film was then pyrolyzed at 100°C for 1 min and 300°C for 4 min, followed by crystallization in a lead-rich rapid thermal annealer for 1 min at 700°C. This process was repeated until a total thickness of ~ 2.0 µm was achieved. Typically, 20 repeats were needed. Afterwards, a thin PbO capping layer was deposited at 6000 rpm for 45 sec with the same pyrolysis and crystallization steps as the PZT layers to remove pyrochlore from the surface of the film. A window was etched via reactive ion etching to gain access to the bottom electrode. The top electrode consisted of sputtering 2 nm of Ti as an adhesion layer followed by 500 nm of Au. Afterwards, the devices were released via backside silicon deep reactive ion etching. An optical micrograph of the resulting devices is shown in Fig. 4.1(b).



Fig. 4.1 Top view of (a) circular diaphragms shorted together and (b) rectangular PMUT designs. The circular diaphragms were designed to have a resonant frequency of  $\sim 6 - 8$  MHz, and the rectangular diaphragms were designed for  $\sim 15$  MHz.

To test electrically whether the permittivity and piezoelectric coefficient would increase with DC bias, samples with an architecture similar to that of the PMUTs but unreleased were fabricated. A 500 µm Si stack with 1 µm of SiO<sub>2</sub> on both sides (NOVA Electronic Materials, Texas, USA) was used as the substrate. The bottom electrode was deposited by sputtering 30 nm of Ti, annealing it at 700°C for 15 minutes with 10 sccm of oxygen flow, and then sputtering 100 nm of Pt at a substrate temperature of 500°C. To facilitate orientation of the balance of the piezoelectric film, a PZT seed layer (Mitsubishi Materials Corporation, Hyogo, Japan) was spun,

pyrolyzed, and crystallized, as described elsewhere [19, 25]. For the MPB composition, 14 mol% lead excess Pb( $Zr_{0.52}Ti_{0.48}$ ) O<sub>3</sub> solution doped with 2% Nb (Mitsubishi Materials Corporation, Hyogo, Japan) was spun on at 2750 RPM for 45 seconds. The film was pyrolyzed at 100°C for 1 min and 300°C for 4 min, followed by crystallization in a lead-rich rapid thermal annealer for 1 min at 700°C. This process was repeated ~ 20 times until a total thickness of ~ 2.0 µm was achieved.

In order to investigate various compositions, an inverted mixing order process was used to prepare PZT solutions with different Zr/Ti ratios [26-32]. In this case, 0.4 M solutions of PZT with Zr/Ti ratios of 52/48, 40/60, 30/70, and 20/80 were used. The procedure is given in the Appendix. These were spun on the hot-sputtered Pt substrates with the Mitsubishi seed layer at 3000 RPM for 30 seconds. The film was pyrolyzed at 250°C for 30 sec and 400°C for 1 min, followed by crystallization in a lead-rich rapid thermal annealer for 2 min at 650°C. The top Pt electrodes were patterned via liftoff and annealed at 600°C for 1 min. These samples were then diced. Pieces were adhered to the center of a Si wafer, and strain gauges were superglued onto the die, whereupon the  $e_{31,f}$  was measured via the wafer flexure method [33].

Next, 14 mol% lead excess Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> solution doped with 2% Nb (Mitsubishi Materials Corporation, Hyogo, Japan) was spun on at 2750 rpm for 45 sec. The film was pyrolyzed at 100°C for 1 min and 300°C for 4 min, followed by crystallization in a lead-rich rapid thermal annealer for 1 min at 700°C. This process was repeated ~ 20 times until a total thickness of ~2.0  $\mu$ m was achieved. The resulting PZT had a Lotgering factor > 97%. The top Pt electrodes were patterned via liftoff and annealed at 600°C for 1 min. The wafer was then diced and clamped to the center of a Si carrier wafer, and strain gauges were glued onto the die.

Following sample fabrication, the effect of DC bias on  $e_{3l,f}$  and  $\varepsilon_r$  were measured on

clamped samples that resembled the PMUT used in underwater acoustic experiments, save for the fact that it was not released from the underlying substrate. Prior to characterizing the relative permittivity and piezoelectric measurements as a function of DC bias, a device was poled at 35 V for 20 min at 150°C. Pre-poling allows the DC bias dependence to be deconvoluted from poling, as was apparent in previous studies. The wafer flexure method was used to characterize  $e_{31,f}$ .

The design, fabrication process, and characterization for the circular 6 - 8 MHz PMUTs are described elsewhere [19, 25]. The PMUT was wire-bonded to a pin grid array (PGA) or circuit board and coated with 2  $\mu$ m of parylene for waterproofing.

The receive sensitivity was obtained with the setup in Fig. 4.1. The bulk transducer, functioning as a pressure source, was excited using a unipolar 5  $V_{pp}$  burst sine waveform at its resonance, 3.5 MHz, at 8.5 mm distance from the receiving PMUT.

For photoacoustic measurements, the PMUT was submerged in a distilled water tank facing a black card, as seen in Fig. 4.2. A tunable (680 – 980 nm) nanosecond laser (Phocus Mobile, Opotek Inc., Carlsbad) delivered 10 ns pulse width laser pulses at 10 Hz pulse repetition frequency and 120 mJ/pulse energy through a custom-fabricated fiber optic bundle (Fiberoptic Systems Inc., CA). For photoacoustic imaging measurements, the PMUT was housed in a custom printed circuit board and optical fiber bundle apparatus with an additional external gain of 20 dB as described elsewhere [19, 25]. Pencil leads of 0.3 mm diameter were suspended in an agar-gel phantom at different heights to test the photoacoustic sensitivity of the PMUT as a function of depth, and to see if DC biasing produced improved depth sensitivity. The preparation of the agar-gel phantom is described elsewhere [13]. A single element of the PMUT was linearly scanned across the fixed target and the photoacoustic A-lines were compiled to form a B-mode photoacoustic image.

For pitch-catch measurements, the PMUT was placed inside a pin-grid array cavity, which

was then filled with distilled water. A glass slide was placed on top of the cavity, acting as a reflector. One PMUT element was excited with a single cycle of unipolar 5  $V_{pp}$  in a sinusoidal burst mode. Another PMUT element functioned as a receiver with an external 39 dB gain. A bias tee was used to apply a DC bias while the PMUT during receive.



Fig. 4.2. Experimental setup for (a) acoustic and (b) photoacoustic measurements. For pitch catch measurements, the bulk transducer source in (a) was replaced with a glass slide.

# 4.3. Results and Discussion

First, the pressure output of a single rectangular diaphragm PMUT was compared to the pressure output of a single element of 20 circular diaphragms shorted together (this was acoustically characterized in Chapter 2). The result is shown in Fig. 4.3. The active areas for the circular diaphragm design (20 circular diaphragms) and the single rectangular diaphragm were  $\sim$ 56550 µm<sup>2</sup> and  $\sim$ 79900 µm<sup>2</sup>, respectively; the rectangular diaphragm has approximately 1.4 times the effective area. Using a hydrophone as a receiver and the PMUT element as a transmitter (at 5 V<sub>pp</sub> unipolar sinusoidal burst at the resonant frequency) the pressure output was  $\sim$  2x greater for the rectangular design than the circular diaphragm. Differences relative to the increased effective

area could potentially be due to multiple elements being excited together via crosstalk. In addition, the displacement and velocity were expected to be different for these devices, as the Si device thickness was 2.5 times thicker in the rectangular design compared to the circular design. Moreover, the target frequency for the rectangular design was different to the circular (15 MHz and 8 MHz, respectively). It is expected that the higher the frequency, the higher the attenuation. In addition, based on equations (1-5) and (1-6), if the frequency increases, so does the pressure output. However, in PMUT applications, the relationship is more complicated; as frequency increases, the PMUT diaphragm can become thicker/stiffer and/or the diaphragm area reduces, which also effects the effective area output.



Fig. 4.3 Hydrophone signal and pressure output for the rectangular diaphragm and circular diaphragm element designs.

The rectangular and circular diaphragms were further compared by measuring their deflection with a laser doppler vibrometer (Polytec, Irvine, CA, USA). An overall frequency spectrum is presented in Fig. 4.4, and the displacement data of the main peaks as a function of actuation voltage is given in Table 4.1. The rectangular diaphragm analyzed here were below the target resonant frequency of 15 MHz, presumably due to over-etching similar to the circular devices in Chapter 2 (see Fig. 2.5 and 2.6). Based on Fig. 4.4, the frequency spectrum has several more peaks and is much more complex than the spectrum of the circular diaphragm (see Fig. 2.5). This complexity in the resonance behavior is not easily explained. Two possible contributions could be (1) variations in the backside etch and (2) the interference of higher harmonics arising from the length mode, which can be seen in Fig. 4.4 (a) peak (b), where a large displacement is seen at 0.543 MHz. Additional sub-modes can be seen within the rectangular diaphragm as the entire diaphragm moves out of plane, as seen in Fig. 4.4 (g-m).

Moreover, the in-air deflection for rectangular diaphragms was significantly different lower than the circular diaphragm (~ 8 nm/V vs 40 nm/V, respectively). One contribution could be the thickness of the Si device layer was 2.5 times thicker for the rectangular design compared to the Si device design. A stiffer diaphragm will vibrate less. In addition to having a larger effective area, one possible reason by which the rectangular diaphragm outputs larger pressure in water compared to the circular diaphragms is that a stiffer diaphragm can vibrate against water loading more effectively than a less stiff diaphragm. It is recommended that COMSOL simulations should be used to evaluate the optimal stiffness for maximum displacement, as well as to analyze the various peaks seen in Fig. 4.4.



Fig. 4.4. (a) Overall frequency spectrum of rectangular PMUTs and the corresponding modes at each peak (b-m). The peaks were (b) 0.543 MHz, (c) 1.332 MHz, (d) 2.862 MHz, (e) 4.39 MHz, (f) 6.48 MHz, (g) 8.78 MHz, (h) 8.99 MHz, (i) 11.44 MHz, (j) 13.42 MHz, (k) 15.08 MHz, (l) 16.39 MHz, (m) 19.89 MHz.

TABLE 4.1: DISPLACEMENT AT MAIN PEAKS			
Actuation	6.48 MHz	8.77 MHz	0.543 MHz
Voltage (V <sub>pp</sub> )	Displacement (nm)	Displacement (nm)	Displacement (nm)
10	62	83	312
8	_	62	_
6	46	47	194
4	21	32	130
2	11	17	65

The second factor that was studied in this chapter is the composition of the piezoelectric layer. The X-Ray diffraction patterns and FESEM images of various PZT compositions are shown in Fig. 4.5. The Lotgering factors are similar and show highly oriented, phase pure perovskite PZT for each composition. As expected, the degree of tetragonal splitting increases as the film becomes more Ti rich. In addition, the grain sizes were determined using the line-intercept method. The grain sizes for 52/48, 40/60, 30/70, and 20/80 were  $212 \pm 19$  nm,  $203 \pm 113$  nm,  $197 \pm 24$  nm, and  $232 \pm 26$  nm, respectively, indicating statistically similar grain sizes for all compositions.



Fig. 4.5. Structural characterization of fabricated samples of various PZT compositions. (a) XRD analysis and (b - e) are surface FESEM images. (\* = substrate peaks)

The baseline dielectric characterization of the films is given in Fig. 4.6. As expected, the permittivity decreases as the film moves off the morphotropic phase boundary (MPB). As the composition approaches lead titanate, the remanent polarization increases due to increased tetragonality, and possibly a reduction in the film stress. It should be noted that for the 20/80 composition, a maximum of 400 kV/cm was applied for the hysteresis loop, as it becomes leaky at greater electric fields, which agrees with literature expectations [21].



Fig. 4.6. (a) Permittivity vs frequency and (b) hysteresis loops of various PZT compositions.

Afterwards, the devices were hot poled to allow the DC bias dependence to be determined with reduced convolution with poling. The permittivity ( $\varepsilon_r$ ) and piezoelectric coefficient ( $e_{31,f}$ ) as a function of DC bias was then investigated. The results are given in Fig. 4.7 for the PZT 52/48 film. At 15 V (75 kV/cm), the permittivity decreases by a factor of 0.6 and the piezoelectric coefficient decreases by a factor of 1.7 relative to their zero bias values. The  $e_{31,f}$  starts to saturate at ~ 10 V, corresponding to the value of the coercive field ~ 50 kV/cm. Based on the normalized voltage coefficient, the receive sensitivity is expected to be improved by ~ 2.5 times with a DC bias of 15 V.



Fig 4.7 (a) Permittivity, (b) piezoelectric coefficient, and (c) voltage coefficient as a function of DC bias 52/48 composition.

In addition, the tunability of the different PZT compositions was investigated. The results are presented in Fig. 4.8. The tunability change for the 52/48, 40/60, 30/70, and 20/80 compositions were 43%, 30%, 16%, and 11%, respectively at an electric field of 75 kV/cm. The PZT 52/48 had the largest value in the piezoelectric coefficient and permittivity tunability, as expected, since the polarizability is at a maximum at the brink of structural instability (i.e. at the MPB). The decrease in the permittivity and piezoelectric coefficient as a function of composition was different. From the MPB to PZT 20/80, the permittivity and piezoelectric coefficient decreased by a factor 65% and 43%, respectively.



Fig 4.8 (a) Permittivity and (b) piezoelectric coefficient, as a function of DC bias with various PZT compositions.

The resulting voltage coefficient, or receive sensitivity, is given in Fig. 4.9. With 0 DC bias, if a PMUT is functioning as a receiver, PZT 20/80 should be used due to its higher voltage coefficient than the other compositions. However, when a DC bias of 75 kV/cm is applied, the voltage coefficient of a 52/48 composition can match and potentially surpass the voltage coefficient of the PZT 20/80 composition.



Fig 4.9 (a) Voltage coefficient versus DC bias for various PZT compositions.

The underwater receive sensitivity and photoacoustic sensitivity as a function of DC bias are shown in Fig. 4.9. The ultrasound receive sensitivity and the photoacoustic receive signal were found to increase by approximately two times, agreeing with the electrical measurements in Fig. 4.10. With no DC bias, the  $e_{31,f}$  and the permittivity were – 10 C/m<sup>2</sup> and 1300, respectively, with  $h_{31,f} = -0.0062$  C/m<sup>2</sup>. At 15 V DC bias, the  $e_{31,f}$  and the relative permittivity were –13.8 C/m<sup>2</sup> and 740, respectively, with  $h_{31,f} = 0.018$  C/m<sup>2</sup>. This is ~ 18% of the voltage coefficient of AlN, which has a piezoelectric coefficient and permittivity of -1.05 C/m<sup>2</sup> and 10.5, respectively [4, 5].



Fig 4.10 (a) Ultrasound receive signal and (b) normalized photoacoustic signal as a function of DC bias based on setups in Fig. 4.1 (a) and (b), respectively. (c) indicates the center frequency and bandwidths as a function of DC bias. The device used for these was PZT 52/48 with 2 µm thickness.

