



**ENERGY HARVESTING WITH MICRO
MACHINES**

THESIS

Noah T. Blach, 2Lt, USAF

AFIT-ENG-MS-17-M-007

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Abstract

A device that harvests heat into usable electrical power would increase overall power efficiency and reduce costs in the armed forces. Traditional combustion engines and moving fluid systems are too bulky and expensive to be placed in many conventional systems or places. Ferroelectric materials can generate power, but only if moved from a cold sink to a hot source using a mechanical device. MEMS devices are mechanical devices made with specialized techniques with feature sizes on the micrometer scale. A MEMS device that moves in response to heat is fabricated, and is used as a mechanical base for developing an energy harvesting device. Membranes with device layers as thin as 2 micrometers are fabricated. Simulation is used to determine resonance frequencies near 100 kHz. Simulations also show the time to reach thermal equilibrium is 1 millisecond. The voltage generated on such devices is shown to be 3 volts in simulations. The ideal thickness of oxide is examined, and is equal to the thickness of the silicon layer. The completed devices show deflections from 1 to 3 microns. Applied voltage produces a deflection of .2 microns. The optimal frequency for harvesting energy is 5 hertz and produces -60 dbV.

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List of Abbreviations

Abbreviation	Page
PZT	lead zirconate titanate 1
AlN	aluminum nitride 1
XRD	X-ray diffraction analysis 7
Rochelle salt	potassium sodium tartrate tetrahydrate 11
PVDF	polyvinylidene fluoride 12
PT	lead titanate 18
PZ	lead zirconate 18
PMN	lead manganese niobate 18
PZNT	$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ 19
PMNT	$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ 19
TrFE	trifluoroethylene 21
FOM	figures of merit 21
SNL	Sandia National Labs 24
SUMMIT	SNL Ultraplanar, Multilevel MEMS Technology 24
DRIE	Deep Reactive Ion Etching 25
C_4F_8	octoflourocylcobutane 25
SF_6	sulfur hexaflouride 25
RIE	reactive ion etching 26
BOE	buffered oxide etch 28
KOH	potassium hydroxide 28
TMAH	tetramethylammonium hydroxide 28
BOE	buffered oxide etch 28

Abbreviation		Page
PECVD	plasma enhanced chemical vapor deposition	35
SiH ₄	silane	36
NH ₄	ammonia	36
SOI	silicon on insulator	42
CTE	coefficient of thermal expansion	45
TEG	Thermoelectric generators	65
IPA	isopropyl alcohol	71
DI	Deionized	71
ARL	Army Research Labs	84
AlN	aluminum nitride	85
AFRL	Air Force Research Laboratories	85
SEM	Scanning Electron Microscope	88
XPS	X-ray Photoelectron Spectroscopy	88
HeNe	Helium-Neon	88
eV	Electron Volts	101

ENERGY HARVESTING WITH MICRO MACHINES

I. Introduction

The ability to harvest waste energy from small scale sources would be useful to power small, autonomous systems that do not require batteries [1]. Such sources include vibrations [2], electromagnetic waves [3], and heat [1]. In the United States, over 50% of energy consumed is lost as waste heat [4], making this an ideal source from which to harvest energy. Piezoelectric and pyroelectric materials combined with MEMS technologies show promise to make energy from these sources available for energy harvesting with potential use in applications such as remote sensors [5].

This project details the fabrication of an energy harvesting MEMS device using only parallel microfabrication methods, suitable for producing many devices at once. In chapter II, the background necessary for understanding this project is presented. One section is devoted to ferroelectricity and includes information on piezoelectricity and pyroelectricity. The materials which demonstrate ferroelectricity such as lead zirconate titanate (PZT) and aluminum nitride (AlN) are explained and enumerated. The following section explains the relevant methods of micromachining and fabrication these materials. This is necessary to understand how a material can be processed and packaged into a useful device. A third section is given to explain the efficiency of harvesting energy and of thermodynamic cycles. Without correctly operating a device on the correct thermodynamic cycle, energy efficiency will not occur, so this section is crucial for the actual operation of the device. Lastly a review of comparable devices is given to show both that this project has not yet been attempted, and that the general goal is of interest to the scientific community. In chapter III, the method-

ology of how this project was executed is given. A step by step process of building a ferroelectric energy harvesting devices is presented, followed by the process for testing such devices once they are made. Details of the setup for finite element simulations are noted as well. A simulated approach is useful, both for designing the device before fabrication, and for simulating the device performance in ways that can not be tested in lab. In chapter IV, the results and analysis of the procedures performed in chapter III are shown. The simulated results of device actuation under different conditions is presented. The results of characterization of the ferroelectric materials in use is given, as well as the results from processing them in laboratory settings. The results of making membranes on scales smaller than previously attempted is shown. In chapter V, the report is concluded with a summary of the findings, this project's contribution to science, lessons learned from this project, and recommendations for future research.

II. Background

There are multiple underlying disciplines which are required for the creation of a MEMS energy harvesting device. This chapter is broken into four parts to provide the necessary background to those disciplines. The first section will detail the history, physics, and practical use of ferroelectric materials, which can potentially enable energy harvesting. The next section will address the modern state of microfabrication processes and capabilities as they relate to this project, and which allow the formation of ferroelectric materials in micro-sized devices. The third section will be a survey of comparable devices in modern literature, to provide a general understanding of what sort of devices have already been created. The last section provides the necessary background to energy harvesting cycles, which are necessary to operate devices with thermodynamic efficiency.

2.1 Ferroelectricity

2.1.1 Introduction to Ferroelectricity

Ferroelectricity is the phenomenon of permanent electrical polarization of a material in response to an applied field [6, 7, 8, 9, 10, 11, 12]. This effect, unknown until the 20th century, has the potential to enable the conversion of heat into energy. Materials which are ferroelectric are also pyroelectric, which is the development of an electrical polarization in response to a change in temperature [13]. In addition, ferroelectric materials are also piezoelectric, which is the generation of an electric polarization in response to a change in stress [14]. Materials with these properties can be used to generate electrical energy from physical quantities such as stress and heat, allowing them to be used for energy harvesting devices [15]. All ferroelectric materials are pyroelectric, and all pyroelectric materials are piezoelectric [16]. The relationship

between these properties is shown in Fig. 1. The quantities of temperature, charge, and strain are all interrelated by piezoelectric and pyroelectric properties, as shown in Fig. 2. This means that none of these properties can be changed without affecting all of the others, and they all must be simultaneously taken into account. In addition to the previous mentioned properties of piezo and pyroelectricity, one can use ferroelectric materials to change the temperature based on an applied electric field or even cause heat in response to applied strain, using the electrocaloric effect and the piezocaloric effect. To make use of these properties in an energy harvesting device, it is important to select a suitable material, which can be aided by understanding the crystal structure of potential materials, and how that affects a materials performance in real-life conditions.

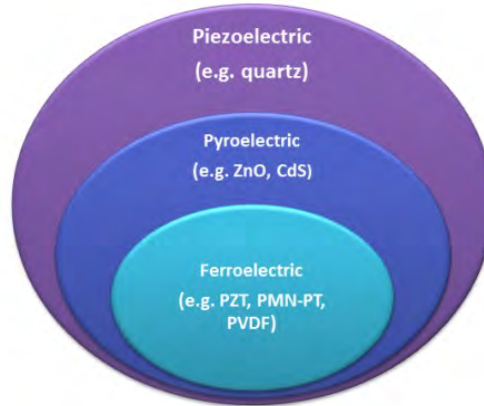


Figure 1. Ferroelectric materials are a subset of pyroelectric materials, which are a subset of piezoelectric materials [16]. The properties a material possesses can change with the temperature. Ferroelectrics have a temperature named the Curie point. Below this temperature, they can possess ferro, pyro, and piezoelectricity. Above this point, all three properties are lost. Some compounds even have upper and lower curie points, and only inside the range will these properties occur. There is no reason that all of a compounds properties must be used, and a ferroelectric material can be used only for its piezoelectric properties, without regard to ferro or pyroelectricity.

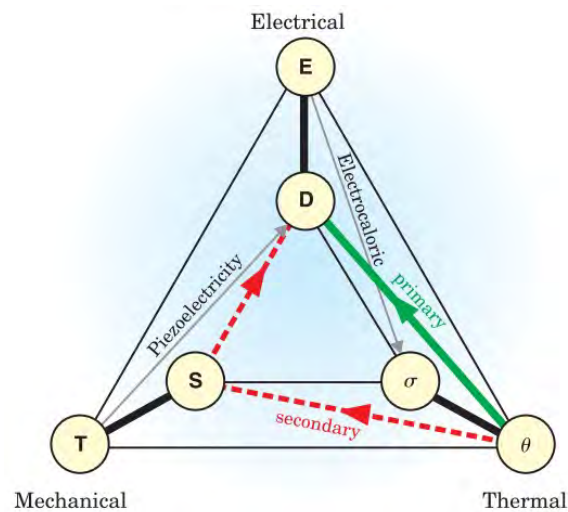


Figure 2. The complete state of a ferroelectric material is incomplete without knowing the stress, electric field, and temperature [13]. A change in one property will cause a change in the others, via the mechanisms shown. The processes that lead to the generation of electricity from heat are shown in green and red. The green arrow is the pyroelectric effect, or the direct conversion of heat to electrical displacement. The red arrows is the secondary pyroelectric effect, which is the generation of strain from heat using thermal expansion, and then the generation of displacement from strain. More complicated effects, such as the tertiary pyroelectric effect, the generation of charge from a nonuniform temperature gradient, are not shown.

2.1.2 Crystal Structure

Unlike properties such as conductivity and tensile strength, which all solids possess, piezoelectric and pyroelectric quantities are identically zero across a wide range of substances, limiting material selection [14]. The appearance of these properties depends entirely on the crystalline structure of a compound. Any crystalline structure that has an inversion center will not be piezoelectric due to symmetry. In addition, the crystal class 432 is not piezoelectric [14]. Of the 20 remaining classes, the 10 polar crystal classes also display pyroelectric properties. Unfortunately for prospective materials scientists, while these conditions are necessary, only a small proportion of chemicals in these classes display ferroelectricity, piezoelectricity, or pyroelectricity of useful magnitude [14]. Unlike a capacitor, where, charge is accumulated only on the ends of the device, ferroelectric materials have change in every unit cell. In ferroelectric crystals, the polarization is due to the spontaneous realignment and movement of atoms inside the crystal lattice in response to stress or temperature change. Atoms exist as ions with charge in the lattice, and the movement of charge will generate current. This movement of atoms is described as a first or second order deformation of the crystal lattice. A first order deformation of the lattice is a change of symmetry, such as a transition from 4mm to 3m symmetry. A second order deformation is the continuous change of a lattice parameter such as cell size while the overall symmetry remains unchanged. Near first order transition points and during second order transitions, a ferroelectric material will exhibit properties such as varying permittivity and heat capacitance in addition to ferroelectric effects. In fact, ferroelectrics were first discovered because researchers exploring for substances with high permittivity for capacitors would occasionally test a ferroelectric near its transition temperature, and find an enormously high capacitance. Because the properties of ferroelectric transitions occur due to the proximity of the material to these phase

change points, and because a change in temperature will alter a materials location on the phase diagram, this causes rapid change of energy-harvesting potential for a given material as temperature changes. In addition, the properties of ferroelectric crystals are highly temperature dependent [17]. This means that any given material will only operate properly in a limited temperature range. Some materials can generate electricity most effectively at this transition point, called the curie point, and not at all above it. Moving the temperature of the device by a few degrees above this point would cause electricity to stop being generated. In addition, stress between the electrode and the ferroelectric will also move the material on the phase diagram, by effectively changing the pressure that the material is under. This means that the choice of electrode can alter the performance of the ferroelectric material, as the conducting electrode and insulating ferroelectric stretch at different rates. Moreover, the lattice mismatch between the electrode and the ferroelectric can cause strain and dangling bonds, affecting the chemical properties of the ferroelectric. Therefore, even after selecting a ferroelectric material, it is necessary to find a suitable electrode, and a suitable temperature at which to operate. Since ferroelectric properties are all dependent upon the crystal structure, the orientation of the crystal drastically change material properties, even if overall chemical composition and crystal structure itself is unchanged. For example, the capacitance difference between different orientations of PZT is shown in Fig. 3. The orientation of a crystal is determined via X-ray diffraction analysis (XRD). In this analysis, the pattern of x-rays diffracted through a single crystal are matched to a library of known compounds to identify the structure, and which orientations and phases are present. A sample PZT XRD spectrum is shown in Fig. 4. For bulk piezoelectric materials, of millimeter thicknesses, surface effects would not be as important, since a single crystal of a material could be grown, cut, then combined with any electrode with negligible surface effects. But for this

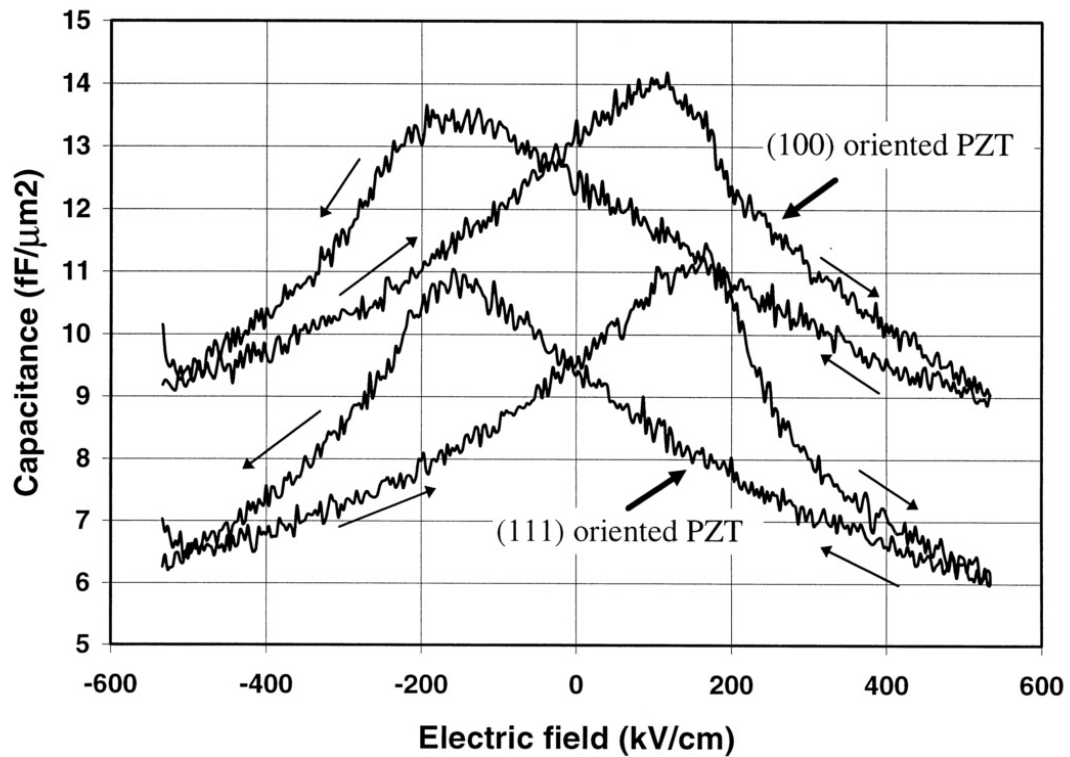


Figure 3. In addition to capacitance, the pyroelectric coefficient, the heat capacity, and other properties are highly dependent on the crystal axis [18]. These properties cannot be changed by the after fabrication, and if a device is made improperly, that orientation is permanent. The reorientation that occurs in ferroelectrics is of the domain walls, but the domain walls move while maintaining the same crystallographic orientation.

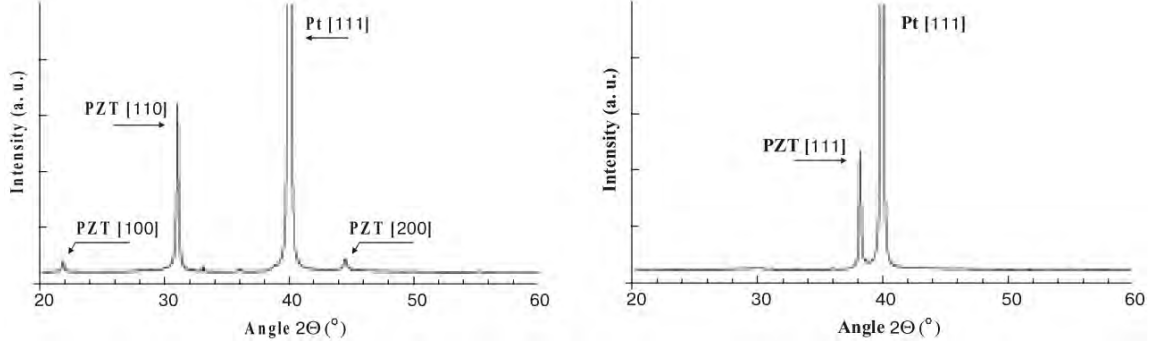


Figure 4. It is normally desired to achieve a single orientation of PZT in a device [19]. The sample with XRD spectrum shown on the left has multiple orientations of PZT, while that shown on the right has only one orientation. Even though the spectrum shown on the left has one orientation, it is polycrystalline, not monocrystalline. The domains in the PZT occur slightly rotated to each other and with grain boundaries, despite having the same principal axis. This necessitates using a simple 2θ scan instead of a $\theta\omega$ x-ray analysis of the material. The platinum in both examples is crystallized in the $\langle 111 \rangle$ orientation, which allows for good lattice matching to the PZT. There are no peaks visible in this plot from the silicon substrate due to the range chosen. Silicon oxide below the sample is amorphous and shows no diffraction pattern.

MEMS energy harvesting device, with a potential layer thickness of one micrometer, surface effects could dominate bulk effects, and the only way to control surface effects is to control the orientation, phase, strain, and lattice mismatch of the electrode and ferroelectric layers.

2.1.3 Mathematical Foundations of Ferroelectric Materials

This project will seek to perform computer modeling of energy harvesting devices, and it is necessary to understand the mathematical background of ferroelectrics to accept why such computer models are fundamentally limited in accuracy. The mathematical basis for ferroelectricity relies on finding the minimum thermodynamic potential of a crystal system, and using Taylor series to estimate the change in energy from the movement of the atoms [6]. These materials exhibit a change in thermodynamic potential under changes in pressure, stress, temperature, and atomic position in the lattice, which complicates thermodynamic calculations. Taylor series can involve up

to the twelfth power in multiple independent variables simply to predict certain ferroelectric phenomena, even before any considerations are taken into the accuracy of such a number [20]. A simple equation for predicting the phase transition point of PZT is [17]

$$\begin{aligned}
g_l(\tau, \mathbf{n}, p) = & \frac{1}{2}\alpha_1(n_1^2 + n_2^2 + n_3^2)p^2 + \frac{1}{4}\beta_1(n_1^2 + n_2^2 + n_3^2)^2p^4 \\
& + \frac{1}{4}\beta_2(n_1^4 + n_2^4 + n_3^4)p^4 + \frac{1}{6}\gamma_1(n_1^2 + n_2^2 + n_3^2)^3p^6 \\
& + \frac{1}{6}\gamma_2(n_1^6 + n_2^6 + n_3^6)p^6 + \frac{1}{6}\gamma_3(n_1^2n_2^2n_3^2)p^6 \\
& + \frac{1}{8}\delta_1(n_1^2 + n_2^2 + n_3^2)^4p^8 \\
& + \frac{1}{8}\delta_2(n_1^8 + n_2^8 + n_3^8)p^8 \\
& + \frac{1}{8}\delta_3(n_1^4n_2^4 + n_2^4n_3^4 + n_3^4n_1^4)p^8 \\
& + \frac{1}{8}\delta_4(n_1^4n_2^4n_3^4(n_1^2 + n_2^2 + n_3^2))p^8
\end{aligned} \tag{1}$$

Here, the $\alpha_i, \beta_i, \gamma_i$, and δ_i are functions of temperature, $\mathbf{n}$ is a polarization unit vector, p is polarization, and the function g is for the overall energy of the system. This equation is much reduced, because of the symmetry of the perovskite system, and because stress is constant, and absent in the model. This equation was used to determine the phase transition of PZT. It is possible for MEMS processes to result in compounds with multiple orientations coexisting, such as with twinning of T and R phases [21]. The intrinsic stress of a material is highly variable and leads to altered material properties [22]. This is only useful once a material exists to be analyzed, however. For a material that is projected, it is necessary to simulate each of the atoms in a unit cell, and determine the hamiltonian of all of the valence electrons. For disordered compounds that may have 30 unit cells to simulate disorder, with 5 to 6 atoms each, this is a challenging task [23]. Even measuring these coefficients for an existing compound is not as simple as measuring properties such as density, because a single compound

has many piezoelectric coefficients. Unlike density which is a scalar property, piezoelectricity is a tensor property [24]. Determining the relationship between stress and electric field depends on the orientation of the electric field and stress relative to each other and the crystal axis, and is a third rank tensor. Pyroelectricity is a first rank tensor, as it only relates to temperature, a scalar rather than stress [24]. The most commonly used piezoelectric coefficients are d_{33} and d_{31} . These coefficients are the ratio of strain parallel to the $\langle 100 \rangle$ into polarization parallel and perpendicular to the $\langle 100 \rangle$ plane. Due to the 2 dimensional nature of micromachining, these axes are more used in MEMS devices than the d_{51} coefficient, which relates shear strain to charge. In simulations it is possible to simply assume a piezoelectric tensor, but accept the material provided could be very different. In particular, for the devices being grown for this project, the intrinsic stress on the three layer wafer could radically change the coefficients from the normal value for the process. For the modeling done with this project, commonly used tensor values of PZT were used.

2.1.4 Piezoelectricity

While ferroelectric materials consist of multiple interrelations among strain, temperature, and electric field, some of these properties can occur independently of each other, enhancing or degrading the energy generated. It is important to understand each individual property and how it might affect a complete device. Piezoelectricity is the polarization of a material due to applied stress, which is observed as generated voltage or charge [7]. Quartz was the first material discovered to have this property in 1880. The common crystal oscillator that uses quartz relies on this piezoelectric property. Quartz and potassium sodium tartrate tetrahydrate (Rochelle salt) were the primary piezoelectric materials until 1942, with the discovery of barium titanate [25]. The research into piezoelectric materials was prompted by the increasing use of sonar.

Piezoelectric materials could detect sonar frequency vibrations and convert them into electric signals for military use. The properties of this material prompted a search for similar compositions and resulted in the discovery of PZT soon after [8]. PZT in various doped forms remains the predominate piezoelectric ceramic to current times. Lead free ceramics have been investigated by replacing lead with bismuth or other metals [26, 27]. These are of interest due to environmental and health concerns over using lead. It would be preferable to use a lead free material for an energy harvesting device if one were suitable. Other than single crystal ceramics, polycrystalline materials, polymers, thin films and composites can also display piezoelectricity. A common polymer piezoelectric material is polyvinylidene fluoride (PVDF) [3]. Polymers have very different mechanical properties than ceramics, such as fracture resistance. If those mechanical properties were necessary, then a polymer piezoelectric material could become useful for energy harvesting. Composites are multiphase materials that can combine the properties of 2 entirely different materials for enhanced properties, and were first rigorously investigated in 1978 for piezoelectric effect [28]. The different types of connectivity in composites are shown in Fig. 5. By combining two different known materials into a composite, it is possible to create a new form that has more desirable properties than either of the starting materials.

For energy harvesting, it is important to choose a material that can convert as much of the mechanical strain into electrical energy as possible. This number is called the coupling factor. Certain designer PZT compounds have high coupling factors of over 70% between strain and electric field [29], facilitating the direct and easy conversion of strain to electricity. In an energy harvesting MEMS device such as the one being designed here, the movement of the device will generate electricity independent of the electric field generated from temperature change. A constant strain will form an electric field once, then cease to produce useful electricity. This is why MEMS piezo-

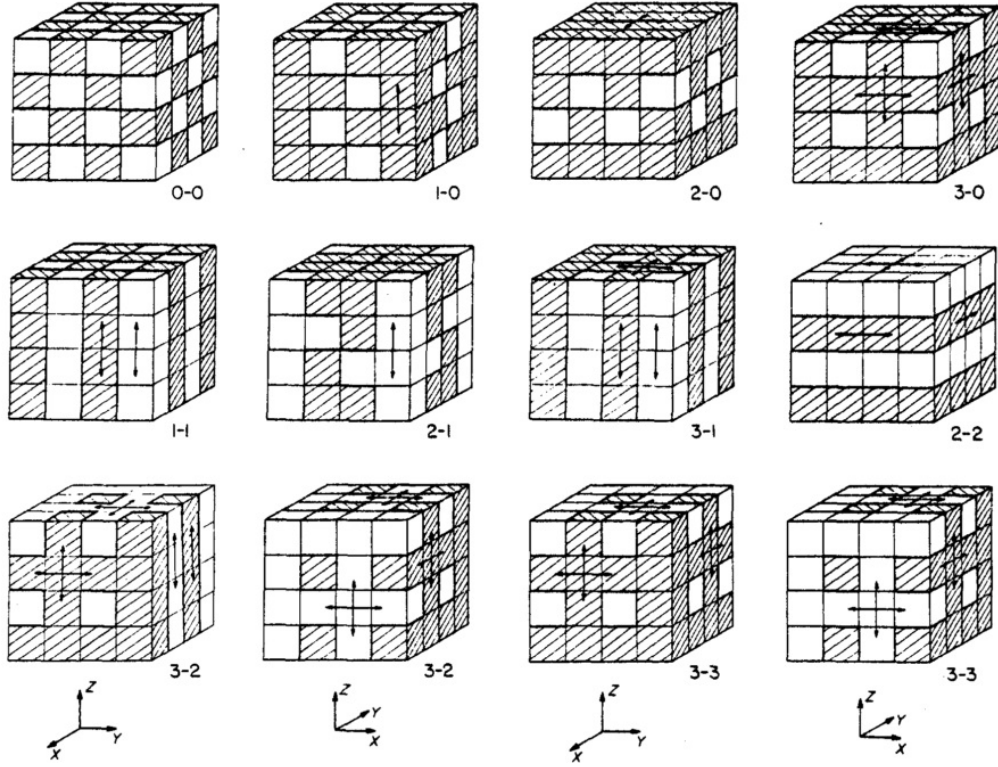


Figure 5. The figures presented are fundamental composite structures that can be used for ferroelectrics. By combining 2 different materials, it is possible to create a structure with the desirable qualities of each component. For example, it might be possible to achieve maintain the piezoelectric properties of one component while having the resistance to fracture properties of another. In addition, certain composites exhibit sum properties, or properties superior to either of the original materials. There are 10 fundamental ways of making regular, symmetrical repeating composites, and they differ in the connectivity between the materials. Each material may be connected in either 0, 1,2, or 3 dimensions. For example, a 2 dimensional connection would be a plane. In 0-0, there is no connectivity between like materials, and each light-colored material has 6 dark material regions adjacent. In 1-1, taking only the light or only the dark material, one would form 1 dimensional rods of each material. In 3-3 connectivity, even though the visualization is complicated, both the light and dark colored materials individually form connected three dimensional lattices [28].

electric energy harvesting devices focus on harvesting vibrations. The piezoelectric tensor is frequency dependent, and thus such a device acts very different over a range of applied frequencies, in addition to the fact that most mechanical structures for such devices only operate at a limited set of frequencies. Outside of energy harvesting, applications of piezoelectric materials include medical ultrasound transducers, military sonar, actuators for adaptive optics, inkjet actuators, buzzers, shock sensors, gyroscopes, resonators, igniters, capacitors, and electronic filters [30, 31].

2.1.5 Pyroelectricity

Another property of ferroelectric materials is the pyroelectric property. Pyroelectricity is a the property of some materials to develop an electric polarization due to change in temperature [32]. This means that with an alternating heat source, a pyroelectric material could generate useable electricity. The first modern analysis of pyroelectricity was performed by Brewster, who discovered that some crystals developed electric fields when heated, and named the term pyroelectricity in 1824 from the Latin prefix pyro [13]. While the ancient Greeks did note pyroelectric crystals, their attribution of these properties to lynx urine later proved inaccurate. In MEMS systems, heating a pyroelectric material will generate stress as the material and the adjacent electrode expand at different rates. This stress induces electric polarization from the piezoelectric effect, and is named the secondary pyroelectric coefficient [13]. This is one example of conflicting effects of ferroelectric materials that must be taken into account before fabricating a real device. This can enhance or degrade the pyroelectric properties of a system. Pyroelectric materials can be used in infrared detection, and can detect temperature changes smaller than $.2 \mu\text{K}$ [13]. In a MEMS energy harvesting device, under a constant thermal load, a pyroelectric material will generate an electric field once, then reach steady state. Only by constantly applying

and removing a thermal load can electricity be generated from pyroelectric materials. This is why movement is essential in a ferroelectric MEMs energy harvesting device, as opposed to a thermoelectric, which has no movement and relies on quantum effects.

2.1.6 Electrocaloric Effect

There is an additional linear property of ferroelectric materials specifically useful in energy harvesting, and that is the electrocaloric effect. The electrocaloric effect is the converse pyroelectric effect, and results in the generation of heat in materials from the movement in charge [33]. This can be used to enhance the energy production of pyroelectric materials [34]. The electrocaloric effect is the key to harvesting heat into energy using ferroelectric materials. Without it, there is a fundamental limitation of the coupling coefficient, often less than 1% for pyroelectric materials. While it is possible to rely on the conversion of heat into strain energy, this is not an energy efficient process due to all of the energy simply lost to entropy. Using the electrocaloric effect with ferroelectric materials is the only way to achieve useful energy harvesting from waste heat with these classes of materials.

2.1.7 Electrostriction

Another significant electromechanical effect occurs in lab materials that must be taken note of, and this is electrostriction. The piezoelectric tensor is more accurately modeled as a linear component and a higher power components. The quadratic term is named the electrostrictive effect [35]. Because the electrostrictive effect is quadratic and therefor an even function, it is not affected by hysteresis which makes this effect useful in some actuator applications. While most materials have a negligible electrostrictive effect compared to piezoelectric effect, certain polymers and relaxor ferroelectrics exhibit enormous electrostriction [36]. Polymers with large electrostric-

tive coefficients are more useful for actuators, as a small change in voltage generates a large displacement. Electrostriction can even occur in compounds that do not display piezoelectricity. This effect can alter the apparent piezoelectric coefficient of a device. This is the only higher order term that will be taken into account for this project; descriptions of other non-linear effects, such as the flexomagnetoelectric effect, while theoretically interesting will be omitted here.

2.1.8 PZT and Perovskite Materials

One notable material that satisfies the conditions of being useful for harvesting energy is PZT, a member of a class of materials called perovskites, having the formula ABO_3 [37, 38]. It is commonly used in MEMS devices for piezoelectric energy harvesting [39]. They have point symmetry $m3m$. In a unit cell, the anion will be at the center, the cation on the corners, and the oxygen forming an octahedron at the face centers. This perovskite structure is shown in Fig. 6 [38]. Simple compounds include BaTiO_3 , and PbZrO_3 , but mixed compounds such as $\text{Pb}(\text{Co}_{.25}\text{Mn}_{.25}\text{W}_{.5})\text{O}_3$ are used as well. Dielectric constants of 10000 near the phase transition are common. These high dielectric constants contribute to high energy harvesting potential. PZT has a stable cubic phase that begins in the range 300 to 500 degrees, depending on the amount of Zr doping. At lower temperatures, a phase boundary occurs near Zr 48% at 0 C to near Zr 58% near 400C[17]. PZT is primarily fabricated near the morphotropic boundary line which separates the tetragonal and rhombohedral states as shown in Fig. 7. PZT can be deposited in a clean room through methods such as sputtering, CVD, or sol-gel deposition [40]. The quality of sputtered PZT films is degraded by lead deficiency which occurs as a result of thermal annealing. This altered state is often a pyrochlore phase instead of a perovskite phase, and is not piezoelectrically active. If this phase were generated in lab in an energy harvesting

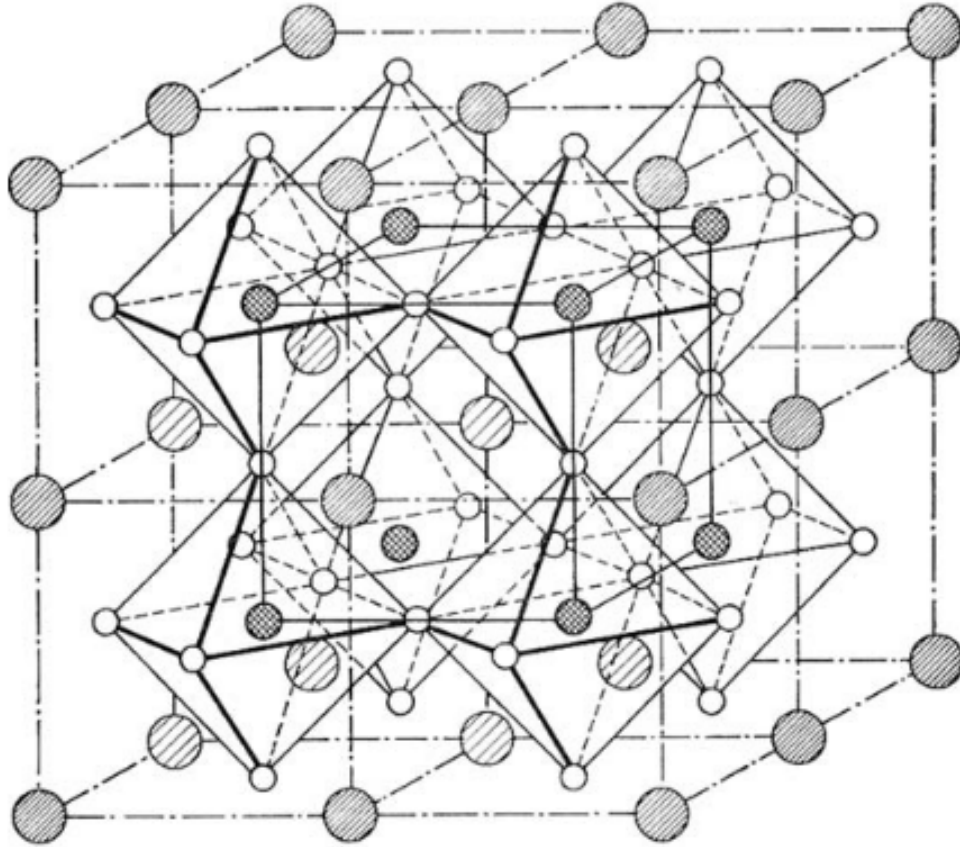


Figure 6. The perovskite crystal structure shown here is shared between PZT, barium titanate, and other ferroelectric ceramics. The octahedra can become distorted and lose some symmetry. The central lead atoms will physically move inside of this lattice, causing movement of electric charge. This is the origin of all ferroelectric effects.