It has been reported that the resonant frequencies and bandwidth can increase as much as 33% with an applied DC bias for air-coupled transducers [5]. This may be a consequence of the applied voltage increasing the in-plane stress of the piezoelectric. The stress can dominate over flexural rigidity and can thus increase the resonant frequency [14]. To examine whether significant changes can be seen in operating frequency and bandwidth as a function of DC bias, the center frequency and bandwidth were extracted from the Fourier transform of the pitch-catch and photoacoustic receive signals, as shown in Fig. 4.10 (c). For both cases, the center frequency (6.89 MHz) and bandwidth (photoacoustic 69% and pitch catch bandwidths were 41%, respectively) remained relatively constant as a function of DC bias (from 0 - 15 V); the center frequency had a standard deviation of 0.6%. The photoacoustic bandwidth and pitch catch bandwidths had a standard deviation of 2% and 8%, respectively. The photoacoustic center frequencies and bandwidth also showed little variation with DC bias, albeit the photoacoustic bandwidth was higher (69%) than the pitch-catch bandwidth (41%). The higher bandwidth for photoacoustics compared to pitch-catch is due to two factors: first, in pitch-catch ultrasound imaging, spatial resolution is governed by the frequency of the transmitted acoustic wave arriving at the receiver, whereas in photoacoustic imaging, the laser pulses have nanosecond-scale excitation with much wider frequency content [15, 16]. Second, the bandwidth for one-direction sound propagation is larger than two-way bandwidth [17].

B-mode photoacoustic images were reconstructed from the raw voltage-time data, as shown in Fig. 4.11 and Fig. 4.12. Without DC bias, a clear photoacoustic signal was only obtained from four of the five pencil leads, the fourth being at  $\sim 3.7$  cm in depth. With 15 V DC bias, the photoacoustic signal was increased for all pencil lead targets compared to those without DC bias.

In addition, the PMUT was able to receive a photoacoustic signal from the fifth pencil lead at 4.3 cm depth. From Fig. 4.11, it can be seen that there was an  $\sim 20$  dB improvement in the image signal. The cause of this is that images with and without DC bias was subjected to log compression together in the same data matrix, e.g. the raw data for Fig. 4.11 (b) and (c) were subjected to one log compression operation for an overall image comparison. Thus, when compressing the two images in a single data matrix, the normalization convoluted both datasets and caused the observed signal intensity difference between the two images to be much greater than 2 times. When the log compression was done separately for each image (where the raw data for Fig. 4.11 (b) was subjected to one log compression and Fig. 4.11 (c) was subjected to another log compression, and so each constructed image was normalized to its own dataset), as shown in Fig. 4.12, the photoacoustic signal with DC bias was  $\sim 2$  times greater than the signals seen without DC bias, agreeing with the electrical measurements. It is observed that the signal-to-noise ratio (SNR) was significantly better with DC bias than without DC bias, and applying the log compression of both images in the same dataset had caused the larger improvement in the imaging signal and quality. It is not clear why this should be the case. The cause of the DC bias improving the signal to noise ratio should be explored in future work.



Fig. 4.11 (a) Picture of the light-guide fiber optic assembly housing the PMUT. The PMUT is facing downward at the agar gel phantom with pencil leads of varying heights. The resulting images are with (b) DC bias and (c) 15 V DC bias operation (75 kV/cm) for 52/48 composition. Log compression was done together with (b) and (c) for comparison.



Fig. 4.12 Images of Fig. 4.11 where log compression was done for separately images for (a) without DC bias and (b) with DC bias.

#### 4.4. Conclusions

This chapter presents a method to increase the transmit and receive sensitivities of PZT based PMUTs. By increasing the effective area ~ 1.4 times and choosing a single rectangular diaphragm element design rather than a series of circular diaphragms connected in series element design, the pressure output increased ~ 2 times. The receive sensitivities increased by ~ 2 times when 15 V (75 kV/cm) is applied to the PZT PMUT, due to the increase in the  $e_{31,f}$  and a decrease in the relative permittivity. Operating at a 15 V DC bias also yielded stronger photoacoustic signals and allowed detection of signals at greater depths compared to without DC bias. When no DC bias is applied, PZT with composition 20/80 has a significantly higher voltage coefficient than all other compositions. When 15 V DC bias is applied, PZT 52/48 can match and potentially exceed the receive sensitivity of PZT 20/80. Thus, operating at higher electric fields in piezoelectric materials can improve sensitivities. It is likely that a comparable improvement could be achieved by

imprinting the PZT; this would be useful as it would allow higher receive sensitivities for the PMUT without the need for a DC bias on receive.

4.5. References

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### **Chapter V: Crack Propagation Energies vs Composition**

# 5.1. Introduction

Thin film-based piezoelectric devices are typically driven to high fields and are subject to higher stresses and strains than are bulk ceramics of the same composition. These thin films often have high levels of residual stresses which affect both the domain structure and piezoelectric properties [1-5]. Moreover, if the combination of residual stress, applied stress, and piezoelectrically-induced stresses exceed a material-dependent threshold, it can induce cracks or delaminations [6-7]. Film thickness, poling conditions, lead content, crystallographic orientation, temperature, dopants, surface quality and grain size [8-16] all influence crack formation in PZT films and ceramics. Cracking in piezoelectric films can also induce subsequent thermal dielectric breakdown events, causing failure [17, 18]. Thus, a knowledge of the mechanical limits of PZT is required to appropriately design usage conditions for the films.

One factor that can influence the propensity for cracking in PZT ceramics is toughening associated either with stress-induced ferroelastic domain reorientation or with stress-induced phase changes. PZT ceramics tend to become tougher as cracks elongate – this is known as R-curve behavior. It is reported that stress-induced ferroelastic domain switching is the primary toughening mechanism in PZT ceramics [15-26]. When a crack-tip domain is exposed to high mechanical stress under an applied load, the ferroelastic domains reorient to reduce the local stresses. An example is shown in Fig. 5.1.



Fig. 5.1. A simplified schematic of ferroelastic switching for ferroelastic toughening. In (a), c-domains in PZT before any stress is applied to the sample. In (b) after a crack forms, when a c-domain switches to a-domain, it reduces the local stress, reducing the drive for crack propagation.

Ferroelastic toughening is influenced by three material properties: coercive stress, saturated strain, and elastic modulus [16-26]. Of these, the coercive stress has the greatest influence on toughness enhancement, as it determines the process zone size [19]. In principle, ferroelastic toughening should increase with greater lattice distortion (e.g., higher tetragonal PZT distortions) such that a given volume fraction of domain reorientation would lead to larger compressive stresses on the crack [14-19]. A second reported contribution to toughening is stress-induced phase transformations. During mechanical loading, adjacent grains interact with one another, generating local stresses which drive transformations between different ferroelectric distortions [27].

The phenomenon of stress-induced ferroelastic domain switching and phase transformation is well documented in literature. Zhang et al. showed that when subjecting PZT ceramics to high compressive stress, the elastic stiffening behavior varied between PZT-5H, PZT-5A, PTZ-4, and PZT-8. Samples de-poled at lower stresses in soft PZT materials compared to hard materials [28]. The coercive stresses for soft ceramics were reported to be ~ 40-50 MPa; for hard ceramics they were ~ 60 – 150 MPa [28]. Seo et al. found that the coercive stresses were dependent on PZT composition, with a minimum of ~ 50 MPa at the MPB and increasing to ~ 200 MPa at 60% PbTiO<sub>3</sub> concentrations [27]. Seo et al. also reported that tetragonal PZT ceramics show lower ferroelastic toughening than rhombohedral compositions [14]. In particular, coercive stress is
strongly dependent on lattice distortion; an increase in the lattice distortion increased the coercive stress, resulting in fewer switched domains and lower toughening [14].

Ferroelastic switching, and thus ferroelastic toughening, can be enhanced in two different ways: having a large c/a ratio (large distortion) and/or having a large starting population of c domains to be available for switching. It is well known that the Zr/Ti ratio influences ferroelectric, ferroelastic, and domain populations in thin films [29-32]. It is likewise known that films under compression induce c-domains, while films under tensile stress induce a-domains [10]. Thus, the Zr/Ti content can potentially affect the degree of ferroelastic switching and ferroelastic strengthening.

The cracking behavior of PZT thin films has been documented in the literature. Finite Fracture Mechanics (FFM) describes two conditions that need to be fulfilled for crack initiation: stress and energy conditions [33-35]. Firstly, the normal tensile stress should be larger than the material tensile test, and secondly, the increment of the potential energy for finite crack length increment should be greater than the material toughness. Cracks initiate only when both conditions are met. The energy criterion depends on the material's ability to store energy before cracking; as the thickness of the material decreases, more work and energy is needed to create new surfaces. Indeed, Coleman et al. showed that for PZT 52/48 films, the crack initiation stress increased when the film thickness decreased [17, 18]. In addition, the characteristic strength of the PZT film/substrate stack decreased with increasing film thickness; it was found that the PZT film thickness functions as the initial crack length that initiates failure of the stack at higher loads [17, 18]. Whether this holds true at compositions off the morphotropic phase boundary has not yet been explored.

Additionally, it has been shown that the electrical and mechanical history of PZT has a strong effect on its propensity of cracking [17, 18, 36]. Thin films experience residual thermal stresses from processing, electrically-induced stresses from piezoelectric responses, and applied stress from bending. In many films, the residual stress state arises from the PZT film cooling down from the crystallization temperature ( $T_{crystallization}$ ) to the Curie temperature ( $T_c$ ). The residual thermal stress,  $\sigma_t$ , is associated with the thermal expansion coefficient mismatch between the film and the substrate, and can be calculated via

$$\sigma_t = \frac{\int_{T_c}^{T_{crystallization}} (\alpha_{CTE,f} - \alpha_{CTE,sub}) dT}{\left[ \left( \frac{1 - \nu_f}{Y_f} \right) + \left( \frac{1 - \nu_{sub}}{Y_s} \right) \left( 4 \cdot \frac{t_f}{t_{sub}} \right) \right]}$$
(5-1)

where  $T_{crystallization}$ ,  $T_c$ ,  $\alpha_{CTE}$ , v, and Y are the crystallization temperature, Curie temperature, thermal expansion coefficient, Poisson's ratio, and Young's modulus, respectively [18, 37]. The subscripts of f and *sub* denote film and substrate, respectively. If the substrate is significantly thicker than the film, Equation (5-2) can be further simplified to

$$\sigma_t = \left(\frac{Y_f}{1 - v_f}\right) \int_{T_c}^{T_{crystallization}} \left(\alpha_{CTE, f} - \alpha_{CTE, sub}\right) dT$$
(5-2)

For PZT, the Curie temperature increases with increasing tetragonality (more PbTiO<sub>3</sub>) [38, 39]. Thus, as the crystallization temperature cools to the Curie temperature, film stress decreases with increasing tetragonality based on Eqn. (5-1) and (5-2). Therefore, PZT films with less residual thermal stress should be able to withstand higher applied stresses.

This chapter investigates the crack initiation stresses of PZT thin films at Ti-rich compositions off the morphotropic phase boundary and examines the possible mechanistic contributions that affect the crack behavior of these compositions.

### 5.2 Experimental Fabrication and Setup

PZT compositions of 52/48, 40/60, 30/70, and 20/80 composition were prepared on fourinch Si wafers with ~ 45 nm TiO<sub>2</sub> and 100 nm of hot sputtered platinum as described in the Appendix. The PZT was prepared and deposited using the inverted mixing order solution procedure described in Chapter 4 and detailed in the Appendix. The samples were all (001) oriented with a target thickness of 2.0  $\mu$ m. 100 nm Pt top electrodes were deposited via sputtering and patterned via lift off on some samples.

The samples were then diced into 1.2 cm x 1.2 cm squares, which were placed in the ballon-3-ball (B3B) measurement setup to evaluate the strength of the entire stack (PZT/Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si) and crack initiation stress in the PZT films, as described by Coleman et al. [17, 18]. A schematic of the B3B setup is shown in Fig. 5.2. Here, the square sample was supported by one ball on the bottom side and three balls on the top surface of the sample. All the balls had a diameter of 7.5 mm. The bottom remained fixed while the load pressed down on three balls on top, generating a biaxial tensile stress at the very center of the sample, with the PZT surface facing upwards. A pre-load of  $\sim 10$  N was employed to hold the sample between the four balls, and all tests were conducted at room temperature with a compression displacement control of 0.1 mm/min on a universal tester (Instron, MA) At least ten samples were tested to failure per composition to obtain a Weibull analysis on the strength of the sample stack. To investigate crack initiation stresses, the samples were loaded at approximately 30% - 95% of the characteristic Weibull strength. Each new load condition required a new sample (all samples were only loaded once). Afterwards, the surface of the PZT was evaluated for cracks via FESEM and dark field optical microscopy.

The different PZT compositions were also tested for microcracking when subjected to an electric field. The samples were driven from the bottom electrode, and hysteresis loops were conducted at incrementally higher electric fields: 200 kV/cm - 500 kV/cm at 100 Hz for each of the compositions. The surface of the top platinum electrode was evaluated for microcracking.



Fig. 5.2. Ball on 3 Ball (B3B) setup.

## 5.3. Results and Discussion

The XRD and FESEM images of the different compositions are shown in Fig. 5.3. They all had similar Lotgering factors (>95%) and (001) oriented single phase PZT, although pyrochlore was present on the surface for the 40/60 and 30/70 compositions. The grain sizes were statistically similar for the 52/48 (195 ± 15 nm), 40/60 (186 ± 36 nm), and 30/70 (218 ± 17 nm) compositions. It was found that the microstructure was significantly different for the 20/80 PZT compared to the other compositions (the grain size of the 20/80 composition was 126 ± 40 nm). It is possible that

the smaller grain sizes in the Ti-rich samples were due to greater lead retention in the tetragonal films. The crystallization temperature of PbTiO<sub>3</sub> is lower than PbZrO<sub>3</sub>, therefore when the Zr/Ti ratio increases, the time for PbO loss increases, and vice versa [40]. Lead is also known to induce more grain nucleation [11, 12]. Thus, the 20/80 composition was excluded for the B3B in this study.

The Weibull modulus and characteristic strength of the stack extracted from the B3B data via Weibull analysis using the Equation 5-3,

$$P_f(\sigma) = 1 - \exp\left(-\left(\frac{\sigma}{\sigma_o}\right)^m\right)$$
(5-3)

where  $P_f(\sigma)$  is the probability of failure at a certain applied stress ( $\sigma$ ), *m* is the Weibull modulus and  $\sigma_o$  is the characteristic Weibull strength (where the probability of failure below this applied stress is 63%) [41, 42].

The resultant Weibull modulus and characteristic strengths for each composition are given in Fig. 5.4 and Table 5.1. The MPB composition was found to have a Weibull modulus and characteristic strength of 11-24 and 1091-1137 MPa, respectively, at 95% confidence interval. This agrees with previous studies conducted by Coleman et al. showing that MPB PZT films reduce the strength of the entire stack and increase the Weibull modulus from that of the Si substrate [9, 18]. That is, the crack in the PZT is the critical flaw size for the entire stack. In this case, the PZT thickness provides a well- defined critical flaw size, resulting in a higher Weibull modulus than that of the substrate [9, 18].