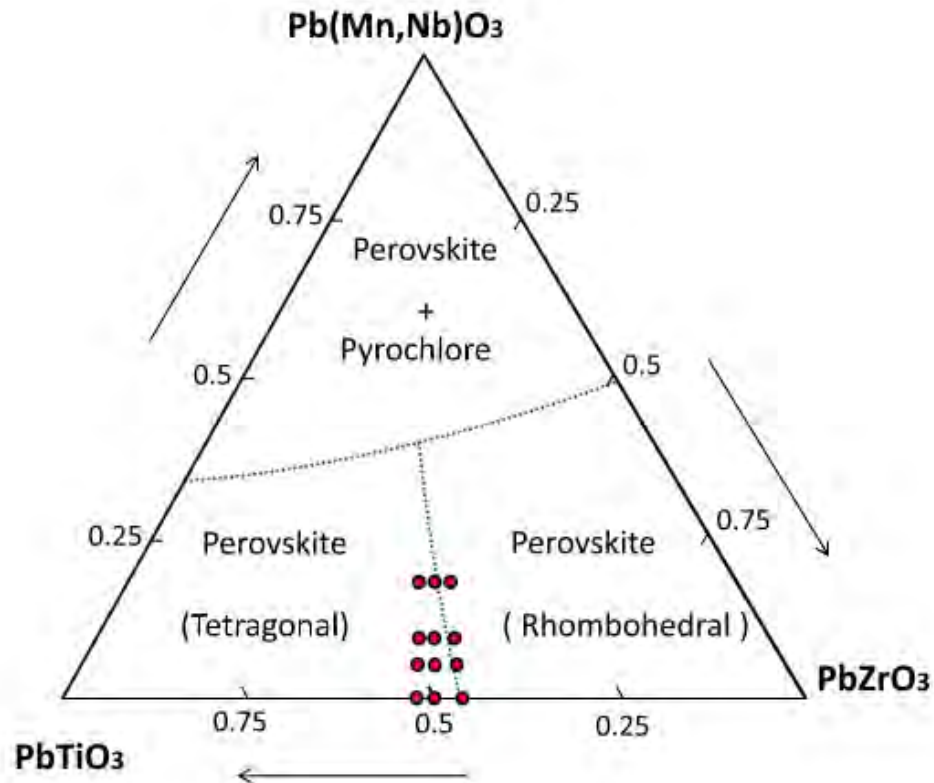


Figure 7. This is a phase diagram of mixtures of lead titanate (PT), lead zirconate (PZ), and lead manganese niobate (PMN). Combinations of these materials have extremely high curie points of over 600°C , which allows them to be used at much higher temperatures than conventional PZT, which is limited to a curie point over 200°C lower. These compounds also display high coupling coefficients and low electrical permittivity. In this phase diagram, the compositions studied were chosen on the phase boundary of the 2 perovskite states, where it would be expected to find the most piezoelectric compositions. PZT compositions near phase change boundaries will show enhanced ferroelectric coefficients [29].

device, there would be zero electricity generated, which makes the avoidance of the pyrochlore phase important. Sputtering targets of PZT can contain 20 % excess lead to counteract this effect [41]. In practical lab settings, the excess lead will evaporate away as lead oxide, leaving a stoichiometrically correct material. Sputtering can often lead to an amorphous rather than a crystalline film, and annealing may be necessary to crystallize the film and enable piezoelectric properties, as shown in Fig. 8. To form patterns for MEMS devices, PZT is normally dry etched using chlorine or fluorine ions [43]. Wet chemical etches for PZT exist but are less common, and requires chemicals that can etch lead oxide, zirconium dioxide and titanium dioxide simultaneously. Such mixtures are uncommon in practical scenarios. One such mixture involves, hydrofluoric acid, hydrochloric acid, nitric acid, and ammonium chloride [44]. Continuous substitutions from one material to the next by incremental doping is possible with this family such as with stiochiometric lead manganese niobate [45], or more simply with doping barium for lead, or titanium for zirconium. PZT can be described as "hard" or "soft", depending on whether there are more n type or p type dopants [46, 47]. Hard PZT has low permittivity, hysteresis, and mechanical loss, whereas soft has the opposite qualities, and higher coupling factors [48]. These materials can be used to tailor PZT towards a specific application.

Specifically for harvesting electricity, some PZT derivatives with more desirable properties include $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZNT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) [49, 50]. These novel compounds have been shown to have superior piezoelectric properties. They have a lower Curie temperature around 150C, above which they lose all piezoelectric properties. They can be grown as single crystals using the Bridgeman technique.

The bottom electrode for PZT based devices is almost always platinum, because the platinum will not react with oxygen in PZT even under elevated temperatures, and

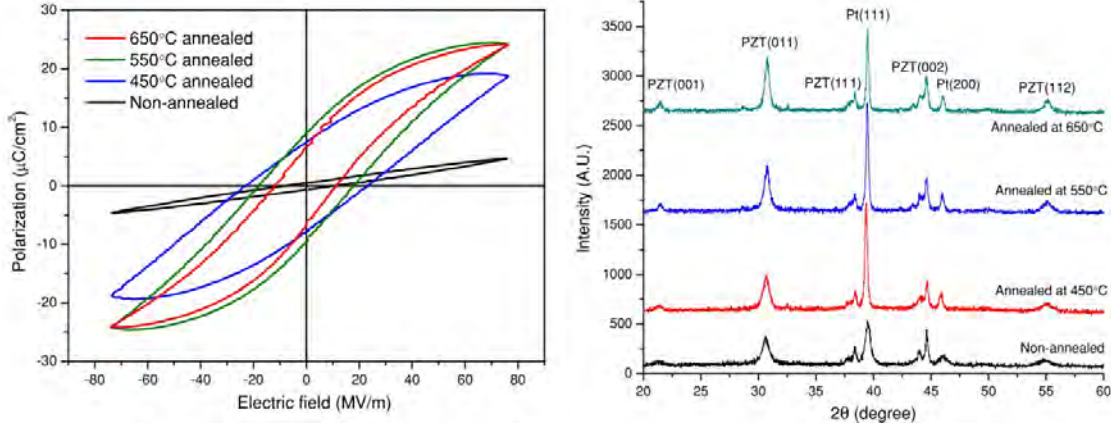


Figure 8. These diagrams show the changes in PZT as it is heated from an amorphous state to 450 ° C, 550 ° C, and 650 ° C. On the left is the hysteresis loop, which shows the remnant polarization. The larger the area inside the loop, the more ferroelectric the sample is. On the right is shown an XRD spectrum of the sample after being annealed at each temperature. This provides evidence of which annealing temperatures correspond to which crystal orientation. With no annealing, the hysteresis loop in black is essentially a line, which indicates the absence of ferroelectricity[42]. At 450 ° C, there is ferroelectricity. The size of the loop is maximized at 550 ° C, and shrinks slightly at 650°C, indicating some ferroelectricity has been lost at this high temperature. The increase in the peak sizes as the temperature increases shows that the PZT is becoming more crystalline at higher temperatures.

is useful for controlling PZT orientation [51]. An electrode that reacts with oxygen and formed an insulating oxide layer would ruin a MEMS device. Common thicknesses for the bottom electrode is near 100-200 nanometers. Titanium is often used as an adhesion layer below the platinum to ensure the platinum does not delaminate from the below substrate[52]. The titanium also can migrate through the platinum, resulting in a titanium or titanium oxide layer on top of the platinum electrode. The surface chemistry of the electrode will partially determine the crystallization axis of the PZT [53]. Titanium oxide in layers of 5 nanometers is shown to encourage the growth of $\langle 111 \rangle$ oriented PZT [54]. Annealing the lower electrode can enhance crystallization properties.

2.1.9 Polymers

An alternative to ceramic PZT for energy harvesting MEMS include an entirely different type of material, polymers. Polymers are lightweight and have other convenient mechanical properties, such as flexibility and resistance to shattering. The first electroactive polymer was a simple rubber band, as discovered by Roentgen in 1880 [55]. Polymers are broadly divided into ionic and field activated polymers [7]. Ionic polymers diffuse ions in an electrolyte solution. Electronic polymers including PVDF are solid and exhibit strain in response to an electric field. Polymers such as PVDF are not sputtered, but rather spin coated onto a substrate. This can potentially require far less processing equipment than ceramic PZT. After being dissolved into a solvent, they are spread as a liquid across the substrate. Evaporation of the solvent leaves a uniform coat of polymer. PVDF is made from monomer units of vinylidene fluoride, and was observed with piezoelectric properties in 1969. The polymerization can be stopped at different lengths to generate the desired chain length of PVDF. Different monomer units can be added, such as trifluoroethylene (TrFE), to increase piezoelectric properties and energy harvesting properties [56, 57]. These compounds are available commercially, as polymerization is an involved process. Polymers are normally dry etched with oxygen, as the extensive carbon bonding makes them immune to wet etch formulas. Polymers also naturally operate at much lower temperatures than ceramics, and have much lower dielectric constants.

2.1.10 Materials Selection

When comparing piezoelectrics materials, some common figures of merit (FOM) are used to compare compounds [58]. For piezoelectric materials, a useful FOM is the square of the piezoelectric coefficient divided by the permittivity. This is equivalent to maximizing voltage times current. For the pyroelectric effect, a similar FOM is

the square of the pyroelectric coefficient divided by the permittivity[58], which is also equivalent to maximizing voltage times current.

Various other indices can be used based upon properties such as loss tangent and material heat capacity [59]. The electromechanical coupling factor, which is the ratio of useful mechanical energy to input mechanical energy for a material is also a useful measure, and such materials as PMN-PZT can exhibit over 90% coupling [60]. This applies to the piezoelectric effect, while the thermal coupling factors for pyroelectric materials is often 1% or less [61], and hence the need to use the electrocaloric effect in energy harvesting.

2.2 MEMS

MEMS devices such as those to harvest electricity share several fabrication processes. A description of these processes is necessary to understand the fabrication of the device for this project.

2.2.1 History of MEMS

MEMS fabrication originated from semiconductor processing industry that was focused on making silicon microprocessors [62]. Silicon is a useful mechanical layer as well, because it does not fatigue, has higher strength than steel, and has large flexibility. The processes for making microelectronics on silicon were adapted to make micro mechanical devices. one frequent use of these devices is embedded sensors, such as accelerometers, gyroscopes, and strain gauges. A micromachined accelerometer is shown in Fig. 9. These sensors consume much less power than conventional sized sensors, and can be placed in mobile devices such as cell phones. Actuators, the complement of sensors, can also be made via MEMS processing. A MEMS actuator is shown in Fig. 10. One characteristic these devices have in common is the reliance

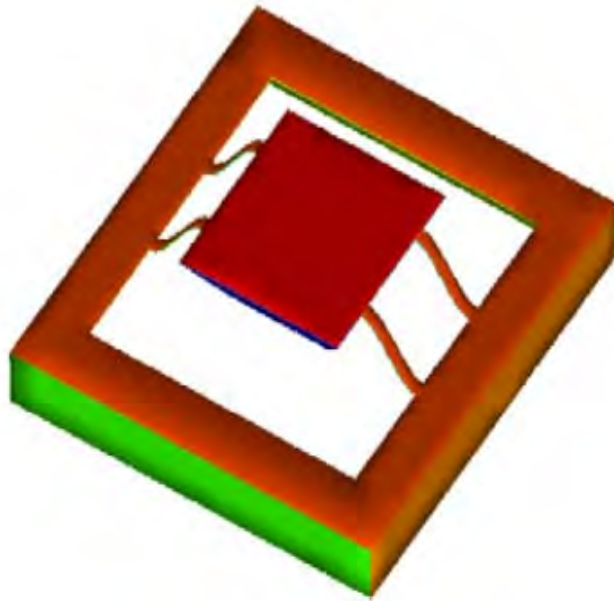


Figure 9. This is an MEMS single axis accelerometer that combines piezoeresistive elements and DRIE etching. The arms will be in response to acceleration. The resistivity of those arms will change while bent, and that change can be detected, allowing for the determination of acceleration. There is a large mass under the center structure, which serves to tune the frequency of the device and allow it to detect lower accelerations. At this scale, the surface area to mass ratio is abnormally high, so to make the machine more sensitive to lower accelerations, mass muss be added [63].

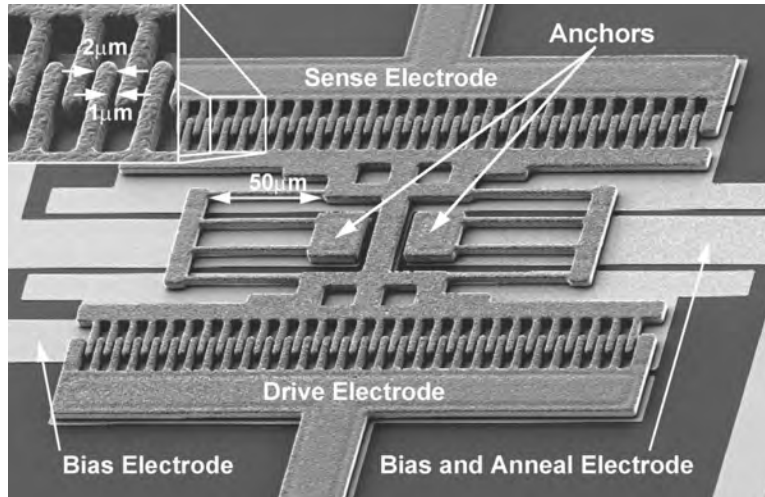


Figure 10. This is a micromachined combdrive actuator. Contrary to macroscale mechanisms which function by using moving joints or spinning wheels, this mechanisms generates movement entirely by bending. On this scale, frictional forces would be too high to effectively use rotors or joints. an electric field brings the moving combs closer to and farther away from the stationary combs, generating movement. The comb drive has a natural resonant frequency based upon the mechanical structure, and an electrical input of that frequency should be used [64].

on bending. Friction and surface tension becomes an increasingly dominant force as the dimensions shrink, so rotors and joints will simply adhere via surface tension, and stop working. This forces a reliance on compliant mechanisms, or those that rely on bending. Making single MEMS devices can be a cost and time intensive process. This can be avoided by using a foundry, such as at Sandia National Labs (SNL). Their SNL Ultraplanar, Multilevel MEMS Technology (SUMMIT) process uses 5 layers of silicon to form complex micromachined structures for multiple users at once. A sample MEMS device fabricated using the SUMMIT process is shown in Fig. 11. The development of MEMS technologies such as these have paved the way for the fabrication of a microscaled energy harvesting device. Some specific tools and processes that will be used for the micromachining of an energy harvesting device are elaborated below.



Figure 11. This is an sample device that can be made by the SUMMIT V fabrication process. The multilevel process allows four layers of polysilicon to be deposited, allowing the fabrication of rotors, joints, and gears. Numerous designs from multiple users can be fabricated in a single run, facilitating the supply of complex MEMS structures to individual users [65].

2.2.2 Deep Reactive Ion Etching

Deep Reactive Ion Etching (DRIE) is a two step process designed for the highly anisotropic etching of silicon [66]. This can allow the creation of a trench in silicon the depth of an entire wafer, allowing for the release of a mechanical membrane from the other side, serving as a base in an energy harvesting device. The first step in DRIE is the coating of a octofluorocyclobutane (C_4F_8) polymer over the entire exposed surface of the substrate. C_4F_8 will self-polymerize once deposited, and the carbon fluorine bonds are extremely stable and etch resistant. Next, sulfur hexafluoride (SF_6) is ionized and used to etch the surface. The ion-etching from the SF_6 has sufficient energy to etch the C_4F_8 polymer wherever contact is made. The ions flow mainly in a vertical direction, resulting in only the bottom of the trench being etched. The chemical reaction with SF_6 is always present, but does not appreciably etch the sidewall. After all of the polymer is removed from the trench bottom, the SF_6 continues to etch the silicon beneath with both isotropic and anisotropic mechanisms

from the chemical and ion-assisted etching components. The process is stopped, and repeated again starting at the deposition of a protective polymer. The trench is almost vertical, but with scalloping resulting from the isotropic etch chemistry. The chemicals used in this process etch silicon dioxide very slowly, so silicon dioxide can be used as a stop layer to precisely stop a deep etch. Common sidewall angles are from 88 to 92 degrees, which is an aspect ratio of 30:1. Etch rates can be as high as 5 micrometers per minute. The selectivity to photoresist is 100:1 and the selectivity to silicon oxide is 200 to 1 [62, 67]. The process flow for DRIE etching is shown in Fig. 12. If the material being etched is not silicon, then reactive ion etching (RIE) is a generalized version of DRIE that can be adapted by using different etching chemicals to target any desired substrate. In addition, simpler RIE processes are normally single step, avoiding any polymerization stage. RIE can even be used to etch compounds such as platinum that are chemically inert, by bombarding with chlorine at sufficiently high velocity.

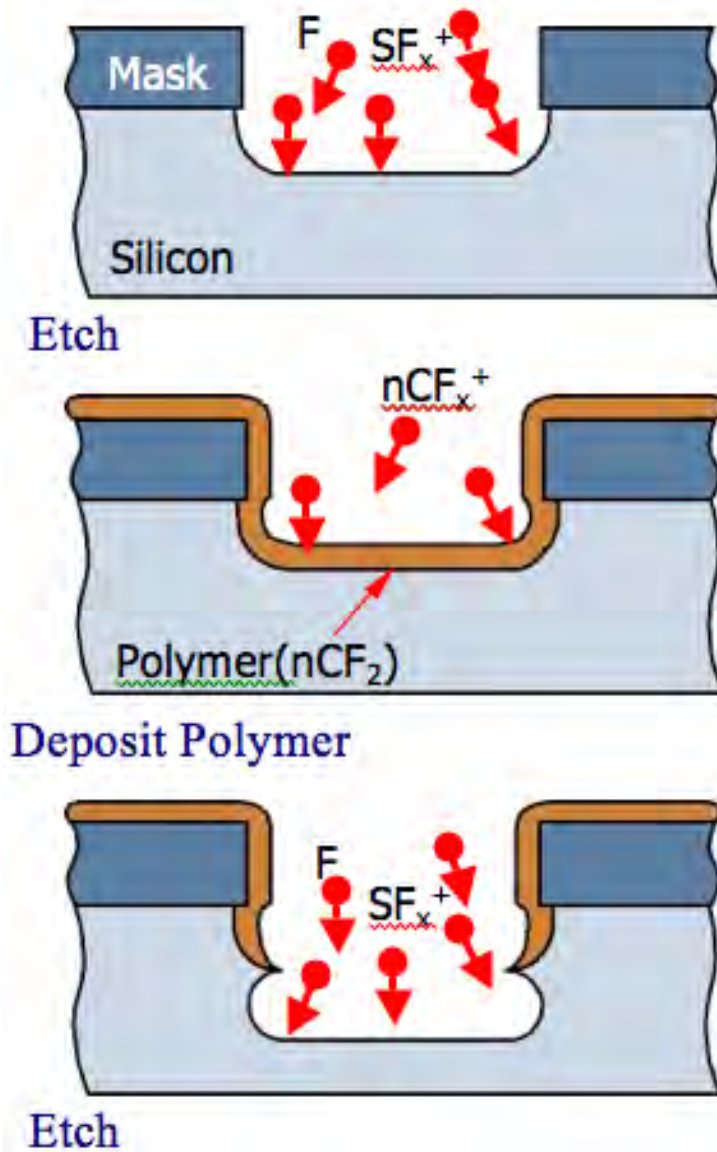


Figure 12. The DRIE process consists of three steps as shown. In the first step, a polymer is deposited in the cavity. In the second, the polymer is anisotropically dry etched so that no polymer remains on the bottom of the cavity. In the last step, the exposed silicon is etched, deepening the trench. This process can be repeated through an entire silicon wafer [68].

2.2.3 Liftoff

Instead of performing an etch, it is sometimes simpler to form a pattern use a technique called liftoff. Liftoff is a patterning procedure following evaporation or sputtering. A photoresist is patterned on a substrate before physical deposition. After deposition, the photoresist which is not firmly adhered to the substrate can be removed or "lifted off", and any material on top of the photoresist would be removed as well. This process is aided by highly directional deposition methods with poor step coverage, such as evaporation. To ensure discontinuity between the 2 regions of deposited material, the thickness of deposited material must be much less than the thickness of the photoresist. In addition, multiple layers of photoresist, with the upper layer overhanging the lower layer, can be used to ensure a discontinuity of the deposited material [69].

2.2.4 Wet Etching

While most substances can be etched by RIE, sometimes a liquid chemical solution can exist that will etch far more selectively. This process, called wet etching is the general process of immersing a substrate in a liquid, which will react to dissolve the exposed material. It can be used to dissolve away a target material, but a specific recipe must be found for each desired chemical to etch [70, 71, 72]. Common etches include buffered oxide etch (BOE) for etching thermal oxide, and iodide solution for etching gold. Etching can be isotropic if it proceeds irrespective of crystal orientation, or anisotropic if one crystal orientation is preferentially etched. A comparison of these etching profiles is shown in Fig. 13. Silicon can be anisotropically etched using potassium hydroxide (KOH) and tetramethylammonium hydroxide (TMAH). This will generate etching profiles as shown in Fig. 14. Silicon oxide is etched using buffered oxide etch (BOE), which is a mixture of hydrofluoric acid, water, and a

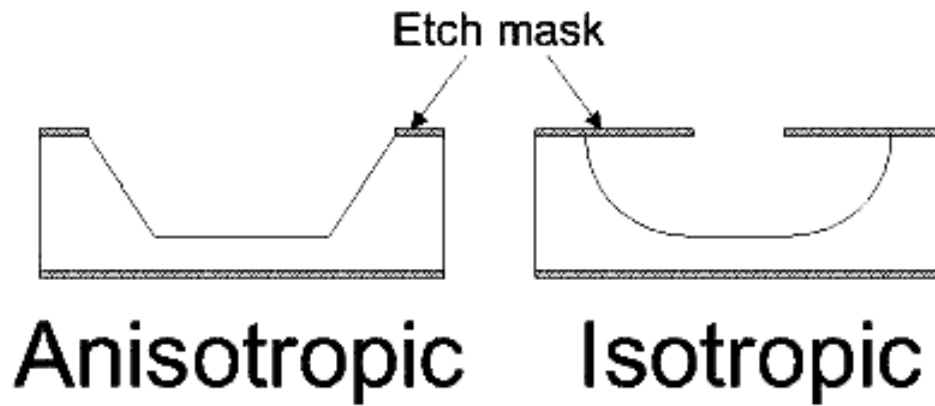


Figure 13. Isotropic etching of silicon results in curved features and undercutting of the etch mask. Anisotropic etching results in angular features [73]. These effects are only different for single crystal substrates. In amorphous or polysilicon substrates, without any crystal axis, all etching would be isotropic. The etch rates and profiles for both can be modified by agitating the liquid etchant mixture, promoting the transfer of dissolved atoms away from the etch site and of unused etching chemicals in. Agitation can also be used to promote smoother features by avoiding bubbles forming at the etch site that will prevent further etching.

buffering agent such as ammonium fluoride[75]. This mixture displays high selectivity to silicon. Isotropic wet etching suffers from overetching, where the liquid will begin to cut under the photoresist and enlarge the pattern.

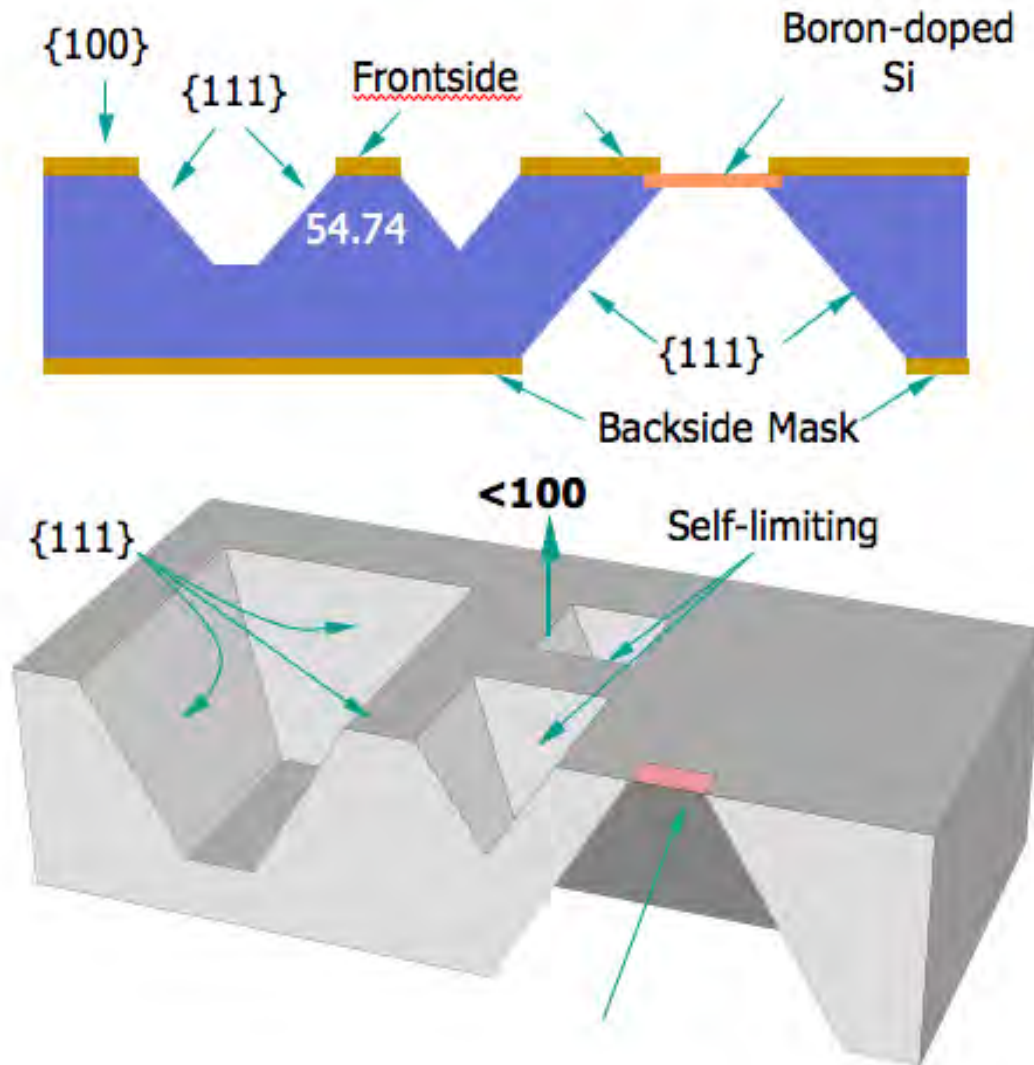


Figure 14. Silicon has crystal planes which have etch at different rates in certain solvents. Solvents such as potassium hydroxide will etch into v-shaped groves as shown, as the $\langle 100 \rangle$ plane is etched faster than the other planes. The $\langle 111 \rangle$ plane is etched the slowest, and the walls shown are defined by those crystal planes. If the etching is stopped prematurely, the profile will appear trapezoidal. If the etching continues until the $\langle 111 \rangle$ planes intersect, an inverted pyramid will form, and etching will proceed very slowly from that point onward. Boron doped silicon can also be used as an etch stop, because it etches much slower than undoped silicon [74].

2.2.5 Evaporation

Depositing single element metals such as gold, platinum, titanium, chromium, or aluminum in a thin film on a substrate allows the formation of electrical contacts in a MEMS device. This is commonly done using evaporation. Evaporation is a type of physical deposition process where a target called the charge is heated until gaseous [76]. The gaseous particles then travel to the target substrate where they recondense into the solid phase due to loss of energy. A schematic of this process is shown in Fig. 15. When the heating is accomplished via electron bombardment, the process is named electron beam evaporation. The electron beam is controlled magnetically to develop even heating over the target. An alternate method of heating is resistive heating, or running current through the boat holding the charge to heat it. Resistive heating is limited because the heating element must be at least as hot as the material to be evaporated. This can lead to vapor pressure from the heating element, and cause contamination even when boats with high melting points such as tungsten are used. Inductive heating consists of placing an inductive coil around the charge. The coil is subject to RF power, which is transferred to the charge. The coil can be cooled without the charge being cooled. This process also can result in contamination. E-beam evaporation is achieved by heating a tungsten filament to eject electrons, which are guided and accelerated by electric and magnetic fields. Voltages from 3 keV to 20 keV are commonly used. E-beam evaporators are often designed with multiple targets in a single chamber to allow for co-deposition. Evaporation is always done in a vacuum so that the gaseous atoms travel directly from the target once they are in the vapor state. With no gas in the confines of the vacuum chamber, there will be no ballistic collisions with other molecules to change momentum or direction. The mean free path needs to be greater than the length of the chamber, which at 10^{-5} torr is 5 meters, although UHV systems work at pressures as low as 10^{-11} torr. Low pressures also

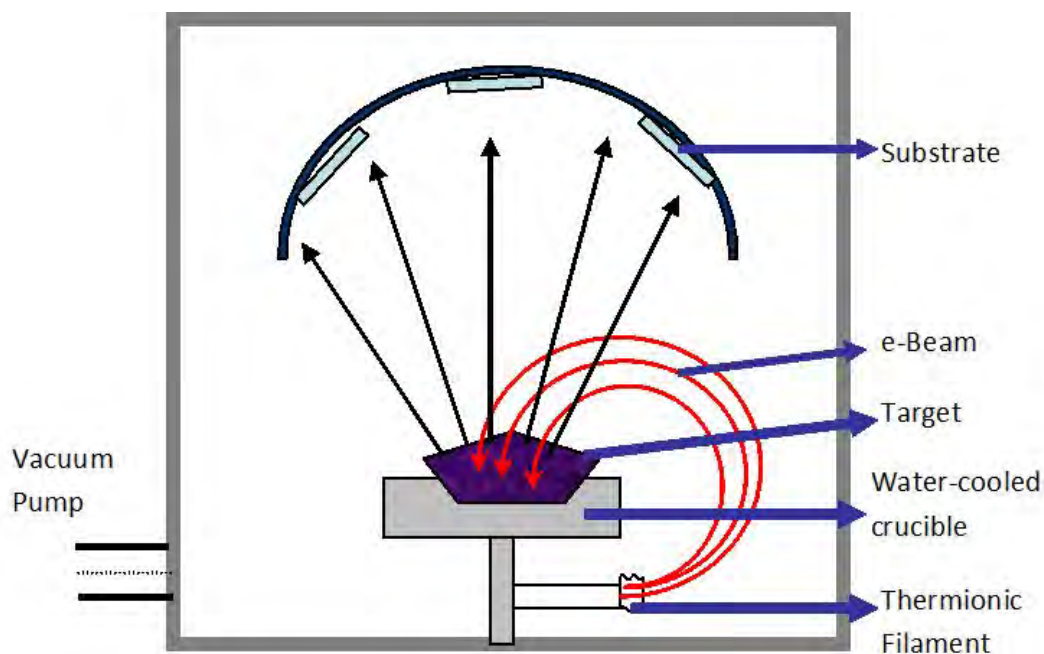


Figure 15. This evaporation process is largely used on pure atomic species. The vaporized compounds will form a thin, conformal coat on any substrate nearby. A compound of two or more atoms would have different vapor pressures for each constituent, and the resulting film would have stoichiometry different than the original sample. Contamination from the boat is minimized, both by having a boat with very low vapor pressure such as tungsten [77]. A thermal evaporator would be largely the same except for the heating source, which would be heat to the crucible instead of heat from an electron gun to the source. This setup is simpler, as heating is more readily accomplished by dissipation of electricity than directing a high energy electron beam. However, this would have the drawback that the crucible would have a temperature at least as high as the source. In electron beam evaporation, one can heat the source and cool the crucible, resulting in much lower crucible temperatures. Since the crucible itself will slowly evaporate and introduce contaminants, reducing its temperature can provide a more pure coating.

prevent contamination from reaction with atmospheric species. This process coats conformally, which results in very small amounts of coating on sidewalls or other high aspect ratio features. To ensure uniform coating over the substrate, it is common to rotate the substrate during evaporation. The amount of heating depends strongly on the target material. Gold has high vapor pressures and require lower temperatures than metals such as tungsten. Most evaporators operate on the order 10^{-2} torr, and a pressure of .1 torr corresponds to 1000 atomic layers per second. Most evaporation targets are elemental compounds, as evaporation will cause dissociation of almost all materials into byproducts. The process of metal condensation commonly results in compressive stress on the substrate. deposition rates can be up to 200 nm per minute. X-ray radiation from the e-beam can result in damage to certain substrates. Lateral diffusion may occur on the surface after condensation due to residual energy. There is a drop off in deposition at increased angles from the source.

2.2.6 Sputtering

When dealing with compounds such as PZT of more than one element, and no simple chemistries from PECVD are available, an alternative technique called sputtering can be used. Sputtering is a physical deposition technique that relies on the kinetic transfer of energy to eject target molecules. Argon or oxygen atoms are ionized and then excited towards the target. At the target, the kinetic energy causes random ejections of molecules, called sputtering [78]. An illustration of this process is shown in Fig. 16. Two electric fields are necessary, one to ionized the gas and one to accelerate the gas towards the target. A DC electric field can be used to sputter against a conductive target, but only an RF source with AC signal can sputter against an insulating target that does not conduct electrons. Sputtering can be used to deposit compounds of multiple materials. The high energies of sputtering gasses,

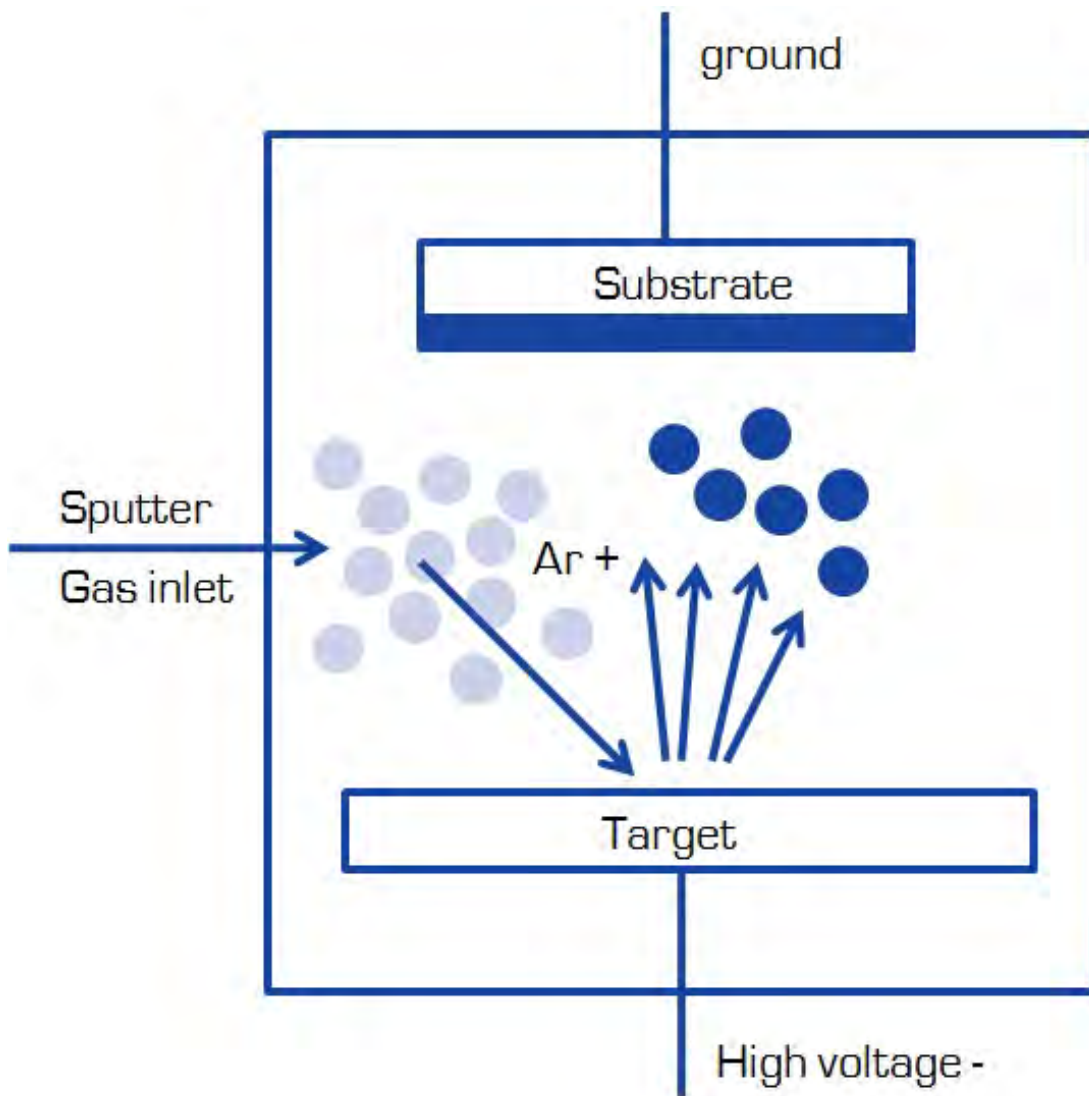


Figure 16. Sputter deposition can use oxygen, argon, or other gases to impinge on the source. The source is dislodged multiple atoms at a time. This process is largely stoichiometric, but deviations can occur between the thin film ratios deposited and the original elemental ratios of the source. The source can be of a wide variety of elements and compounds [79]. The argon ions can build up charge on the target as they interact. In a conducting metal target, the charge would dissipate. In an insulating target, the charge will remain, and it is necessary to use alternating RF power to bombard the target.

from 10 to 50 eV, allow the material to diffuse across the surface of a substrate once it has impacted, allowing for better coverage and smooth deposition. Sputtering is anisotropic, but has better step coverage than evaporation because of the mobility of the high energy atoms and because of the higher pressures involved. The pressures are high enough to cause collisions between the sputtered atoms, randomizing trajectories. The sputter yield is the number of target atoms ejected per incident atom. The higher the energy, the larger the sputter yield. Sputtering is slower than evaporation because so much energy is wasted in the process. In evaporation, all heat energy is spent evaporating atoms and is then carried away. In sputtering, ejecting one atom can take 100 times the energy of evaporation of that atom. The resulting energy is dissipated into the target, which will then need to cool.