Fig. 5.3. (a) XRD of PZT compositions and FESEM images of (b) 52/48, (c) 40/60, (d) 30/70, and (e) 20/80. The asterisks indicate substrate peaks. The grain sizes and Lotgering factors were all statistically similar apart from the grain size achieved as seen in part (e).

In contrast, the Weibull modulus for the 40/60 and 30/70 composition were 4.6 – 6.2 and 2.5-3.6, respectively, at 95% confidence interval. This was much lower than the value for the MPB composition. Moreover, the characteristic strength for the 40/60 and 30/70 compositions were 1453 - 1705 MPa and 1355 - 1807 MPa, respectively, at 95% confidence interval. This was little changed from that of the SiO<sub>2</sub>/Si substrate (Weibull modulus and characteristic strength of 2.3 – 2.8 and 1647 - 2126 MPa, respectively). That is, as the PZT composition increases in tetragonality, the Weibull moduli and characteristic strength approach the Weibull moduli and characteristic strength of the SiO<sub>2</sub>/Si substrate. A low Weibull modulus indicates a wide distribution of critical flaw sizes, which is known to be the case for Si [43-46]. Thus, the lower Weibull modulus with increasingly tetragonal compositions suggest that either a) the non-MPB PZT films have cracks with a broad distribution of critical flaw sizes, such that the film thickness does not act as a characteristic flaw size and/or b) the PZT layer does not crack prior to failure of the SiO<sub>2</sub>/Si stack.



Fig. 5.4. Probability of failure vs. failure stress for 2-micron thick PZT films with different Zr/Ti ratios on  $Pt/TiO_2/SiO_2/Si$  substrates

Composition	Characteristic Load	Characteristic	Weibull Modulus	
_	(N)	Strength (MPa)		
52/48	130	1137	17	
	[125 – 135]	[1091 – 1183]	[11 - 24]	
40/60	180	1579	6.7	
	[166 - 195]	[1453 - 1705]	[4.6 - 8.2]	
30/70	181	1581	3.0	
	[155 - 207]	[1355 - 1807]	[2.5 - 3.6]	
SiO <sub>2</sub> /Si	216	1887	2.5	
	[189 - 244]	[1647 – 2126]	[2.3 - 2.8]	

Table 5.1: Characteristic Load, Characteristic Strength, and Weibull Modulus for Various PZT Compositions on SiO<sub>2</sub>/Si Substrates and SiO<sub>2</sub>/Si Substrate Reference [17, 18]. Brackets indicate 95% confidence intervals.

To evaluate crack initiation stress, specimens with the 40/60 and 30/70 films were loaded at either ~ 30% or ~90% of the characteristic Weibull strength. In neither case were cracks were discernable on the PZT surface. This contrasts with the data on PZT 52/48 films, where obvious cracks were visible in the electron microscope below the stack strength; these cracks extended through the PZT thickness and served as the flaws that lowered the stack strength and increased the Weibull modulus [17, 18]. Absence of pre-cracking (and hence absence of a characteristic crack length) in the PZT 40/60 and 30/70 compositions is consistent with the low observed Weibull modulus and the high stack failure strength. That is, the PZT film thickness did not act as the critical flaw size for stack failure; a wide distribution of flaws in the SiO<sub>2</sub>/Si substrate governed failure in samples with tetragonal PZT films.

There are at least two mechanisms that might contribute to the reduced observation of cracking in the tetragonal films, relative to the MPB PZT contributions. First, in tetragonal PZT, ferroelastic domain switching between a and c domains can act to reduce local stresses, and so could increase the toughness. To ascertain the different domain populations of the films in this study, the {002} XRD peaks of the different compositions were analyzed via Pseudo-Voigt peak fitting in LIPRAS software. While two peaks were initially fitted to the data (corresponding to the

a and c-domains), a better result was achieved when three peaks were fitted (*a*-domain, rhombohedral, and *c*-domain), as seen in Fig. 5.5. Evidence of the rhombohedral phase was present even in compositions far from the MPB via XRD peak fitting. This can potentially arise from composition gradients during the sol-gel deposition process, the influence of film stress, and/or inhomogeneity in the sol-gel solution. For example, Ti-rich conditions at the bottom of the layer led to Zr/Ti gradient formation as PbTiO<sub>3</sub> provides favorable nucleation in comparison to PbZrO<sub>3</sub> [12, 47, 48]. Moreover, Vaxelaire et al. found that the crystallographic gradient correlated to Zr/Ti chemical gradients; thus, the entire PZT film may not be at the MPB even if produced using a precursor solution with the correct average stoichiometry, but can instead alternate between rhombohedral (Zr-rich zones) and tetragonal (Ti-rich zones) [49].



Fig. 5.5 Pseudo-Voigt fits of the {002} XRD peak for (a) 52/48, (b) 40/60, and (c) 30/70 films.

To verify the presence of concentration gradients, Scanning Transmission Electron Microscopy (STEM) was used in conjunction with Energy-Dispersive X-Ray Spectroscopy (EDS). The samples were prepared creating a cross section with a Helios 660 and a Scios 2 Focused Ion Beam (FIB)/SEM. Trevor Clark did the FIB preparation and Ke Wang the TEM. Regions of interest were protected with beam-induced carbon deposited via the electron beam and then the ion beam. The ion beam deposition and milling are performed at 30 kV with currents as high as 30 nA for trenching, with the exception of the final polishing step at 5 kV. The cross-sectional TEM specimens were observed by FEI Titan<sup>3</sup> G2 double aberration-corrected microscope at 300 kV. The STEM images were collected using a High Angle Annular Dark Field (HAADF) which had a collection angle of 52-253 mrad. EDS maps and line scans were collected by using a SuperX EDS system under STEM mode. The results are shown in Fig. 5.5. The PZT 52/48 composition had Zr gradients that fluctuated from 45 to 60 mol% at the 25<sup>th</sup> and 75<sup>th</sup> percentile range from the box-and-whisker plots shown in Fig. 5.6; this is comparable to reported composition fluctuations in other PZT sol gel solutions on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates [50, 51]. The interquartile range for the mole fraction Zr was similar for all compositions 16.1, 16.1, and 15.2 mol% for 30/70, 40/60, and 30/70 compositions, respectively. The interquartile range for the mole fraction of Pb was also similar for all compositions (20, 16, and 16 mol% for 30/70, 40/60, and 30/70 compositions, respectively. It is believed that one cause of the observed rhombohedral phase is these concentration gradients. The presence of mechanical strains, local strains, or a shift in the MPB due to non-stoichiometry and the presence of lead on the B-site [52, 53] are additional factors that could induce a rhombohedral phase off the MPB.



Fig. 5.6. TEM line scans of PZT compositions (a) 52/48 (b) 40/60 and (c) 30/70. The films were acquired such that the position is perpendicular to the substrate. Position 0 is the film surface. The extrema correspond to each of the crystallization layers, with high Ti and Pb concentrations near the bottom of each crystallized layer and high Zr contents at the top of each crystallized layer (d) box-and-whisker plots of the gradients of Zr, Pb, and Ti for each composition.

Returning to the X-ray data, XRD peak fittings are shown in Fig. 5.5. Each fit had ~ 99% adjusted  $R^2$ , indicating good fits to the experimental XRD data. The three peaks correspond to *c*-domains, *a*-domains and the rhombohedral phase. The lattice parameters and area underneath the fitted peaks were extracted from Pseudo-Voigt fits via MatLab and are given in Table 5.2. Fig. 5.7 compares the extracted lattice parameters to those reported by Shirane et al. [54]. When the average film compositions were more Ti-rich, the rhombohedral phase fraction decreased and the

a-domain volume fraction increased. Furthermore, the concentration of c-domains increased with increasing tetragonality.

	Area under fitted curves (%), lattice parameters for each composition					
Туре	52/48	40/60	30/70			
<i>c</i> -domain	1.27%, 4.141 ± 0.007 Å	1.53%, 4.138 ± 0.012 Å	12.00%, 4.121 ± 0.007 Å			
Rhombohedral	58.95%, 4.073 ± 0.003 Å	45.81%, 4.055 ± 0.003 Å	28.46%, 4.073 ± 0.005 Å			
<i>a</i> -domain	39.78%, 4.065 ± 0.004 Å	52.66%, 4.015 ± 0.001 Å	59.54%, 3.996 ± 0.001 Å			

Table 5.2: Lattice Parameters and Percentage Domain Population versus Different Compositions



Fig. 5.7. XRD fittings for the fabricated PZT compositions (a) 52/48, (b) 40/60, and (c) 30/70 and comparison to the lattice parameters from Shirane et al. [54].

The second potential contribution to a higher characteristic strength for tetragonal films is that they have slightly lower residual stresses than MPB films and can thus withstand higher loading stresses, increasing their characteristic strength. To ascertain this, phenomenological parameters were inserted into Equation (5-1); data used in the calculations are given in Table 5.3. It was found that the thermal stresses in the film did not significantly vary between compositions based on phenomenological calculations; the thermal stresses were 82.0 MPa, 87.2 MPa, and 79.9 MPa for the 52/48, 40/60, and 30/70 compositions, respectively. It should be noted that this calculation only addresses the thermal strain on cooling from the crystallization temperature to T<sub>c</sub>, and does not account for any stress relaxation associated with development of the domain state on cooling through  $T_{C}$ 

Material	Poisson's	Elastic	Thermal	Curie	Crystallization	Thickness
	Ratio	Modulus	Expansion	Temperature	Temperature	(µm)
		(GPa)	Coefficient	(°C)	(°C)	
			(1/K)			
PZT 52/48	0.35	95	$4.8 \cdot 10^{-6}$	392.6	650	2.0
PZT 40/60	0.33	116	$4.8 \cdot 10^{-6}$	418.4	650	2.0
PZT 30/70	0.32	119	$4.8 \cdot 10^{-6}$	440.2	650	2.0
Si	0.3	180	$2.6 \cdot 10^{-6}$	Х	Х	500
SiO <sub>2</sub>	0.3	130	$0.5 \cdot 10^{-6}$	X	X	1
Pt	0.39	276	8.9 · 10 <sup>-6</sup>	X	X	0.100

Table 5.3: Mechanical Properties for PZT Sample Stack Used in B3B [18, 53-57]

In addition to examining cracking induced by mechanical loads, the microcracking behavior of each composition was investigated using electric fields of increasing magnitude. For this experiment, the same samples described in Chapter 4, Fig. 4.4 were used. The resultant images are shown in Fig. 5.8. Two findings were of particular interest. Firstly, with increased tetragonality, higher fields are needed to induce cracking. Secondly, as the Ti concentration increased, the average crack density increased; the average crack density (# of crack intersections/ length of line drawn on an optical image) for the 52/48, 40/60, and 30/70 composition were 0.0692  $\pm$  0.0102, 0.1251  $\pm$  0.0270, and 0.1961  $\pm$  0.0364 intersections per micron, respectively. For the 20/80 composition, no visible cracks were observed even after large fields were applied. At least in part, the lower cracking propensity for the more tetragonal films is due to the lower film piezoelectric coefficients than for the MPB composition.



Fig 5.8. Optical images of the top electrode at various electric field magnitudes of hysteresis loops for (a) 52/48, (b) 20/80, (c) 40/60, and (d) 30/70. Enhanced images of the cracks for using the line intercept method to determine the density of cracks are shown for (e) 52/48, (f) 40/60, and (g) 30/70.

In 20/80 compositions, the hysteresis loops show high leakage above 400 kV/cm [47, 48, 57]. In addition, the remanent polarization incrementally increased with multiple applications of an applied electric field of 300 kV/cm, as shown in Fig. 5.9. The 20/80 film did not appear to crack

(as shown in Fig. 5.9 (b). This "wakeup effect" (here exacerbated by an increase in leakage contributions to the loop) is common in hafnium oxide-based films. One source of wake-up is depinning of domains from strong local internal fields. In this work, one potential source of pinning is the concentration gradients in Pb, Zr, Ti, and possible O through the film thickness. It has previously been reported that wakeup effects are more common in Ti-rich phases than Zr-rich PZT [47, 48, 58].



Fig. 5.9. Hysteresis loops for 20/80 composition. It is seen in (a) that the 20/80 composition is leaky, and in (b) there is the wakeup effect (exacerbated by the leakage) after applying 300 kV/cm for multiple iterations.

### 5.4 Conclusions

PZT of 52/48, 40/60, 30/70, and 20/80 compositions were fabricated via the IMO sol-gel method to investigate their respective cracking behaviors. The PZT 52/48 behavior was in good agreement with the work by Coleman et al. [9]. As the composition moved towards PbTiO<sub>3</sub> (a Ti-rich tetragonal regime), the characteristic strength increased while the Weibull modulus decreased to values comparable to that of the Si substrate. It was found that the residual thermal stress accumulated due to thermal expansion differences between the crystallization temperature and the Curie temperature did not significantly vary between average 52/48 to 30/70 compositions; it is

unknown if there was a difference in the relaxation of the stresses due to domain formation below the Curie temperature. Thus, it is speculated that the higher stack strengths are associated with increased toughening due to either ferroelastic switching or phase switching in samples with more Ti-rich PZT. Based on peak fitting, the fabricated PZT compositions had a mixture of a-domain, c-domain, and rhombohedral phases for all compositions; the rhombohedral phase decreased while both a and c-domain fractions increased with increasing tetragonality. TEM line scans confirmed the existence of Zr/Ti concentration gradients in all compositions. This may account for the rhombohedral peak found in the XRD peak fitting, although local strains, local homogeneity, and Pb<sup>4+</sup> on the B-site can also potentially affect the formation of rhombohedral phase. It was also found that with increasing tetragonality, the microcracking density increased as the electric field increased.

From an acoustic device perspective, maximum displacement is desired for actoustic sources. To maximize the displacement, a maximum lateral strain or applied electric field is needed. In scenarios where the PZT compositions do not crack, PZT 52/48 would be ideal due to its large piezoelectric coefficient. Practically, however, the PZT samples do crack in some device configurations (e.g. depending on the release state, the clamping conditions, and the PZT film thickness). Thus, off-MPB compositions are potentially of interest in actuators due to the reduced propensity for cracking, albeit with a tradeoff associated with the need to apply higher electric fields.

It should be noted that in this chapter, the cracking and failure behavior investigated was for clamped films (e.g. films on the substrates, without patterning). In the next chapter, the cracking and failure behavior for released films will be discussed.

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# Chapter VI: Comparison of Released and Non-Released States of PZT-based Multilayer Actuator Devices

### 6.1. Introduction

Piezoelectric multilayer actuator (MLA) devices are often used to replace single layer devices of similar overall thickness due to their high-volume efficiency, coupled with the high output strain at small applied voltages [1-8]. In particular, for the same actuation voltage, a larger displacement can be achieved with multiple layers versus a single layer as the electric field levels are higher [4, 7]. In MEMs medical devices such as PMUTs and microcatheters, this voltage reduction is useful, as it improves safety.

It is critical to note, however, that moving from single layer to multilayer actuators has important implication in terms of reliability. In particular, MLA have both higher active areas, and high fields than single layer actuators of comparable dimensions. Since degradation and failure are more likely as area and field increase, MLA can only be utilized if adequate reliability is achieved. At present, there are no extant studies on reliability in thin film MLA. PZT-based devices are often operated for extended periods in harsh conditions, at elevated temperatures and in uncontrolled humidity. In these conditions, time-dependent dielectric breakdown often occurs; the material's insulating properties fail, and the device becomes conducting. Factors that govern when and how dielectric breakdown and failure occur also affect the stability of the piezoelectric properties. Therefore, understanding failure mechanisms in multilayer piezoMEMS devices is of interest.

Numerous factors influence the time-dependent dielectric breakdown of perovskite ferroelectrics, including microstructure, bulk defect chemistry, defect chemistry at the

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electrode/film interface, thickness, stoichiometry, doping, and electrode materials [9-28]. For example, in SrTiO<sub>3</sub> and BaTiO<sub>3</sub> film, ceramics, and crystals, degradation has been attributed to oxygen vacancy migration. On electromigration, these oxygen vacancies accumulate near the cathode and form a depletion region near the anode [18, 19-21, 24-28].

Defect chemistry and its role in breakdown is more complex in PZT films relative to BaTiO<sub>3</sub> or SrTiO<sub>3</sub>, due to variations in stoichiometry caused by lead evaporation during high temperature processing. Understanding how the defect chemistry, including oxygen vacancies, contributes to failure in PZT devices is crucial. It has been reported that oxygen vacancy migration contributes to PZT film resistance degradation, as oxygen is the most mobile ion in PZT at ambient temperatures [14, 15, 28]. That is, oxygen vacancies migrate under applied electric fields and accumulate near the cathode region, changing the barrier height at the electrode interfaces. PZT films modified with acceptor dopants (i.e.  $Fe^{2+, 3+}$ , and  $Mg^{2+}$ ) have shorter lifetimes than PZT with donor dopants as the acceptors favor oxygen vacancy formation [15, 29]. However, Akgun et al. showed that with increasing Mn-dopant concentration, the activation energy for failure increased from 0.76 eV to 1.33 eV from 0.5% to 4 mol%, respectively [13-15]. It was proposed that the multivalency of the Mn ion allows for electron and/or hole hopping. The Mn ions were distributed throughout the film and thus reduced the likelihood of electron accumulation at the cathode/film interface [14, 15].

The effect of the mechanical release state on reliability is also of interest. Releasing a device removes the underlying substrate, thus removing the substrate clamping effect. This may cause the thermal boundary conditions to change, as there is no underlying substrate (typically Si) to act as an effective heat sink. For instance, Lundh et al. demonstrated that released PZT thin films can generate significant AC Joule heating when actuated at high electric fields (~ 390 kV/cm),

particularly under bipolar operation [30]. Thus, the ability to generate local hotspots for breakdown events can change between clamped versus released films and affect lifetime. Coleman et al. found that released PZT films were less susceptible to failure by cracking, likely due to a reduction in film stress associated with bending, with a possible additional contribution due to enhanced domain wall motion. That is, clamped films cracked under high electromechanical load whereas released films did not under the same conditions [31]. Thus, the release state of the device may play an important role in the mechanism of failure, cracking, and the activation energy to failure. Currently, there is no data comparing HALT data for released and non-released samples. Therefore, this chapter examines the breakdown behaviors of clamped and released PZT films from MLA devices.

### 6.2 Experimental Setup

The fabrication process for the MLA is shown in Fig. 6.1, optimized by Wanlin Zhu and Jung In Yang. The substrate was a ~ 400-micron Si wafer, with a stack of 165 nm Pt, 37 nm TiO<sub>2</sub>, 80 nm of Al<sub>2</sub>O<sub>3</sub>, 1  $\mu$ m of SiO<sub>2</sub>. A seed layer of PMZT (12 wt%, 20% lead, 44/56 Zr/Ti ratio, and 2% Mn doping) (Mitsubishi Materials, Inc.) was deposited via sol-gel deposition at 3500 RPM for 45 seconds, pyrolyzed at 200 °C for 2.5 min, and crystallized at 700 °C for 1 min with 2 slpm O<sub>2</sub> flow. This was done so that the Mn would prevent accumulation of electronic charges on Ti atoms at the cathode/PZT film interface and improve lifetime [14, 15]. Afterwards, the majority of the film was deposited via sol gel processing with PZT solution (14 wt% lead, 52/48 Zr/Ti ratio, and 2% Nb doping) (Mitsubishi Materials, Inc.), with a spin speed of 2750 RPM for 45 seconds and two pyrolysis steps (100 °C for 1 min and 300 °C for 4 min). Two spin/pyrolysis sequences were followed by a crystallization step at 700 °C for 1 min with 2 slpm O<sub>2</sub> flow. This cycle was repeated

until the total thickness was 750 nm. A capping layer with the same composition as the seed layer was deposited at 4500 RPM for 45 seconds with the same pyrolysis and crystallization steps.

Afterwards, a blanket layer of 100 nm platinum was sputtered at a substrate temperature of 320 °C to minimize lead loss. A thin lanthanum nickelate layer (Mitsubishi Materials, Inc.) was used as a seed layer to help promote (001) orientation of the subsequent PZT layer. The lanthanum nickelate solution was spun on the platinum surface at 3000 RPM for 20 seconds, dried at 75 °C for 2 min, pyrolyzed at 400 °C for 5 min, and crystallized at 700 °C for 1 min with 2 slpm O<sub>2</sub> flow. Then, the second PZT layer was formed using similar processing techniques. A final 100 nm platinum layer was sputtered at room temperature.

Following deposition of the blanket layers, the electrodes and PZT layers were then patterned via reactive ion etching (the conditions are listed in the Appendix). During the etch process, there are several potential sources for damage to the PZT film (1) hydrogen liberated from the photoresist can be trapped in the PZT, (2) crystallographic damage can occur at bombarded surfaces, and (3) the surface chemistry of the film can change if one ion is more easily removed than another. Thus, the wafer was treated to a two-step anneal developed by Wanlin Zhu and Jung In Yang to reduce any etch damage; the two steps were 500°C for 30 min in a box furnace and 650°C for 5 min in the RTA. It is not known whether both steps are needed.

Afterwards, 94 nm of aluminum oxide was deposited at 200 °C by PEALD as a passivation layer after 1064 cycles. Vias were then patterned via RIE for electrical access to the intermediate electrodes. A blanket 15 nm layer of Cr was added as an adhesion layer, followed by 150 nm of Au; these layers were patterned via wet etching (conditions are in the Appendix). The devices were then released via DRIE. It should be noted that the masks were designed such that released and unreleased devices experienced the same process conditions.



Fig. 6.1. Process flow for the fabrication of MLA devices.

Highly Accelerated Lifetime Testing (HALT) was used to determine the lifetime of the MLA devices and investigate the degradation mechanisms. The samples were diced into 1.5 cm x 1.5 cm square dies that were mounted into DIP packages with silver paste. For MLA devices, the electrode configuration was arranged in such a way that the device would be driven via the middle electrode while the top and bottom electrodes were grounded. A positive voltage was applied to the middle electrode. For each measurement condition, the median time to failure (t) was extracted. Datasets at three different temperatures (at constant field) and three different fields (at constant voltage) were used to calculate the voltage acceleration constant (n), and activation energy ( $E_a$ ) via the Prokopowicz and Vaskas lifetime model,

$$\frac{t_1}{t_2} = \left(\frac{V_2}{V_1}\right)^n \exp\left[\frac{E_a}{k_b} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{6-1}$$

where V, T, and  $k_b$  are the voltage, temperature, and Boltzmann's constant, respectively [32].

Optical and FESEM images were taken after HALT measurements to characterize breakdown events. A thermal camera was used to examine the device surface while an electric field was applied at elevated temperatures; this was done to determine the heating behavior of the MLA device.

In addition, videos were taken from the optical microscope while high voltage (> 35 V, which is > 460 kV/cm) was applied at room temperature to observe (1) the number of breakdown events as a function of applied electric field and time, and (2) the nearest distance between breakdown events.

#### 6.3. Results and Discussion

Failure in clamped films was comparable to behavior that has been reported previously [40]. Images of the breakdown for clamped devices are given in Fig. 6.2, and the current vs time behavior is given in Fig. 6.3 (c). The failed clamped devices showed blackened regions, which are attributed to thermal breakdown events [33]. Moreover, as time increases, the current steadily increases; over this background is distributed several current spikes. As reported elsewhere, these thermal breakdown events can evaporate Al<sub>2</sub>O<sub>3</sub> passivation layer, electrode, and the piezoelectric layers. This manifests in a sharp current increase, and several of these events typically occur before the devices short, as shown in Fig. 6.3 (c). It should also be noted that the size of the thermal breakdown events was  $\sim 8 \,\mu\text{m}$  in diameter, which is similar in magnitude to what has been reported by Coleman et al [31]. Moreover, many of these breakdown events were connected via cracks, as shown in Fig. 6.2 (d). This suggests that the electrical and mechanical failure of the device is coupled, agreeing with previous reports [31].



Fig. 6.2. Breakdown behavior of a clamped device. (a) shows failure events for a clamped device on the macro scale when the device was subjected to 170 °C at 24 V (313 kV/cm). Several electrodes show dark spots regions – these are thermal failure events. (b) is an FESEM of one of the failed devices. The yellow arrows indicate thermal breakdown events. A breakdown pathway connects these thermal breakdown events from the top electrode to the middle electrode of the MLA device. (c) shows the FESEM image of a device that was subjected to 55 V (718 kV/cm). (d) shows a magnified view of three of these thermal breakdown events. The breakdown events are connected via cracks indicated by the light blue arrows.



Fig. 6.3. Example of (a) scenario 1 and (b) scenario 2 of the current vs time behavior for *released* MLA devices. In (a), the sample reached a current of 100 times the base current. Superimposed on this background current rise is numerous current spikes. In (b) the sample failed before the current reached a 100-fold increase relative to the minimum current. For contrast, (c) shows a typical current vs time behavior for a *clamped* MLA device.

It was observed that the released devices behaved differently from the clamped devices in five different ways. First, the released devices had more anomalous failures (often immediately or within the first minute of applying an electric field) compared to the clamped devices. In some cases, all twenty diaphragms would mechanically fail immediately upon application of an electric field.

Secondly, two different behaviors of current vs. time were seen for the released devices, as shown in Fig. 6.2 (a) and (b). The first scenario is that the sample surpassed the two orders of magnitude above the base current and had many current spikes prior to breakdown. In the second

case, the sample did not reach two orders of magnitude above the base current; the current rose incrementally with time followed by a sharp spike in the current value, then decreased quickly to the minimal measurable current value. This was due to either a loss in contact with the electrode or a detached diaphragm. Released samples predominantly showed the second scenario. In clamped devices, the current surpassed an increase of two orders of magnitude upon failure.

Thirdly, the FESEM images showed different thermal breakdown events in the released and clamped devices; this can be seen in Fig. 6.2 for the clamped films and Fig. 6.4. for the released films. It can be noted that the breakdown events were different in size. In released devices, the thermal failure events were quite small, less than 5  $\mu$ m in diameter, suggesting that the dissipated energy per failure event was relatively small. In released devices not subjected to HALT conditions, the black spots were not detected, as shown in Fig. 6.3 (e). Breakdown events in clamped devices were more catastrophic, as seen in Fig. 6.4 (a) and (b).

Also, in clamped devices, breakdown events were connected via cracks, as shown in Fig. 6.2 (d); this was not the case for released devices, as seen in Fig. 6.4. (b) and (c). This is in good agreement with observations by Coleman et al., who showed that released films were less susceptible to failure by cracking and clamped films had correlated breakdown events with cracks connecting to each site [38]. It should also be noted that the breakdown events occurred on the electrode surface; no evidence of thermal breakdown events occurred on the sidewalls, as seen in Fig. 6.4 (d).



Fig. 6.4. Breakdown behavior of a released device. (a) Top-down optical image of a released device. The images in (b) and (c) were located in the asterisk symbol marked in (a). (b) shows thermal breakdown events as black marks on the film surface. (c) provides a zoomed in image of a specific breakdown event. (d) is an image of the region marked as a triangle in (a), showing no evidence of obvious thermal breakdown events at the sidewall of the PZT pattern. The features in (d) seem to be redeposited PZT from RIE etching; such features are present at the sidewalls of clamped samples and virgin samples as well. (e) indicates the surface of a pristine released device, where there is no obvious evidence of the black dots seen in (b). (f - h) show failure events for a released device on the macro scale. (f-h) show that the membrane had cracks that outlined the perimeter of the bottommost platinum layer, and also cracks that seem to come from the edges of the membrane. (i) shows that there are no cracks propagating into the SiO<sub>2</sub> surrounding the membrane. (j) shows a crack at the membrane/electrode fan out interface, but no cracks propagating into the SiO<sub>2</sub>.

Fourthly, in released samples, the membranes mechanically failed after prolonged application of an electric field. Fig. 6.4. (f-j) shows the state of released devices after being
subjected to HALT measurements. Cracks that outline the bottom electrode and cracks from the film edge into the membrane can be seen. Fig. 6.4 (i) shows that near the membrane edge, the membrane broke off cleanly; there are no cracks that propagate into the SiO<sub>2</sub> (off the membrane). Based on the images, the region most prone to failure (and potentially the region of highest stress) is most likely the very edge of the membrane. A second high failure region is the perimeter of the PZT with respect to its bottommost electrode. Currently, it is not known whether the crack initiation that causes the whole diaphragm starts at the edges of the diaphragm and propagates inward, or whether a crack initiates at the middle of the diaphragm and the cracks propagate outward. If it is the former, adding a thicker passivation layer or a membrane anchor can potentially strengthen the edges of the membrane. If it is the latter, potentially using a thicker passivation layer or leaving a thin layer of residual device Si can strengthen the membrane itself.

Finally, the HALT data and Arrhenius plot for clamped and released films are given in Fig. 6.5. The lifetime data for each condition is given in Table 6.1. At low temperatures ~ 150 - 170 °C, the lifetime between clamped and released films are comparable (e.g. at 150 °C with 313 kV/cm (24 V), the lifetime for clamped and released films were 18.71 hrs and 19.01 hrs, respectively. The lifetime measurements start to diverge at higher temperatures (at 200 °C with 313 kV/cm (24 V), the lifetime for clamped and released films were 0.99 hrs and 5.30 hrs, respectively). A final point to note is that the activation energy to failure was different for released and clamped films. It is of note that for any given HALT condition, failures by scenarios 1 and 2 did not correlate in lifetime; no clusters of data points or data thresholds corresponding to scenario 1 or scenario 2 were evident. The activation energies for clamped and released devices were 1.02  $\pm 0.17$  eV and 0.46  $\pm 0.20$  eV, respectively for a temperature and electric field range of 150 °C -

220 °C and 313 kV/cm – 392 kV/cm, respectively. The obtained activation energy for the clamped devices agrees with reports in the literature [33, 35].