2.2.7 PECVD

To deposit electrically insulating materials to protect layers and devices from shorting out, evaporation is not suitable, but another process is. In plasma enhanced chemical vapor deposition (PECVD), plasma is generated through RF heating that creates ions that can overcome the potential energy barrier to react [80]. PECVD can therefore use a lower temperature and a higher pressure to achieve higher deposition rates than other technologies. The use of plasmas can result in stoichiometrically inaccurate films, and hydrogen incorporated into the film[81]. In any specific reaction, the rate is limited by either the mass flow or the temperature. At low temperatures, there are an abundance of reactants, but few overcome the activation energy barrier. At high temperatures, all of the reactant can dissociate faster than new reactants are flowed into the chamber, and the flow rate limits deposition speed. Films can deposit with GigaPascals of tensile stress. Nickel, titanium carbide, titanium nitride, aluminum oxide, and tungsten can also be deposited via this method[62]. For

the deposition of silicon, silane (SiH_4) will spontaneously decompose into silicon and hydrogen[62]. The excess hydrogen flows away, leaving the silicon behind on the substrate. If oxygen or nitrous oxide is added to the silane mixture, the silane will react to form silicon dioxide[62]. Silane and ammonia (NH_3) react to form silicon nitride. The actual deposition chemistries are highly complicated. Even the decomposition of pure silane involves the intermediates SiH_2 and Si_2H_6 . Concentration gradients can exist in the chamber, which makes accurate modeling challenging.

2.2.8 Annealing

Annealing is the process of heating to a high temperature, and can be done in vacuum or in the presence of an atmosphere. The high temperature can provide energy to overcome the activation barrier to transition to a more thermodynamically stable state. Undesirable states include lattices damaged from ion implantation and films that are amorphous. In PZT, annealing can result in change of the crystal phase and orientation to increase piezoelectric properties [82].

2.2.9 Optical Lithography

Common to all deposition and etching techniques is the need to form a pattern in the material. Otherwise, the only structures that could be formed are flat layers of different materials stacked on top of each other. The method of forming these patterns relies on optical lithography. Lithography is from the greek words for stone and write, and was a process first used to images onto paper by exposing stone to light. Optical lithography is the process of using a mask and shining light through it to copy a pattern. Modern lithography is about 200 years old, having been used in the early 19th century to copy paintings. In optical lithography, light is shone through the photomask to a material below that can record the pattern. Photosen-

sitive resins used for this purpose are called photoresists. This process is shown in Fig. 17. After exposure, a process is used to either selectively remove the photoresist that has been exposed to the light source, or the photoresist that has not been exposed to the light source. These resists are called positive and negative, respectively. Once the photoresist has been developed, a chemical deposition or etching process is performed. An etching process will ideally only etch the substrate where it is not covered by photoresist, forming a pattern. Alternatively, a deposition process will coat the entire wafer, but the areas on top of the photoresist can be later removed. Once the deposition or etching has occurred, the remaining photoresist is removed, leaving the final pattern. Photomasks are commonly made on fused silica with an opaque layer, such as chromium. Chrome can be removed via laser ablation to form a pattern in the photomask, or can be chemically etched away. A single photomask can be used many times to generate complicated patterns. In multilayer devices, the exposure device must be capable of aligning layers. Different photoresist chemicals can be exposed with different frequencies of light, ranging from the visible into the UV. The shorter the wavelength of light, the smaller the resolution that can inherently be obtained, as light cannot be practically used for this purpose with features smaller than one wavelength. When features are so small that they are near a wavelength of light, diffraction effects can cause the pattern to transform if there is distance between the mask and the substrate. Sherifs are used so that the desired pattern is formed after diffraction. To overcome this problem, contact exposure systems place the mask in contact with the photoresist. This can result in contamination of the mask. Projection printers can be used to scale a mask down, by focusing the light as it passes through the mask to the wafer. Proximity lithography is similar to contact lithography, except the mask is maintained several micrometers from the substrate [76]. The resist must be applied uniformly and at the correct thickness to produce

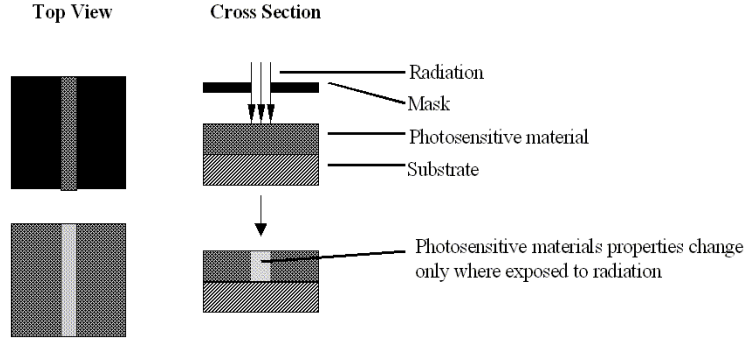


Figure 17. In optical lithography, a light source is projected through a patterned photomask, partially exposing a light sensitive material, or photoresist. This process can be repeated with the same mask on a different substrate. Since creating a photomask can take several hours and an exposure process can take several minutes, reusing this mask can greatly accelerate the process of making micro-sized patterns. Despite the name optical lithography, UV and not visible light is often used, as the shorter wavelength causes smaller diffraction defects [83].

reliable features, and is often spin or spray coated for this purpose.

2.2.10 Wafer Bonding

Wafer bonding can either be used to create a stronger wafer base, create multilevel devices, or to create sealed cavities. For this project, wafer bonding is the only method capable of forming the base wafers on which the device will be fabricated. The two main types of bonding are direct and indirect. In direct bonding, large amounts of heat, pressure, or electric field cause the wafers to chemically bond to each other. Indirect bonding is the process of using a glue or adhesive. Anodic bonding is the bonding of silicon to glass. SOI wafers can be made this way, by bonding a silicon wafer to a thermally oxidized silicon wafer, and then thinning one of the wafers to make a device layer. SOI wafers have a limit of 4 micrometer silicon oxide layer thickness due to the limits of thermal oxidation. SU-8 has been shown to be effective for low temperature bonding [84]. Gold eutectic bonding has also been investigated, and operates based on the gold-silicon eutectic less than 400 °C. The combined mixture of gold and silicon melts below the gold melting point of 1000

°C and the silicon melting point of 1400 °C, and is one of the largest decreases in melting points from combining 2 elements known. Low temperature bonding could potentially be useful to create a large cold sink on top of an energy harvesting device.

2.2.11 Thermal Oxide Growth

A method of forming an electrically insulating layer or a masking layer for etching in MEMS fabrication is thermal oxide growth. Silicon can be chemically changed into silicon dioxide by reaction with water or oxygen at high temperature. At room temperature, a 1 nanometer film of silicon oxide will form on silicon and is called the native oxide. At higher temperatures, oxygen can diffuse further into the substrate. Oxide growth is a slow process, and can take up to an hour for a 150 nanometer thick layer. The glass is not crystalline like quartz, but rather has short term order. By adding phosphorus or boron containing elements during the heating, boron or phosphorus doped glass can be formed. This glass may have tuned electrical properties, or different etching properties. The silicon oxide has a lower density than the original silicon and thus this process increases the volume of a wafer.

2.2.12 Dopant Diffusion

In some devices, modification of the resistivity of silicon can be useful to form pn junctions or form silicon sensors. To accomplish this, a single crystal silicon wafer can be doped by either implanting high energy ions into a silicon substrate, or by allowing atoms to diffuse into silicon at high temperatures. Additional methods exist to introduce dopants into an ingot during crystal growth. A silicon wafer is either placed in contact with a solid source such as a highly doped glass, or nearby a source that will emit gaseous particles. Diffusion of the particle into the silicon is governed by Fick's second law of diffusion, a differential equation, $\frac{\partial c_x}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c_x}{\partial x} \right)$.

The result shows that the concentration will increase over time, but decrease with depth into the silicon, causing a concentration gradient. The decay with depth is rapid, and is proportional to a square exponential. If a n type dopant is diffused into a p type wafer, this can create a pn junction. The limit on diffusion is the solubility of the dopant in silicon, around 10^{21} atoms per cubic centimeter. Silicon often has near 10^{13} impurities per cubic centimeter from fabrication, so doping to a concentration lower than this would be irrelevant. Temperatures from 900 to 1200 °C are common to allow a rapid diffusion of particles into a silicon wafer. One method of controlling the total amount of dopants is to perform an initial doping with a known concentration to a short distance, called pre-deposition. The source is then removed, but high heat is applied during the drive in process to force the already implanted atoms further into the wafer.

2.2.13 Compliant Devices

MEMS devices that do not use hinges are called compliant. The only movement that can occur without hinges or rotors is bending. While this limits the types of devices that can be fabricated, non-compliant MEMS devices encounter increasing friction and surface tension effects as dimensions are reduced [85]. An example of a compliant mechanism is shown in Fig. 18.

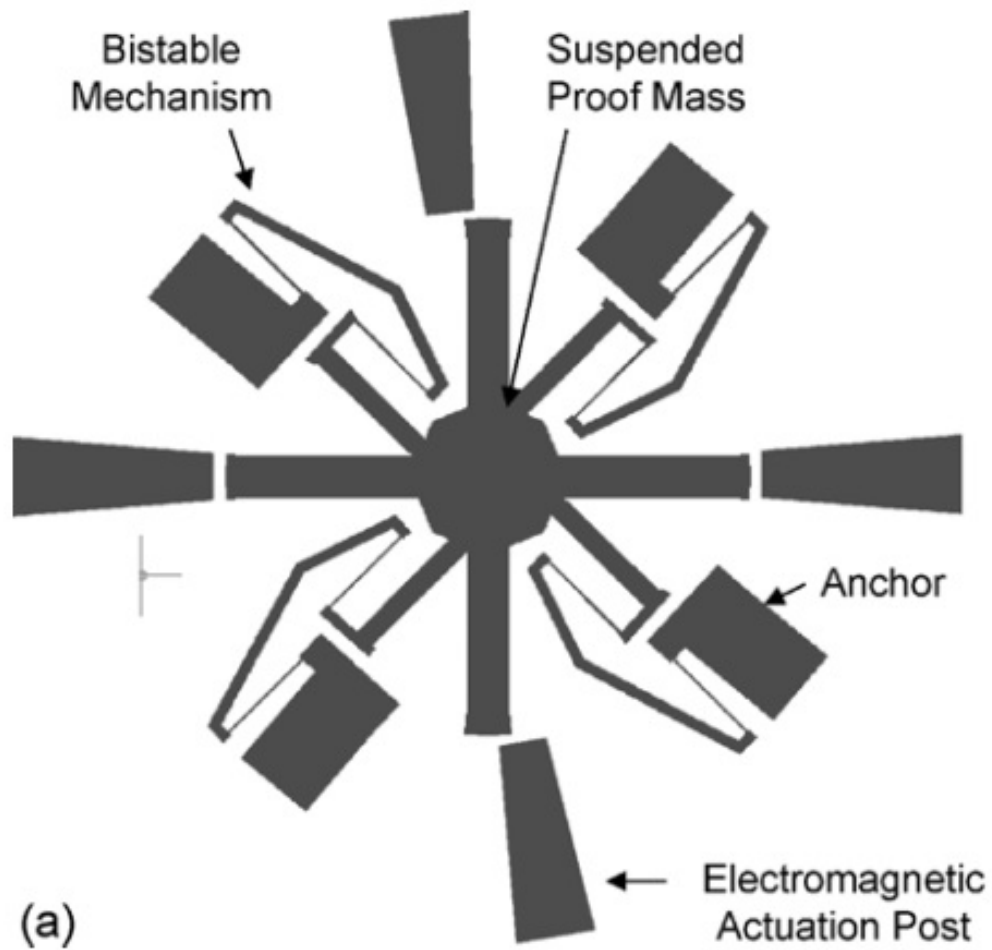


Figure 18. This is an example of a MEMS rotary actuator, which is different than macro rotors because there is no traditional pin in this mechanism. The rotation only occurs due to bending in the elements and initiated by electrostatic forces. The overall device is limited in total deflection because without a true rotor, it is fixed to the anchors. [85].

2.2.14 SOI Wafers and Bistable Membranes

To form a suitable base for an energy harvesting device, a simple silicon wafer is not suitable. Instead, an silicon on insulator (SOI) wafer is a three layer stack consisting of a silicon handle, a silicon oxide box layer, and a silicon device layer. The oxide layer can act as an insulating layer. The device layer and box layers is often from 1 to 10 microns thick. The handle layer is the remainder of the 500 micron wafer. The different thermal expansion coefficients between the silicon device layer and the silicon oxide box layer results in stress on the device. An example process using an SOI wafer is shown in Fig. 19. SOI wafers can be used as a base wafer for manufacturing novel devices. The presence of the box layer allows for the single crystal silicon to be etched to a precise depth by using the silicon oxide as a stop layer. This etching can be done from both sides. Accelerometers, gyroscopes, and pressure sensors have been manufactured using these wafers. A resonator made from etching through an SOI wafer is shown in Fig. 20. If an SOI wafer is DRIE etched from the handle side entirely to the etch stop with no processing on the front side, the only remaining material of the half millimeter wafer will be the thin device and box layers. This method is shown in Fig. 21. These layers are thin enough to buckle under the compressive stress remaining from the manufacturing process, resulting in a buckled membrane structure. This structure can easily deflect about 2% of the width of the membrane for common dimensions. The membrane is dynamically unstable, which means the structure has a wide range of movement for a small input force. The membrane can respond to both pressure and heat change to actuate in the z-axis. Membranes of this type can be actuated in response to heat [89]. The movement properties can be altered by the addition of aluminum to the membrane [90]. The membrane is a more complicated form of a cantilever. Intrinsic stress in a simple cantilever would result in a device as shown in Fig. 22. When clamped

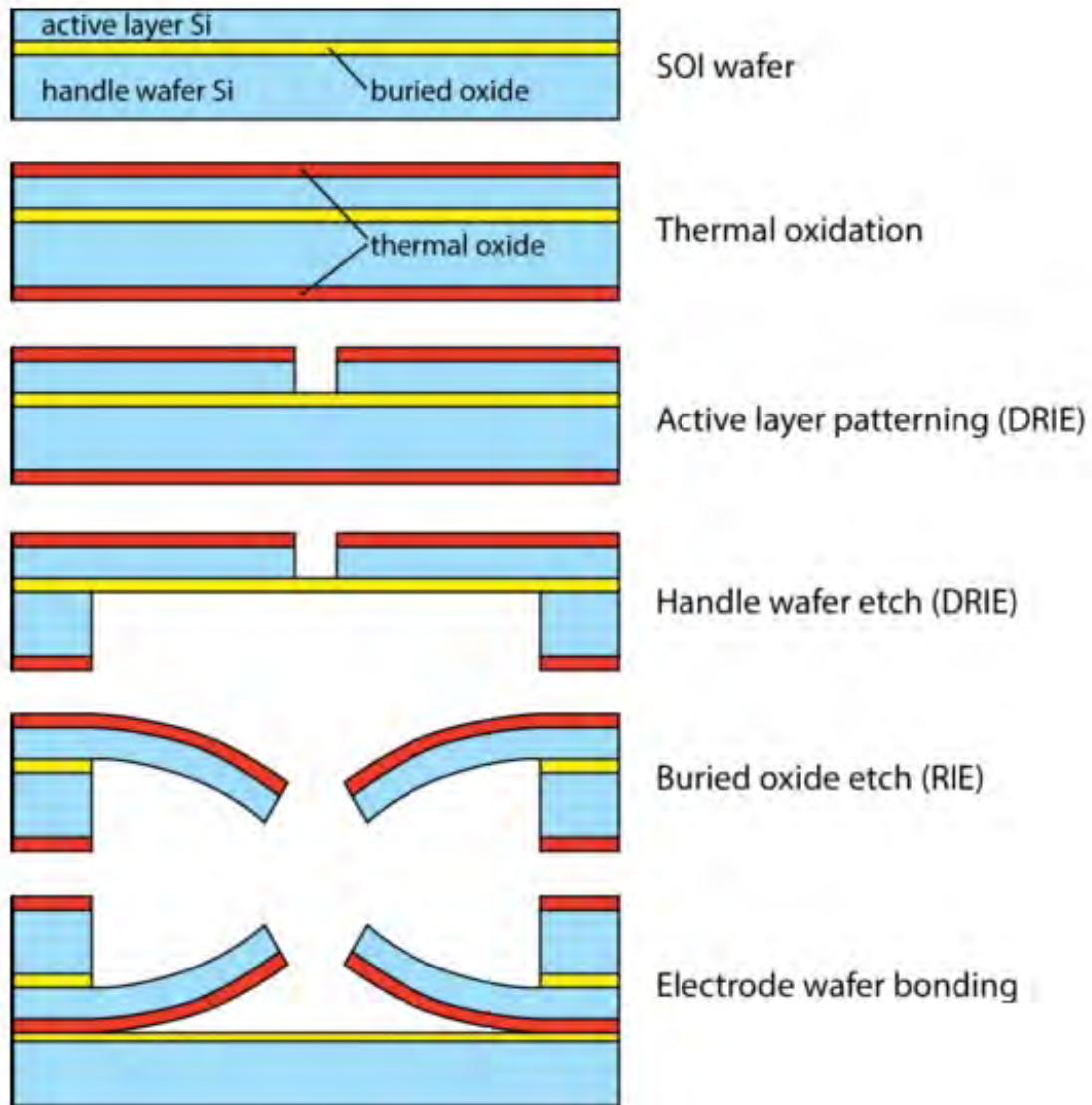


Figure 19. Devices such as these can only be made effectively starting with SOI wafers, which allow the steep vertical features with an exactly defined etch stop[86]. In this example, the starting SOI wafer was thermally oxidized. Then, DRIE etching was used to pattern the top, and then the bottom. Wafer bonding was used to bond to another wafer to create the final device.

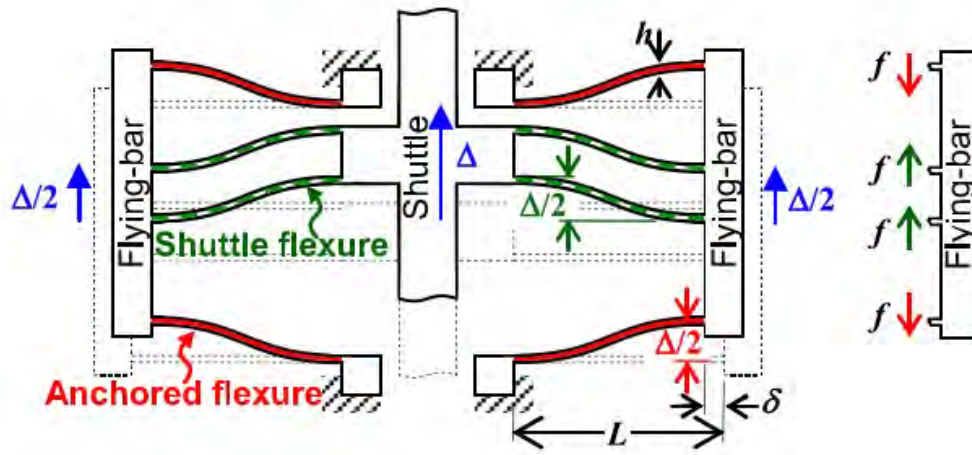


Figure 20. The thick moving layers in this device are enabled by SOI starting materials [87]. In contrast to the comb actuators seen earlier, which are made with very flat layers of deposited silicon, these flexures extend deeply in the z-axis, because they have been machined from the bulk silicon wafer. This design is exceptionally sturdy and resistant to torquing.

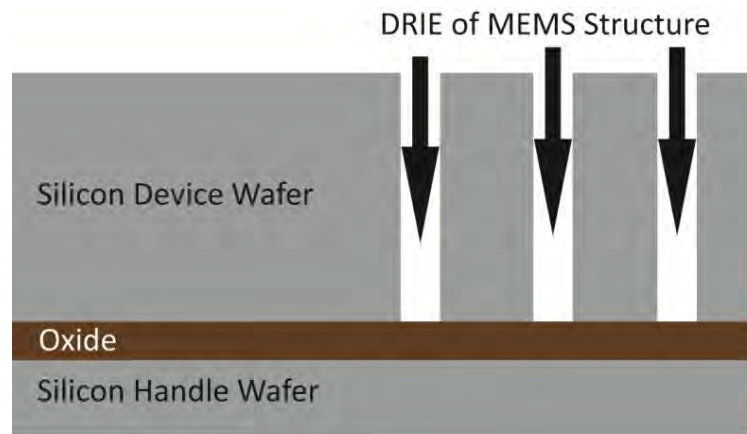


Figure 21. THE DRIE of an SOI wafer uses the silicon oxide layer as a natural etch stop. The DRIE process etches silicon oxide hundreds of times more slowly than silicon, ensuring that even a thin silicon oxide layer will be unaffected by the etching process. These trenches can be at a slight angle of several degrees from vertical depending on the process [88].

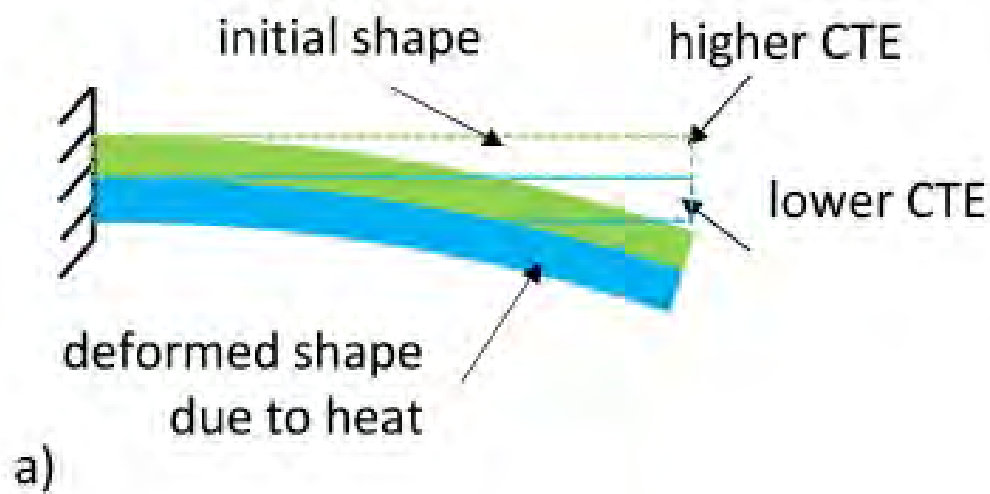


Figure 22. The cantilever made of any 2 arbitrary materials will bend in response to heat or cooling. The initial shape may be already deflected due to intrinsic stress [91]. The higher the coefficient of thermal expansion (CTE) mismatch, the larger the deflection. The deflection also depends on the mechanical strength of the compounds involved. This cantilever could be fixed at both ends, making a bistable cantilever. It would be unstable at the even position, and would always be curved up or down. If fixed on all four edges, it would become a bistable membrane.

at both ends, it would become a bistable device as shown in Fig. 23. The position would be a multivalued function of temperature, as shown in Fig. 24. While this buckling normally takes a smooth spherical form, larger membrane can attain more complicated equilibrium shapes as shown in Fig. 25. The motions of all of these devices can be modeled as the device having a spring constant, $F = kx$.

2.2.15 Scaling of Devices

Lastly, it remains to justify why ferroelectrics should be combined with MEMS for energy harvesting, since ferroelectric materials could be combined with macro sized devices for the same purpose. It is important to determine the effects of scale, if any, on MEMS energy harvesting devices. Previous research has shown that frequency is proportional to x^2 , transmitted thermal power, electrical power per surface area, and mechanical power per surface area are proportional to the linear dimension [92]. Deflection, capacitance, and voltage are proportional to x^{-1} , while snap temperatures and internal stress remained unchanged. This implies that as devices are made smaller such as in Fig. 26, the rate of energy transfer and the power generation will increase. The total energy delivered from one cycle of a pyroelectric device is proportional to its volume [93]. However, the cycle rate is inversely proportional to volume, as the heat capacity of a device is proportional to its mass. Increasing the surface area contact as a device becomes larger allows a device that delivers more total energy per cycle

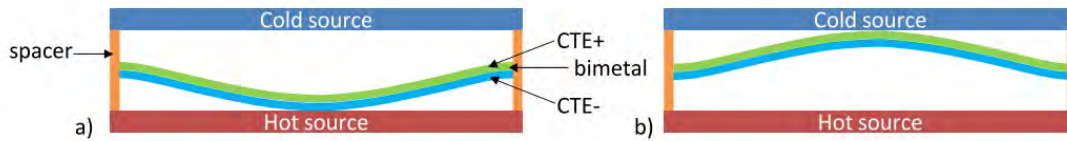


Figure 23. This is a generalized pyroelectric bimorph for energy harvesting. The structure has no stable state while not in contact with one of the sinks[91]. as it moves up or down, and heats and cools, the pyroelectric material generates energy. The high contact force of the doubly fixed cantilever ensures good contact.

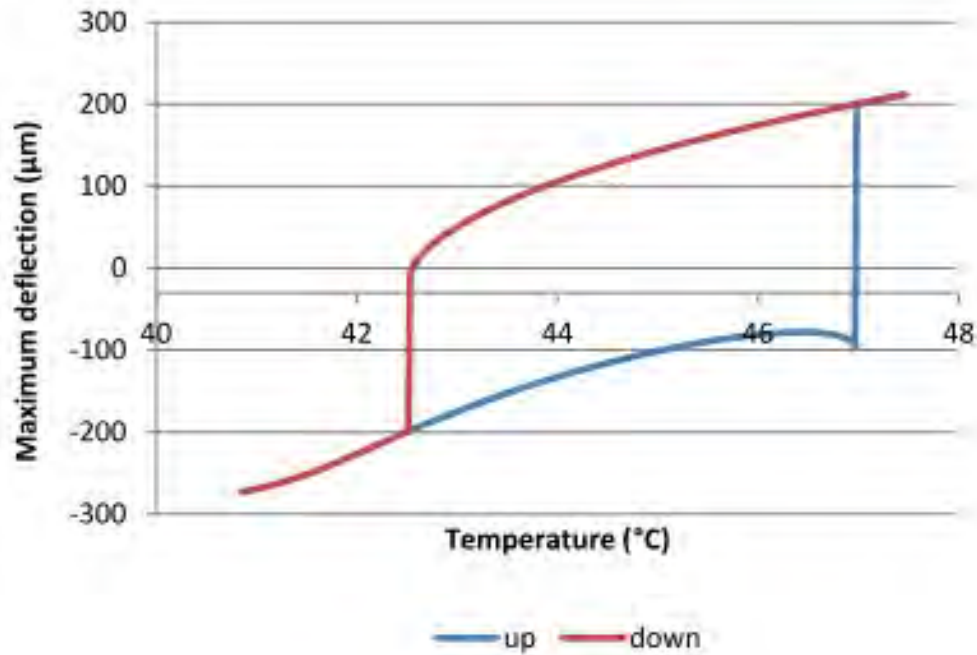
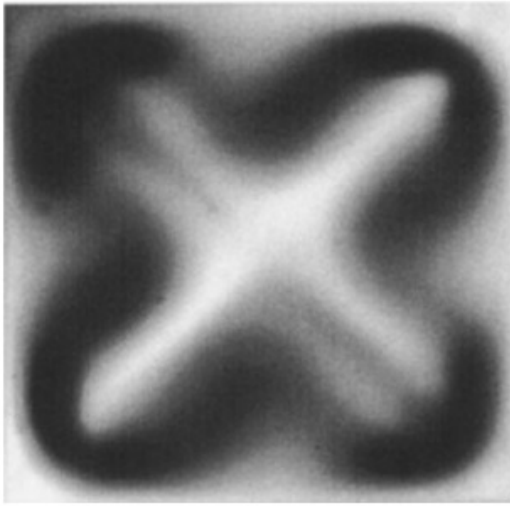
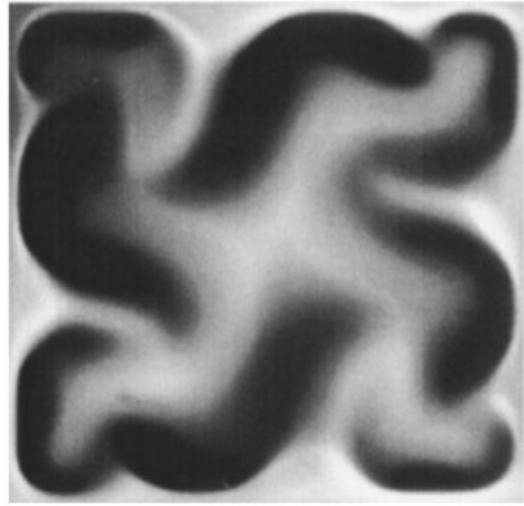


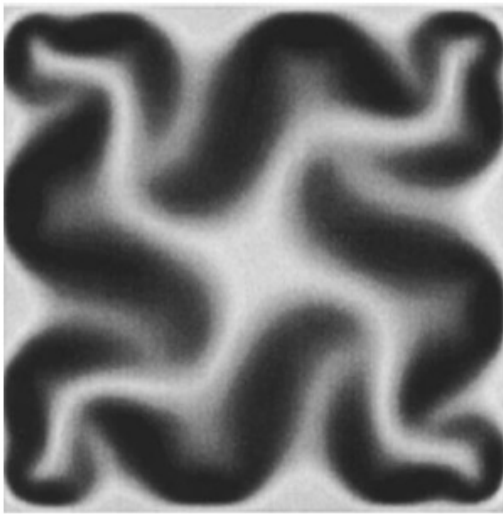
Figure 24. This is a plot of the vertical deflection of the mechanical layer in Fig.31 over temperature. At low temperatures beneath 42.5 °C, the cantilever will snap down. At temperatures above 47°C, the cantilever will snap up. At temperatures in between, the thermal mismatch of the elements in the cantilever are insufficient to force it to move, so it will stay in whatever position it is in. This means that maintaining a heat source over 47 °C and a sink under 42.5°C will cause perpetual motion of this machine. The goal of most bistable mechanisms would be to reduce gap between the sink and source temperature as much as possible, so that a very small change in temperature could still move the device[91].



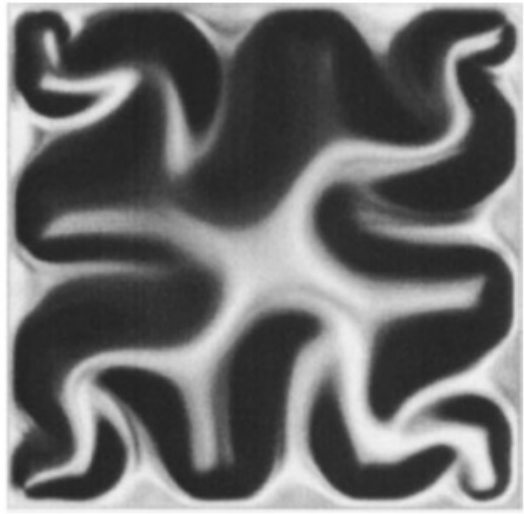
(a)



(b)



(c)



(d)

Figure 25. If SOI membranes are too large, the stress between the layers will create overbuckled shapes instead of a smooth curved shape. Membranes (a) through (d) show increased buckling away from the simple curved shape. Successive membranes are larger and hence more flexible, displaying increased buckling. This implies a maximum lateral size for any membrane for any given thickness of SOI wafer. Some rotational symmetry of order 4 does still exist on these wafers, and the pattern is not entirely random or disordered.

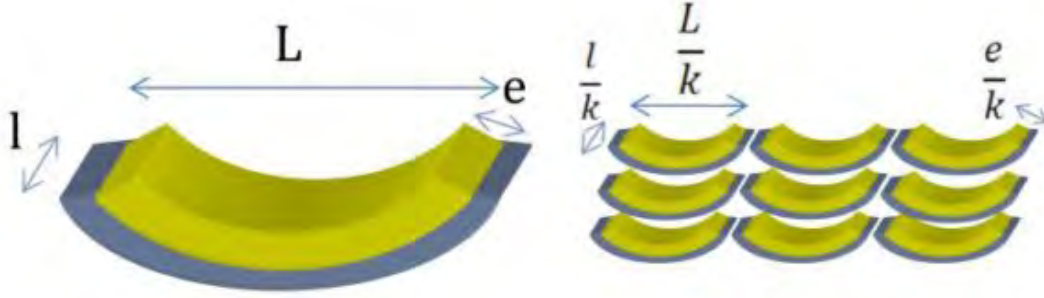


Figure 26. The down scaling of the devices is shown to increase energy production [92]. In this diagram, the surface area of the original device is maintained as it is replaced with 9 smaller devices, even as the volume is reduce by three times. On the mems scale, this implies volume, and hence mass reduction of multiple orders of magnitude compared to macro sized devices. With less mass involved in the devices, the frequencies increase rapidly.

at a higher cycle rate. This means that minimizing devices size by using MEMS will lead to much more powerful devices.

2.2.16 Piezo Resistivity

Determining the position of a MEMS device in situ would allow the analysis of a MEMS device functionality based on position. For micrometer deflections, optical viewing is insufficient for tracking motion, and electrical sensing can be used. Piezo resistivity is the change is resistance of a material in response to applied stress[94]. Deformation in the crystal lattice moves the energy levels of a material, changing the resistivity. While resistivity is a scaler quantity, applied stress can occur in multiple axes. Piezoresistivity is thus a tensor and not a simple scaler. All materials exhibit some degree of piezoresistivity. Single crystal silicon has one of the largest responses of all materials, almost 2 orders of magnitude larger than common conductors such as gold. This makes single crystal silicon useful as a sensor to stress. A sensor can be formed by forming a channel of highly doped silicon on a sample through which the current will flow. As the stress on the region changes, the resistivity of

the path changes. While the strain cannot be measured point by point, it is instead an average of the strain along the entire path. To increase sensitivity, the geometry of a piezoresistive design is important [95]. The direction of the piezoresistive strip should be along the strain axis. This leads to a ladder design, where the piezoresistive strip crosses and recrosses the bending of the device, to minimize the proportion of material parallel to the the strain.

2.3 Designs of Energy Harvesting Devices

Energy harvesting from heat with MEMS has been attempted with other geometries. A review of devices that share similarities to the device proposed in this work follows.

2.3.1 Pyroelectric Cantilever Design

An 8 millimeter silicon cantilever was fabricated with a piezoelectric/pyroelectric layer. Onto the tip of the cantilever was placed a proof mass. The mass served to lower the resonant frequency of the cantilever, and to provide contact to the upper and lower substrates. The cantilever was electrostatically actuated from the up to the down position. Above the cantilever was placed a hot source, and below was placed a cold source. The cantilever was actuated at 60 hertz and electrodes along the cantilever would carry power out of the system. The piezoelectric layer was also pyroelectric, and as it was heated and cooled, would generate energy. In addition to being electrostatically actuated, the cantilever would naturally resonate as heated and cooled due to the different coefficients of expansion of the bilayer cantilever [96]. The device is shown in Fig. 27.