Fig. 6.5. HALT data and Arrhenius plot for clamped and released films. (a) Arrhenius plot for clamped versus released films measured over the temperature range of  $150^{\circ}$ C –  $220^{\circ}$ C at 24 V (313 kV/cm) (b) and (c) are individual HALT data comparing clamped and released films for (b) 24 V (313 kV/cm) at 200°C and (c) 24 V (313 kV/cm) at 150°C. (d) and (e) are individual HALT data for released films at (d) 24 V (313 kV/cm) at 150 °C and (e) 30 V (392 kV/cm) at 150°C. The red dots are where the device reached two orders of magnitude above the base current and the black dots are where the device did not reach two orders of magnitude.

	Temp (°C)	Voltage (V) / Electric Field (kV/cm)	t <sub>50</sub> (hrs)
Released	150	30 V, 392 kV/cm	3.22 [0.57 - 5.86]
Released	150	26 V, 339 kV/cm	21.70 [6.69 - 36.70]
Released	150	24 V, 313 kV/cm	19.01 [13.58 – 24.44]
Released	170	24 V, 313 kV/cm	18.20 [11.40 - 25.00]
Released	200	24 V, 313 kV/cm	5.30 [3.36 - 7.24]
Clamped	150	24 V, 313 kV/cm	18.71 [14.03 - 23.40]
Clamped	170	24 V, 313 kV/cm	12.98 [9.17 – 16.78]
Clamped	170	28 V, 366 kV/cm	7.84 [4.88 - 10.80]
Clamped	180	24 V, 313 kV/cm	6.73 [3.95 - 9.51]
Clamped	200	24 V, 313 kV/cm	0.99 [0.70 - 1.31]
Clamped	220	24 V, 313 kV/cm	0.52 [0.40-0.64]

Table 6.1. Lifetime Measurements for Clamped and Released Samples at Different HALT Conditions. Brackets indicate 95% confidence interval range

There are several ways in which the released devices differ from the clamped films, which could, in principle, change the activation energy associated with resistance degradation. In particular, the release process induces changes in both the mechanical and the thermal boundary conditions. The released devices are free to deform by flexure, which should reduce the propensity for cracking under field; this could increase the reliability of the released devices. However, the released device has no underlying silicon to act as a heat sink. Thus, they may be more prone to Joule heating, such that the local temperature could differ from the set temperature. If the latter were the case, then the apparent activation energy could drop.

In order to assess the importance of this second possibility, a series of released devices were filmed until failure via a thermal camera, to directly ascertain temperature increase. The device was placed on a hot stage (Cascade, Inc.) with an applied 22 V (287 kV/cm). Snapshots of the device at the initial application of the electric field are shown in Figure 6.6(a); snapshots taken

after six hours are shown in Fig. 6.6(b). The change in temperature between the initial state of applying the electric field and after a certain amount of time was examined, rather than the absolute temperature. This was because when an electric field is applied to the device, reflectance changes due to the change in the angle of incidence associated with local curvature of the membrane. These can cause temperature artifacts [30], as is observed by the bright red ring at the perimeter of the released region. In the future, thermoreflectance calibrations should be done at t<sub>0</sub>, immediately after the electric field is applied. This might allow curvature-induced artifacts to be reduced. In practice, each surface (e.g. Pt, PZT, and SiO<sub>2</sub>) would need to be calibrated separately to facilitate more quantitative measurements of the local temperature.

It is apparent from the figures that =no significant Joule heating was found in the released device, even as the current rose from 9.54 nA to 223 nA (the electrical degradation/breakdown regime). In fact, any temperature rise, if present, was under 1 K in magnitude. Therefore, the difference in activation energies between released and non-released devices cannot be attributed to a global increase in Joule heating in the absence of the underlying Si. It is apparent that any thermal failure events were either too small or too short-lived to be captured in this experiment.



Fig. 6.6 Original screen readout of the top-view of a device with a thermal camera (a) when the voltage is applied and (b) six hours later. The excited actuator is marked with the yellow arrow. Both the maximum and the minimum temperature color bars are 140.9°C and 77.4°C, respectively, indicating no significant change even after six hours, at which point the current had increased by more than two times. Note that the apparent high temperatures are associated with bending, rather than with a real high temperature near the device perimeter [30].

At present, the reason for the difference in HALT activation energies of clamped and released films is not known. Potential factors which should be pursued in future work include: (1) The fact that the released films did not, in general, reach two orders of magnitude increase from the base current and (2) the activation energy for failure in released films of  $0.46 \pm 0.20$  eV could potentially correspond to oxygen vacancy migration [23, 27]. Additional HALT measurements at lower and higher temperatures are needed to determine whether there is a change in the activation energy for failure with set temperature. It is also recommended that additional characterization techniques such as thermally stimulated depolarization current (TSDC) and in-situ impedance measurements are needed to determine the major carrier types and charge transport mechanisms in PZT films.

Finally, the voltage acceleration factor was determined, and is presented in Fig. 6.7. The voltage acceleration factor from Equation (6-1) was found to be 3.3 and  $8.6 \pm 3.9$  for clamped and released films, respectively. These values are similar to prior reports for PZT films (~4 – 10) [15, 36]. However, it is noted that of the possible conduction mechanisms, none have a fourth/fifth order relationship between current and electric field. Thus, a model developed by Garten et al. was employed [36, 37], which assumes that Schottky barriers dominate the leakage characteristics. This assumption is consistent with previous reports on comparable films [38]. The Schottky conduction model is given via

$$\ln\left(\frac{J_{Sch}}{T^2}\right) = \ln(A) - \frac{q \cdot \phi_B}{k_B T} + \frac{q \cdot \sqrt{q \cdot \frac{E}{4\varepsilon_0 \cdot \varepsilon_\infty \cdot \pi}}}{k_B \cdot T} E^{0.5}$$
(6-2)

Where A,  $\varepsilon_{\infty}$ , J,  $q \cdot \phi_B$ ,  $k_B$ , T, E, and q are the effective Richardson constant, high frequency permittivity, current density, Schottky barrier height, Boltzmann's constant, temperature, electric field, and electronic charge, respectively.

Thus, the new fitting equation derived by Garten et al. was found to be

$$\frac{t_1}{t_2} = \frac{T_2^2 \cdot e^{\frac{-q \cdot \Phi_B}{k_B T_2}} \cdot e^{\frac{q \cdot \sqrt{q \cdot \frac{E_2}{4\epsilon_0 \cdot \epsilon_\infty \cdot \pi}}{k_B \cdot T_2}}}{T_1^2 \cdot e^{\frac{-q \cdot \Phi_B}{k_B T_1}} \cdot e^{\frac{q \cdot \sqrt{q \cdot \frac{E_1}{4\epsilon_0 \cdot \epsilon_\infty \cdot \pi}}}{k_B \cdot T_1}}$$
(6-3)

At constant temperature, the fitting equation would thus be

$$\frac{t_1}{t_2} = e^{\beta E_2^{1/2} - \beta E_1^{1/2}} \tag{6-4}$$

where  $\beta = [q^3/(4\pi\epsilon_i)]/k_BT$ . Thus, the natural log of the t<sub>50</sub> was plotted against the square root of the applied voltage, with the extracted slope being the adjusted acceleration factor. The refitted data is given in Fig. 6.7 (b). The adjusted voltage acceleration factor was found to be 1.3 and 3.3 ± 1.4 for clamped and released films, respectively. While more measurements will need to be done to determine whether the voltage acceleration factor is significantly different between the two states, the obtained values are close to values reported in literature of ~ 2 - 2.5 [15]. It should also be noted that the conduction mechanism can vary due to the way processing affects the defect chemistry. Thus, the assumption of Schottky conduction being the dominant mechanism of these films should be directly confirmed by leakage current measurements.



Fig. 6.7. Voltage dependence of median time to failure and fittings via (a) Eyring equation and (b) the model developed by Garten et al. and Randall et al. [36, 37].

An optical microscope was used to observe breakdown events when high voltage (> 450 kV/cm) was applied to clamped devices at room temperature. The location of breakdown sites, distance between breakdown events, and number of failure events per unit time were extracted as a function of the applied voltage (field). Images of the top electrode with different voltages taken at different times is shown in Fig. 6.8.



Fig. 6.8. Top view of non-released devices at an applied electric field of 457 kV/cm (35 V) (a – b, c – d), 522 kV/cm (40 V) (e – f), 587 kV/cm (45 V) (g – h), 653 kV/cm (50 V) (i – j), 718 kV/cm (55 V) (k – l), 783 kV/cm (60 V) (m – n, o – p), 849 kV/cm (65 V) (q – r), and 914 kV/cm (70 V) (s – t). (a), (c), (e), (g), (i), (k), (m), (o), (q), and (s) correspond to the initial time when the voltage was applied. (b), (d), (f), (h), (j), (l), (n), (p), (r), and (t) correspond to the time after the device has shorted.

The cumulative breakdown events as a function of time and a histogram of nearest breakdown events for different electric fields are shown in Fig. 6.8 and 6.9, respectively. In devices with lower applied electric fields, breakdown events occurred over a longer time compared to devices with higher applied electric fields. This was most evident in samples where 457 kV/cm (35V) was applied; in these samples, breakdown events appeared one by one over a long time period (299 sec and 154 sec). In samples with an applied 914 kV/cm (70 V), several breakdown events occurred over a shorter time period (8.9 sec), as seen in Fig. 6.9. However, it should be noted that this data is limited by the camera resolution; it was difficult to view breakdown events within 9 µm and the recording software was limited to 30 frames per second.

It was notable that all of the data sets seemed to show a characteristic "S" shaped curve for the accumulation of breakdown events as a function of time before failure. To assess whether the distributions were self-similar, a characteristic time ( $t_{char}$ ), was defined as the time at which 50% of the failures occurred before the device shorted. The  $t_{char}$  for each electric field condition is shown in Table 6.2. As expected, it was found that  $t_{char}$  decreased with increasing electric field; multiple reports show that dielectrics fail faster when subjected to high electric fields [13-15, 28, 33]. All data points were then normalized by dividing the actual time by  $t_{char}$ . As seen in Fig. 6.8, these normalized datasets largely overlap.

	Figure 1 and
Electric Field (kV/cm)	Characteristic Time (sec)
457 (35 V)	256
457 (second device) (35 V)	119
522 (40 V)	17.5
587 (45 V)	16.3
653 (50 V)	9.8
718 (55 V)	10.5
783 (60 V)	9.1
783 (second device) (60 V)	7.2
849 (65 V)	8.3
913 (70 V)	7.5

Table 6.2. Characteristic Time vs Electric Field for Clamped Films



Fig. 6.9. Cumulative breakdown events for various voltage conditions for clamped films. (a) shows the cumulative percentage breakdown events for all voltages, while (b) is a zoomed in version of (a) to see the higher electric field data more clearly. (c) shows the cumulative percentage breakdown events versus the time divided by the characteristic time for each electric field conditions. The  $t_{char}$  was defined by the time in which the cumulative percentage of breakdown events was 50%.

Finally, the nearest distance between breakdown events was not randomly distributed. The nearest distance between breakdown events was under 50 µm separation distance for all electric fields investigated. There is also a tail in the distribution to longer separation distances. Unfortunately, the resolution of the optical microscope precluded determination of whether the

center of the distribution changed with voltage. These data provide more numerical proof that thermal breakdown evens in PZT films are correlated [31]. However, based on the data shown in Fig. 6.8 and 6.9 two devices measured with similar applied conditions (466 kV/cm and 800 kV/cm) show some variation in the spatial and time distributions to the breakdowns. Thus, it is recommended that more samples should be tested per condition to supplement these findings.



Fig. 6.10. Histogram data of various electric fields vs. distance to nearest breakdown event.

## 6.4 Conclusions

The lifetime and breakdown behavior in clamped and released films were investigated. The current vs. time data in released films showed two families of responses: (1) when the membrane broke, the current did not exceed two orders of magnitude from the base leakage current and (2) the current reached two orders of magnitude from the base value, with superimposed current spikes. Thermal breakdown events for released films were much smaller (< 5  $\mu$ m) compared to clamped

films; these events were not connected via cracks (unlike clamped films), a finding in agreement with the literature [31]. Released films were more likely to have anomalous failures (broken membranes almost immediately upon voltage application). Finally, the activation energy was found to be  $1.02 \pm 0.17$  eV and  $0.46 \pm 0.20$  eV for clamped and released films, respectively. Thermal imaging of the membrane indicated no significant heating in released films despite the absence of Si beneath the PZT.

Thermal breakdown events were studied in clamped films; these events were correlated in space and time. The nearest breakdown events were often within 50 µm from each other. The time for each voltage application to reach 50% of cumulative breakdown decreased with increasing voltage (devices failed quicker at higher voltages). At lower voltages, breakdown events were much more spaced out in time.

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#### **Chapter VII: Summary and Future Work**

# 7.1. Summary

This thesis discussed the design, fabrication, and characterization of PMUTs for their suitability in imaging and particle manipulation applications, as well as possible ways to improve their acoustic attributes. The PMUTs were strongly {001} oriented, with high permittivity (>1000), remanent polarization (> 20  $\mu$ C/cm<sup>2</sup>), and <6% variation amongst elements on a device.

For particle manipulation applications, deterministic 1D control of 4  $\mu$ m SiO<sub>2</sub> beads and gold nanorods was achieved. By carefully designing the diaphragms to be in close proximity to one another (in this case, the pitch was 75  $\mu$ m), the particles could be moved from one element to another without the need of microfluidic flow.

For imaging applications, ultrasound and photoacoustic images were achieved. An ultrasound image of an 18 mm x 18 mm clay/glass target was raster scanned. Photoacoustic signals of various targets were achieved: pencil lead targets in agar gel and under chicken tissue, an ICG dye-filled tube in agar gel and under chicken tissue, blood filled in tubes, and a single hair follicle.

To improve the acoustic characteristics of the transducers, several avenues were examined. First, by increasing the effective active area of vibration by 1.4 times and changing from a multicircular-diaphragm element design to a singular rectangle diaphragm design, the pressure output was increased by  $\sim 2$  times. It should be noted that the circular and rectangular diaphragm design was designed for different frequencies (10 MHz and 15 MHz, respectively). Based on Equation (1-6), the general relation between pressure and frequency is if frequency increases, pressure also increases. However, in PMUT applications, the PMUT diaphragm generally becomes thicker/stiffer and/or the diaphragm area reduces to obtain a higher resonant frequency, which also effects the effective area output. In addition, several different PZT compositions were tested as well as the application of a DC bias. It was hypothesized that since the receive sensitivity depended on the permittivity and piezoelectric coefficient, both can be influenced by DC bias. The permittivity and piezoelectric coefficient decreased by different rates (65% and 43%, respectively, when comparing PZT 52/48 and PZT 20/80) from 0 kV/cm to 75 kV/cm (15 V). When no DC bias was applied, PZT 20/80 had the highest receive sensitivity compared to other compositions, due to the reduction in the permittivity being greater than the reduction of the piezoelectric coefficient when moving off the MPB. When a relatively low 15 V (75 kV/cm) DC bias was applied, PZT 52/48 was able to match the receive sensitivity of PZT 20/80.

In addition, the crack initiation stresses for different PZT compositions were also investigated. The results for PZT 52/48 were in good agreement with work conducted by Coleman et al [1, 2]. For the 40/60 and 30/70 compositions, the characteristic stack strength increased while the Weibull modulus decreased to values typical to that of Si. It was speculated that the more tetragonal compositions showed addition toughening due to ferroelasticity or phase switching. Based on peak fitting of the XRD scans, the volume fraction of c-domains increased as compositions became more Ti-rich. This would allow for more switching from c to a-domains when the samples were under biaxial tensile stress at the midpoint of the sample. TEM line scans indicated concentration gradients were present for all compositions, which may have contributed to the observation of rhombohedral phase off the MPB.

Finally, the breakdown behavior of multilayer actuator PZT based devices was investigated. The activation energy for highly accelerated lifetime testing was found to be  $1.02 \pm 0.17$  eV and  $0.46 \pm 0.20$  eV for clamped and released films, respectively. Thermal imaging of a released device showed no significant temperature changes over time under field; thus, the change in activation energy cannot be attributed to a substantial local rise in temperature. Two different failure modes were observed: (1) many diaphragms broke before the current reached two orders of magnitude increase over the base leakage current and (2) in other diaphragms, the current rose two orders of magnitude from the base current, and was marked by short current spikes associated with individual thermal breakdown events. Additionally, in released films, no cracks connected the breakdown sites (which were usually < 5  $\mu$ m in lateral dimensions). In clamped films, the breakdown sites were connected via cracks and were much larger in size.

For clamped films, it was found that breakdown events were not randomly distributed in space; they were often within 50  $\mu$ m of one another. Moreover, at lower voltage applications, breakdown events were spaced out over a longer time period.

### 7.2. Future Work: Transparent PMUTs on different substrates with improved properties

In photoacoustics, the arrangement of the laser source and the ultrasound transducer is important. One common arrangement is illumination from the side of the transducer, between the ultrasound transducer array and the target. Compared to perpendicular illumination, photons in the side-illumination geometry need to travel a longer distance before reaching the object, resulting in lower fluence and a weaker signal. The light source can be integrated as two fiber bundles along the length direction of a 1D transducer array, however, this method does not illuminate the area under the transducer, producing a blind spot in front of the transducer. It is difficult to use this approach with 2D arrays, as a large area under the 2D transducer array is not illuminated.

Ideally, the light should be incident in the same direction as the acoustic waves. Dangi et al. drilled a hole through the center of a PMUT device and inserted an optic cable. They demonstrated successful photoacoustic imaging, as shown in Fig. 7.1. However, fabricating such

a device is challenging and labor intensive. An entirely transparent transducer, in which glass was used instead of Si as the substrate and allowed light to shine through from behind, is therefore of interest.



Fig. 7.1 (a) and (b) indicate a fiber optic cable inserted through the center of the PMUT. This was achieved by puncturing a hole through the center as shown in (c). The resultant photoacoustic imaging is shown in (d), where the target is a black card in the shape of the letter "P." Figure from reference [3].

The work of Yeager et al. is valuable in designing transparent transducers as they showed that  $e_{3I,f}$  (needed to achieve good transmit power and receive sensitivity) is more sensitive to the polar axis fraction than to film composition. This can be seen in Fig. 7.2 [4].



Fig. 7.2 Comparison of polar axis fraction, composition, and electrical properties. Data extracted from Yeager et al. [2].

Yeager et al. systematically changed the thermal expansion coefficient mismatch between PZT and the substrate to encourage a higher polar axis fraction by placing the PZT film in compressive stress. As a result, tetragonal PZT films on CaF<sub>2</sub> substrates showed predominantly out-of-plane polar axis orientation.

Therefore, fabricating PZT on transparent substrates with large thermal expansion coefficients would increase  $e_{31,f}$  and make the device stack completely transparent. CaF<sub>2</sub> wafers are thus interesting, as they have a high thermal expansion mismatch with PZT (the thermal expansion coefficient of CaF<sub>2</sub> and PZT is 18.85ppm/°C and 4.8 ppm/°C, respectively) [5-7]. A proposed PMUT fabrication process with a transparent stack is presented in Fig. 7.3. First, 100 nm of ZnO could be deposited via atomic layer deposition on the CaF<sub>2</sub> wafer, patterned via lithography and wet etched in acetic acid. The ZnO would serve as a sacrificial layer that on removal gives the device its suspended diaphragm structure. Then, a passive elastic layer of SiO<sub>2</sub> deposited via PECVD should be deposited and annealed to remove hydrogen trapped in the resulting film [8]. A bottom electrode could be deposited via CSD or sputtering and patterned via reactive ion etching. The PZT layer would then be deposited via sputtering or CSD. The top electrode can then be deposited via sputtering and patterned via lift off.

Transparent or nontransparent materials can be used for the top and bottom electrodes, and there are tradeoffs for either. If the entire stack is transparent or semitransparent, there will be fewer blind spots for imaging with the array when the light source is placed behind the transducer. One candidate for a transparent top electrode would be indium tin oxide, which can be sputtered and annealed to improve conductivity [9]. Sputtering of indium tin oxide is often done at elevated substrate temperatures (usually > 200 °C) that are not suitable for traditional liftoff resists such as LOR 5A and SPR 3012 [10, 11]. Inorganic liftoff can circumvent difficulties associated with this patterning step [12].

Despite the feasibility in processing and the benefits, transparent/semi-transparent electrodes can be susceptible to heating from absorbing the photoacoustic light source, which can cause the elements to act as thermoacoustic source, reducing the signal to noise ratio [13].

Transparent electrodes such as ITO generally have lower electrical conductivity (and thus higher resistivity) than non-transparent electrodes such as Pt or Au [9, 11, 12]. This results in difficulty in achieving high frequency devices (e.g. > 10 MHz) with large area elements without RC time constant issues. If the electrode material is non-transparent such as Pt or Au, some light will be reflected back to the source. It is thus expected that less heating would occur from the light source if nontransparent electrodes were used. The higher conductivity in this type of electrode would also decrease RC time constant issues for higher frequency devices. However, using an array of non-transparent electrodes only allowing light in between elements may result in blind spots.

After the top electrode is patterned, the bottom electrode can be accessed via reactive ion etching. Then, etch pits connecting to the bottommost ZnO could be patterned. The whole wafer would then be immersed in an acetic acid bath at elevated temperatures with agitation to remove the ZnO and release the device [14, 15]. These etch pits could be sealed off either with photoresist or an inorganic material such as PECVD SiO<sub>2</sub>, to prevent water from leaking to the back of the diaphragm. The device/electrical connections should be waterproofed with parylene. Based on reports of transparent CMUTs in the literature, the transmittance of the stack should be at minimum  $\sim$ 30% -70% between 700 - 900 nm to be usable [5, 9, 16-19].



Fig. 7.3. (a) Proposed transparent PMUT fabrication on  $CaF_2$  substrates. Illustrations are not drawn to scale. (1) Starting with a  $CaF_2$  substrate, (2) the sacrificial ZnO layer can be deposited via ALD and patterned via wet etching. (3) the passive elastic layer can then be deposited via PECVD, followed by (4) sputtering and RIE patterning of the bottom electrode. (5) PZT can then be deposited, followed by (6) sputtering and inorganic liftoff for the top electrode patterning. (7-9) etch pits can then be made to the bottom ZnO layer as well as to gain bottom electrode access via reactive ion etching. (10) The device can then be waterproofed using a lamination layer such as photoresist. (b) Top-view of rectangular and circular diaphragms for transparent PMUT fabrication.

A preliminary run was done using CaF<sub>2</sub> wafers. A target thickness of 100 nm of ZnO was deposited via ALD, patterned with SPR 3012, and wet etched in a 50% acetic acid bath at 50 °C. However, it was noted that when the wafer experienced temperature changes > 90°C, it began to crack. Thus, it is suggested that when handling wafers with high thermal expansion coefficients, one should not place any concentrated stress on the wafer, even with tweezers. The CaF<sub>2</sub> wafer could be mounted on a 6-inch carrier wafer for handling to prevent this.

In addition to CaF<sub>2</sub> wafers, other substrates with larger thermal expansion coefficients than PZT (4.8 ppm/°C) can be tested, such as SrTiO<sub>3</sub> (9.4 ppm/°C), MgO (10.8 ppm/°C), and Ni (13.3 ppm/°C) [5, 6, 7]. Ni is particularly interesting, as it has been proven to improve the piezoelectric coefficient by ~ 27% compared to Si substrates due to the induced compressive stress that increases the out-of-plane polarization direction [20-24]. Additionally, it is easily micromachined and can be made flexible, allowing the PMUT to conform to various curved surfaces [20-23].

### 7.3 Testing density of transparency with PMUTs for photoacoustic imaging.

One drawback of transparent stacks is that transparent electrodes such as indium tin oxide and semitransparent lanthanum nickelate have relatively low electrical conductivity (and thus high resistance) compared to metals such as gold and platinum. Thus, a transparent device would be limited by RC time constants at higher frequencies (i.e., > 5 MHz), particularly when long elements are needed. Ideally, highly conductive metals such as platinum, copper, silver, or gold would be used, but these materials are not transparent. Arranging these nontransparent elements on transparent substrates in such a way that light can pass between them may provide a solution. The distance between elements can be systematically increased or decreased to ascertain the optimal pitch needed to allow sufficient light to pass through and obtain a usable photoacoustic signal. Moreover, the effect of light on adjacent elements will need to be examined, as light may heat the elements, which in turn may create noise in the receive signal.

## 7.4. Improving electrode adhesion

While fabricating and testing the PMUT devices, it was noted that the adhesion between the bottom electrode and the substrate and the top electrode to its underlying layer (i.e., BCB) degrades over time. Initially, when the bottom electrode was sputtered, the electrodes passed the tape test. Even after the full fabrication process, the electrodes remained adhered after the tape test. However, over a period of months, the electrodes became more difficult to wire bond and peeled off, as shown in Fig. 7.4. It is hypothesized that over time, moisture from the ambient seeped into these interfaces, weakening the interface between the electrode and its underlying layer. In addition, the bottom electrode had a weakened interface because it was exposed to the most processing. Moreover, noble metals (such as Au and Pt) were used; their low chemical reactivity yielded poor adhesion to the oxide underlayers. It is noted that ACF bonding induced less electrode delamination compared to wedge wire bonding.



Fig. 7.4. When wire bonding to the bottom electrode, as the bonder is lifted, the electrode is lifted as well, indicating poor adhesion to the underlying  $TiO_2/SiO_2$  layer.

Testing different adhesion layers, subjecting them to different treatments and assessing their long-term adhesion is of interest, as delamination of the top electrode degrades the piezoelectric properties [23]. Oriented  $TiO_2$  is commonly used for the bottom electrode to obtain a strong (111) orientation for hot-sputtered Pt, which serves as a template for {001} PZT growth [24]. For top electrodes, however, extremely thin adhesion layers are needed. Ti and Cr oxidize, which can result in a capacitor in series-induced degradation of the functional properties. One way to circumvent this is to sputter an extremely thin (~ 2 nm) adhesion layer of Ti. At these thicknesses,

the film is discontinuous such that the Ti can bond the electrode to the PZT, without significant capacitor in series problems. Other types of adhesion layers such as ZnO, Al<sub>2</sub>O<sub>3</sub> and their long-term reliability can be explored [25-28].

#### 7.5. Cross talk reduction

Cross talk occurs in PMUT devices driven at resonance and manifests in the device vis propagation through the substrate and propagation through the fluid in water. Cross talk is problematic as it degrades the resolution of acoustic images [29-31]. It was seen in Chapter 2 that when driving a PMUT element at resonance, diaphragm oscillation was observed across nearly the entire device. From in-air LDV measurements, the adjacent element oscillates with amplitudes as high as 33% of the driven element, indicating crosstalk potentially propagates through the substrate. In addition, when two separate devices (e.g., on two distinct substrates) were placed together in the pin grid array and one device was excited in water, diaphragms on the second device were seen to oscillate even ~ 2 mm away from the driven device, indicating that cross talk propagates easily through fluid. The source of electrical cross talk was investigated by exciting one element in an array and grounding elements adjacent to it to the bottom electrode. This should eliminate electrical cross talk. However, oscillation of adjacent elements still occurred. Therefore, understanding what initiates cross talk and finding methods to eliminate it are of interest.

Cross talk that propagates mechanically through the substrate can be reduced by removing the Si device between elements and/or replacing it with an acoustic absorber (i.e. polymers such as polytetrafluoroethylene, polyurethane, polymethylmethacrylate).

## 7.6. Investigation of released vs. clamped devices

The activation energies for failure of clamped and released multilayer actuator (MLA) films were found to be different, as shown in Chapter 6 (1.02  $\pm$  0.17 eV and 0.46  $\pm$  0.20 eV), respectively). They were also shown to fail in different ways: in released films, the breakdown events were not connected via cracks and were far smaller ( $< 5 \mu m$ ) compared to clamped films. Released films experienced more anomalous failures in time and broke before reaching two orders of magnitude from the base current. Therefore, an investigation of the difference in activation energies of clamped and released devices is needed. Characterization techniques such as thermally stimulated depolarization current (TSDC), Charge-Based Deep Level Transient Spectroscopy (Q-DLTS), and in-situ impedance measurements will assess the major carrier type and associated charge transport mechanisms in MLA films. This, in turn, should provide some understanding of why the activation energies differed. Moreover, prolonged HALT measurements should be conducted over a broad temperature range to assess whether there is a change in failure mechanism (and thus activation energy) as a function of temperature, as it was seen from the Arrhenius plot that the clamped and released points converge at low temperatures (~ 150 °C). Additional HALT data will also be needed to determine if the voltage acceleration factor depends on the applied electric field range. Moreover, the top and bottom PZT layers in the multilayer stack should be evaluated individually to compare their lifetimes, voltage acceleration factor, and activation energy.

It is interesting to note that no temperature changes were found in MLA samples after prolonged exposure to the electric field, even in the breakdown regime of the current vs time behavior. It is also interesting that in many cases, the diaphragm broke before reaching two orders of magnitude increase over the base leakage current, but not immediately on voltage application. If the failure was purely mechanical in origin, then the diaphragm should have broken immediately upon application of the voltage, rather than some time after the voltage application since the deflection is static. In addition, the probability of failure vs time to failure in Fig. 7.5 seems to show a change in current vs time behavior over time under voltage. At 24 V (320 kV/cm), the devices predominately reached two orders of magnitude from the base current. At 30 V (400 kV/cm), the devices predominantly did not reach two orders of magnitude from the base current and displayed the characteristic current spikes that were described in Chapter 6. It is hypothesized that at high enough voltages, when the thermal breakdown events seen in Fig. 6.3 (b) and 6.4 (h) of Chapter 6 occur, the energy dissipation can create a shockwave large enough to cause the diaphragm to break before the membrane is able to reach two orders of magnitude, potentially by exacerbating cracks and fragile points on the edges of the diaphragm. This can be tested by using a high-speed optical camera on the surface of the device similar to the thermal camera setup in Fig 6.6. in Chapter 6. A laser doppler vibrometer (LDV) can also potentially sense if there are any acoustic emissions from the diaphragm (or indeed on adjacent diaphragms). In addition, fabricating or attaching sensors near the devices can potentially sense the acoustic emission by the energy dissipation of the thermal breakdown events during HALT measurements. Acoustic emission has been demonstrated to be useful in measuring crack growth/microcracking, and can potentially identify the presence of shockwaves generated by the energy dissipation from thermal breakdowns [32-35].