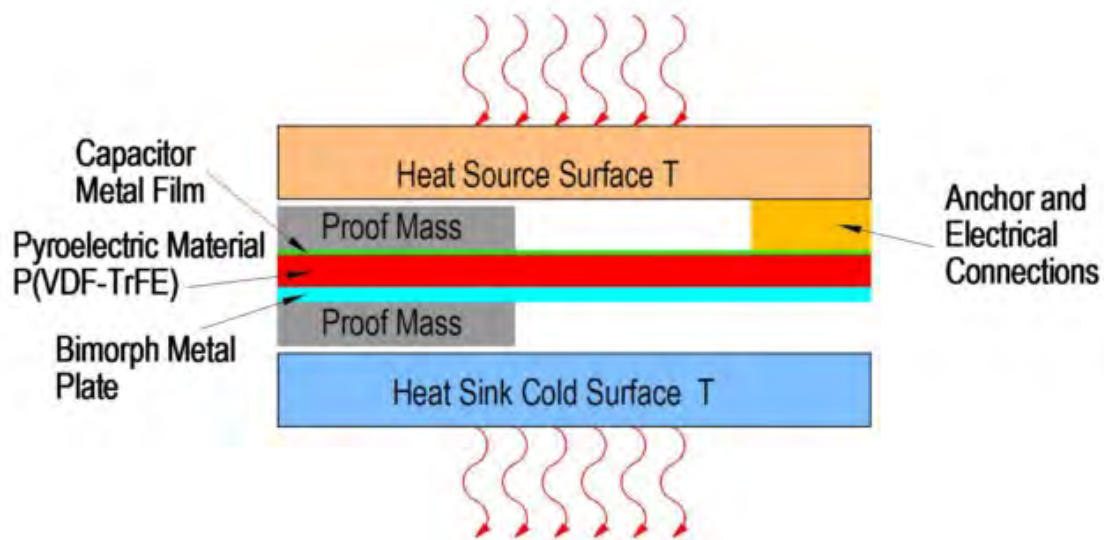


Figure 27. This is the schematic of a MEMS thermal energy harvesting device. This mechanical layer is made of a single end fixed cantilever, in red. The blue material is PVDF, the pyroelectric that will generate electrical charge when heated or cooled. When the cantilever is up, it will heat as it contacts the hot source. As it lowers and contacts the cold source, it will cool. The proof masses are made to slow the actuation of the device. The green layer has different coefficient of thermal expansion than the rest of the cantilever, causing it to bend as the temperature changes. In the event that the cantilever reaches a stable state not in contact with either the hot or cold source, it can be electrostatically actuated to either upwards or downwards. This device was made down to a one square millimeter scale [97].

2.3.2 Vapor Transition Design

A bistable 9 square millimeter silicon membrane was fabricated. The base of the wafer was bonded to a pyroelectric crystal, and the cavity filled with a fluid with vapor transition point near room temperature. When placed membrane side down on a hot surface, the membrane would expand, sending the entire machine upwards into contact with a hot surface. The engine would cool, and the membrane would flip into the opposite state as the vapor cooled into a liquid. The change in temperature from the pyroelectric layer was harvested into electrical energy. The device is shown in Fig. 28.

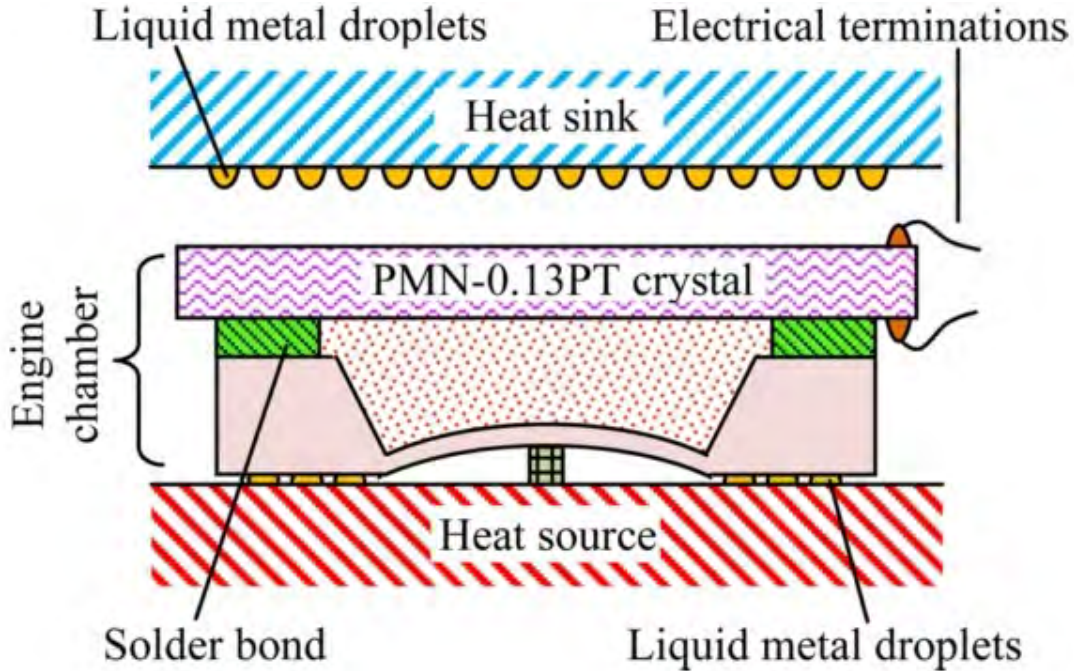


Figure 28. This device consists of an SOI wafer that has been etched out to create a cavity. The cavity was then filled with a phase change fluid, and then sealed with a macroscopically cut single crystal of PMN-PT. When the device heats, the membrane actuates upwards and makes contact with the cold sink, which causes it to cool. The acuation is not from the properties of the membrane, but rather from the phase change material in the filled cavity expanding and contracting. The entire device actuates upwards and downwards. While the movement is from the phase change material, the electricity is generated from the PMN-PT heating and cooling [98]. This energy harvesting device is relatively slow due to the macroscale thickness.

2.3.3 Bistable Metal Bimorph Design

A metal bimorph cantilever was manufactured with metals of dissimilar coefficients of expansion. The metal was compressed to become bistable, with a stable up and down position. As the temperature was increased, the bimorph would be more stable in the up position, and snap through. Once in contact with the upper surface, the bimorph would cool down. Sufficiently cooled, it would snap back to the down position. The change of temperatures on the pyroelectric material on the bimorph would generate electricity. The bimorph had a range of temperatures where both the upper and lower states were stable, so the upper contact and lower contact must be within the temperature range for the device to function. The bimorph had dimensions on the centimeter scale, and was constructed using macroscopic techniques [91].

2.3.4 Piezoelectric Cantilever Design

Piezoelectric materials when combined with MEMS can be used to form vibration energy harvesting devices[15]. The most common geometry is using a cantilever fixed at one end, similar in design to a springboard. On top of the native silicon is placed electrode layers and the piezoelectric layer. A SOI wafer can be used to define the etch stop layer for the backside etch. Commonly a large proof mass is left unetched on the end of the cantilever. The additional mass reduces the vibration frequency. The desired frequency for these devices is commonly in the hundreds of hertz. The frequency without the additional mass would be in the kilohertz. Significant research has been performed to determine the optimum length, tapering, and other geometrical parameters of these cantilevers [99].

2.3.5 Passive Devices Design

Passive devices are those that move only from temperature changes, not from electrostatic forces. Using the difference in thermal expansion between nickel and silicon, a completely passive thermal actuator is developed [100]. The expansion of the nickel is forces the movement of the device. While expansion could result in torque, the mechanical structure of the device with 5 parallel bars prevents any out of plane skewing. The device is shown in Fig. 29.

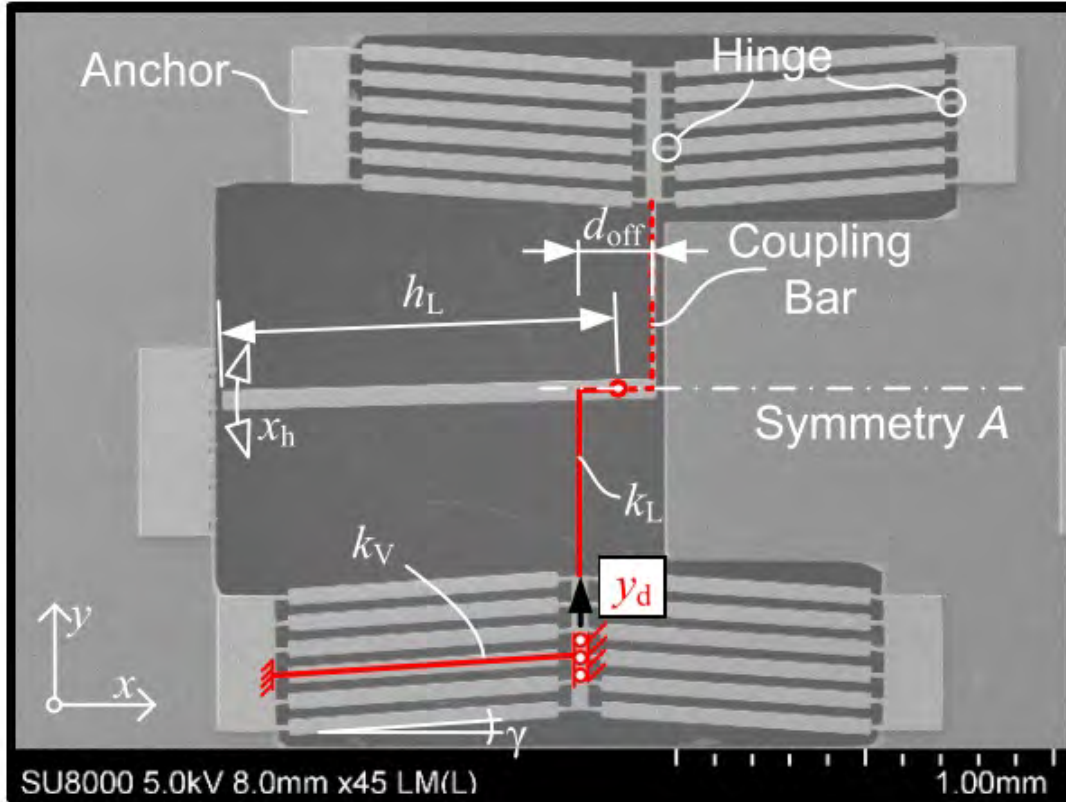


Figure 29. This thermal actuator uses expansion of materials from heating to generate movement [100]. The darker areas are single crystal silicon from an SOI wafer. The lighter areas are silicon electroplated with nickel. During heating, the nickel areas expand faster than the silicon, becoming longer. This forces the bars to bend in the y-axis. The force on the center bar causes it to move. Despite the fact the thermal expansion is in itself almost a very small force, this system multiplies the overall deflection twice. Once is by using the bars almost perpendicular to their growth direction, causing large lateral movement. The second is by using a traditional lever to multiply the deflection.

2.3.6 Static Piezoelectric Layer Design

Instead of using a moving membrane with a piezoelectric element, a bimetal membrane was designed to press against a static piezoelectric element. The bimetal would snap through in response to a heat differential. This device, shown in Fig. 30 [101], is one of the few to separate the moving element from the piezoelectric element.

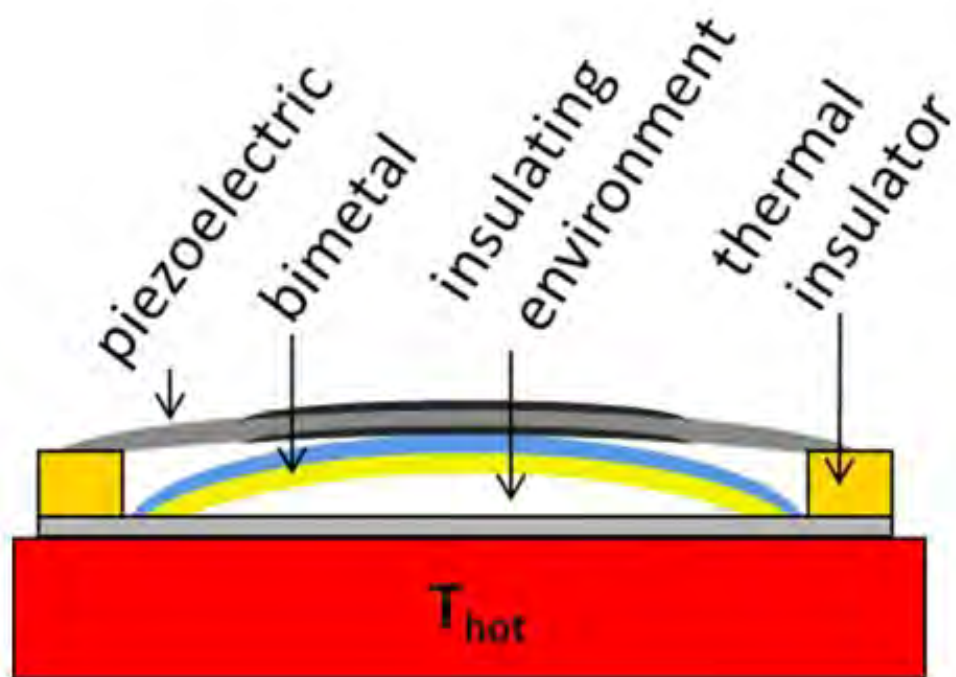


Figure 30. This is an example of an alternate structure for an energy harvesting cantilever. Instead of placing the piezoelectric material on the moving membrane, the moving membrane instead presses against the piezoelectric element, which is fixed. Since electricity is only generated where contact is made, a potentially large device may only generate electricity across a small area of piezoelectric material [101]. This device has the advantage of design simplicity, as there is no need to place the piezoelectric element onto the moving device.

2.3.7 Novel Thermal Energy Harvesting Configurations

The change in capacitance using constant charge and a moving capacitor can be used to harvest energy as shown in Fig. 31. A macrosized design involved a 100 μm thick steel beam was used as a base layer before PVDF was deposited on the structure. The applied stress of the holding device forced the 10 cm long beam into a bistable state [102]. Applied mechanical vibrations could then be harvested via energy from the structure. The device was made from macroscopic fabrications methods. A magnetically induced bistable cantilever device with one end fixed to the substrate was fabricated to harvest energy. The bistability resulted from a magnet attached to one end that interacted with a magnet fixed on the substrate to render the no deflection state energetically unfavorable. The energy was harvested by a PZT layer placed on the cantilever, which was stressed by the motion. The input to the system was physical vibrations [103]. The system is displayed in Fig. 32.

2.3.8 Similar Characteristics of Heat Harvesting Devices

While there are numerous different designs, the one commonality between all of these designs is frequency and heat flow. The frequency should be as high as possible, to maximize the power of the system. Frequency increases as size decreases, which pushes the trend toward smaller systems. The other issue is thermal management. A device must channel heat properly. This is an interesting issue. Unlike electricity, which can be controlled on an off via transistors, heat flow cannot be stopped in a device, and it will continue by all paths available. The device that is to change temperature must insulate heat, otherwise it would allow too much heat to pass through. However, the rest of the device must also insulate heat, so as to not waste energy. Silicon, a conductor of heat, will waste heat through the substrate if it is connected to the heat source. The thermal considerations are paramount for designing an energy

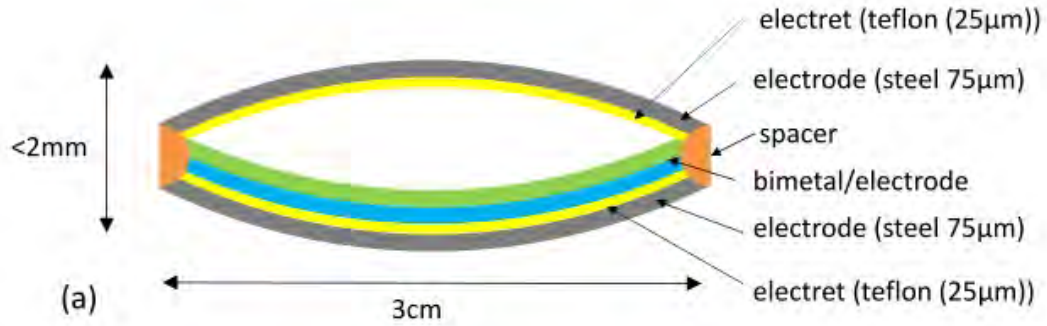


Figure 31. An electret is a material that stores accumulated charge for long periods of time. As long as the charge does not dissipate, this allows it to act as a ferroelectric material. As the electret moves up and down, the stored charge moves with it, creating variable capacitance. This can be harvested as usable electrical energy. The mechanical layer here is a cantilever similar to Fig. 22, except that it is fixed at both ends, creating a permanent curved shape. Depending on the temperature, it will either be upwards in contact with a cold sink, or downwards in contact with a hot sink. The sink it is in contact with cools or heats it, forcing the material in the opposite direction[91].

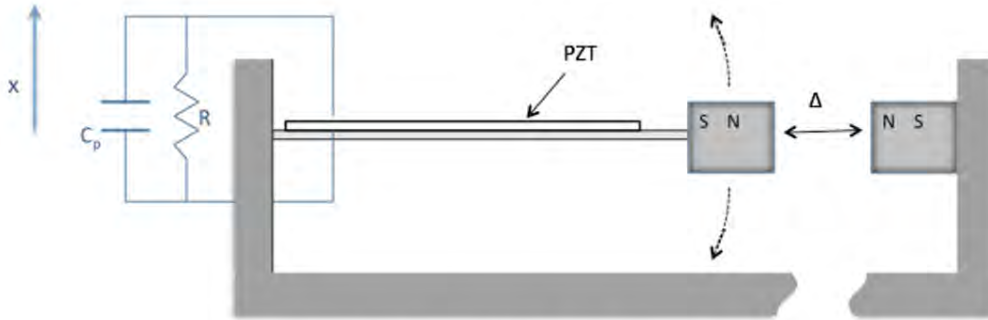


Fig. 1. Schematic of the bistable harvester considered.

Figure 32. This is a novel bistable device to harvest vibrations from a wide range of frequencies. Instead of tension, magnetic force prevents the undeflected state from being stable, and induces significant non-linearities into the system. The deviations from linear behavior allow the machine to vibrate over a wide range of frequencies. Since many vibrations sources are irregular and have a wide range of frequencies produced, this design could be exceptionally useful in real environments [103].

harvesting device for waste heat.

2.4 Efficiency of Energy Harvesting

So far, materials selection has been discussed to determine a preferred ferroelectric material. MEMS processes of how to form a device have been discussed, as well as a review of comparable devices. What remains is specific discussion of MEMS materials useful for energy harvesting devices, and a discussion of energy harvesting itself.

2.4.1 Energy Harvesting Cycles

Since the goal of harvesting energy is to increase the efficiency of the overall system, it is natural to want an efficient energy harvesting system as possible. This can be done by using the proper thermodynamic cycle, which are conceptually thought of as paths in entropy-temperature space or polarization-electric field space. By withdrawing the power at the correct time in the cycle, the amount of power not lost to entropy can be minimized. Some common energy harvesting cycles are detailed below.

Carnot Cycle.

The Carnot cycle is the thermodynamic cycle that converts the greatest amount of heat possible into energy[61]. The Carnot cycle is traditionally plotted on a Entropy-Temperature axis, where the cycle forms a square with adiabatic and isothermal lines. The Carnot cycle can also be plotted in terms of polarization, pressure, volume, or electric field. While the equations in terms of these parameters are less natural, they are more useful to work with for piezoelectric materials because polarization and electric field are measurable constants. Volume of the material or the pressure the material is under are difficult to measure for solid thin films in this setting. If a material follows the Carnot cycle, it will convert the maximum amount of potential power into realizable power, with the minimum amount lost to entropy.

In practical settings, it is impossible to simultaneously know both the polarization of the material and the electric field as time changes, although they can be controlled by applying an external electric field. Alternative cycles that are possible to realize include the resistive cycle, the Ericsson cycle, and the SSDI cycle. The most common cycles are shown in Fig. 33.

Active Energy harvesting.

The SECE cycle is one of the most simple to implement [61]. The energy is removed at the maximum temperature and minimum temperature of the pyroelectric material. The efficiency of this method is k^2 . SSDI is similar so SECE, except that the material is taken to its maximum polarization by the electric field before heating. Then the heating/cooling of the electric field provides for the movement of charge. The efficiency of this cycle can be near the Carnot limit. The resistive heating cycle is the simplest cycle to implement. It consists of no external electric field, and the device generates a polarization that is slightly different than its electric field due to hysteresis. The efficiency of this cycle is extremely low, and can graphically be seen by its lack of similarity to the Carnot cycle. The efficiencies of the active energy harvesting cycles are in table 1. The resistive cycle will have efficiency near k^2 , which

Table 1. Efficiencies of Energy Harvesting Cycles[61]

Cycle	Efficiency
Carnot	$\nu_{Carnot} = 1 - \frac{\theta_c}{\theta_h}$
SECE	$\nu = \frac{k^2}{1 + .5k^2\nu_{Carnot}}\nu_{Carnot}$
SSDI	$\nu = \frac{k^2}{1 + k^2\left(\frac{2\beta}{1-\beta} + \frac{\nu_{Carnot}}{2}\right)}\frac{1+\beta}{1-\beta}$
Resistive	$\nu = \frac{\pi}{4}k^2\nu_{Carnot}$

is often on the order of .1%. Using an active cycle can increase energy gathered by

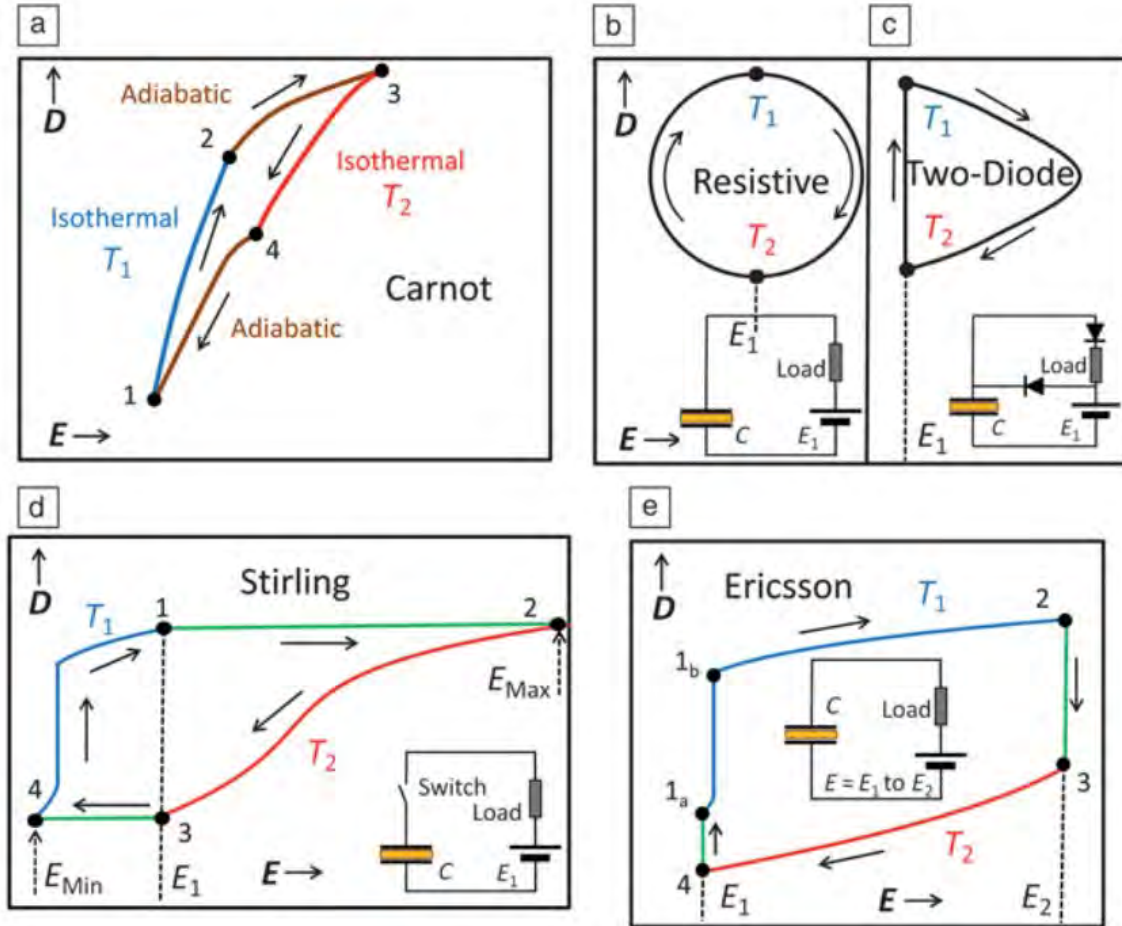


Figure 33. This is a graphical plot of the most important energy harvesting cycles, displayed on D-E plots [33]. The power generated is proportional to the area inside the curve. Part (a) is the Carnot cycle, consisting of adiabatic and isothermal components. While this is the most energy efficient cycle, there is no simple nature to these curves on a D-E plot. The resistive cycle is modeled as a pair of sinusoidal curves displaced by 90^{circ} , which generates a circle. The Stirling cycle has a horizontal component where the electric field is modified, and the Ericsson cycle has a vertical portion where the electric displacement is modified. Because displacement and electric field are more simple to control in a lab setting than entropy, the Ericsson and Stirling cycles are easier to implement than the Carnot cycle. The resistive cycle is simple to implement, but very inefficient.

an order of magnitude.

Stirling, Erickson, and Olsen cycles.

The Erickson cycle is an isostress and isovolume cycle used for piezoelectric materials. As stress is a much more rapid process than thermal change, the Erickson cycle is a much faster process [48]. The Erickson cycle has been shown to have efficiencies of over 50 percent, compared to the resistive cycle where 1 percent efficiencies are standard [33]. The Olsen cycle is the electrical equivalent of the Erickson cycle, and consists of isovoltage and isocharge transitions [56]. This is practical to control for pyroelectric materials, because voltage and temperature can be held constant while the other is changed, if in a controlled environment. The same amount of charge is put into and removed from the device during a heating cycle, but the charge at higher voltage results in more power. The area inside the curve of the P-E diagram represents the total power generated from one cycle. The Olsen cycle is shown in Fig. 34.

2.4.2 Thermoelectric Generator

While energy harvesting devices using MEMS and ferroelectrics may be possible to use for harvesting waste heat, there are alternatives. Thermoelectric generators (TEG) operate using the Seebeck Effect. When two dissimilar metals or semiconductors are joined, a junction will form due to the different Fermi energy levels of the materials. A TEG junction and operation is shown in Figs 35 and 36. If one side of this junction is selectively heated, more electrons on that side of the junction will achieve the thermal energy necessary to be excited to the conduction band from the valence band. This will happen continuously as the material remains hot. If these electrons are at a higher potential than the other side, they will flow to the cool area

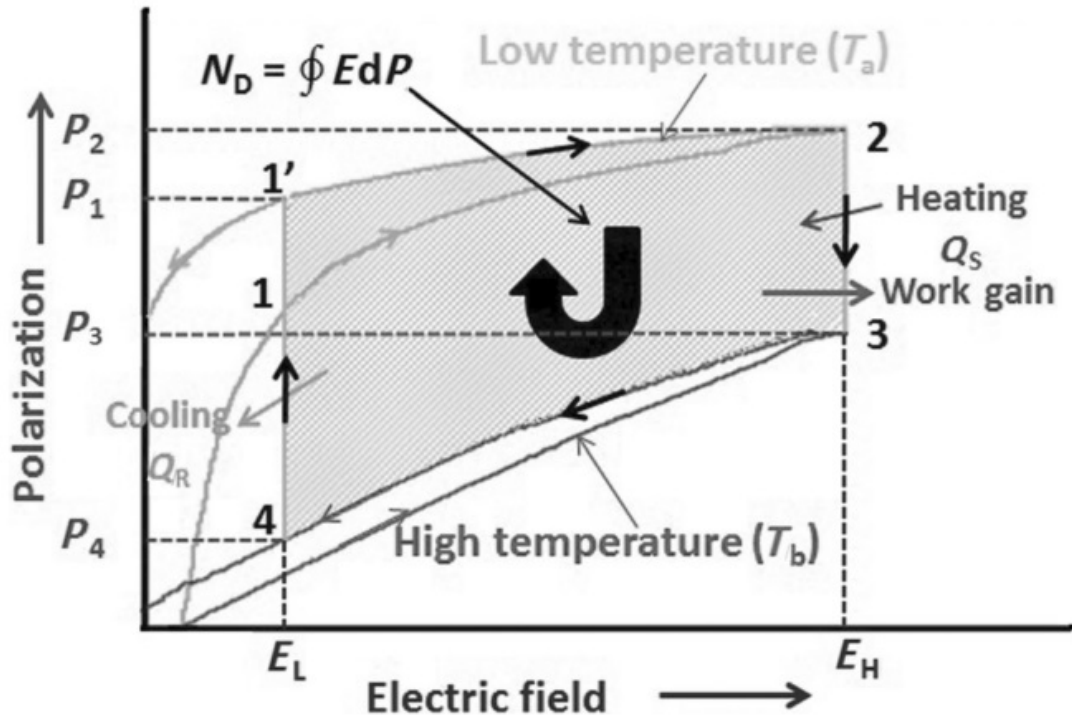


Figure 34. The Olsen cycle is one of the primary energy harvesting cycles used for pyroelectric materials [26] The total work performed is the area inside the circle. The wasted energy is the energy it takes to heat up the substance. The vertical lines are heating, which produces a change in the polarization. The sloped lines are where the energy is harvested, where the removal of electric field and polarization yields electricity.

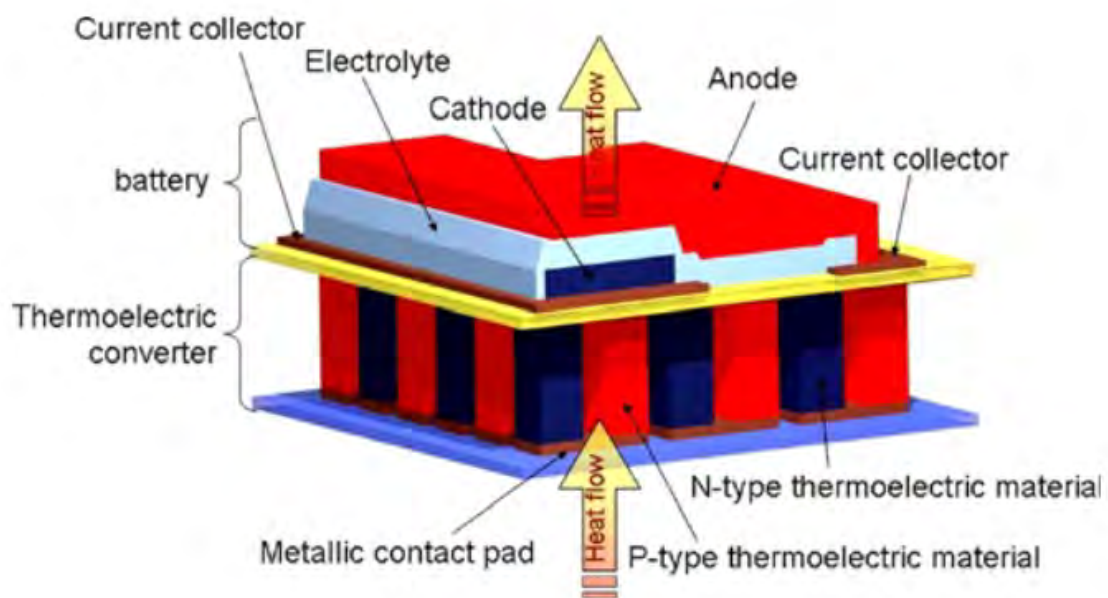


Figure 35. A TEG is a three dimensional structure, with blue n-type and red p-type channels. The heat flows in through the bottom and out the top, a constant process. The bottom electrode is common to all of the electrical channels. The top electrode is subdivided into cathode and anode for harvesting voltage. [104].

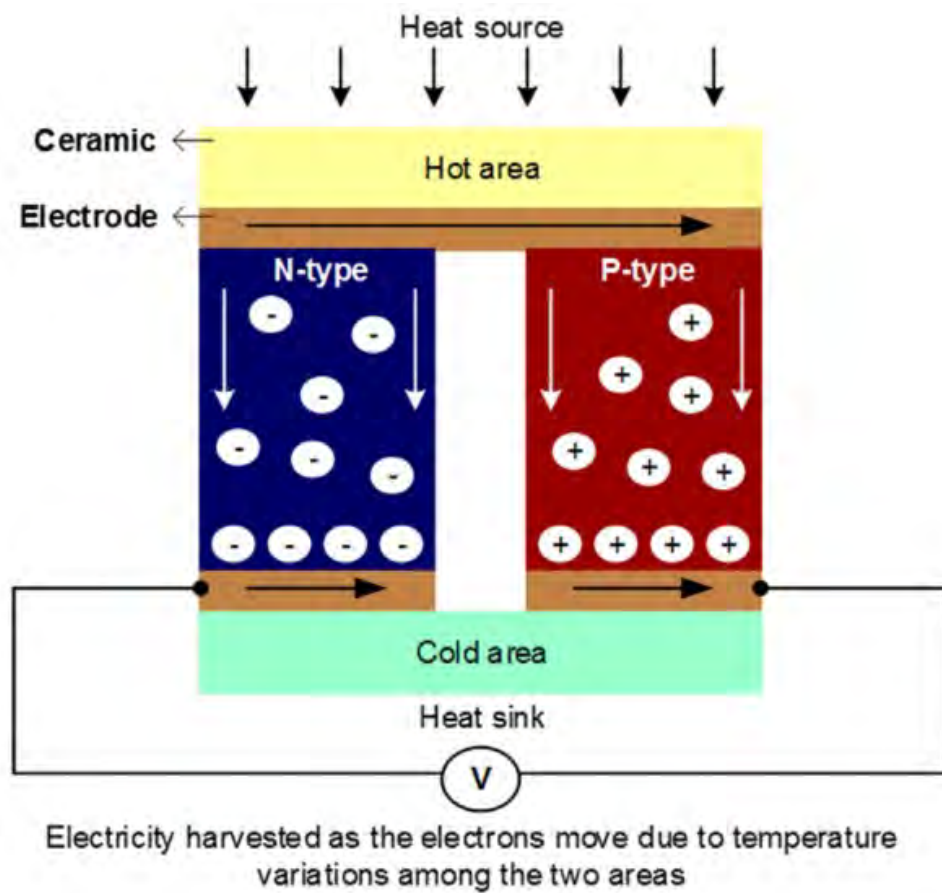


Figure 36. The electrons are at different energies levels and temperatures in the different sides of the device, generating current [105]. However, heat can flow through the material as phonons, causing loss. Often waste heat vastly exceeds useable electricity, making these devices very inefficient.

resulting in current flow. Thermoelectric generators are used in space exploration to provide energy from the decay heat of nuclear materials. They require no moving parts and have long lifetimes. The only barriers to their common use is cost, health hazard, and efficiency. Some materials used in TEG are toxic, restricting their widespread availability. They often contain exotic blends of rare metals, driving up cost. The efficiency is fundamentally limited by the loss of heat to phonons. As a Seebeck junction is heated, a vast majority of the heat will not excite electrons into the conduction band, but phonons in the lattice. While research is being done to provide improved materials, they are not yet commercially viable outside of deep space probes. This limitation is the reason to pursue other energy harvesting technologies, such as ferroelectrics. TEG can be fabricated by microengineering techniques.

2.5 Summary of Background

Based on the limited efficiencies of TEGs, and the potential efficiency of ferroelectric materials, it is natural to pursue the construction of an energy harvesting device from ferroelectric materials. Due to the increased frequency and power generation from MEMS devices there is incentive to combine MEMS and ferroelectric materials. While MEMS energy harvesting devices have been made, none have used the advantages of a bistable membrane. The construction techniques necessary for the creation of this device have been detailed, and the next chapter will contain the procedure of how to fabricate this device.

III. Methodology

3.1 Methodology Overview

There are several components to the construction of this device. First, the construction of procedure of a device is detailed that has built in heating capabilities from a resistive heater, and deflection measurement capabilities from piezoresistors. Then, the procedure for fabricating simpler energy harvesting devices without these features is given. Since the material itself needs to be characterized so that the performance of the device can be separated from the performance of the material, materials analysis needs to be performed distinct from device testing. These procedures follow the fabrication procedures. Lastly, the setup for simulation of the device is given that is later used to predict device properties.

3.2 Design Method for Device with Built-in Heating and Deflection Capabilities

The steps below give the construction process for a MEMS energy harvesting device. This particular design uses PZT as the ferroelectric material, and an SOI membrane as the moving layer. Piezoresistors are used to sense deflection, and a heating layer is included. These eliminate the need of complex optical equipment to detect membrane motion, and allow the simple injection of heat into the membrane.

3.2.1 Preparation of the Sample for Processing

To begin, each SOI wafer is cut into smaller pieces, so that each piece may be fabricated independently. The wafers are covered with protective S1818 photoresist and diced into 1 inch squares before processing. This allows a single 3 inch wafer to be subdivided into four samples, allowing more attempts at making a device. After

dicing, the S1818 photoresist is removed by application of acetone. This step can be neglected if it is desired to use an entire 3 inch wafer for processing.