Fig. 7.5. Probability of failure versus time to failure for MLA devices at HALT conditions (a) 30 V at 150 °C and (b) 24 V at 150 °C. The red dot points indicate cases where the device reached two orders of magnitude from the base current, whereas the black data points did not.

## 7.7. Finite Element Analysis

The resonant frequency was calculated for the PMUTs using the theory of thin plates. It is recommended in the future that finite element analysis simulations should be done to determine the optimal electrode geometry, passive layer thickness, diaphragm deflections, as well as to analyze the various peaks seen in Fig. 4.4.

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# **Appendix – Processing Tips and Tricks**

A.1. M4L Plasma Cleaning: The plasma cleaner is mainly used for processing steps: descum and photoresist removal after etching. Essentially, it removes organics from the surface of the substrate. The McKinstry research group has developed several descum recipes, such as:

Table A.1. Different Plasma Cleaning Recipes				
Recipe #	Author	Parameters		
1	Margeaux Wallace/Aaron	50 sccm He, 150 sccm O <sub>2</sub> , 200 watt power for 2		
	Welsh/Yongqiang Qiu et	minutes, regulating 550 mTorr pressure		
	al.			
2	Beth Jones et al.	50 sccm He, 100 sccm O <sub>2</sub> , 300 watts for 2 minutes,		
		regulating 550 mTorr pressure		
3	Margeaux Wallace/Aaron	50 sccm He, 100 sccm O <sub>2</sub> , 300 watts for 1 minute,		
	Welsh/Yongqiang Qiu et	regulating 200 mTorr pressure		
	al.			
4	Nicole Kirchner-Hall et al.	50 sccm He, 150 sccm O <sub>2</sub> , 200 watt power for 2		
		minutes, regulating 550 mTorr pressure		

Recipes 1 and 2 are typically used before photolithography steps to clean the substrate. Recipes 3 and 4 are typically used for post-development to remove residual scum layers potentially left behind by the photoresist. Dr. Lyndsey Denis et al. showed that preparing two baths of developer and moving the sample from one bath to the other halfway through development, with light
agitation, avoids residual scum layer. This allows "fresh" developer to remove the residual photoresist left in a pattern by avoiding local saturation of developer with photoresist.

Photoresists that have been exposed to reactive ion etching typically need additional steps to be removed (more than just acetone and IPA). This is particularly true for photoresists that have reticulated from heating during the etching process. In these scenarios, the sample can be immersed in Baker PRS 3000 heated to 85 °C for several minutes (upwards of 20 minutes to an hour in some situations), followed by an IPA  $\rightarrow$  acetone  $\rightarrow$  IPA rinse. When the reticulated photoresist still isn't removed by these solvents, an aggressive plasma clean using the M4L can be used. These recipes were provided by Mike Labella and Bob Benoit from the Army Research Lab and the parameters are given in Table A.2.

Table A.2: Different Aggressive Descum Parameters		
Process	Parameters	
Mike Labella et al.	<ul><li>50 sccm He, 300 sccm O<sub>2</sub>, 300 watts power,</li><li>550 mTorr pressure regulation for 5 minutes</li></ul>	
Bob Benoit et al.	50 sccm O <sub>2</sub> , 400 watts power, 1000 mTorr pressure regulation for twenty minutes	

It should be noted that in some cases, multiple cycles of an oxygen plasma and immersion in heated Baker PRS 3000 is needed to remove reticulated photoresist. It should also be noted that as the plasma clean time increases, the instrument will also begin to heat, and the rubber seal of the M4L door may expand and thus vacuum may not be optimal. Thus, it is recommended to only clean for 5 minutes at a time with these recipes. These recipes, in general, can remove most organics: photoresist, reticulated photoresist, thick Protek samples, etc.

# A.2. Sputtering Processes:

The following processes were developed for sputtering devices:

Recipe Name	Pressure	Sputter Time / (thickness)	Power (watts)	Temp setpoint (°C)
Jake Ti gun 3	2	25 / 2 nm	200	20
200 300		360 / 30 nm		
Pt gun 1 1000 A	2.5	417 sec / 100 nm	200	20
Pt gun 1 1000 A	2.5	417 sec / 100 nm	200	600
600 ???				
Au gun 1 500 A	2.5	1000 sec / 520 nm	200	20

# A.3. Photolithography Processes:

The following photolithography processes were developed and optimized:

# A.3.1 For typical liftoff processes (i.e., lift off processes compatible with sputtering 100 nm

**Pt):** 

- Use the M4L for descum (50 sccm He / 150 sccm O<sub>2</sub> / 550 mTorr pressure regulation / 200 watts / 2 minutes)
- Heat sample on a hotplate > 100°C (suggested by Dr. Thomas Jackson, heating the sample above 100°C to minimize water/moisture on the sample).
- 3. LOR 5 A: dynamic or static spin with 4000 RPM for 45 seconds, followed by a soft bake at 180°C for 1 minute. Note that one should cover the dispense hole on the spin cover

immediately after photoresist application; this reduces any potential debris from falling on the sample.

- 4. SPR 3012: dynamic or static spin with 4000 RPM for 45 seconds, followed by a soft bake at 95°C for 1 minute.
- Expose on the MA/BA6 tool at 64 80 mW/cm<sup>2</sup> of power (i.e., 10 seconds on the MA/BA6 Gen 2 which outputs 8 mJ/cm<sup>2</sup> per second).
- 6. Develop using CD-26 developer for 90 seconds, followed by a DI water rinse and dry. It should be noted to avoid a scum layer from forming, one should move the sample to a fresh CD-26 bath at the 45 second mark. It should be noted that LOR 5 A is not a light-sensitive resist, and so increasing exposure power and time would not affect it.
- 7. Use M4L descum recipe 3.
- 8. Sputter 100 nm of Pt electrodes (or the electrode type of your choosing).
- Place sample in an acetone bath. After ~ 1 minute, one can "encourage" the unneeded Pt by squirting it with an acetone bottle, as well as brief sonication for 5-10 seconds.
- 10. After the unneeded Pt has flaked off, the sample should be washed with IPA before putting into the CD-26 bath for ~ 5 10 minutes to remove the LOR 5A. This time is dependent on how thick the LOR 5A was spun on the sample, and how large the sample is. A tip by Dr. Carl Morandi is that you can switch to a different CD-26 bath at the halfway mark. One may notice a slight-yellow tint in the CD-26 solvent if any photoresist development occurred.
- 11. Afterwards, the electrode should be annealed for 1 minute in an RTA in air at 550°C, to improve the interface between the electrode and the sample.

#### A.3.2. For liftoff processes on large topography features

In some cases, a sample will have patterned features already deposited on the substrate/film and will need to deposit photoresist on these features. While samples with topography of small heights (in the hundreds of nanometer range) can follow typical liftoff procedures, it was found that samples with greater than 5 µm of topography require more specialized photoresist spinning procedures. This is because with high topography samples, photoresist does not uniformly coat the entire wafer and photoresist is starved toward the edges of high topography features, as shown in Fig. A.1. To circumvent this, instead of using positive photoresist and sputtering, negative photoresist can be used. For example, in the current thesis, it was desired to have electrodes on top of high topological features. In this case, the whole sample can be blanket-sputtered with Au, and then a negative photoresist will be applied on top to protect against wet etching using Au etchant. The negative photoresist starvation on the edges of topography will not be an issue; it would allow the Au etchant to remove the Au on the edges.

In particular, nLOF2020 was used as it is a single-layer liftoff resist and, using the same mask as positive photoresists, will leave photoresist in areas that are in the trenches and clear features that are on the very top of the features. The procedure was as follows to achieve a 2 micron thick nLOF2020 photoresist:

- 1. Blanket-sputter the sample with Au.
- 2. Spin nLOF2020 at 4000 RPM for 30 seconds and bake at 110°C for 60 seconds.
- 3. Expose sample on the MA/BA6 at  $70 \text{ mJ/cm}^2$ .
- 4. Post exposure bake the sample at 105 °C for 60 sec.
- 5. Develop for 60 sec.

- 6. Use the M4L plasma descum recipe 3.
- 7. Use gold etchant (KI and H<sub>2</sub>O) to remove the gold. Note that the etch rate is extremely fast

(< 1 min for 500 nm, depending on level of agitation)

8. Remove photoresist with PRS 3000 at 85°C for 10 minutes



Fig. A.1. (a - c) Top view of patterning SPR3012/LOR5A liftoff resists on sample with high topography. There is clear inhomogeneity in the resist, as the photoresist does not cover certain areas of the rectangular trenches, and residual photoresist is in the areas for metal deposition (d) indicates the liftoff process, where it is especially difficult to achieve fast and optimal liftoff due to the poor resist profile, as indicated by the blue arrow.

# A.3.3. For protection against dicing

A protection layer is often needed when using a dice saw to divide the wafer into devices. This is to prevent debris from scratching the device. Oftentimes, spin coating a thin layer of photoresist (such as a single layer of SPR 955) is enough. However, some devices have been released from the substrate (such as via DRIE) and thus spin coating photoresist is difficult, as released devices can break much more easily. In these scenarios, MicroSpray by Micro Chem is used to spray coat rather than spin photoresist. After spraying a thick layer of photoresist on a sample, the sample should be placed at a hot plate that is at room temperature before gradually ramping up to 110 °C. This gradual ramping was found to be crucial, as since the photoresist is thick due to spray-coating,

immediately placing the sample on a hot plate at 110°C will result in nonuniformity from bubbling. The sample should be heated at 110°C for 10 min.

### A.3.4. For protection against etching

The selection and processing of photoresist to protect a sample during etching was divided into two spheres: wet etching and dry etching.

For wet etching, such as etching away oxides (i.e., SiO<sub>2</sub> and PZT), HMDS and SPR 1827 are used:

- Spin HMDS for 2000 RPM for 15 seconds. In addition, before taking it off the vacuum chuck, use a cleanroom-grade Q-tip to apply photoresist on the edges of the sample to decrease the chance of delamination, as acids may attack the interface between the photoresist and sample.
- 2. Bake sample at ~  $115^{\circ}$ C for 5 minutes.

For dry etching, two photoresists were used for experimentation: multiple coats of SPR 955, or a single "thick" coat of AZ 4620.

#### A.3.5. Using SPR 955 (4 – 10 μm):

- Place sample on a hot plate at 105°C for 1 minute to remove water from the surface of the sample
- 2. Spin coat HMDS at 2500 RPM for 15 seconds and bake at 105°C for 1 min.
- Layer 1: Spin coat 955 photoresist at 2000 RPM for 30 seconds and bake at 105°C for 5 min.
- Layer 2: Spin coat 955 photoresist at 2000 RPM for 30 seconds and bake at 105°C for 5 min.

- Layer 3: Spin coat 955 photoresist at 2000 RPM for 30 seconds and bake at 105°C for 2 min.
- Expose on the MA/BA6 for 4 cycles, each with 8.5 seconds exposure time at 8 mW power and 30 sec wait time between cycles.
- Develop in CD 26 for 3min, 30 sec, switching to a fresh batch of CD 26 at the halfway mark with light agitation.
- 8. Use the M4L descum recipe 3.
- Soft bake the photoresist at 90°C for five minutes per layer coated prior to etching to remove any potential residual solvent.

Each layer of 955 photoresist yields approximately  $2.5 \ \mu m$ . Other processing conditions with SPR 955 is given in Table A.3.

SFR 755 FHOTORESIST PARAMETERS			
Number of 955 Layers at 2000 RPM	Exposure Parameters	Develop Time	Thickness (µm)
2	2 cycles, 8 mW, 9 sec per cycle, 30 sec wait time	2.5 min	~ 4 - 5
3	4 cycles, 8.5 sec exposure, 30 sec wait time	3 min, 30 sec	~ 6 - 8
4	5 cycles, 10 sec, 30 sec wait time	5 min	~ 8 - 10

TABLE A.3	
SPR 955 Photoresist parameters	

# A.3.6. Using AZ 4620 (10-15 μm)

1. Prebake sample at 105 °C for 1 min.

- 1000 RPM for 30 sec with AZ 4620 photoresist for 15 micron thickness or 1500 RPM for 30 sec with AZ 4620 for 10 micron thickness
- 3. Bake at 90 °C for 1 min and at 105 °C for 3 min.
- 4. Wait for one hour to allow the photoresist to re-hydrolyze.
- Expose for ~50 mJ/cm<sup>2</sup> per micron (850 mJ/cm<sup>2</sup> for 15 μm thickness or 900 mJ/cm<sup>2</sup> for 10 μm thickness
- Develop in AZ Developer 400K 1:4 for five min, switching to a fresh batch of AZ Developer 400K 1:4 at 2.5 min.

Tangentially related, hard masks such as ~ 80 nm of  $Al_2O_3$  deposited via atomic layer deposition at elevated temperatures (i.e., 175°C to 200°C) also serve as high-quality masks for etch patterning. For instance, it has been reported that the selectivity between alumina and silicon is ~ 1: 3800 [M. D. Henry et al, *Nanotechnology*, vol. 20, 2009.]. For the current work, 15 microns of AZ 4620 has been demonstrated to withstand 2 microns of PZT etching and ~ 400 microns of Si DRIE with optimal cooling conditions.

### A.3.7. For using thick negative photoresists (greater than 50 µm):

One of the more convenient ways to construct a lab-on-chip device (i.e., microfluidic channels) is to provide a mold with the desired channel dimensions and coat the PDMS on top of this mold. Upon curing and peeling off the PDMS, the features would be transferred from the mold to the PDMS. The mold is a template for the microfluidic channel device. Oftentimes, the mold for the microfluidic channel should be tens of micrometers in height. SU-8 photoresist was used to creature features of  $\sim 50 - 60 \,\mu\text{m}$  in height. The following process was used to achieve a  $\sim 60 \,\mu\text{m}$  thick photoresist.

- 1. Use the M4L descum recipe 1.
- Spin statically at 2300 RPM for 45 seconds. Then, bake at 65°C for 2 min and 95°C for 8 min.
- Expose 4 cycles, with each cycle having 12.5 second exposure time at 8 mW power, 30 second wait time between cycles
- 4. Post exposure bake the sample at 65°C for 2 min and 95°C for 6.5 min.
- Develop in SU-8 developer for 6 min, with light agitation and switching to a fresh batch of SU-8 developer at the 3 min mark.

### A.4. Etching Process:

The following etch processes for these materials were developed/used during this Ph.D.