3.2.2 Fabrication of Piezoresistive Elements

The first component to fabricate in this design is the piezoresistors, since they can only be formed directly on the silicon itself. The piezoresistive elements are designed in a Wheatstone bridge configuration. This allows very small changes in resistance to be more accurately detected. The samples are solvent cleaned with acetone, methanol, water, and isopropyl alcohol (IPA). This cleaning process, which is repeated many times during this fabrication, ensures that all particles are removed from the sample. The sample is dried at 110 °C for 2 minutes, then cooled. The drying process ensures that all of the solvents have evaporated off of the sample. The samples are placed in a diffusion furnace to grow an oxide layer 150 nanometers on the silicon substrate. This oxide layer prevents diffusion of the boron into the silicon substrate later on in the process. The samples are again solvent cleaned, plasma ashed and coated with S1818 photoresist. The resist is exposed in the MJB3 mask aligner, and the wafer is developed in 5:1 Deionized (DI) water to developer solution. This results in the piezoelectric pattern existing in the photoresist, but not in the oxide. The wafer is then placed in the TRION RIE machine and dry etched to etch through the silicon dioxide using CF_4 . The photoresist prevents some portions of the sample from being etched, forming the piezoresistive pattern. The sample is solvent cleaned to remove the photoresist and any other particles. At this point, the sample now still will have a 150 nanometer oxide layer, except in special areas where the piezoresistors will be placed. The sample is placed in a diffusion furnace adjacent to a boron target, and heated to 950C for 10 minutes to allow boron to diffuse into the sample. The sample is then removed and cooled. The sample is placed in a buffered oxide etch (2:5:1

HF:DI water; whatever) to remove all silicon dioxide from both sides of the wafer. This complete the patterning for the piezoresistive traces. This process is shown in Figs. 37, 38, an 39. .

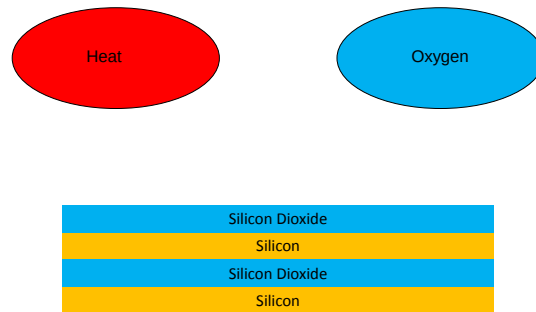


Figure 37. Heat and water vapor cause the growth of a 120 nanometer thermal oxide layer on the surface of the SOI wafer. This process is performed inside a furnace that can reach over 1000 °C. This process has a practical limit of growing layers of 4 micrometers thick, as the process slows as thickness increases. The growth of this layer causes the silicon layer to shrink, as some silicon is converted to silicon dioxide. The overall structure is larger, as silicon dioxide is larger per mole than silicon.

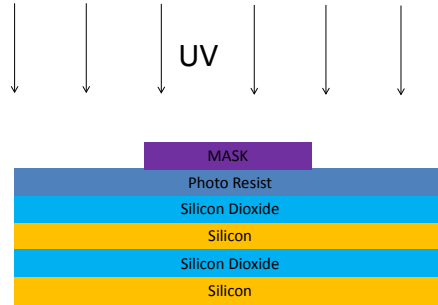


Figure 38. Photoresist is applied to the wafer, exposed and developed. This will cause a pattern of photoresist to appear on the wafer in the shape of piezoresistors. The photoresist will prevent some parts of the wafer from etching.

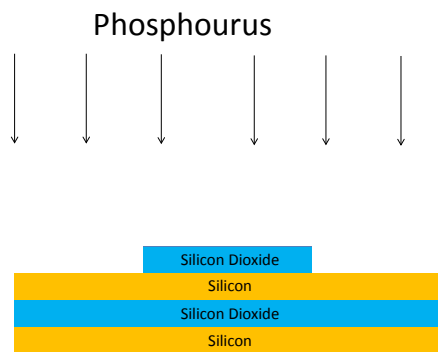


Figure 39. After the photoresist is removed by washing in acetone, boron is diffused into the wafer by placing a dopant source adjacent to the sample at 1000 degrees C. A borosilicate evaporates off of the boron source, and coats the sample. The boron will then diffuse from the borosilicate glass into the silicon. The boron will not spread through the protective oxide layer, leaving most of the sample unaffected. The borosilicate glass is later removed via HF etching.

3.2.3 Deposition and Patterning of Heating Traces and Piezoresistive Contacts

Since the piezoresistors are not useful without a place to make electrical contact, it is necessary to deposit gold pads to make electrical contact with the resistors. In addition, a step is saved by depositing a heating layer at the same time. This heating layer is simply a thin gold trace deposited across the substrate. When current flows through it, the resistive heating will heat the sample. To accomplish this, the sample is solvent cleaned, coated with S1818 resist, prebaked, exposed, and developed. The sample is then placed in the evaporator, and 30 nanometers of titanium and 150 nanometers of gold are deposited on the sample. After removal, the gold covering the resist is removed with tape by the liftoff procedure. After additional with acetone, the fabrication of the gold traces is complete. This is shown in Figs. 40, 41, and 42.

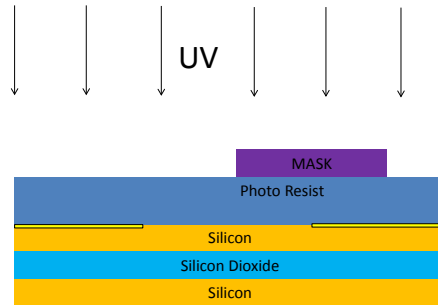


Figure 40. The piezoresistors need to have electrical contacts, and a gold heating layer needs to be deposited. Since this will be done via liftoff, another layer of photoresist is applied, exposed and patterned.

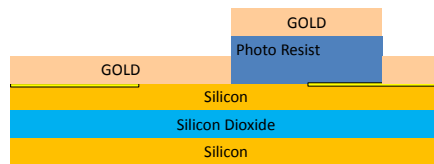


Figure 41. 150 nanometers of gold and 20 nanometers of titanium for adhesion are thermally evaporated across the sample. The titanium ensures adhesion of the gold to the silicon.

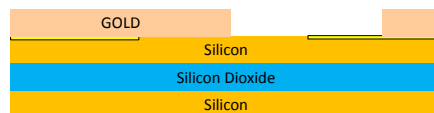


Figure 42. A liftoff procedure removed the gold that adhered to the photoresist, and the remaining resist is removed via acetone. At this point, the gold heaters are fully functional, as are the contacts to the piezoresistors.

3.2.4 Deposition and Patterning Silicon Nitride for Electrical Insulation

After this is complete, a insulation layer of Silicon nitride is deposited to prevent electrical contact between the gold heater layer and the pyroelectric layer. The sample is solvent cleaned and plasma ashed. The sample is then placed in the Trion PECVD chamber, to grow a layer of silicon nitride 250 nanometers across the sample. The sample is then solvent cleaned and plasma ashed again. S1818 is applied to the sample exposed and developed using the standard procedure. The silicon nitride is then etched in the Trion RIE. The photoresist is then removed using the solvent cleaning procedure. This leaves the gold pads exposed for contact, but the gold heating layer electrically insulated. This is shown in Figs. 43, 44, and 45.

3.2.5 Deposition and Patterning of the Lower Electrode for the Energy Harvesting Ferroelectric Material

It is necessary to have an electrode on each side of a ferroelectric, otherwise the generated charge can never be moved to a storage device. In this same step, the electrical contact that goes from the bottom electrode to a probe contact pad is formed. The sample is solvent cleaned, coated with S1818 resist, prebaked, exposed, and developed. The sample is then placed in the sputtering machine and platinum is sputtered deposited. The lower electrode is formed out of platinum, which is

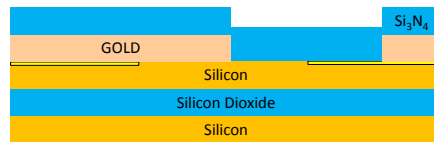


Figure 43. A layer of silicon nitride is grown using PECVD for insulating the just deposited gold layer and the electrode layers above. The silicon nitride is 250 nanometers thick, which is thick enough to entirely encase the 150 nanometer gold electrodes

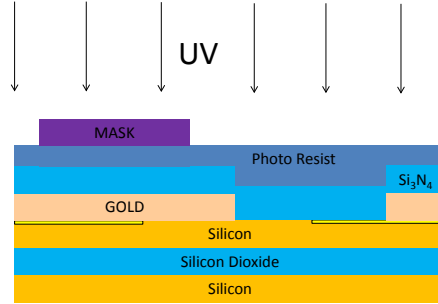


Figure 44. A layer of photoresist is applied, exposed and patterned to prepare to etch the silicon nitride. The pattern will leave silicon nitride only above the active device area, and leave the rest of the device open for electrical contact.

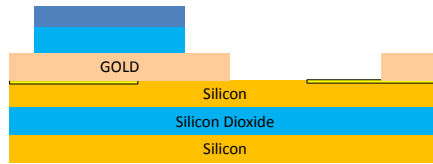


Figure 45. Reactive ion etching is used to pattern the silicon nitride, which is largely immune to wet etching. The photoresist is then removed by using acetone, and the device area is now protected by silicon nitride.

customary for PZT. Titanium is used as an adhesion layer to ensure contact of the platinum to the below substrate. The sample is then lifted off as in the evaporation procedure. Because sputtering is a conformal deposition technique, the liftoff is not as immediate. Many applications of tape and sonication in acetone are necessary to complete the patterning of this layer. The crystallization of the platinum is analyzed in a crystal XRD machine. Surface composition is determined using the XPS. The surface composition can affect the orientation. The surface composition varies as the titanium adhesion layer migrates through the platinum, forming a TiO_x layer as it partially oxidizes at high heat. These steps are shown in figures 46,47, and 48.

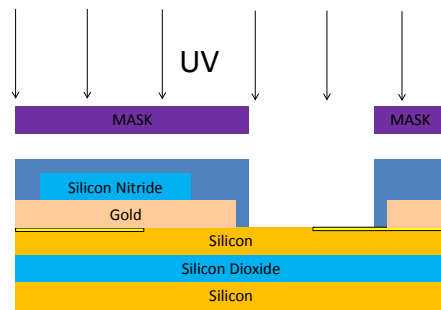


Figure 46. A platinum layer is going to be deposited to serve as the lower electrode for the PZT. To prepare for the liftoff of the next platinum layer, photoresist is applied and patterned.

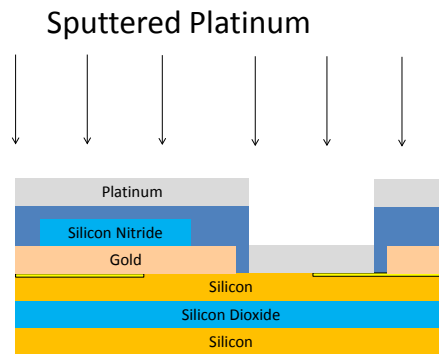


Figure 47. Platinum is sputtered onto the sample, using titanium as an adhesion layer. The platinum adheres to the sample where there is no photoresist. The platinum shape covers the active area.

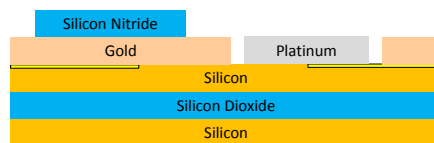


Figure 48. The liftoff procedure completes the pattern definition of the bottom platinum electrode. The sample is cleaned with acetone to remove the remaining solvent.

3.2.6 Deposition and Patterning of the Ferroelectric Material

After the deposition of the bottom electrode, the sample is ready for the deposition of the ferroelectric material. The PZT is bought as a 2 inch target with composition $\text{Pb}(\text{Zr}_{.52}\text{Ti}_{.48})\text{O}_3$. It is placed in the sputtering machine and sputtered deposited. The sputtering power is maintained below 2.5 watts per square centimeter, because higher powers cause cracking as the material forms. The thickness is maintained below 1 micrometer, as larger thickness require complicated procedures to ensure proper film quality. The composition includes limited amounts of argon to encourage the crystallization in the $\langle 111 \rangle$ orientation. The substrate is heated for the same reason. After deposition, the sample is analyzed for composition, phase and orientation in the XRD. The sample is annealed at 650 C for 5 minutes, and analyzed again. The sample is then solvent cleaned and plasma ashed before patterning. To pattern the PZT, the sample is placed in the TRION RIE and etched with chlorine. These steps are shown in Figs. 49,50, and 51

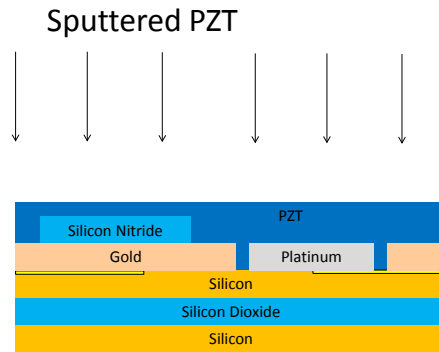


Figure 49. 1 micrometer of PZT is sputtered across the entire surface. This is one of the longest steps, as PZT sputters at rates of 40 nanometers an hour.

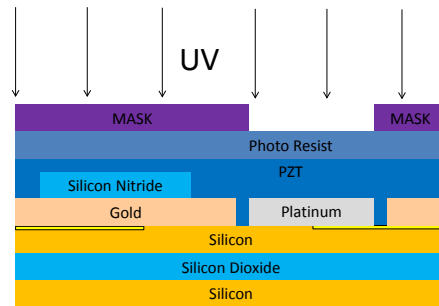


Figure 50. Photoresist is patterned to prepare for PZT etching. Since the PZT covers the electrodes for the piezoresistors and heating element, it must be removed.

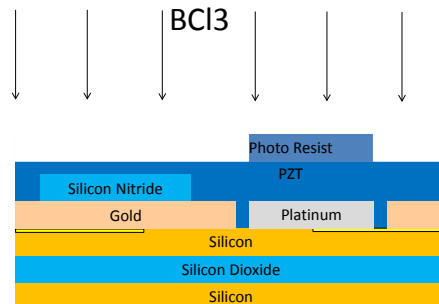


Figure 51. The PZT is reactive ion etched by boron trichloride, to make the contact pads on the sample accessible.

3.2.7 Deposition and Patterning of the Upper Electrode for the Energy Harvesting Ferroelectric Material

The final step to making a complete device is to deposit an upper electrode to cover the PZT. Similar to the bottom electrode and heating steps, the contact pads that run to the upper electrode are formed at the same time. The sample is solvent cleaned and spin coated with S1818 resist. The resist is prebaked, exposed, and developed in the pattern for the upper electrode. A 150 nanometer gold layer and 10 nanometers titanium adhesion layer are deposited across the substrate using a electron beam evaporator. The pattern is formed by liftoff the undesired gold from the substrate. Multiple tapping runs are performed, as well as sonication in an acetone bath. This is shown in Fig. 52.

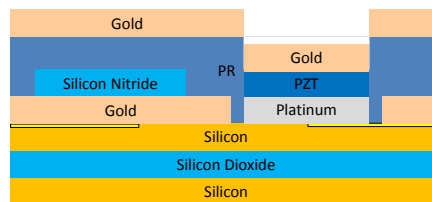


Figure 52. The liftoff sequence is repeated again for the deposition of a top gold electrode. This completes the formation on the top side of the device.

3.2.8 Membrane Release via DRIE

While the device is formed, it is still adhered firmly to the silicon substrate. It is necessary to removed the silicon on the backside via DRIE to yield a moveable membrane. To accomplish this, the reverse side of the sample is solvent cleaned. SU-8 negative photoresist is spin coated on the sample for 30 seconds at 4000 rpm. The sample is prebaked at 65 C for 2 minutes and at 95 C for 5 minutes. The sample is exposed in the EVG mask aligner with back side alignment capability. The sample is developed in SU-8 developer solution. The sample is then placed in a DRIE (bosch Process) machine for plasma etching. This process released the membranes. The process is shown below in Figs. 53 and 54.

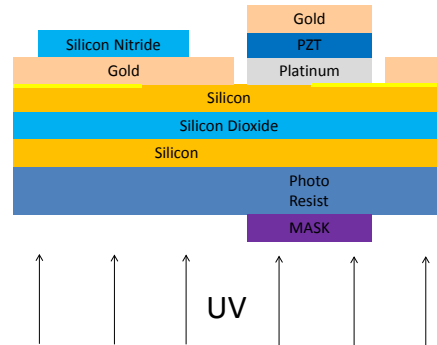


Figure 53. A negative photoresist is used to pattern the bottom side of the wafer for DRIE. The mask pattern must be inverted and flipped in the x-y plane to use for backside alignment with a negative photoresist.

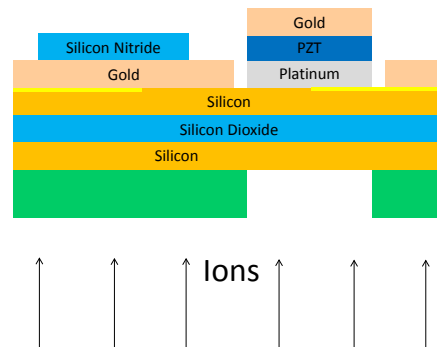


Figure 54. The hardened negative photoresist provides a mask for DRIE etching of the wafer. The device is now complete, and free to move.

3.3 Design Method for Device Using External Heating and Deflection Measurement Methods

The fabrication from top to bottom of the device allows the creation of customized devices, such as those that have heating layers, piezoresistors, and and patterned bottom electrodes. In addition, previously tested materials were available from groups that are dedicated to materials processing. Using these materials prevents the fabrication of features below the ferroelectric, but does provide for simpler testing of the basic features. The processes tested with these materials are detailed below.

3.3.1 Method of Fabricating Simplified Device Using PZT

PZT wafers are obtained from Army Research Labs (ARL). The wafers are 6 inches in diameter, with a 500 micrometer handle, 1 micrometer buffered oxide layer, and 2 micrometer device layer. The large size of the wafers is due to the process requirements at ARL. The devices are thermally oxidized to form a 100 nanometer silicon oxide insulation layer. A lower electrode of platinum with a titanium adhesion layer is deposited. Lead titanate is deposited as an orientation layer, followed by one micrometer PZT. The PZT is deposited by a sol-gel technique. An upper electrode of platinum is sputtered to 100 nanometers thickness. One wafer had the upper electrode deposition step skipped to allow analysis of the PZT material. Wafers in this condition are received for patterning. PZT samples are patterned with S1818 and etched in an RIE chamber with a chlorine chemistry to etch a pattern into platinum to form the upper electrodes. The wafers are reverse patterned with SU-8 at 25 microns thickness in a MA6 mask aligner and DRIE etched to release the membranes. This completes the processing for these samples.

3.3.2 Method of Fabricating Simplified Device Using AlN

Even though PZT is the material of choice for this project, aluminum nitride (AlN) material is readily available, and is also tested in a similar manner. Aluminum nitride piezoelectric material is deposited on wafers by Air Force Research Laboratories (AFRL). The samples provided are .25 square inches. No insulating layer is used, as is typical for the AlN process. The lower electrodes of titanium nitride is deposited by sputtering. The one micrometer of aluminum nitride is also deposited by sputtering. Aluminum nitride samples have an upper electrode of gold deposited by evaporation. The gold is patterned with S1818 photoresist and wet etched with iodide solution to form the upper electrode. The wafers are reverse patterned with SU-8 at 25 microns thickness in a MA6 mask aligner and DRIE etched to release the membranes. This completes the processing for these samples.

3.4 Laboratory Test Setup

Once a device has been made, it is necessary to test and evaluate it with specialized equipment to test the performance. The tools and procedures for this are given below.

3.4.1 Micromanipulator Setup for Piezoresistive Testing and Power Generation Testing

The micromanipulator station is a microscope equipped with electrical probes which can be connected to equipment via BNC connector. The mechanical probes on the tips are designed to be brought into contact accurately and precisely with a substrate. The probe tips can make contact with a half millimeter length square pad without difficulty. This means that using the micromanipulator, one can put voltage to a specified area on a micromechanical sample, such as a heating pad or piezoresistive pad. Adjacent to the micromanipulator are ohm-meters, oscilloscopes,

and voltage sources which can be connected in any combination to provide power to or measure signals from the sample. This device is used at multiple different stages of the device. The station can provide heat to the sample up to 400 °. The heating feature allows the voltage of a ferroelectric energy harvesting device to be sampled while it is being heated. Before any fabrication is performed, the sheet resistance of each sample is measured. This would allow for some determinations of piezoresistive doping by noting the junction voltage. After piezoresistive doping, the resistance of a single piezoresistive trace is measured, at a series of temperatures. Determining the resistance of a piezoresistor is key to using it as a strain sensor. After deposition of the gold heating layer, the resistance of the gold heater is measured, and the resistance of the wheatstone bridge is measured. The resistance of the gold layer allows one to know how much current through the resistor corresponds to how much heat. The measurement of the wheatstone bridge allows the determination initial offset of the piezoresistors. If they are not entirely equal, one side of the bridge will show a bias. In addition, the resistance of the wheatstone bridge is sampled to ensure that electrical contact had occurred and is not inhibited by any native oxide layer. The probe station is next used again after completed fabrication of the device, to test the energy harvesting properties. First, four contacts from the wheatstone bridge are connected to the probe station, while the station is heated to a known temperature. This allowed the determination of resistivity change due to temperature. Two contacts from the probe station are connected to the heating pads, and four are connected to the wheatstone bridge. This setup allows for the resistance change to be measured at different temperatures, and the temperatures determined by comparing to the results from the known DC heating source. Both the AC and DC voltage sources are used in this configuration. To test PZT effectiveness, 2 probes are connected to the heating substrate while one oscilloscope probes is connected to each of the upper and lower

PZT electrodes. A common ground is used between the equipment. The oscilloscope is also connected to the signal generator. In a reverse setup, the signal generator is connected to the piezoelectric electrodes, and four probes are used to connect to the wheatstone bridge. This setup allows the measurement of force from the piezoelectric layer when used as an actuator.

3.4.2 White Light Interferometric Determination of Membrane Deflection

The Zygo white light interferometer is capable of determining vertical deflection of the membrane[106]. While being heated to a series of different temperatures, the membranes are placed under the interferometer and observed. This provides data to correlate heat and deflection. The interferometer is effective of measuring displacements of over 100 nanometers. The device encounters some difficulties when analyzing samples with inherent interference due to thin layers, or which have varying reflectivity over the samples area.

3.4.3 Optical Imaging of Energy Harvesting Devices

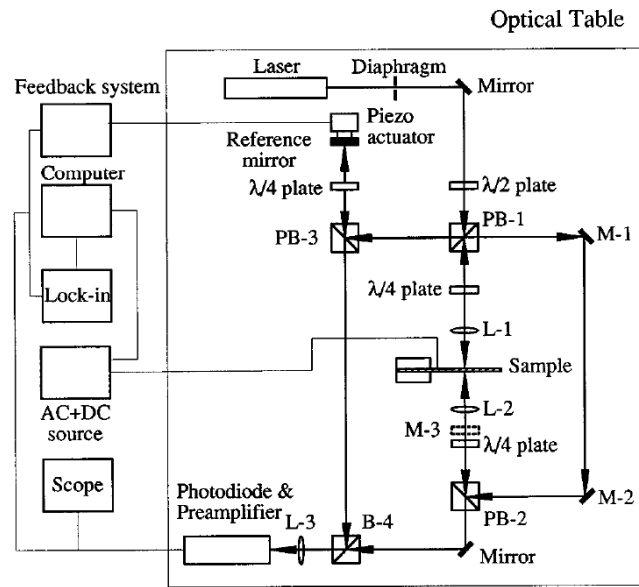
Optical imaging for these samples is performed using Ziess optical microscope. Imaging is used regularly during lithography to ensure that development of photoresist has proceeded satisfactorily, to observe overall material quality, and look for defects. It is also used to determine that wet etching of oxide has not over etched. Zooms range from 5x to 100x.

3.4.4 X-ray measurements to Determine Composition and Crystal Structure of Materials

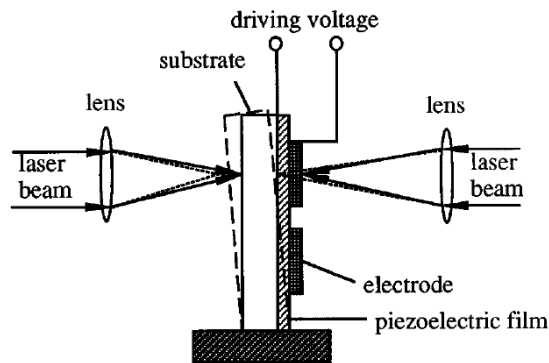
To analyze the PZT for composition and crystallization, an XRD and Scanning Electron Microscope (SEM) are used. These are essential characteristics of ferroelectric materials, and taking these measurements allows this material to be compared to materials in other lots. The XRD is used to determine phase, crystallinity and orientation of the PZT. X-ray Photoelectron Spectroscopy (XPS) equipment is provided by AFRL and used to determine surface chemistry of PZT thin film, and helps determine the quality of the film surface. SEM and EDS are used to obtain composition data on the PZT sputtered film, and to view the overall topography.

3.4.5 Interferometric Determination of Piezoelectric Quantities

An interferometric system using 4 beam splitters is used to measure piezoelectric coefficient of the material [107]. Measuring the piezoelectric coefficient is used to separate the efficiency of the system from the efficiency of the ferroelectric material. The setup is capable of measuring changes in deflection of down to 1 femtometer, and can be used at frequencies from 100 Hertz to 100 KHz. The setup of this system is shown in Fig. 55. This setup is capable of measuring piezoelectric expansions with femtometer precision. The stabilized Helium-Neon (HeNe) laser is sent through a diaphragm to avoid stray reflections. Then, a mirror redirects the beam through a half waveplate, where it is split by a polarizing beam splitter PB-1. The polarizing beam splitter sends half the light to PB-3 in the reference arm. From there, all the light in the reference arm is reflected through a quarter wave plate, and reflects off a mirror mounted on a piezoelectrically actuated platform that reduces vibrational effects on the system. The light then goes back through the quarter wave plate, through the beamsplitter PB-3, and recombines with the signal light at beamsplitter B-4. The



(a)



(b)

Figure 55. In image (a), the overall beam path for an interferometric measuring system is shown. This system is uniquely suited for determining piezoelectric coefficients over a wide range of frequencies. Part (b) of this diagram shows the action of the laser near the sample. The lenses are arranged so that the laser focuses at the front and back surface of the substrate. Because this measurement is based on the curvature of the substrate, having a point measurement eliminates non-linearities that would otherwise occur. The sample must be mounted in such a fashion as to have the top and bottom electrodes of the piezoelectric accessible, and must be double side polished to allow for reflections off both sides.

light that is originally passed through PB-1 becomes the signal. This light passes through a quarter waver plate and is focused in lens L-1 on the front side of the substrate. after reflecting off, the same lens collaminates the light, and the quarter wave plate again rotates the polarization. The polarizing beamsplitter than reflects the light towards mirrors M-1 andM-2, and it enters polarizing beamsplitter PB-2, which reflects all of the light towards the sample. The light again passes through a quarter wave plate and a lens, and focuses on the backside of the sample. The light reflects off the sample, collaminates in the lens L-2, rotates again in the quarter wave plate, and passes through the polarizing beam splitter. The light reflects off a mirror, recombines with the reference arm at B-3, is broadened at L-3 into a photodiode. The photodiode is connected to a lock in amplifier to display the resulting voltage, and to the feedback system which eliminates vibrations.

3.4.6 Optical Spectroscopy for Material Properties

Spectroscopy is a useful tool for analyzing the involved materials, to determine permittivity and potential phases. Electrical permittivity affects the effective power generated by a piezoelectric material, and this information is given by ellipseoemetry. Information on spurious phases which can detriment power generation can be found in Raman spectroscopy. Horiba ellipsometry and Raman spectroscopy tools are used to analyze the PZT and AlN samples for optical properties. Ellipsometry is analysis based on the change of polarization of light after encountering a sample [108]. While ellipsometry can be reflection or transmission based, for analyzing the thin films in this study only reflection ellipsometry is applicable. Raman spectroscopy is the stimulation of a sample with a powerful light source, and the analysis of the scattered light near but not at the same frequency [109]. The vibrational and rotational modes of the atoms mix with the source light, producing scattered radiation with a frequency

shift that matches the energy band of the sample. The samples are analyzed at room temperature and in lab atmosphere. Ellipsometry analysis is performed with a large spot size of over one square millimeter, at an angle of 70 degrees. The large spot size reduces noise in the measurement. The wavelengths analyzed are from 200 to 2400 nanometers, the full extent of the machine. Raman spectroscopy is performed using a 532 nanometer laser, chosen because of the prevalence of this source. The Raman shift is sampled from 50 inverse centimeters, to the machine limit of 15000 inverse centimeters. Most runs indicate no significant features with massive shift, and subsequent analysis is performed on a much narrower Raman shift bounds.

3.5 FEM Setup for Device Simulation

Coventorware is an FEA tool designed to simulate MEMS structures. FEM simulations are performed in Coventorware using a 3000 element mesh on the membrane, as shown in Fig. 56. It is not possible to make the model smaller, as accuracy would sharply decrease with fewer elements beyond this point. It is possible to simulate one quarter of the membrane with 2 mirror planes at 90 degrees, or one eighth of the membrane with 2 mirror planes at 45 degrees. These models decrease processing time, but eliminate the possibility of finding and non-centrosymmetric modes. The one-eighth model also can not be used with a square mesh due to the 45 degree angle. The top layer in red is the piezoelectric PZT. The blue layer in the middle is silicon. The gold layer on the bottom is silicon oxide, with physical parameters chosen from thermal oxide growth. The default Coventorware properties for PZT material are used. The center square in the red PZT a logical designation for the inside of the PZT, so that the inside and outside may be treated differently, such as heat being injected only on the inside of the membrane, and withdrawn on the outside edges. The membrane is extended in the z direction for sake of clarity. The actual device would have a

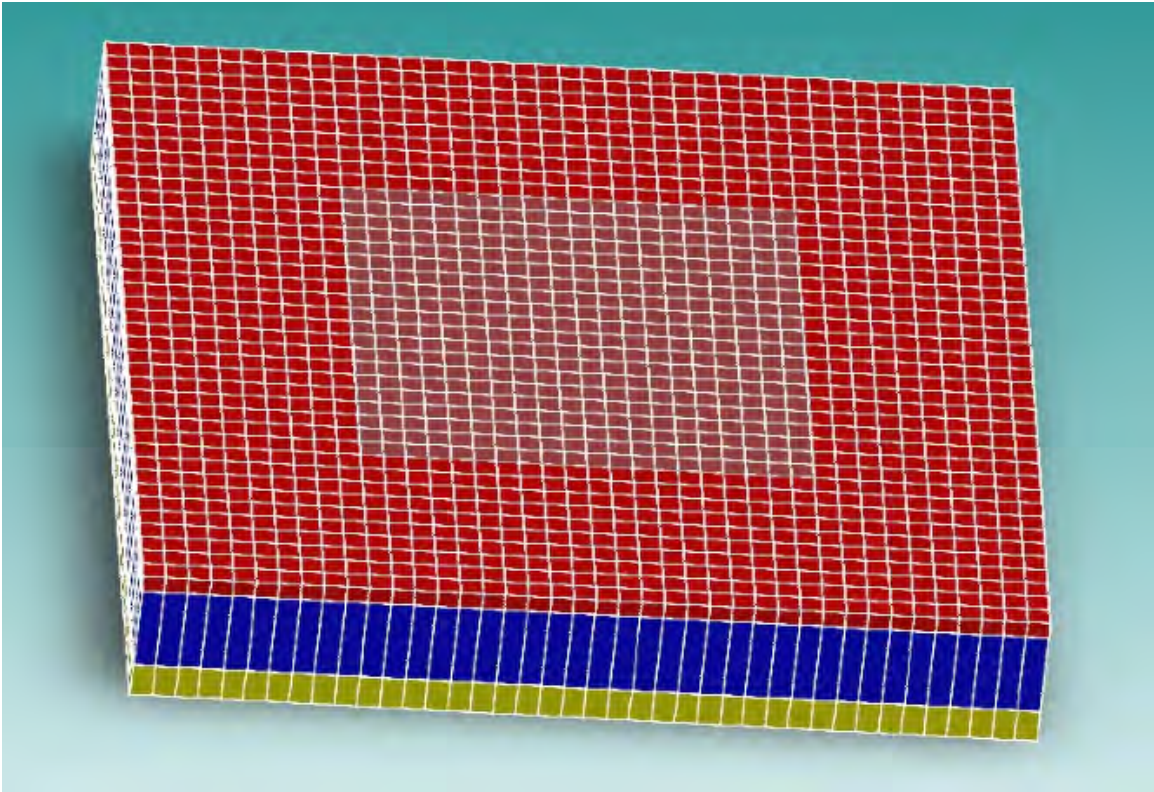


Figure 56. This is the physical model of the membrane in FEM software. The different colors represent different materials. Red is PZT, blue is silicon, gold is silicon oxide. The central square of light red is the area where heat will later be injected in simulation.

150:1 width to height ratio, and be difficult to visualize. Simulations done include mechanical only to find a stable position, thermal simulations to model heat flow, piezoelectric simulations to model resulting voltage, temporal models under constant force to model membrane actuation speed, temporal models to determine membrane actuation force to flip the membrane from one state to another, harmonic analysis to model resonant frequencies, piezoelectric to model deflection with applied voltage. Most simulations are performed using python scripting to run a series of simulations at different settings, such as layer thicknesses, forces, and membrane width.

IV. Results and Analysis

4.1 FEM Modeling Results

The results from the different tests run with FEM modeling and their significance are given below.

4.1.1 Simulations to Determine Membrane Heat Flow Characteristics

First, the device is tested to determine how heat flows, the heat pattern on the device at thermal equilibrium, and the time to reach thermal equilibrium. The device is simulated to take 1 millisecond to reach equilibrium temperature, if heat is injected at the center and diffuses out through the edges, as shown in Fig. 57. If heat is injected through the top and rejected through the bottom of the membrane, equilibrium temperature is reached in tens of microseconds. While the thermal oxide should normally provide a large barrier to thermal heat flow, the dimensions are so different along the two axis as to make heat propagation down through the insulating oxide faster than the horizontal propagation across the membrane. Heat propagation is proportional to surface area and inversely proportional to length. The length down through the membrane z-axis is 100 times shorter than the lateral dimension of the membrane, while the cross section is 100 times greater for the downward flow. This simulation is performed holding the ends at constant temperature and injecting constant power to the middle section of the membrane. The membrane is modeled as being fixed in its unstable equilibrium position for the duration of the test. The deflections experienced by the membrane do not alter the heat flow.