#### A.4.1. RIE (ULVAC) Process:

The following dry etching procedures were used to etch PZT, alumina, SiO<sub>2</sub>, and Pt. The etch rates for full 4-inch wafers are given. Note that etch rates can vary considerably due to a variety of factors, such as sub-mounting (etch rates will increase due to inadequate cooling), sufficient Helium cooling, etc. It is thus recommended to etch only 50% of the targeted thickness, and then ascertain the remaining thickness via ellipsometry and reoptimize the next etch time accordingly. It should also be noted that when coating on thick resists for etch protection in the ULVAC, the sample may have accumulated thick photoresist on the perimeter of the wafer, known as the edge bead. This edge should be cleaned off with acetone/IPA about 2 mm from the wafer edge. If not, the photoresist can reticulate, and the sample can become stuck in the chamber tool. In addition, samples should not be exposed to extended periods of etch time. This is because the

sample and the chamber will be exposed to significant heat with prolonged etch time. This can cause photoresist to reticulate, photoresist features to become compromised, and increasingly faster etch rates over time. Thus, it is best to etch for only a short amount of time (i.e., 20 seconds), followed by a cooldown time where the gases are still flowing but the plasma is off (i.e., 60 seconds). This prevents the overall chamber from heating up and causing photoresist reticulation. In addition to the cooling steps, the He flow indicating optimal cooling is less than 2 sccm.

Table A.4 - Recipe Name: CCPZTSWKETCH (For PZT Etching)Etch Rate: 1.2 – 1.9 nm/min		
	Step 1	Step 2 (Cooling)
APC Press Set (mtorr)	3.8	3.8
Trigger press (mtorr)	22.5	22.5
PFC Press (torr)	10	10
PFC Flow (sccm)	0	0
Ar flow	10	10
O2 Flow	0	0
CF <sub>4</sub>	7	7
N <sub>2</sub> flow	0	0
HBr Flow	0	0
BCl <sub>3</sub> Flow	0	0
SiCl <sub>4</sub> Flow	0	0
Cl <sub>2</sub> flow	3.5	3.5
Antenna RF Power Set (W)	600	0
Antenna AMC No (Pos)	1	1
Bias RF Power Set (W)	150	0
Bias AMC No (Pos)	1	1
Process Time set (sec)	20	60

Star Electrode (0:OFF/1:ON)	0	0
EPM No (0 -31)	0	0
Over Etch (%)	0	0
EPM Set No (0-31)	0	0
Bias V <sub>pp</sub> Low Set (V)	0	0
Bias V <sub>pp</sub> High Set (V)	0	0

Table A.5 - Recipe Name: CCAl2O3 (For Alumina Etching)   Etch rate: ~36 nm/min		
	Step 1	Step 2 (Cooling)
APC Press Set (mtorr)	5	5
Trigger press (mtorr)	15	15
PFC Press (torr)	10	10
PFC Flow (sccm)	0	0
Ar flow	0	0
O <sub>2</sub> Flow	0	0
CF4	0	0
N <sub>2</sub> flow	0	0
HBr Flow	0	0
BCl <sub>3</sub> Flow	30	30
SiCl <sub>4</sub> Flow	0	0
Cl <sub>2</sub> flow	6	6
Antenna RF Power Set (W)	1000	0
Antenna AMC No (Pos)	1	1
Bias RF Power Set (W)	75	0
Bias AMC No (Pos)	1	1

Process Time set (sec)	20	60
Star Electrode (0:OFF/1:ON)	0	0
EPM No (0 -31)	0	0
Over Etch (%)	0	0
EPM Set No (0-31)	0	0
Bias V <sub>pp</sub> Low Set (V)	0	0
Bias V <sub>pp</sub> High Set (V)	0	0

Table A6 - Recipe Name: CCSiO2 (For Silicon Dioxide Etching)Etch Rate: ~4.5 nm/sec		
	Step 1	Step 2 (Cooling)
APC Press Set (mtorr)	10	10
Trigger press (mtorr)	22.5	22.5
PFC Press (torr)	10	10
PFC Flow (sccm)	5	5
Ar flow	0	0
O <sub>2</sub> Flow	0	0
CF4	40	40
N <sub>2</sub> flow	0	0
HBr Flow	0	0
BCl <sub>3</sub> Flow	0	0
SiCl <sub>4</sub> Flow	0	0
Cl <sub>2</sub> flow	0	0
Antenna RF Power Set (W)	500	500
Antenna AMC No (Pos)	1	1
Bias RF Power Set (W)	200	200

Bias AMC No (Pos)	1	1
Process Time set (sec)	220	220
Star Electrode (0:OFF/1:ON)	0	0
EPM No (0 -31)	0	0
Over Etch (%)	0	0
EPM Set No (0-31)	0	0
Bias V <sub>pp</sub> Low Set (V)	0	0
Bias V <sub>pp</sub> High Set (V)	0	0

Table A.7 - Recipe Name: CCJYPTEtch (For Pt Etching)   Etch Rate: ~50 nm/min		
	Step 1	Step 2 (Cooling)
APC Press Set (mtorr)	3.5	3.5
Trigger press (mtorr)	15	15
PFC Press (torr)	10	10
PFC Flow (sccm)	0	0
Ar flow	40	40
O <sub>2</sub> Flow	0	0
CF4	0	0
N <sub>2</sub> flow	0	0
HBr Flow	0	0
BCl <sub>3</sub> Flow	0	0
SiCl <sub>4</sub> Flow	0	0
Cl <sub>2</sub> flow	30	30
Antenna RF Power Set (W)	700	0
Antenna AMC No (Pos)	1	1

Bias RF Power Set (W)	100	0
Bias AMC No (Pos)	1	1
Process Time set (sec)	30	15
Star Electrode (0:OFF/1:ON)	0	0
EPM No (0 -31)	0	0
Over Etch (%)	0	0
EPM Set No (0-31)	0	0
Bias V <sub>pp</sub> Low Set (V)	0	0
Bias V <sub>pp</sub> High Set (V)	0	0

## A.4.2. RIE (PT720) Process:

The following recipes were developed and optimized by Dr. Tianning Liu et al. for removing the scum layer after BCB curing (described in section A.5) and removing TiO<sub>2</sub> and/or Ti [1]:

Material	Pressure	DC Bias (V)	Gas Flow Ratio (sccm)	Etch rate				
	(mTorr)							
Ti or TiO <sub>2</sub>	150	65	CF <sub>4</sub> /O <sub>2</sub> /Ar: 24/6/6	~ 6 nm/min				
BCB (etch)	100	100	CF <sub>4</sub> /O <sub>2</sub> : 20/80	65-100 nm/min				
× ,								
BCB (scum)	100	100	CF <sub>4</sub> /O <sub>2</sub> : 3/47	N/A				

Table A. 8: PT 720 Reactive Ion Etching (PlasmaTherm)

### A.4.3. Wet Process:

To remove any oxides (such as PZT but particularly  $SiO_2$  that cover the entire backside of wafers), it is sometime useful to use wet etches that would stop on the Si (111) and prevent any roughness that may arise from using RIE process. In order to remove the thermal oxide/an oxide from a full four-inch wafer, the following process is recommended:

1. Spin HMDS at 2000 RPM for 15 seconds on the substrate and bake at 110°C for 1 min

- Spin 1827 at 2000 RPM for 30 seconds. Use a Q-tip to apply photoresist on the edge of the wafer. Bake at 115°C for 5 min
- Place the wafer on a wafer holder at a 45-degree angle, with the protected side facing downward. Place the whole setup in a small plastic container.
- 4. Use BOE 6:1 and then hydrochloric acid. Use a syringe and alternate spraying BOE 6:1 and hydrochloric acid. You will notice that the surface chemistry will change when all the SiO<sub>2</sub> has been removed, the droplets of the HCl and BOE 6:1 de-wet from the Si surface.

Oftentimes, the procedure above is used to etch PZT to gain access to the bottom electrode for electrical measurements. If one is worried about using such hazardous chemicals such as BOE 6:1, a quicker and more convenient way is to use a blade and scratch a small area of the sample, exposing the bottom electrode. To have a more reliable connection, one can use the Quorum Sputter Coater to sputter 100 nm of Pt on this scratched area (a procedure that only takes 5- 10 minutes total). A microscope slide can be used to mask areas where Pt is not desired.

**A.5. BCB Processing**: Dr. Tianning Liu's process was used to achieve 0.9 microns thickness of Bis-Benzocyclobutene (BCB) [1]. This material can be used as an insulation layer to deposit wirebonding pads on as well as reducing parasitic capacitance:

- 24 hours before processing, bring the BCB solution to room temperature (for a 0.9 micron film, the solution has a volumetric ratio of 2 BCB to 1 mesitylene solvent, and is normally stored in the cleanroom freezer). Keep the BCB solution sealed at all times.
- 2. Spin coat statically at 900 RPM for 6 seconds and then at 3000 RPM for 40 seconds.

- 3. Bake on a hotplate at 60°C for 2 minutes
- 4. Expose on the MA/BA6 tool for 12 seconds at 6 mW power.
- 5. Post-exposure bake for 5 minutes at 60°C on hot plate.
- Immediately develop in DS3000 at 40 °C for 4 minutes (use a thermocouple to confirm the temperature, sometimes setting the temperature at 53°C and waiting for at least thirty minutes to stabilize).
- 7. Transfer the sample into a clean DS3000 bath at room temperature.
- 8. Blow dry with a nitrogen gun (this step usually takes  $\sim$  5 minutes).
- Cure the BCB in an oven under vacuum at 239°C with slight bleed of Nitrogen for at least 7 hours (or overnight).
- 10. Cool down the sample to less than 100°C before removing the sample.
- 11. To remove the BCB descum layer, use the PT 720 with the settings of 47 sccm  $O_2/3$  sccm  $CF_4$  gas flow with pressure of 100 mTorr and a DC bias of 100 V for 2 minutes.

#### A.6. PDMS

PDMS was tested as a waterproofing/matching layer for PMUTs, as well as the main substrate for microfluidic devices. The PDMS thickness is controlled via 3D printing a "dish" that has an adequate height. The smallest thickness achieved without tearing was  $\sim 1.5$  mm. The following process was used for PDMS:

- Pour into a weight tray Elastomer 184 Silicone Curing Agent and Elastomer 184 Silicone Base in a 10:1 ratio. For a full 4 inch wafer, it typically takes ~ 15 g.
- 2. Mix the solution for 5 min.
- 3. Put in a desiccator under vacuum for 30 40 min (until most of the bubbles have gone)

- 4. Put sample into the 3D printed dish and pour the PDMS into it.
- 5. Spread the PDMS across the sample. Using a flat object (i.e., a ruler), sweep the top of the dish to achieve as uniform of a height as possible.
- 6. Put in an oven for 45 min at 80°C.

#### A.7. ACF Cable Fabrication:

The following processing parameters provided by Dr. Tianning Liu et al. to fabricate flexible cables for ACF bonding [1].

- Be sure when handling the 3 μm Cu/Polyimide/3 μm Cu sheet to keep it as flat as possible to minimize wrinkles.
- 2. Sonicate a piece of Cu/Polyimide/Cu sheet in acetone for 5 minutes.
- 3. Rinse with IPA and dry.
- Use the M4L oxygen plasma to remove organic residue with the settings of: 50 sccm He, 150 sccm Oxygen, 200 watts, 550 mTorr for 1 minute
- 5. Tape the sheet on a Si carrier wafer.
- 6. Spin coat SPR 3012 photoresist at 2000 RPM for 45 seconds.
- 7. Take the sample off the carrier wafer and bake at 95°C for 2 minutes.
- 8. Etch with Transene copper etchant CE-100. This will remove the metal on the side where the photoresist is not protecting the copper.
- 9. Expose on the MA/BA6 for 12 seconds at 8 mW power.
- 10. Develop in CD 26 for 1 min and 30 sec.
- 11. Use 0.5% KMnO<sub>4</sub> + 0.5% KOH solution for two minutes to clean up the conductive seeding layer.

- 12. Remove photoresist in acetone. Wash with isopropanol afterwards.
- Immerse the cable pattern in Bright<sup>TM</sup> electroless plating solution at 80°C for 10 minutes to plate gold on the copper.

#### A.8. PZT solution preparation:

An inverted mixing order process developed by Schwartz et al. was used to make PZT solution of various compositions [2-5]. The general solution flow was developed with Travis Peters and is as follows to prepare 20 mL of 0.4 molar PZT solution. The amounts are given in Table A.9 for the 52/48 composition, and were adjusted accordingly for each PZT composition

	Pb II Acetate Trihydrate	Zr n-butoxide	Ti butoxide	Nb butoxide	Acetic Acid
Molecular Wt. (g/mol)	379.34	383.68	340.32	463.5	60.052
Molal Factor	1.1	0.5096	0.4704	0.02	4
Moles (mol)	0.0088	0.0040768	0.0037632	0.00016	0.032
Grams (g)	3.3381	1.955	1.320	0.07416	1.9217
Volume (mL)	N/A	1.8639	1.3203	0.0585	1.8302

Table A.9. Inverted Mixing Order Amounts for PZT 52/48 Composition

- 1. Add 1.8639 mL of Zr n-butoxide to a glass beaker
- 2. Add 1.320 mL of Ti butoxide to the Zr n-butoxide solution
- 3. Add 0.0585 mL of niobium butoxide into the Zr/Ti solution
- Use parafilm to seal the top of the beaker and sonicate for 5 min to allow adequate mixing.
- 5. Add 1.8302 mL of acetic acid into the Zr/Ti/Nb solution

- 6. Sonicate for an additional 5 min.
- 7. Add 2 mL of methanol
- 8. Add 3.3381 g of lead acetate trihydrate into the solution.
- Place the solution on a hotplate set at 100°C for 30 min (until all the lead is dissolved) with light agitation.
- 10. Pour solution into a graduated cylinder to ascertain the volume of the solution.
- 11. Add a 1:1:5 volumetric solution of methanol/distilled water/acetic acid into the graduated cylinder until the desired concentration is reached. For example, if 13.5 mL is needed for a total of 20 mL PZT solution, then pour in sequence 1.929 mL of methanol, 1.929 mL of H<sub>2</sub>O, and then 9.642 mL of acetic acid.

### Appendix References:

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#### **VITA**

#### **Christopher Cheng**

Christopher You-Yee Cheng was born in Decatur, Indiana to Chi-June Ko and Thim Kian Cheng. He grew up in Parsippany, New Jersey until third grade before moving to Minnesota where he lived from fourth grade to the end of his undergraduate career. He graduated from Eden Prairie High School in June 2011. He then began his studies at the University of Minnesota, Twin Cities Honors Program. He switched majors three times, starting as a biomedical engineer to chemical engineer before double majoring in Materials Science and Engineering and Chemistry, graduating cum laude. He has also worked in three different research labs at the University of Minnesota, as well as in three different divisions as a summer intern at 3M. In August 2016, Chris joined Dr. Susan Trolier-McKinstry's group at the Pennsylvania State University, specializing in the fabrication and characterization of piezoelectric micromachined ultrasound transducers. With Dr. McKinstry as an advisor, Chris was able to work in a variety of labs (such as Dr. Sandy Cochran's lab in Glasgow, Scotland, and Dr. Ronald Polcawich's PiezoMEMS team at the Army Research Lab in Adelphi, Maryland) and was awarded the National Science Foundation as well as the National Defense Science and Engineering Graduate Research Fellowships. Upon graduation, he will be working at Intel.