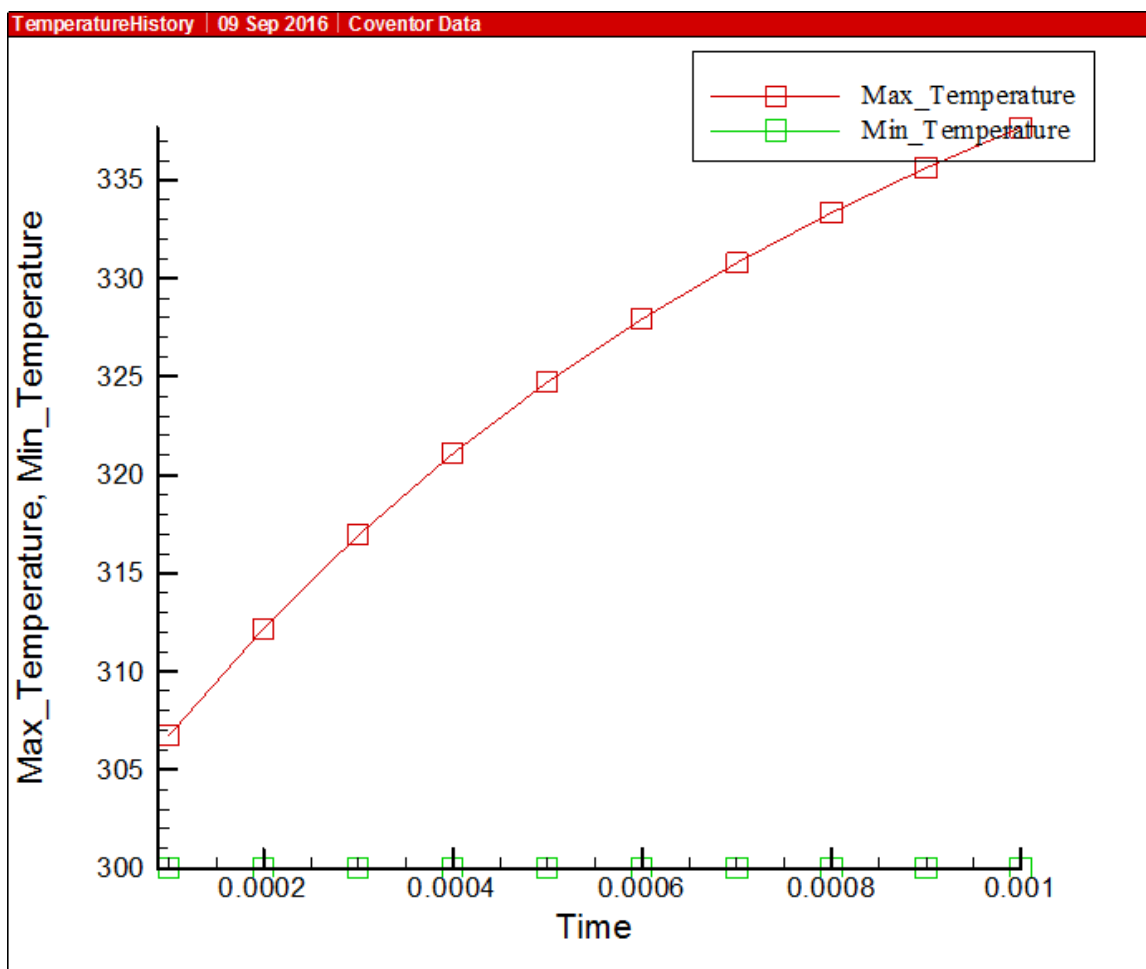


Figure 57. This is a plot of the maximum and minimum temperatures on a membrane as heat is injected into the center and is allowed to flow out the edges. The simulated one square millimeter membrane reaches near is equilibrium heat value in 1 millisecond.

4.1.2 Simulations to Determine Characteristics of Membrane Movement

Since it is not practical in a lab setting to observe this membrane in motion optically, simulations are enacted to determine what sort of motions occur in the membrane. The membrane is initialized at the unstable neutral position, and the results are observed both with and without force applied. With even a small force in the kilopascal range applied to the bottom, the membrane takes 30 microseconds to reach the stable point, as shown in Fig. 58. With no actuating force, the membrane possesses a very small oscillation, exponentially growing in size, until the same results are observed as previously. Near the equilibrium point, the small driving force dominates other vertical forces, but once even a small deflection is achieved, the natural stress on the membrane becomes the significant factor in actuation speed. A periodic oscillation near 100 Khz is observed for membranes of 1 millimeter size. This vibration became less significant as the size of the membrane is decreased. Having a driving force opposite to the direction of deflection for a deflected membrane produces a much more rapid actuation. This is mainly because the forces involved are much larger. The force needs to be enough to push the membrane across the unstable equilibrium point.

4.1.3 Simulations to Determine Harmonic Resonance of Membrane Structure

Based on previous results, the membranes are investigated for harmonic frequencies. At harmonic frequencies, the device may have greatly enhanced motion, which may enhance energy harvesting. Multiple such frequencies are found, the lowest of which is 100 Khz for a 1 millimeter square membrane. The frequency increased with decreasing membrane size, and the overall magnitude of the vibration decreased with

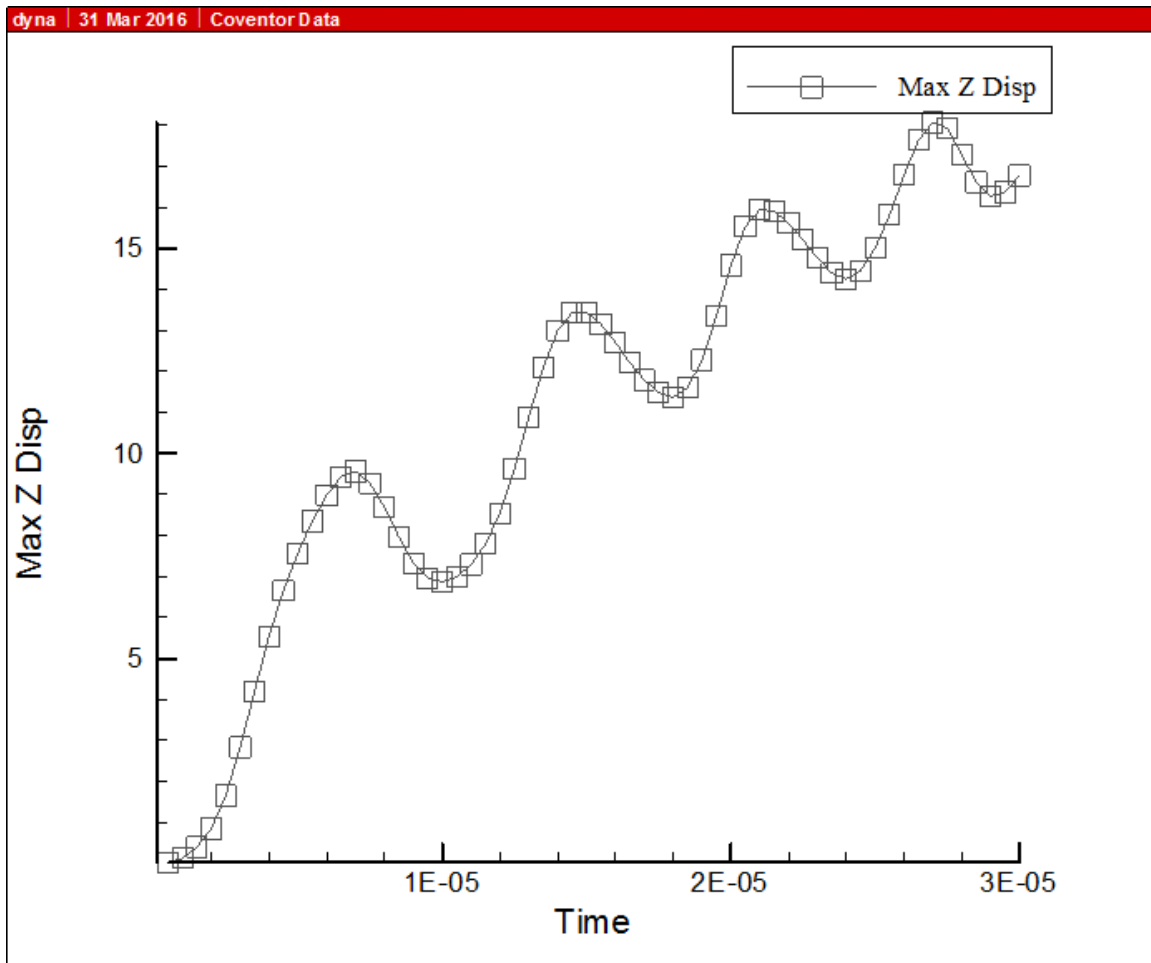


Figure 58. The membrane is predicted to reach its maximum deflection in near 30 us, with a resonance frequency near 100 kHz.

decreasing membrane size. The bandwidth of the resonance frequency is less than 1% of the center frequency.

4.1.4 Simulations to Determine Piezoelectric Response

Lastly, it remained to simulate the expected electrical response of the piezoelectric layer. The maximum voltage of the PZT layer is proportional to the membrane deflection, as shown in Fig. 59. The voltage distribution along the membrane is shown in Fig. 57. The voltage is determined by fixing the bottom surface of the piezoelectric layer as a ground layer. The resulting voltage is determined by fixing the bottom surface of the piezoelectric layer as a ground layer. As there is a one element thick mesh, the voltage is computed by the software as a simple tensor product of the stress at that element multiplied by the provided piezoelectric coefficients. One can visually see this by comparing the voltage and stress plots for the membrane model, and noting their similarity. While models are run to analyze the effect of injecting a voltage on the PZT material on membrane deflection, no noticeable change in deflection is seen. The voltage generated on the piezoelectric material due to the membrane stress is shown in 60.

4.2 Laboratory Results

Before the ferroelectric material is processed, it is first analyzed to determine its material properties. This allows comparisons to later material received in the lab, and can also be used to confirm the quality of the material.

4.2.1 Ellipsometry Data from Energy Harvesting Materials

A Horiba ellipsometer is used to analyze the AlN and PZT for optical properties. The data is presented below in Figs. 62 and 61. The data for aluminum nitride is not

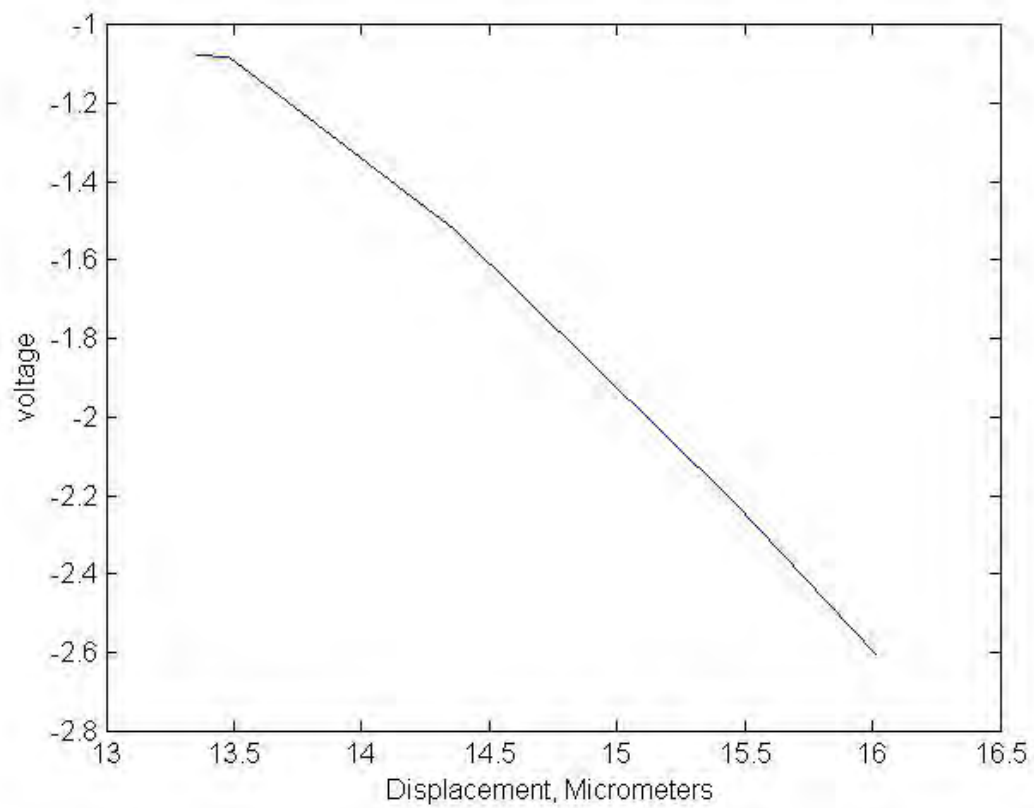


Figure 59. The voltage response is expected to be proportional to membrane deflection

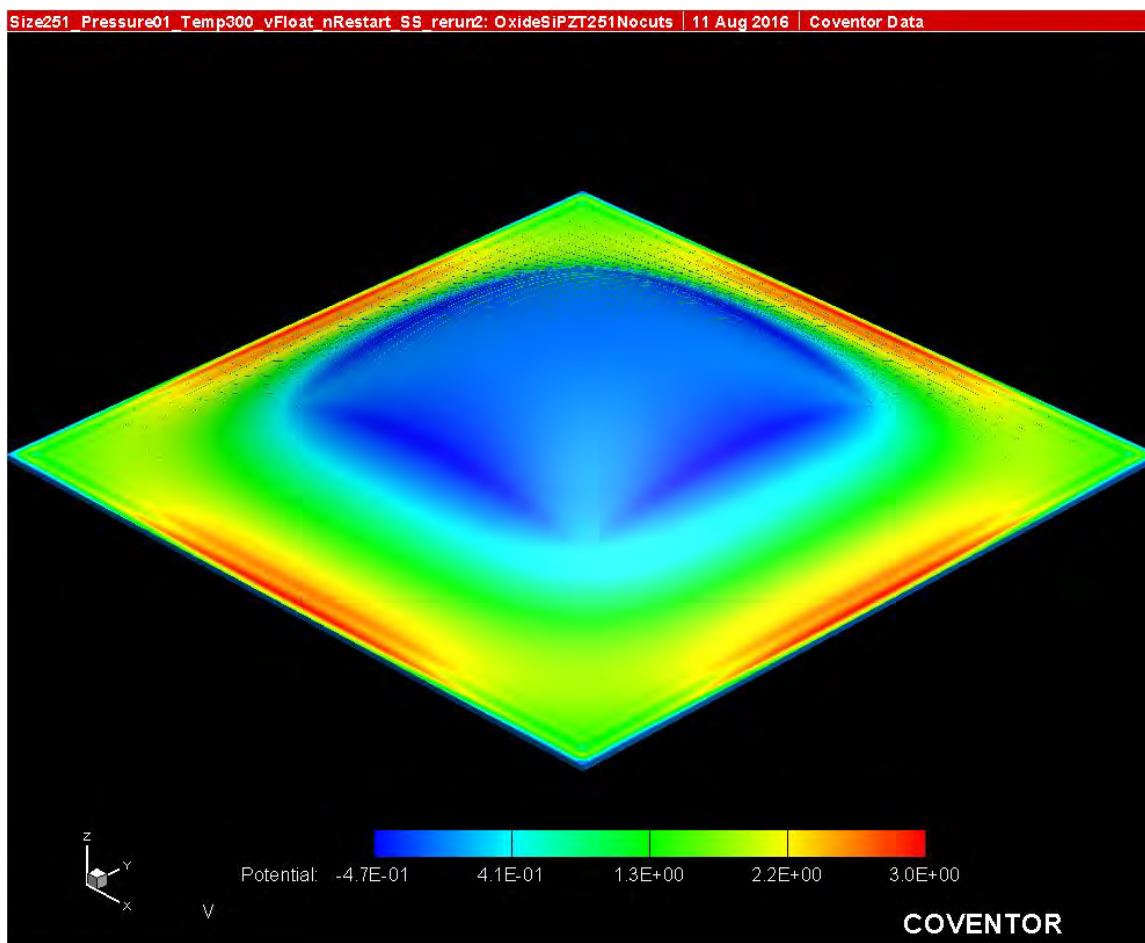


Figure 60. The simulated membrane shows high voltage response at the locations of highest stress along the edges of the square membrane.

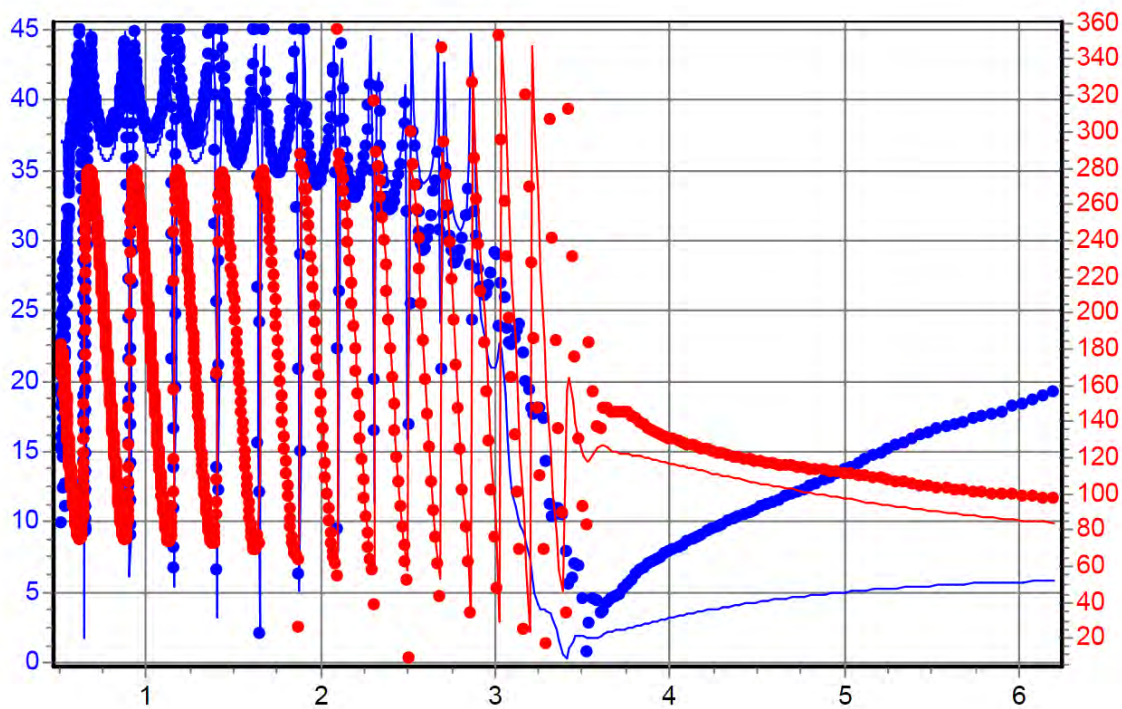


Figure 61. Phase and absorption from 200 to 2400 nanometers with fitting to built in model shown. The bandgap is clearly visible at 3.6 Electron Volts (eV), above which the material properties change and the model is no longer accurate.

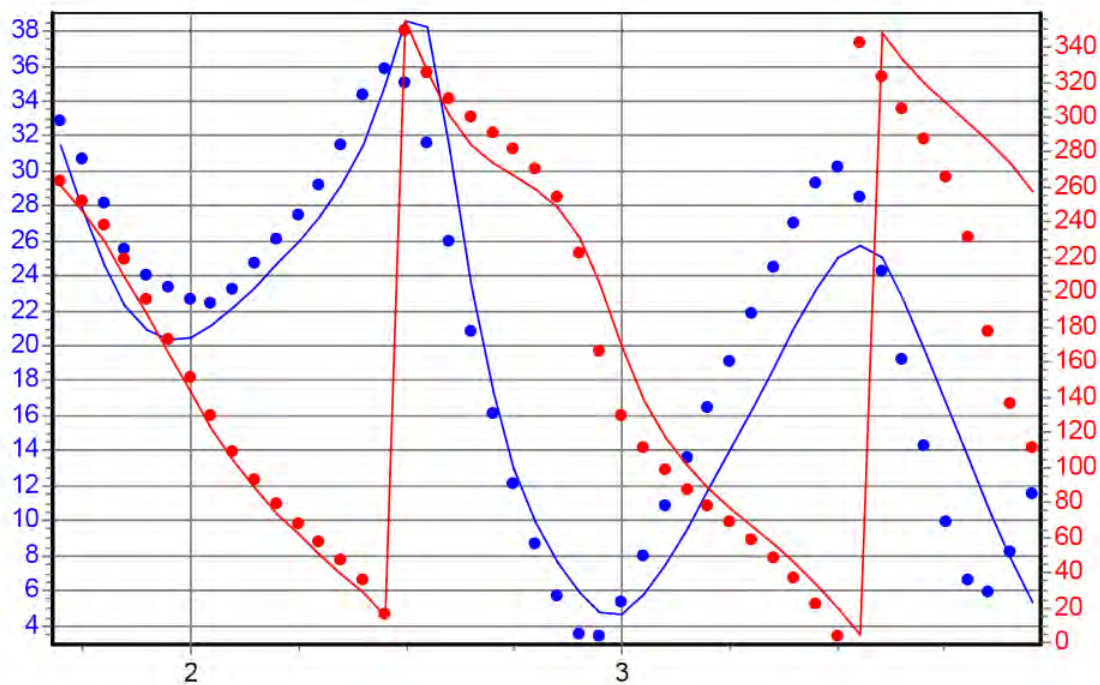


Figure 62. Phase and absorption with fitting to built in model shown. Data at the higher and lower wavelengths is not as important for AlN and is not shown

well matched for the by the model, possibly indicating the reference and the presented sample vary in optical properties. Aluminum nitride can be a non-stoichiometrically grown in the sputtering process, resulting in differing properties depending on the exact elemental ratio. The results for PZT show a clear change in behavior near 3.6 eV. This is indicative of the bandgap of PZT. While the provided model is accurate at higher wavelengths, at energies near and above the bandgap the model begins to diverge from the sample measurements. This particular fit cannot model the material simultaneously above and below the bandgap.

4.2.2 Raman Spectroscopy Data from Energy Harvesting Materials

AlN and PZT are analyzed with a raman spectrometer for more optical properties. The data is shown below in Figs. 63 and 64. The fingerprint from the raman spectrum can be used to confirm the material provided [110], with the critical window for properties being near 500 cm^{-1} for PZT. An additional band is shown near 2500 cm^{-1} , this may indicate a band useful for identification that is neglected in most current scans of PZT. The AlN raman data shows the expected spike at 600 cm^{-1} , but also shows a large response for all values. This likely indicates a corrupt baseline, and the only true spike is the one near 600 cm^{-1} .

4.2.3 Results of Membrane Deflection from Varying Device Geometry

Various membranes are analyzed for deflection over varying thickness of the buffered oxide layer. Using the Zygo interferometer, the deflection of membranes of is compared between wafers of different oxide layers. This test is performed on multiple sizes of membranes. The wafers with a 2 micrometer oxide layer show more deflection than those with a one micrometer oxide layer, as shown in Fig. 65. This result holds regardless of the lateral size of the membrane. This test is also used to confirm that

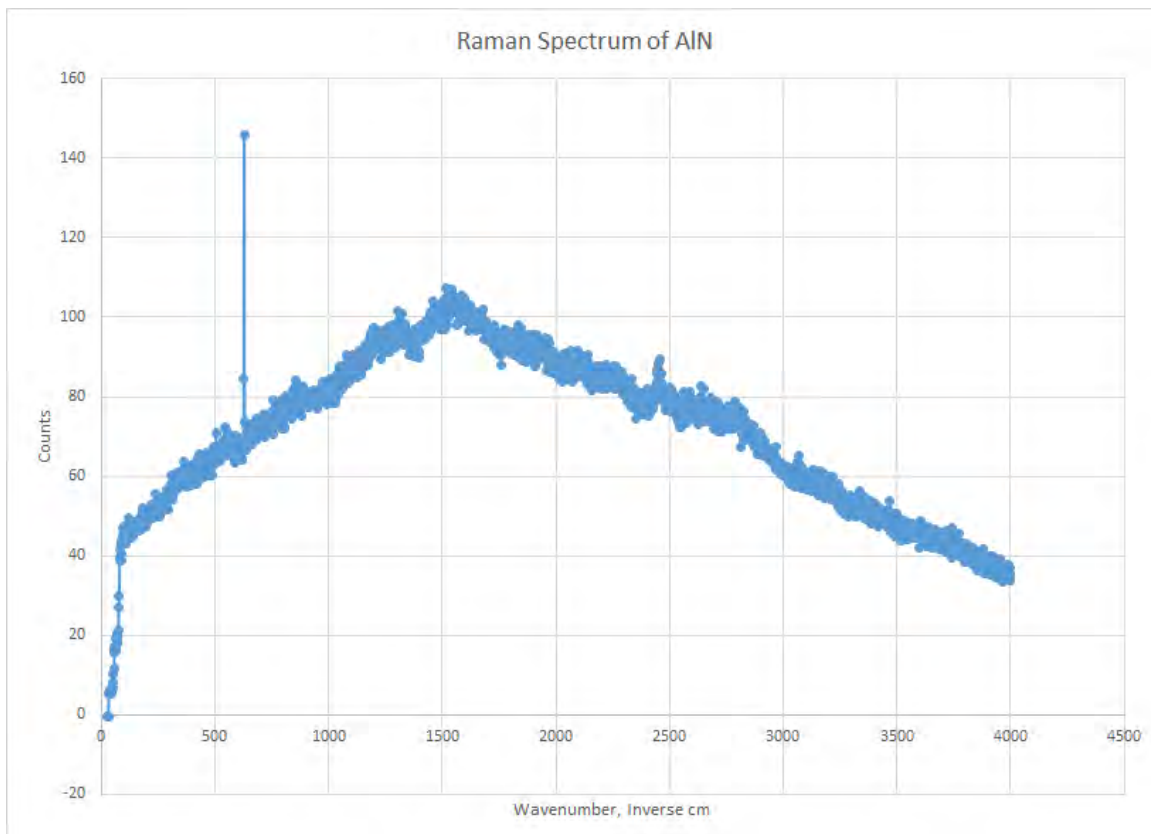


Figure 63. The Raman spectrum of AlN taken with a 532 nm frequency doubled Nd:YAG laser. The single peak at 600 inverse wavenumbers is due to the E_2 transition. There are no other significant peaks shown, and the general curve is due to a false baseline.

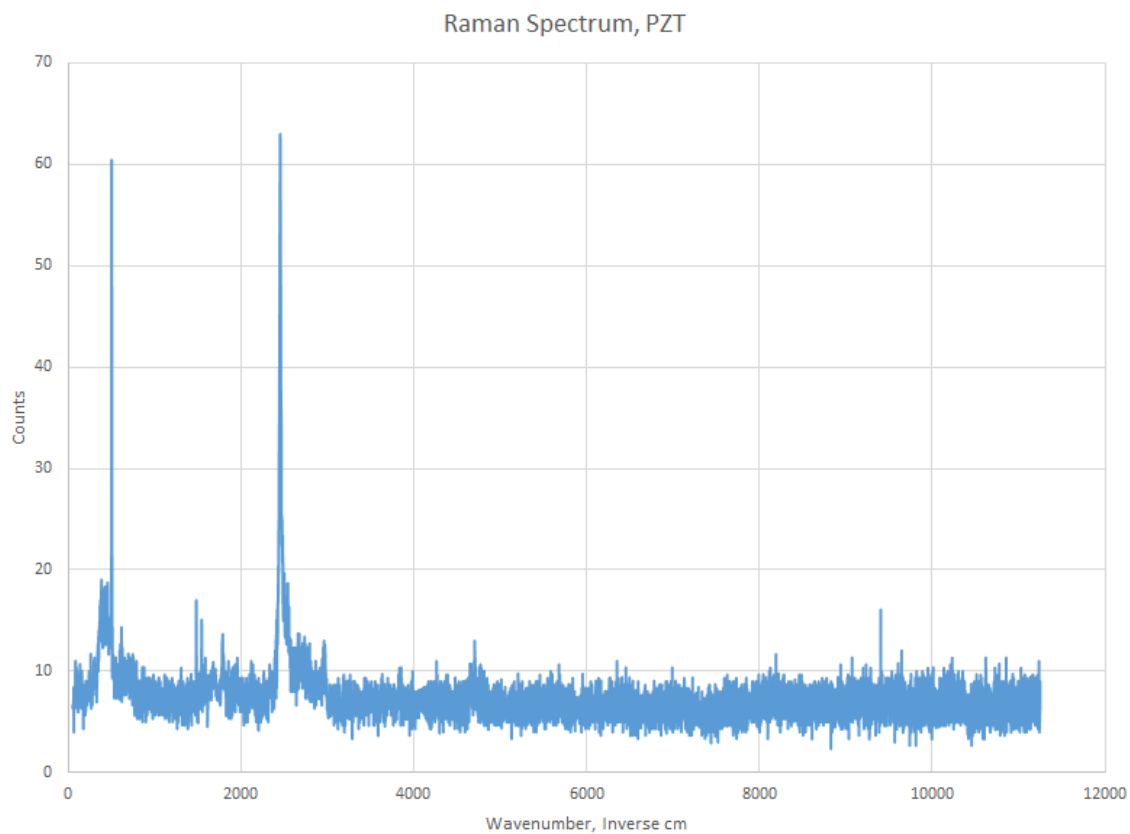


Figure 64. The Raman spectrum of PZT taken with a 532 nm frequency doubled Nd:YAG laser. While the peak near 500 inverse wavenumbers is expected, it is notable that the peaks near 200 inverse wavenumbers are absent. The peak at 2500 inverse wavenumbers is generally beyond the range of most spectroscopy results reported.

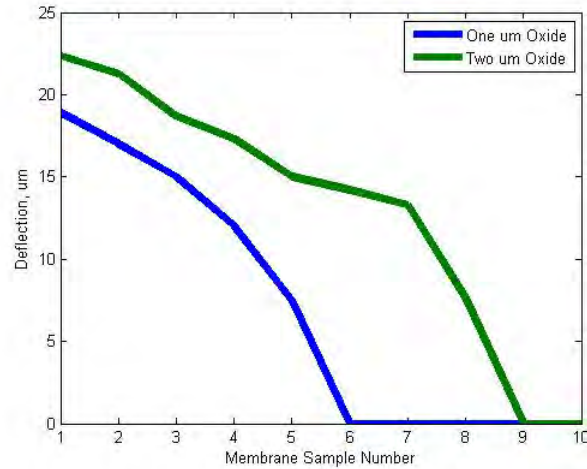


Figure 65. This shows a comparison between maximum membrane deflection on SOI wafers with one and two micrometer oxide layers. The membranes labeled one through ten were of decreasing surface area. For all surface areas of membranes, the two micrometer SOI wafer produced larger deflections. The thinner layers of oxide, while providing less strength to the structure, provide less strain. equal amounts of silicon oxide and silicon maximize the relative strain, and the deflection from the generated device.

2 micrometer device layer wafers could properly form SOI membranes. In our lab, it is yet unconfirmed that SOI membranes of this thickness could be processed and handled without breaking. This test confirmed that wafers of this thickness were useable for SOI membranes, and therefor as layers in energy harvesting devices. In addition, lithography is performed on deflected membranes of this size as proof of concept. The test reveal that a buffered oxide layer equal to the thickness of the silicon layer provide optimal deflection, and that there is a minimum critical size of membrane at any given thickness. This agrees with the FEA results. Therefore, the optimal size is 500 micrometers lateral dimension of membranes with this thickness SOI wafer. The pattern of decreasing membrane deflection with decreasing membrane size is shown regardless of the pattern of square, triangle, or circle, as shown in Fig. 66. A microscope picture of an etched membrane is shown in Fig. 67.

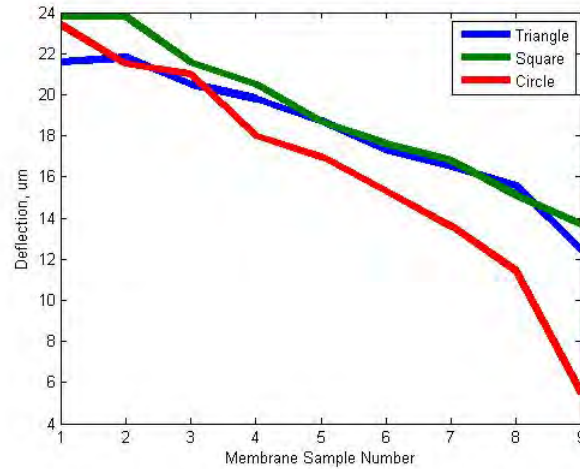


Figure 66. This shows a comparison between the deflections of membranes of different shapes on a two micrometer oxide SOI wafer. The maximum is roughly the same for each shape. The slight shift between the curves is because the different shapes have different surface areas. This shows that minimal difference in deflection should be expected between the shapes.

4.2.4 Piezoresistors Bistability, and DRIE Characterization

The piezoresistors are shown in Fig. 68. The piezoresistors are not able to be evaluated in the desired manner due to aluminum leaching into the silicon to make the entire silicon surface conductive. The process did confirm the suitability of aluminum diffusion to doping the silicon p++ for ohmic contacts with a sheet resistivity of 3 Ohms. The etch using potassium hydroxide to remove this surface layer of aluminum is unsuccessful. This is an unexpected result, as both aluminum and silicon can be effectively etched by KOH. The implications of this are for creating etch stop layers of aluminum doped silicon, even though both can be etched by KOH. The bistability of wafers with a 1 micrometer thick layer of aluminum is determined to be absent even at elevated temperatures, with temperatures up to 200 °C. This confirms that a thicker layer of aluminum is needed for bistability, and that higher temperatures cannot compensate for a thinner layer of aluminum. It is also confirmed that gold is unsuitable for use as a contact to silicon, and will form a liquid phase at near 400 °C.

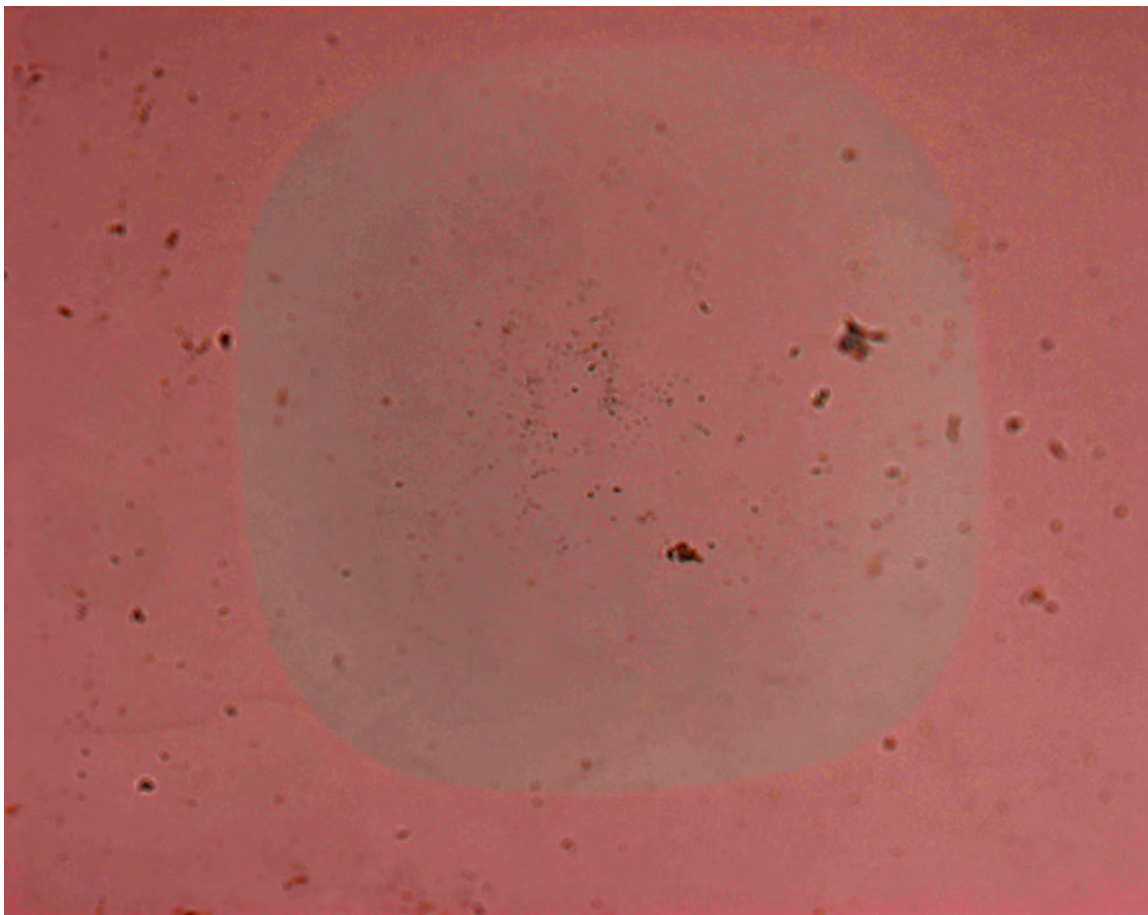


Figure 67. The membrane is presented in false color to increase visibility. The membrane is only deflected 15 micrometers from the surface, so there is no depth change visible, and the coloration change is due to the difference in reflected light. Under a microscope, one could view the pattern of the light to determine whether it is flipped up or down. For the smaller membranes, this fact is not evident to the naked eye. The rounding at the corners is due to the DRIE process. The chemicals lack access at the 90° corner, and etch slower. This results in rounding. As the membranes got to 350 micrometers and smaller, the rounding became so significant that the triangles and square patterns would appear as circles after 500 μm of etching. It is for this reason that circles were selected for the final membrane shape, because squares at these dimensions would appear very distorted.

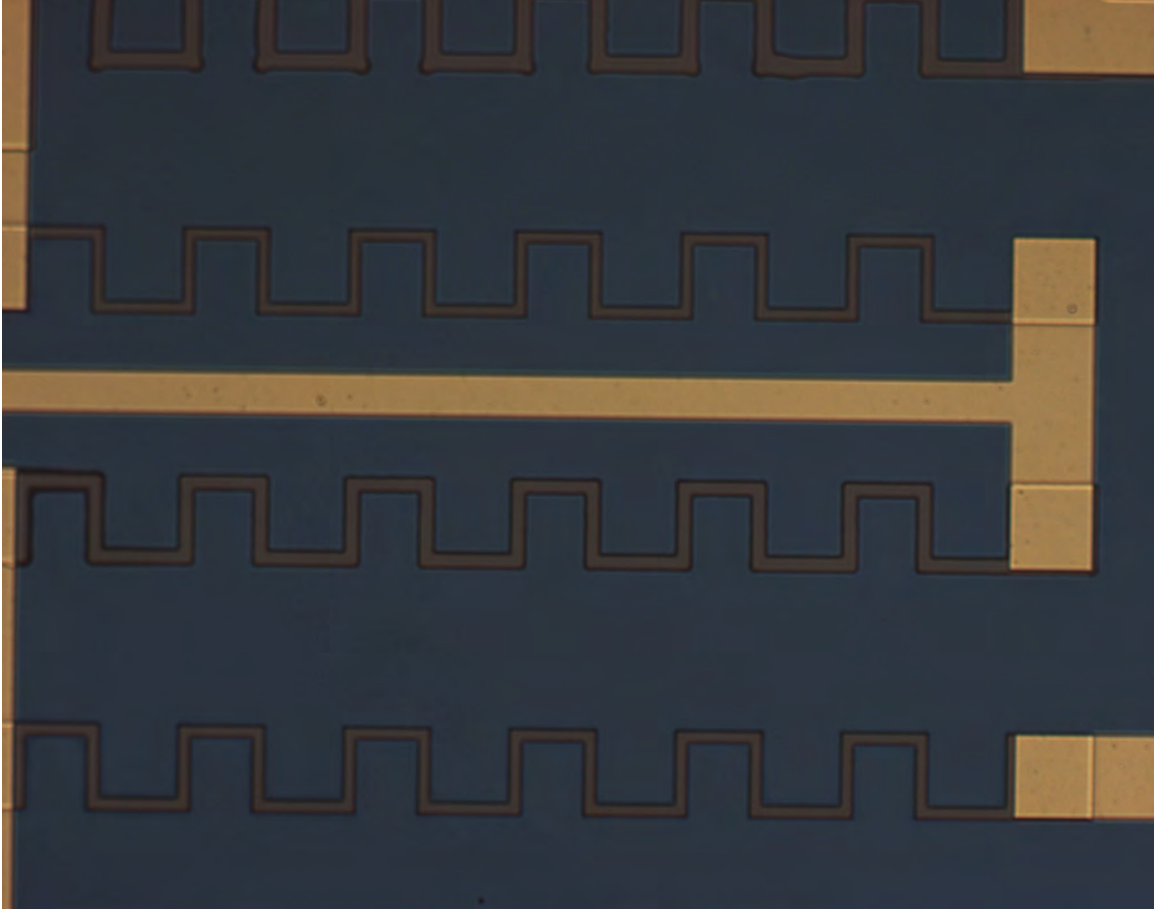


Figure 68. An image of the piezoresistive setup. The blue color is a result of the subwavelength oxide layer on top of the membrane. In most samples, but not this one, the protective oxide is removed as is not necessary. Electrical insulation is provided by the pn junction between the piezoresistors and the substrate, and by the high resistivity of the substrate. The thick gold colored bars are gold electrical traces. The zigzag patterned shapes are the doped piezoresistors. Their different coloring comes from the fact that the blue oxide is etched away above them to allow the boron to diffuse through. The zigzag shape accounts for the piezoresistor going into, the back out of the membrane. Since only the vertical component is strained by the membrane moving, this zigzag shape allows the expansion of vertical trace length. Three of these are reference and will not be on an etched membrane, and only one will be located on an etched membrane.

Once solidified, the gold could be found in clumps as large as 6 micrometer tall, even though the contact is deposited 200 nanometer thick. This is shown in Fig. 69 . This presents an interesting way to form gold nanodots, as surface tension will pull together the gold into a large a clump as possible on the micro-scale. In addition, the slope from the DRIE process is analyzed using the zygo interferometer. The slope using the DRIE etch is almost -10 degrees, resulting in structures nearly 100 micrometers wider than the mask intended on a 500 micrometer deep etch. In addition, certain DRIE etch holes are incomplete on features of 300 micrometers in diameter and smaller, while completely etched to the thermal oxide etch stop on the larger holes. This is indicative of a slower etch rate with the steeper aspect ratio of the smaller holes. While unintended, this large slope from DRIE can be fully compensated for by shrinking the initial etch pattern. Furthermore, the potential to make a structure with negative slope deep inside the silicon has potential for fabricating novel micro-structures.

4.2.5 PZT Deposition

PZT is sputtered and compared to the original target for composition with the EDS tool. The results confirm that the stoichiometry of the target and of the thin film are not the same, and that the sputtering process successfully altered the stoichiometry of the thin film. EDS output is shown in Figs. 70 and 71. The process also confirms a sputter rate in the AFIT sputtering system of near 40 nanometers per hour at 2.5 watts per square centimeter power density. The resulting film shows cracking on the silicon substrate, but a good film quality on the platinum electrode. This is shown in Fig. 72. The complete device as made in the AFIT lab is shown in Fig. 73. This means that platinum is a suitable electrode choice for PZT deposition, and that the cracks on the silicon substrate will extend up to the platinum. The electrode area must exceed the area where PZT is desired to be functional.

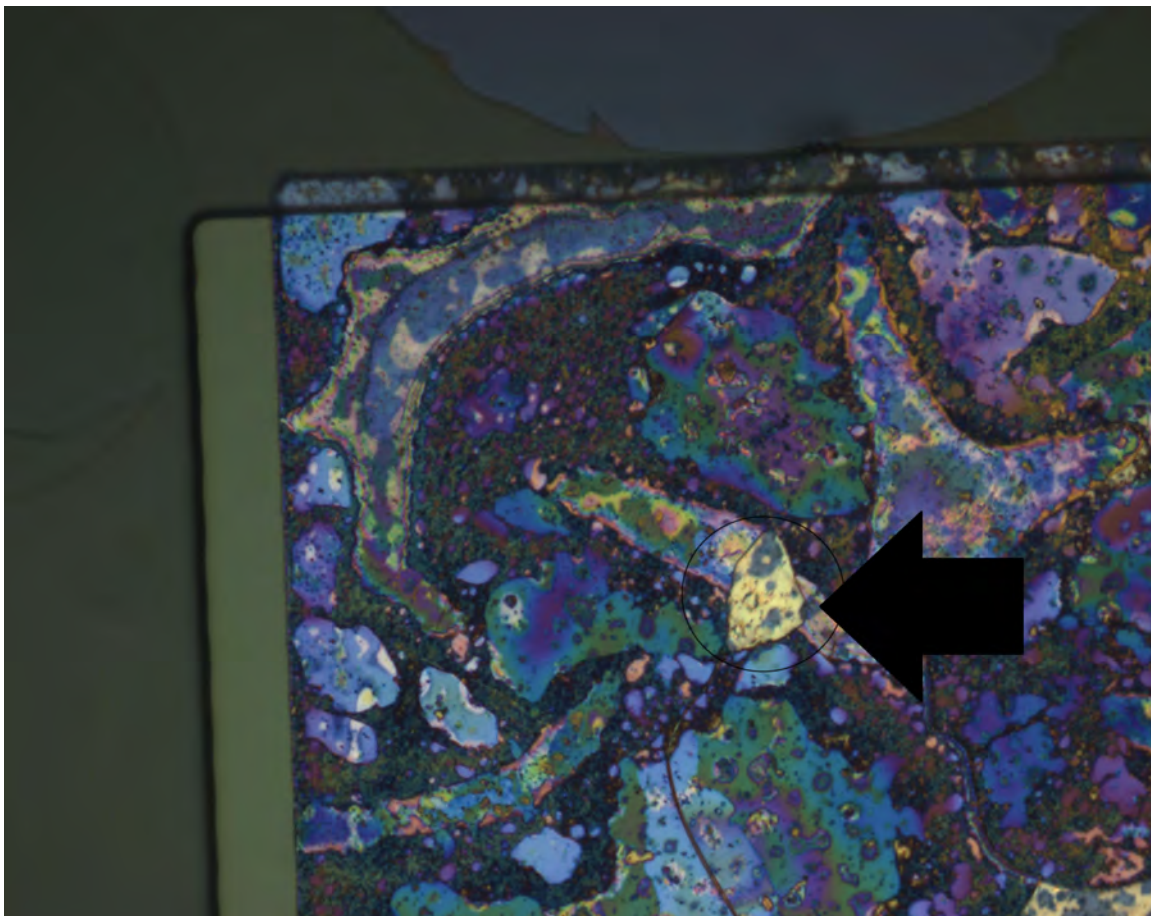


Figure 69. This is an optical microscope picture of a gold contact pad after annealing. The multicolored square is an effect of the silicon becoming liquid as it mixes with the gold and randomly moving. The dark area on the top and left is photoresist. The gold clumps, indicated by the black arrow, are so tall the microscope cannot keep the structure in focus at with the rest of the surface, and are examined by profileometry.

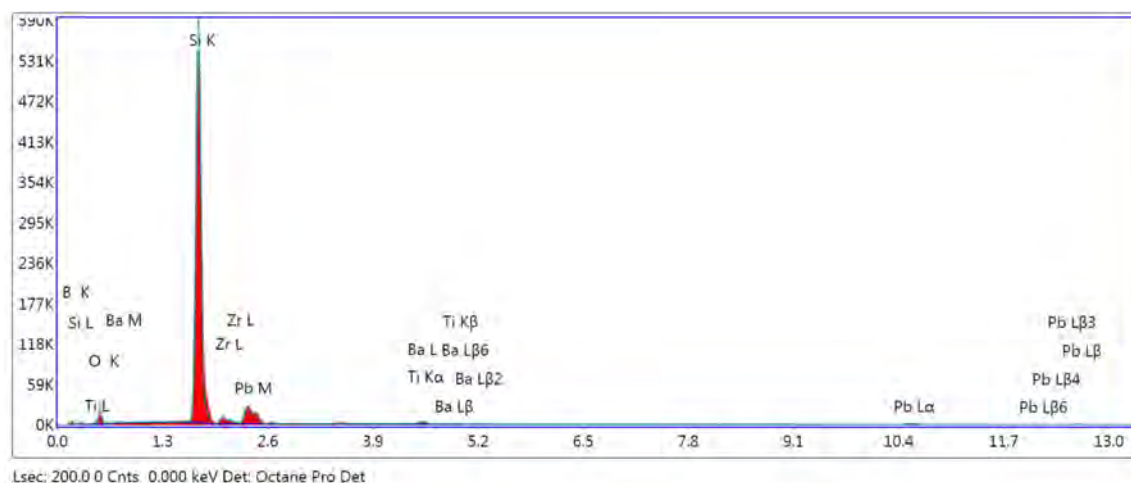


Figure 70. The lead, zirconium and titanium are almost not visible due to the thinness of the layer. The elemental ratios are different than that of the source. While the lack of calibration means that these numbers cannot be taken in absolute terms, there comparison to the source is still meaningful, and shows that the sputtering is preferentially titanium.

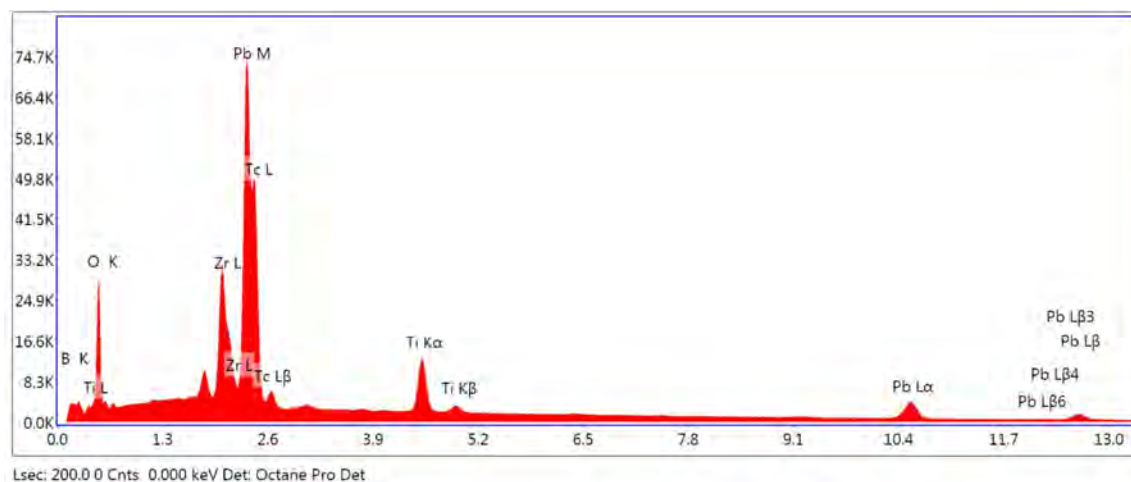


Figure 71. An EDS of the PZT sputtering source. The analysis shows the source to be lead deficient, even though as purchased the source should be stoichiometric. The EDS numbers below are subject to some error, especially the oxygen values. It is possible that the EDS is uncalibrated, which has caused these errors.

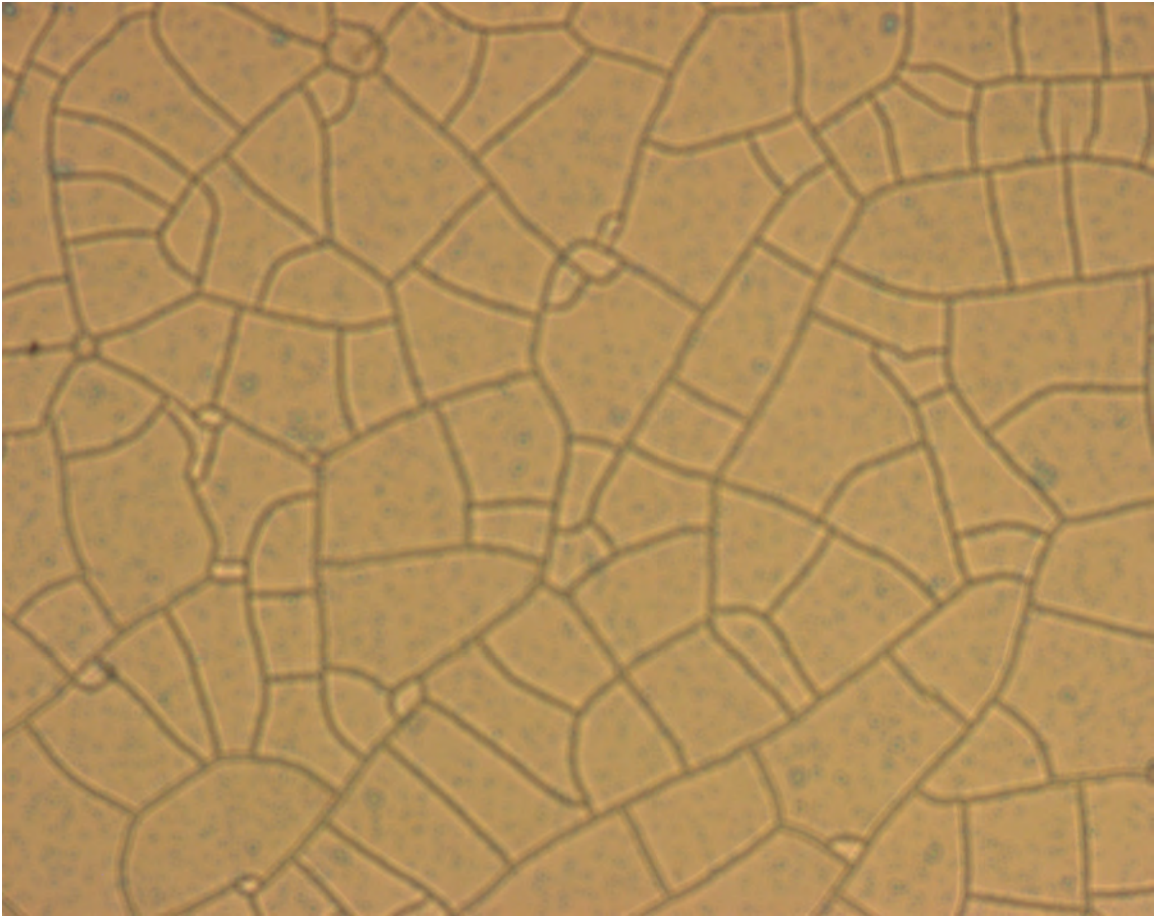


Figure 72. The effect of depositing PZT on a silicon substrate is shown. The cracks would cause electrical shorting were a electrode deposited on top. The gold color is from the PZT. Below is a substrate of silicon. This area is adjacent to a platinum pad, but the cracks extend up to the platinum electrode, making shorting there likely as well, and the device not useable.

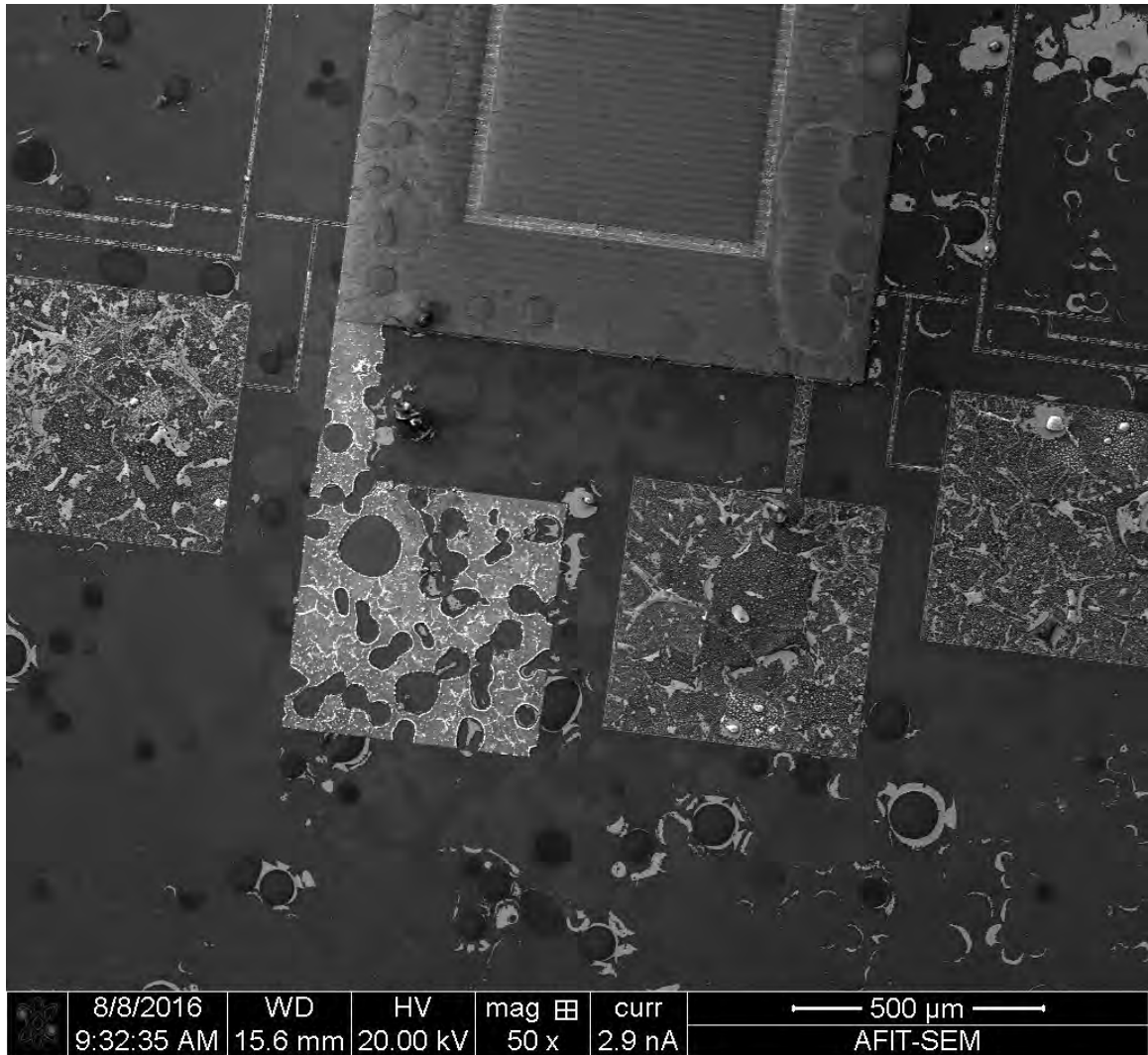


Figure 73. An SEM image of a device designed to harvest thermal energy. The four small squares are probe pads for electrical contact, and the large square at top center is the energy harvesting area.

4.2.6 X-ray Results and Surface Imaging Results

Evaporation results in the lab show adhesion difficulties to PZT with evaporated films. To investigate this result, XPS is used to probe the qualities of the PZT surface. XPS results in Fig. 74 show that PZT accumulates a carbon monoxide surface layer. This carbon monoxide layer is shown in literature to be due to the dangling lead bonds at the film edge. Application of nitric acid and immediate placement of the substrate into the evaporation device can this effect. XRD results in Figs. 75 and 76 show the orientation preference of PZT and the underlying platinum electrodes. The platinum is oriented in both the $\langle 100 \rangle$ and $\langle 110 \rangle$ modes. This confirms that the sputtering process at AFIT is not at sufficiently high temperature to orient the platinum. The PZT is mainly in the $\langle 110 \rangle$ orientation after annealing but amorphous before annealing. This shows that a high annealing temperature is required to achieve any PZT orientation, while cold-sputtered platinum will crystallize. The platinum still shows multiple phases even after annealing. This is unexpected, as platinum should orient at over 400°C. The already deposited PZT film could have prevented the very thin platinum layer from orienting. This shows it may be preferable to hot sputter the platinum, or anneal before PZT is deposited.

4.2.7 Device Testing

The final device is fabricated using the method described in section 3.3.1. The SEM and zygo images of the backside of the completed device are shown in Fig. 77 and 78. The pattern on the front side of the device is shown in Fig. 79. The completed device is placed on the zygo interferometer to measure steady state deflections. Deflections ranged from 1.4 to 3.2 microns. A image of a completed membrane on the interferometer is shown in Fig. 80. Probes were placed on the electrodes and voltage is applied to determine if this device could act as an actuator. This setup is shown in

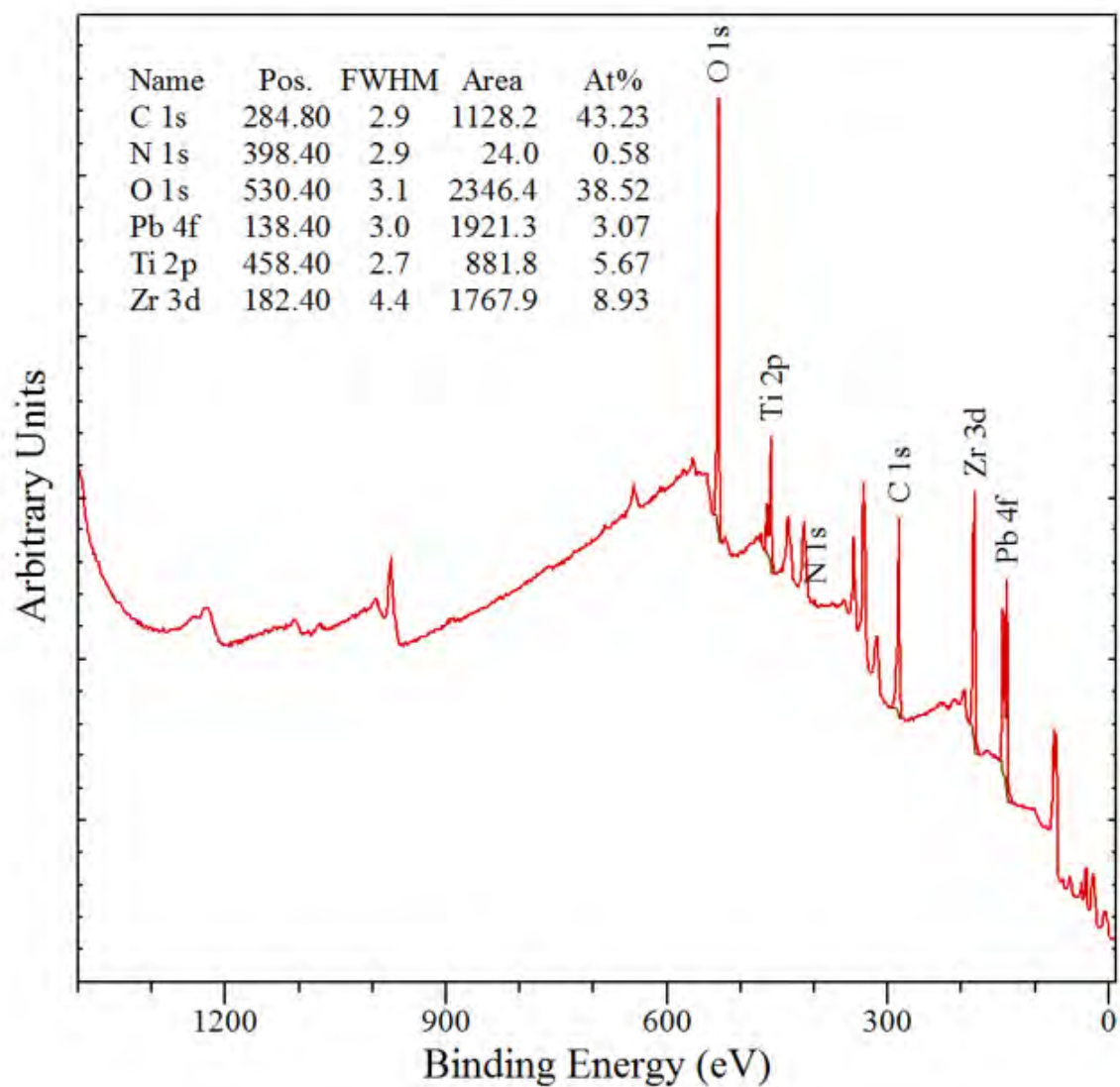


Figure 74. The XPS shows the surface condition of the PZT thin film. The primary feature of not is carbon on the surface of the film, which is caused by carbon dioxide adsorbing as carbon monoxide to the dangling surface bonds. These could be removed with nitric acid.

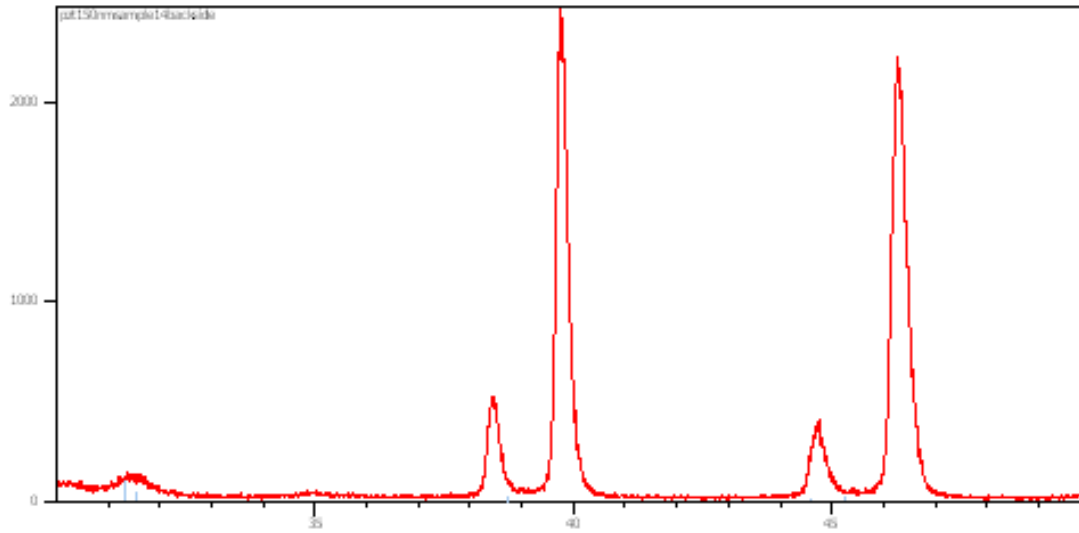


Figure 75. The XRD shows the crystal orientation of the PZT. The large platinum peaks are still visible to the right of the PZT peaks. This indicates that despite the annealing, the platinum is still in multiple orientations, and the procedure of annealing platinum after PZT deposition is unsuccessful.

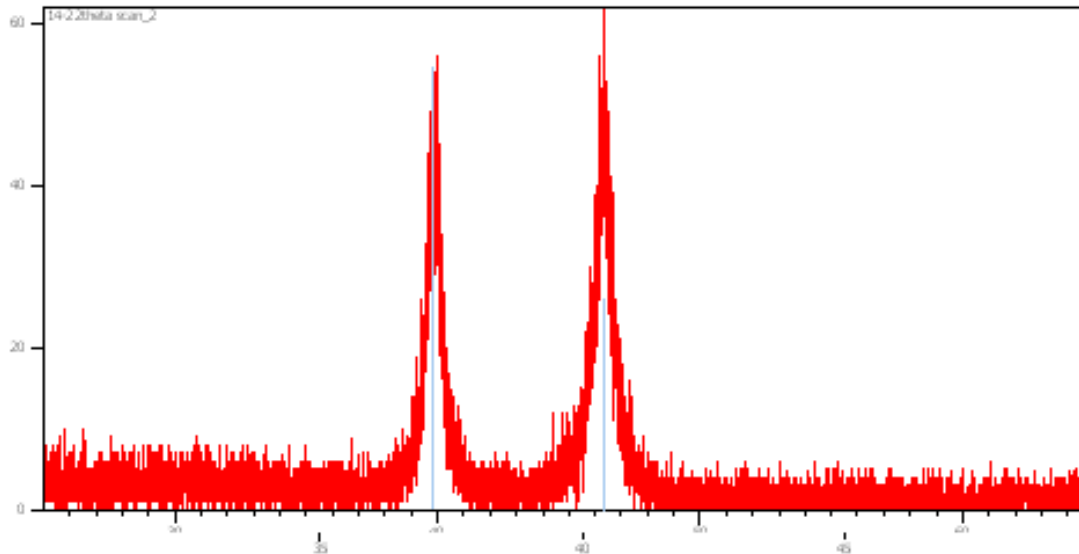


Figure 76. The XRD shows the crystal orientation of the platinum, in both the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. This indicates that the platinum is crystalline, but in multiple orientations. This is not suitable for thin film PZT.

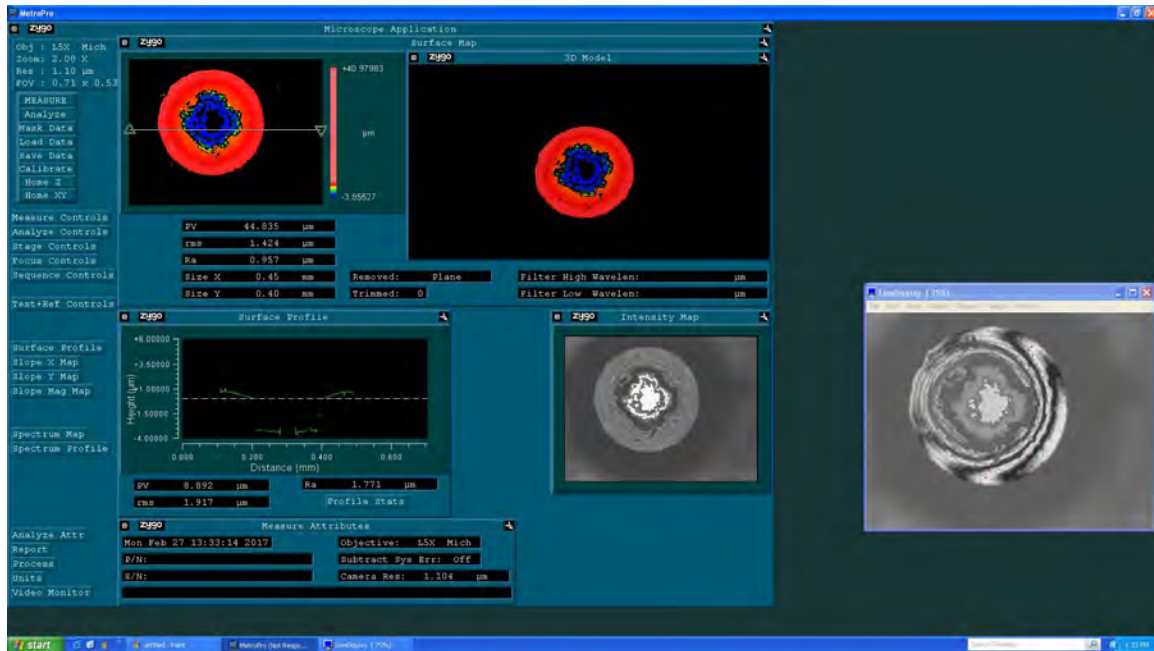


Figure 77. This image shows the image the back side of a completed energy harvesting device taken with a Zygo interferometer.

Fig. 81. The probes can be seen attached to the device in Fig. 82. The membrane showed decreasing deflection when .1 volts is applied, and then showed no change in deflection as the voltage is increased further. This shows that the device is effective at responding to voltage, but has a limiting voltage of beneath .1 volts. After this test is complete, the completed device is subjected to a range of pressures up to 10 psi. The device showed monotonically increasing deflections as pressure is increased. This data is shown in Fig. 83. Then, to test the ability to harvest energy from vibrations, the device is placed on a test bench with 10 psi of pressure applied and removed at frequencies up to 20 hertz. This setup is shown in Fig. 84. Probes attached to the electrodes gathered the resulting energy. This data is shown in Fig. 85. The device showed the most energy gathered near 5 hertz, with a resulting voltage of -60 dbV. The background noise with the pressure not applied is near -100 dbV, placing this far above the noise floor.

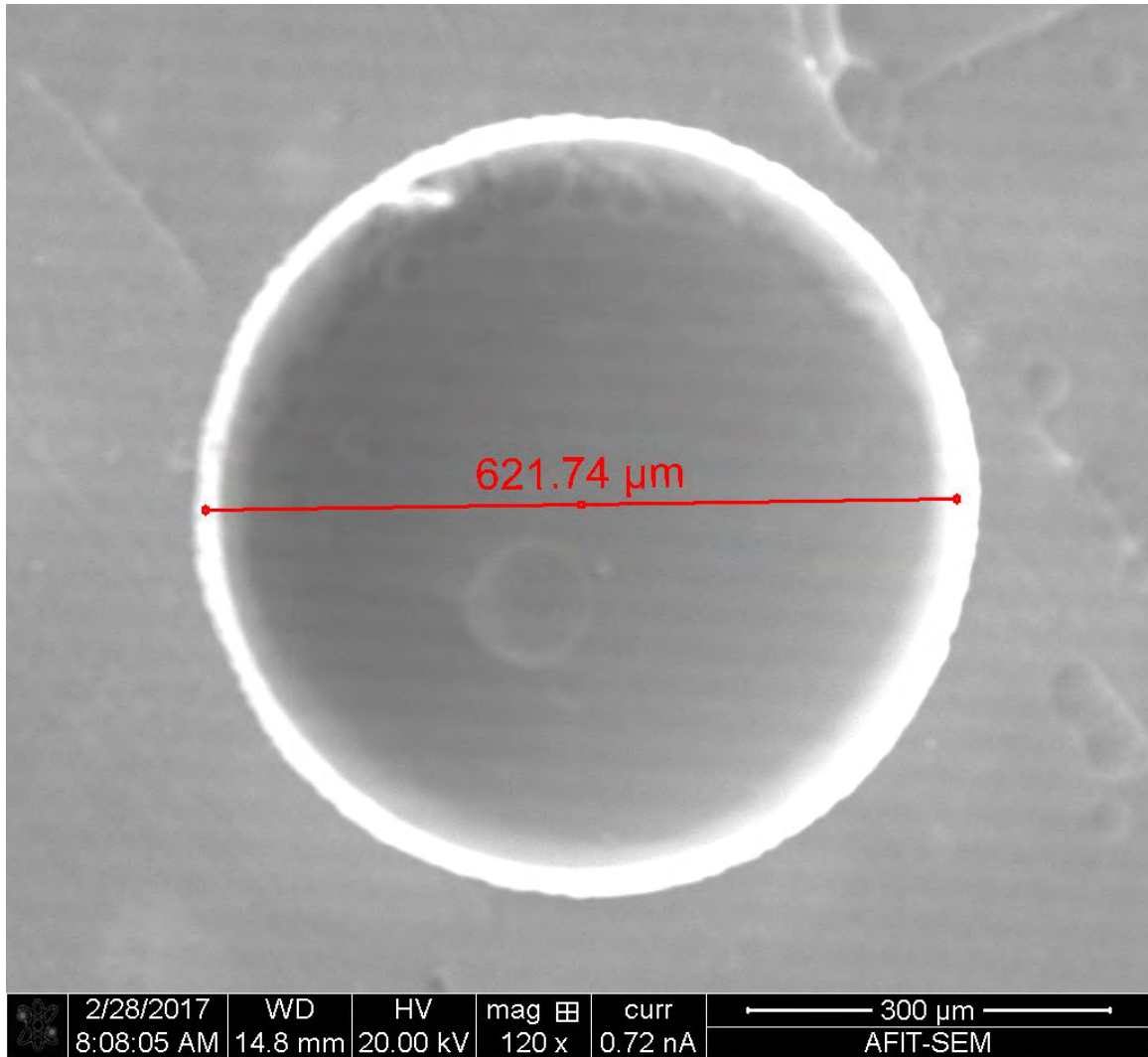


Figure 78. This is an SEM image of the backside a completed device do harvest energy. The cavity is the depth of the handle layer. This hole is formed many times on the sample for identical devices.

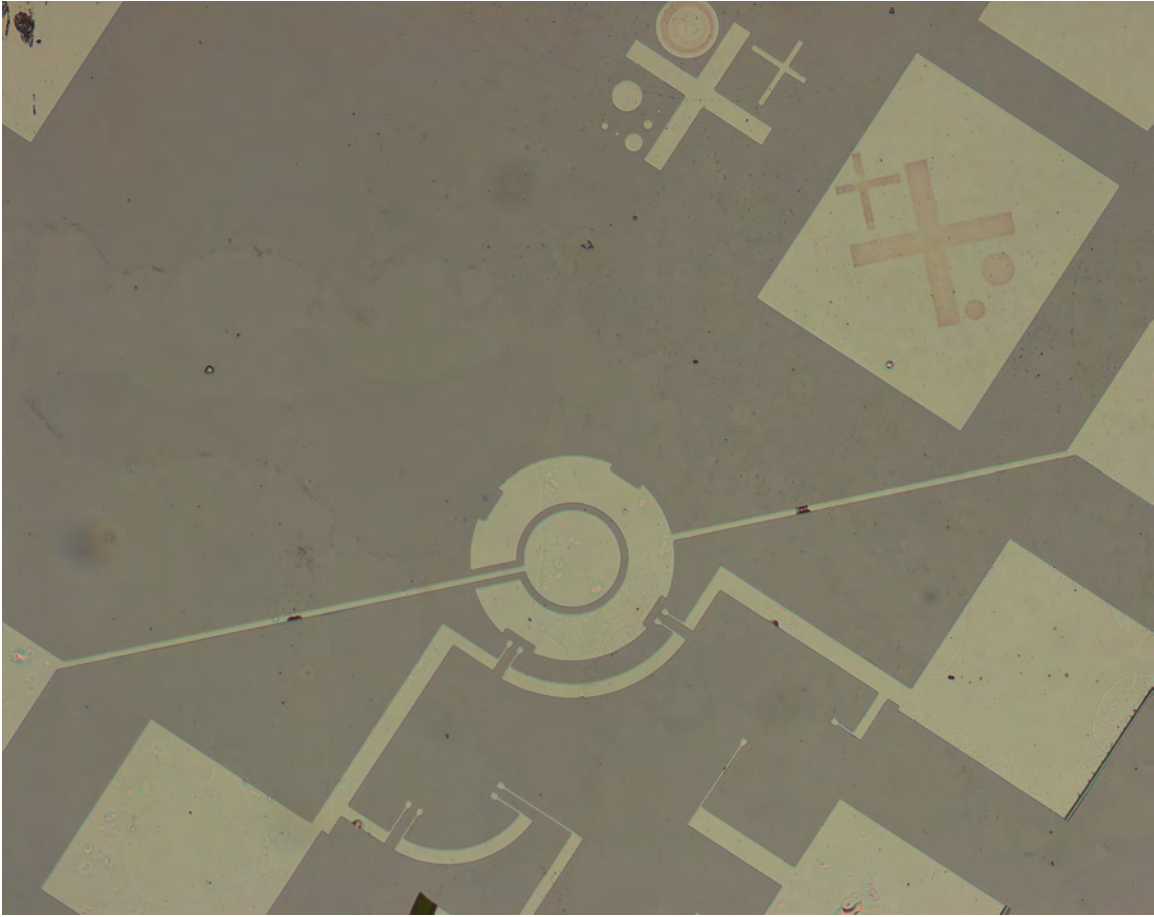


Figure 79. The energy harvesting device, shown here with an AlN piezoelectric layer, is also realized on PZT with an identical electrode configuration. This device experienced shorting between the top and bottom electrodes through the material due to material defect, which rendered the device not useful, and precluded further fabrication.

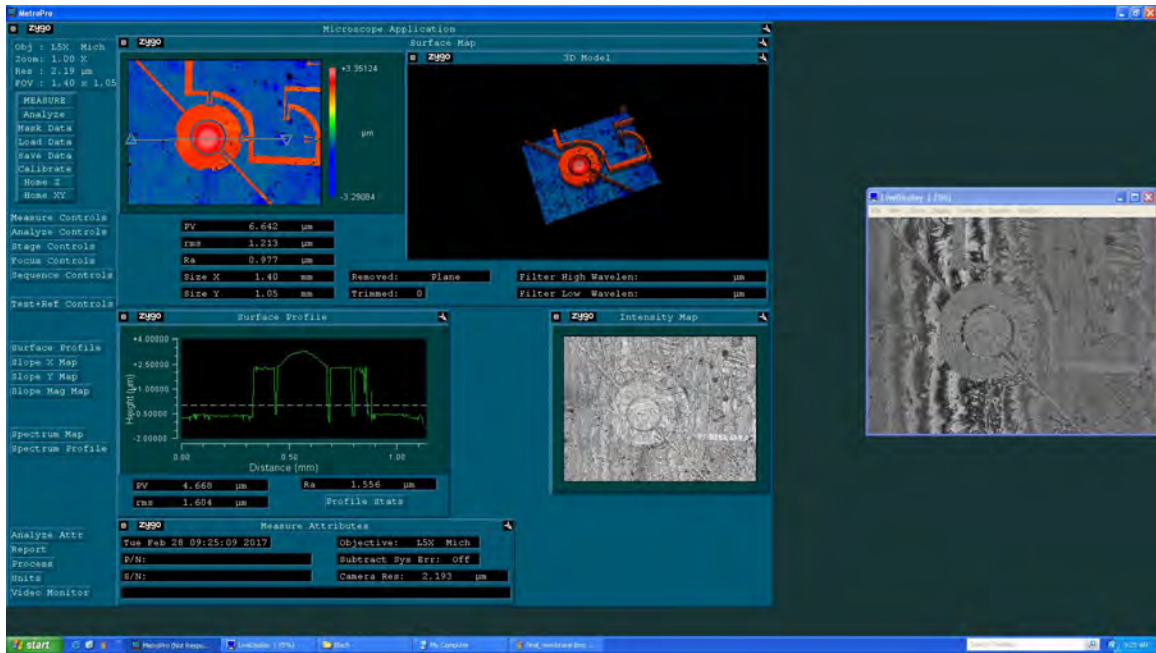


Figure 80. This zygo image shows a completed energy harvesting device. The bump in the center is the deflection due to the membrane formation. The jumps in height are due to the selective etching of the electrodes.

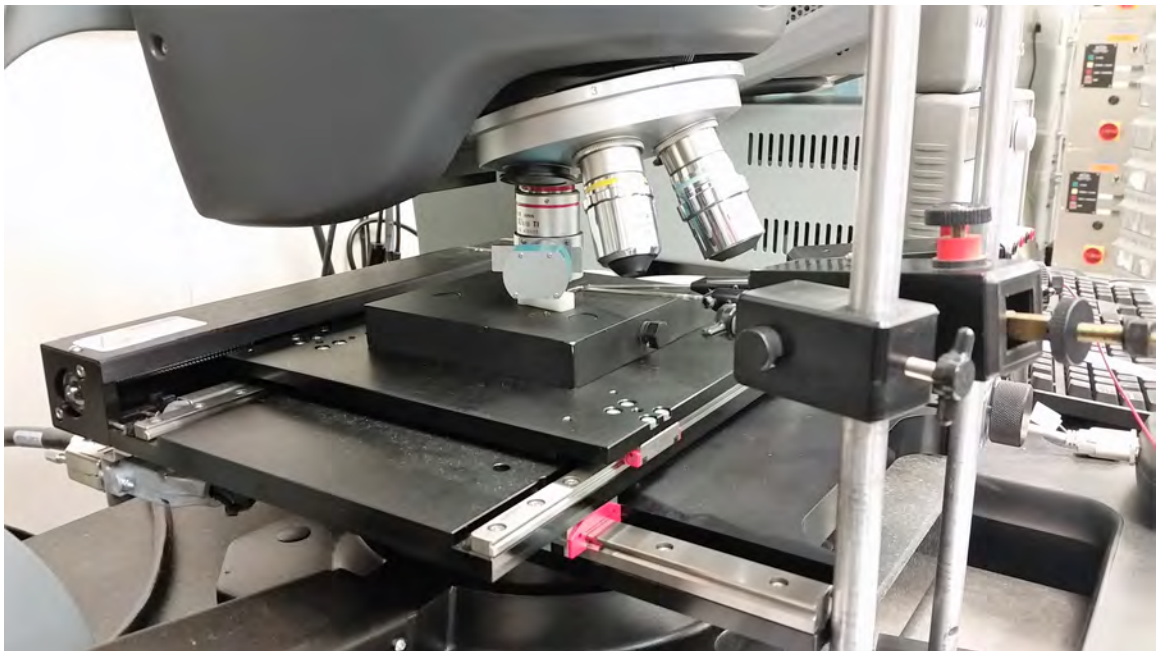


Figure 81. The device is fixed to the test bench, and pressure could be applied to the back of the device. Portable probe stations are connected to the electrical contacts on the sample to apply voltage.

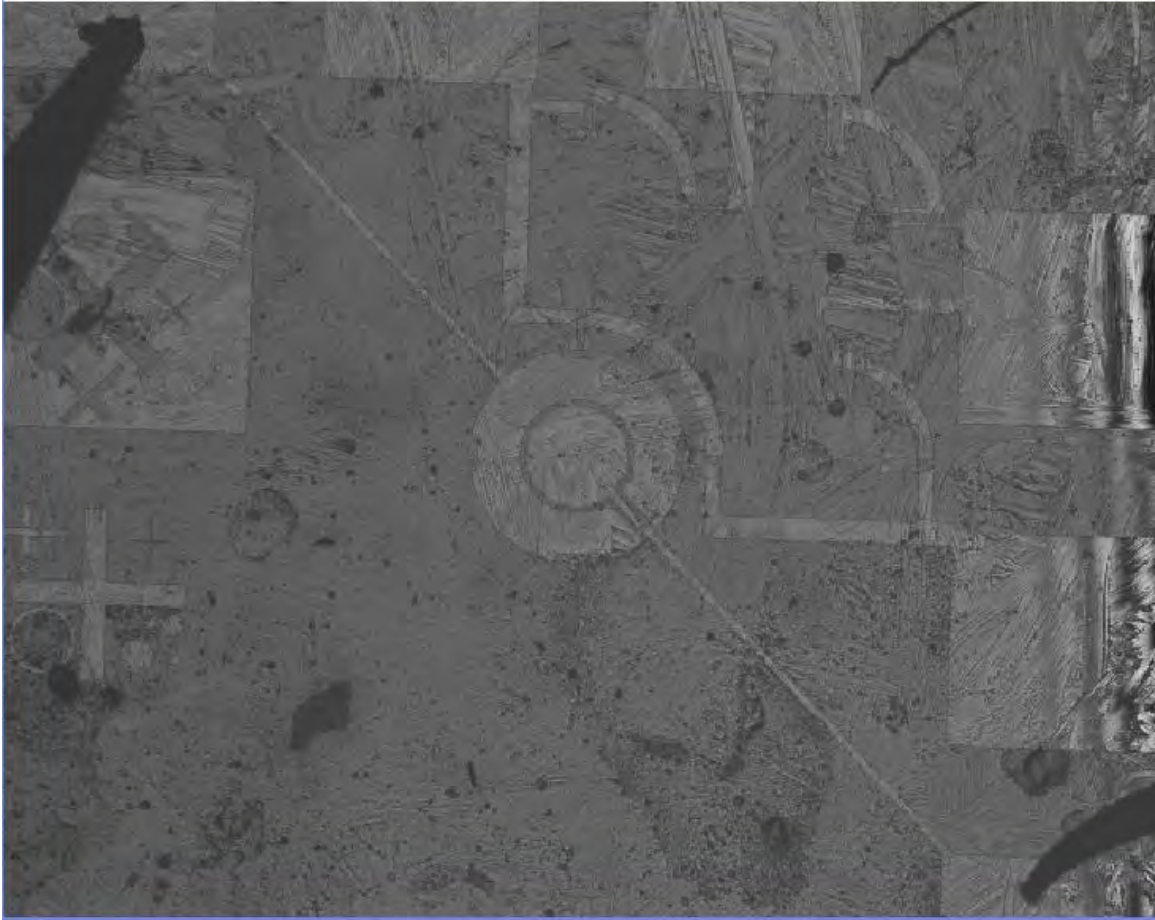


Figure 82. This image from the Zygo microscope shows the moveable probes placed in contact with the electrodes of the device. As voltage is applied to the electrodes, movement can be measured with the Zygo interferometer.

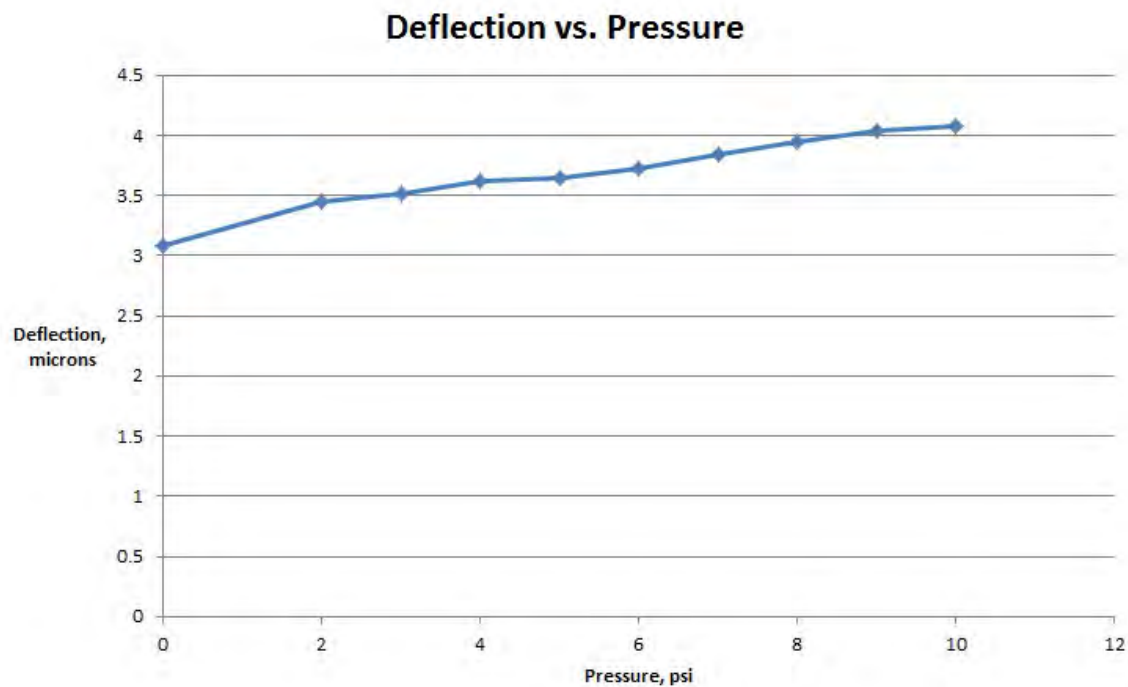


Figure 83. The device is subjected to varying pressures on the back side and measured for the resulting deflection. The device showed an increase in deflection for increasing pressure.

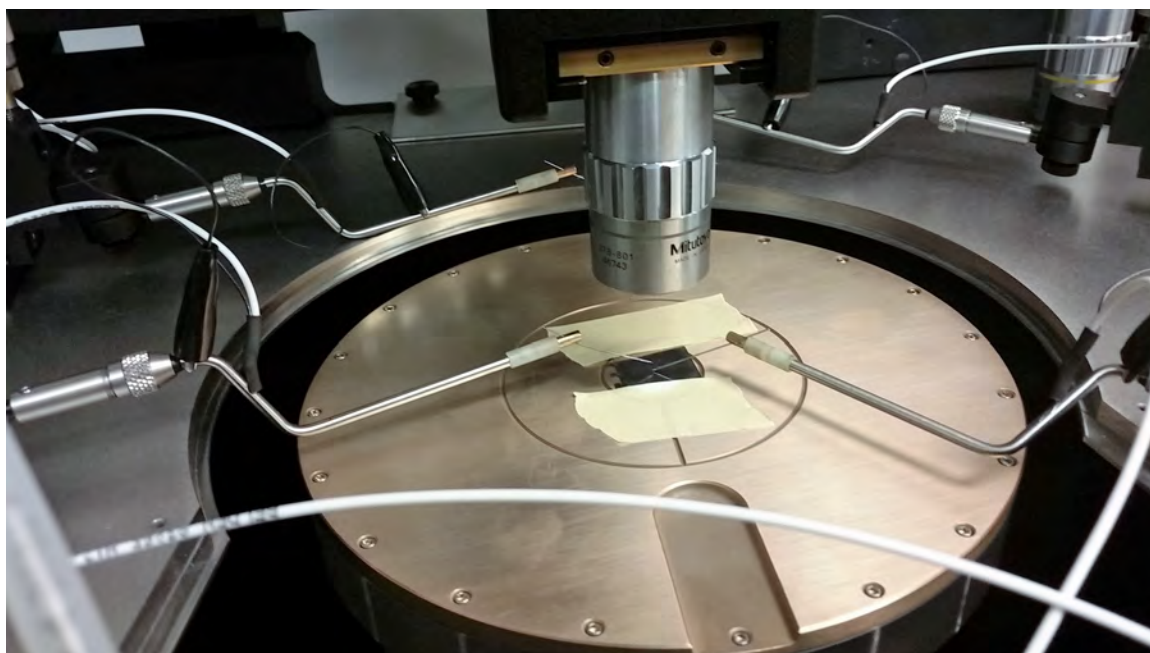


Figure 84. The device is secured to the micromanipulator station. Probe tips make electrical contact to the device. Pressure is applied to the backside at frequencies of up to 20 hertz.

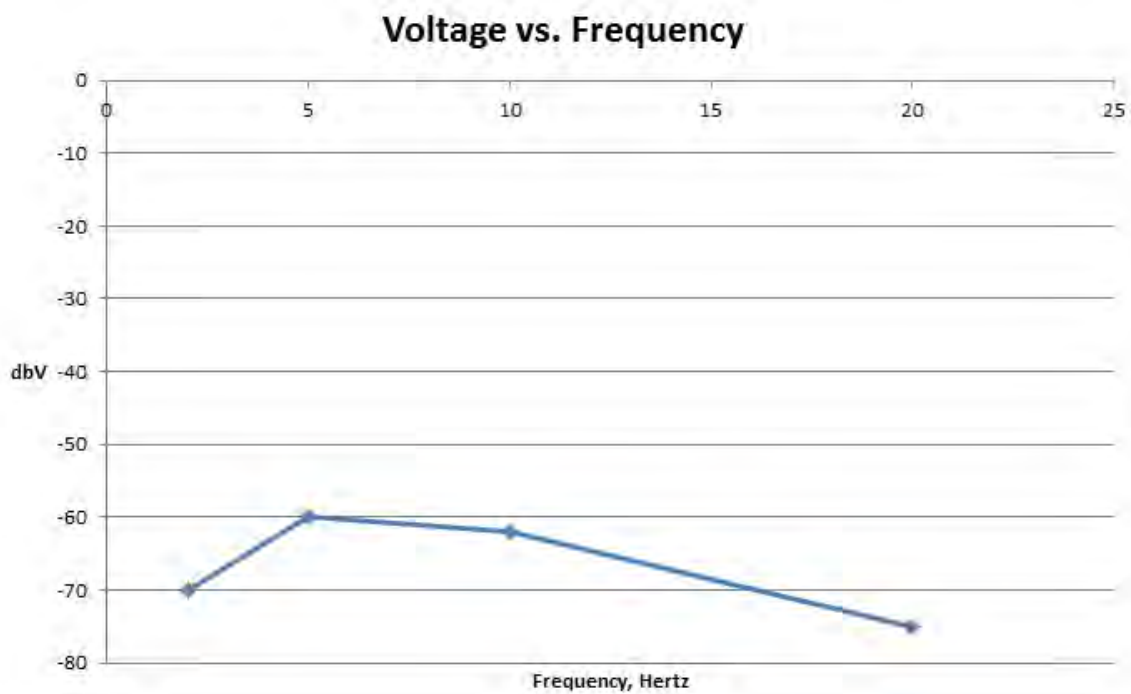


Figure 85. The device is subjected to 10 psi of pressure, at varying frequencies up to 20 hertz to determine the optimal frequency for harvesting energy of the device. The device showed the greatest voltage response at 5 hertz, which is the optimal frequency in this range to harvest energy.

V. Conclusions

After attempting various methods of fabricating a thermal energy harvesting device, several conclusions can be made. Firstly, regarding material selection, PZT and AlN materials are analyzed for their potential for energy harvesting materials in a MEMS SOI membrane structure. The materials are analyzed with ellipsometry, raman spectrometry, XRD, XPS, and SEM to determine material quality. Experiments are performed to determine the etching and processing characteristics of these materials. The spectroscopy results show good match to the predicted properties of these materials, which confirms that they could continue to be used. This shows that it is feasible to dry etch PZT, but not AlN. While it is possible to wet etch AlN, it would also etch the underlying titanium nitride electrode. If AlN are to be used with this project, there would have to be a modification to platinum electrodes, which are compatible with AlN, or a change to a shadowmasking process for deposition. Without etching, it is not possible to access the bottom electrode and perform full characterization of the material. A successful etching process for platinum is performed on the PZT electrodes. PZT fabricated in lab shows numerous material interactions impacting fabrication, such as adhesion and cracking. While PZT fabrication in lab does allow more customization, it is more feasible to receive PZT samples from other sources. This does not allow the possibility of processing between depositions of the electrodes and the PZT, not allowing certain designs. The investigation of the mechanical membranes yields that SOI wafers with two micrometers of silicon can be used as the basis for fabricating SOI membranes with DRIE. The shapes of these membranes is limited due to the rounding effect of DRIE, and the smallest size possible for these membranes is established at near 500 micrometers across. It is determined that a two micrometer thick thermal oxide layer produces more deflection than a one micrometer oxide layer, allowing more membrane movement and hence

more charge generated in an energy harvesting device. The possibility of making the membranes fully bistable with less aluminum than similar projects proves that higher temperatures cannot compensate for thinner aluminum stress layers. The piezo-resistive experiments confirm that aluminum is a suitable choice of contact for making p++ contacts to boron doped silicon, and the effective surface resistance of these contacts. It also shows an unexpected etching result, of an aluminum doped silicon layer that is resistant to KOH etching. This could be useful in creating novel stop layers, as this shows a combination of two materials both subject to KOH etching that is immune to this etching. The overall resistivity of the silicon piezoresistors is established, and it is shown that even the native oxide layer which grows on silicon piezoresistors in contact with air will impede electrical contact. The use of gold as an electrical contact to silicon is attempted, forming a pn junction. Gold is then annealed on silicon, forming into thick microglobules. A interferometric detection system for use in this project is operated and determined suitable for characterizing these materials. Lastly, testing on the completed devices shows the deflection of the fabricated devices, the ability to harvest energy at different frequencies, the ability to act as an actuator, and the pressure response of the devices. This project suggests some future directions for this energy harvesting project. First, more investigation is needed into expanding the deflection of the membranes, and investigating the mechanical effects of additional layers on the silicon membranes. While the switch to simultaneous deposition of PZT and the electrodes adds convenience, no built in heating resistor can be included. Thus, a localized heating source of a small chopped laser needs to be found to properly analyze these devices. Additional studies should be directed at the effects of SU-8 as a thermal insulating and bonding layer. It is the most easily available material to provide thick separation and thermal insulation for potential use in a MEMS structure.

Appendix A. Process Followers

Wafer	Purpose	Mask	Process	Print Date
Any Wafer	General Instructions		Bilayer Liftoff	July 23, 2015, 12:52 PM
Init.	Process Step	Notes	Date	Time
	INSPECT WAFER: o Note any defects o Verify Correct material	<u>Start Date</u> <u>Start Time</u>		
	SOLVENT CLEAN: Using Spinner o 30 sec acetone rinse at 500 rpm o 30 sec methanol rinse at 500 rpm o 30 sec DI water rinse at 500 rpm o Dry with nitrogen at 500 rpm o Dry wafer with nitrogen on clean texwipes o 2 min 110°C hot plate bake			
	SF11 Photoresist COAT wafer piece: o Flood wafer with SF11 photoresist o 30 sec spin at 4,000 rpm, ramp=500 o 120 sec 200°C hot plate bake			
	Clean UV MASK – Under solvent hood o 30 sec acetone rinse o 30 sec methanol rinse o 30 sec isopropyl alcohol rinse o Dry with nitrogen			
	1805 Photoresist COAT wafer piece: o Flood wafer with 1805 photoresist o 30 sec spin at 4,000 rpm, ramp=500 o 75 sec 110°C hot plate bake			
	Expose 1805 with UV MASK o Sample Exposure o Position mask in Mask Aligner o Expose wafer for 4 sec using contact mask aligner			
	1805 DEVELOP: o 45 sec develop with 351:DI (1.5) at 500 rpm o 30 sec DI rinse at 500 rpm o Dry with nitrogen at 500 rpm o Dry wafer with nitrogen on clean texwipes o 2 min 110°C hot plate bake			
	Inspect Lithography on microscope o Are features clean and open, with sharp definition (developed completely)?			
	Expose SF11 o Sample Flood Exposure o Expose wafer for 200 sec , using CP setting (Constant Power) o Verify machine readouts are close to the following: 800 Watts 19 MW/cm² 30 Volts 35 Amps			
	SF11 DEVELOP o 60 sec bucket develop 101 developer o 30 sec DI rinse by hand o Dry wafer with nitrogen on clean texwipes o 2 min 110°C hot plate bake			
	Inspect Lithography on microscope o Are features clean and open, with sharp definition (developed completely)?	<u>Finish Date</u> <u>Finish Time</u>		

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Figure A-1. Process follower for liftoff procedure.

Wafer	Purpose	Mask	Process	Print Date
Si	PyroElectric Membrane		Bottom Electrode	

Init.	Process Step	Notes	Date Time
	INSPECT/Clean Sample: o Note any defects	<u>Start Date</u> <u>Start Time</u>	
	Bottom Electrode Deposit #1 o Sputter deposit Titanium 10 nm thick o Gas 100% Argon o Substrate Temperature 400 C o Power _____ Less than 2.5 W/cm ² o Time _____ o Pressure _____ o Optical microscope inspection o SEM inspection for surface profile and for surface composition		
	Bottom Electric Electrode Deposit #2 o Sputter deposit Platinum 100 nm thick o Substrate Temperature 400 C o Gas 100% Argon o Power _____ Less than 2.5 W/cm ² o Time _____ o Pressure _____ o Optical microscope inspection		
	Bottom Electrode Deposit #3 o Sputter deposit Titanium 5 nm thick o Gas 80% Argon 20% oxygen o Substrate Temperature 400 C o Time _____ o Total pressure .4 Pa _____ o 2.5 W/cm ² o Optical microscope inspection o SEM inspection for surface profile and for surface composition		
	Perform "Lift off" o Place tape on sample o Remove tape o Repeat until Platinum layer largely removed o wash in acetone o place in ultrasonic bath for 5 minutes		
	Clean SOI sample: DO NOT USE METHANOL o Place Sample on spinner device side up @ 500 rpm 90s o Rinse Sample in acetone 20 s o Rinse Sample in DIW 20 s o Rinse Sample in IPA 20 s o Dry on hot plate 120 s @ 110C o Let cool		

Process Step #1

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Figure A-2. P
 rocess follower to fabricate lower electrode

Wafer	Purpose	Mask	Process	Print Date
SOI	PyroElectric Membrane		PiezoResistive Layer	
Init.	Process Step	Notes	Date Time	
	Inspect/Clean SOI Wafer: - o Note any defects - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let mask cool	<u>Start Date</u> <u>Start Time</u>		
	Thermally Grow Oxide - o Place in plasma asher device, 75 W for 5 minutes - o Shut down plasma asher - o Turn off oxygen flow - o Thermally grow 2000 angstroms of silicon oxide			
	Clean SOI Wafer: - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let cool			
	Deposit Resist for oxide patterning - o Clean mask with nitrogen - o Rinse mask in acetone 20 s - o Rinse mask in methanol 20 s - o Rinse mask in DIW 20 s - o Rinse mask in IPA 20 s - o Spin on S1818 onto Sample, 4000 rpm, ramp up 500rpm, 30 s - o Bake Sample on hotplate for 75s at 110C - o Insert mask into mask aligner - o Place sample below mask on mask aligner - o Perform alignment - o Expose on mask aligner for 8 sec - o Develop Sample with 351:DI (1:5) at 500 rpm for 30 sec - o Clean Sample with DI at 500 rpm for 30 sec - o Dry Sample with Nitrogen at 500 rpm - o Dry Sample on Texwipes with nitrogen - o Shut down MJB3 with correct procedure (30 minute cooldown)			

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Figure A-3. Process follower to fabricate piezoresistive layer.

Wafer	Purpose	Mask	Process	Print Date
Si	Expose Electrode			
Init.	Process Step	Notes	Date Time	
	Prepare Sample: o Note any defects o Place on spinner device side up @ 500 rpm 90s o Rinse Sample in acetone 20 s o Rinse Sample in methanol 20 s o Rinse Sample in DIW 20 s o Rinse Sample in IPA 20 s o Dry on hot plate 120 s @ 110C o Let sample cool o Spin on S1818, 4000 rpm, ramp up 500 rpm, 30 s o Bake sample on hotplate for 75s at 110C	<u>Start Date</u> <u>Start Time</u>		
	Prepare Mask: o Clean Mask with nitrogen o Rinse Mask in acetone 20 s o Rinse Mask in methanol 20 s o Rinse Mask in DIW 20 s o Rinse Mask in IPA 20 s			
	Expose Sample: o Load mask into mask aligner o Align mask to alignment marks on wafer o Expose sample on mask aligner for 8 sec o Develop sample with 351:DI (1:5) at 500 rpm for 30 sec o Clean sample with DI at 500 rpm for 30 sec o Dry sample with Nitrogen at 500 rpm o Dry sample on Texwipes with nitrogen o Place sample on hot plate for 120 s at 110C o Shut down MJB3 with correct procedure (30 minute cooldown)			
	Etch Sample: USE ONLY PLASTIC TWEEZERS o Don PPE (Gloves, mask, apron) o Place enough Gold etchant in plastic container to immerse a wafer sample o Place sample in Gold etchant for 4 minutes o Rinse Sample DIW for 30 seconds o Dry sample with nitrogen o Transfer Gold etchant to used Gold etchant container			

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Figure A-4. Process follower for fabricating heating layer.

Wafer	Purpose	Mask	Process	Print Date
SOI	PyroElectric Membrane		Insulating Layer	
Init.	Process Step	Notes	Date Time	
	Inspect/Clean SOI Wafer: - o Note any defects - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let mask cool	<u>Start Date</u> <u>Start Time</u>		
	Grow Oxide o PECVD 400 nm Silicon Oxide			
	Clean SOI sample: - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let cool			
	Clean mask - o Clean mask with nitrogen - o Rinse mask in acetone 20 s - o Rinse mask in methanol 20 s - o Rinse mask in DIW 20 s - o Rinse mask in IPA 20 s			
	Deposit resist and pattern - o Spin on S1818 onto Sample, 4000 rpm, ramp up 500rpm, 30 s - o Bake Sample on hotplate for 75s at 110C - o Insert mask into mask aligner - o Place sample below mask on mask aligner - o Perform alignment - o Expose on mask aligner for 8 sec - o Develop Sample with 351:DI (1:5) at 500 rpm for 30 sec - o Clean Sample with DI at 500 rpm for 30 sec - o Dry Sample with Nitrogen at 500 rpm - o Dry Sample on Texwipes with nitrogen - o Shut down MJB3 with correct procedure (30 minute cooldown)			

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Figure A-5. Process follower to etch insulating silicon nitride layer.

Wafer Purpose Mask Process Print Date

Si **PyroElectric Membrane** **Multiple Etchs**

Init.	Process Step	Notes	Date Time
	INSPECT Sample: - o Note any defects - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let sample cool	<u>Start Date</u> <u>Start Time</u>	
	PZT Deposit - o Sputter deposit PZT 1000 nm thick - o Target Pb_{1.1} (Zr_{0.53}Ti_{0.47})O₃ with 10% excess Pb - o Gas 80% Argon 20% O₂ - o Sputtering Pressure 4.1 Pa - o Power 2.25 W/cm² - o Time - o Substrate Temperature 400 C - o Optical microscope inspection - o SEM inspection for surface profile and for surface composition		
	PZT Anneal - o Anneal 650 C 60 min, heating 10C/min, 1C/min cool down - o Optical microscope inspection - o SEM inspection for surface profile and for surface composition		
	Clean SOI sample: - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let cool		
	Prepare Mask: - o Clean Mask with nitrogen - o Rinse Mask in acetone 20 s - o Rinse Mask in methanol 20 s - o Rinse Mask in DIW 20 s - o Rinse Mask in IPA 20 s		

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Figure A-6. Process follower to deposit and anneal PZT.

Wafer Purpose Mask Process Print Date

Si PyroElectric Membrane Top Electrode

Init.	Process Step	Notes	Date Time
	Prepare Sample: - o Note any defects - o Place on spinner device side up @ 500 rpm 90s - o Rinse Sample in acetone 20 s - o Rinse Sample in methanol 20 s - o Rinse Sample in DIW 20 s - o Rinse Sample in IPA 20 s - o Dry on hot plate 120 s @ 110C - o Let sample cool - o Spin on S1818, 4000 rpm, ramp up 500 rpm, 30 s - o Bake sample on hotplate for 75s at 110C	<u>Start Date</u> <u>Start Time</u>	
	Prepare Mask: - o Clean Mask with nitrogen - o Rinse Mask in acetone 20 s - o Rinse Mask in methanol 20 s - o Rinse Mask in DIW 20 s - o Rinse Mask in IPA 20 s		
	Expose Sample: - o Load mask into mask aligner - o Align mask to alignment marks on wafer - o Expose sample on mask aligner for 8 sec - o Develop sample with 351:DI (1:5) at 500 rpm for 30 sec - o Clean sample with DI at 500 rpm for 30 sec - o Dry sample with Nitrogen at 500 rpm - o Dry sample on Texwipes with nitrogen - o Place sample on hot plate for 120 s at 110C - o Shut down MJB3 with correct procedure (30 minute cooldown)		
	Top Electrode Deposit - o Evaporate 50nm titanium - o Evaporation deposit Gold 200 nm thick		
	Perform "Lift off" - o Place tape on sample - o Remove tape - o Repeat until gold layer largely removed - o wash in acetone - o place in ultrasonic bath for 5 minutes		

Process Step #1

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Figure A-7. Process follower to etch top electrode.

Appendix B. Lab Equipment



Figure B-1. DRIE tool used in device fabrication

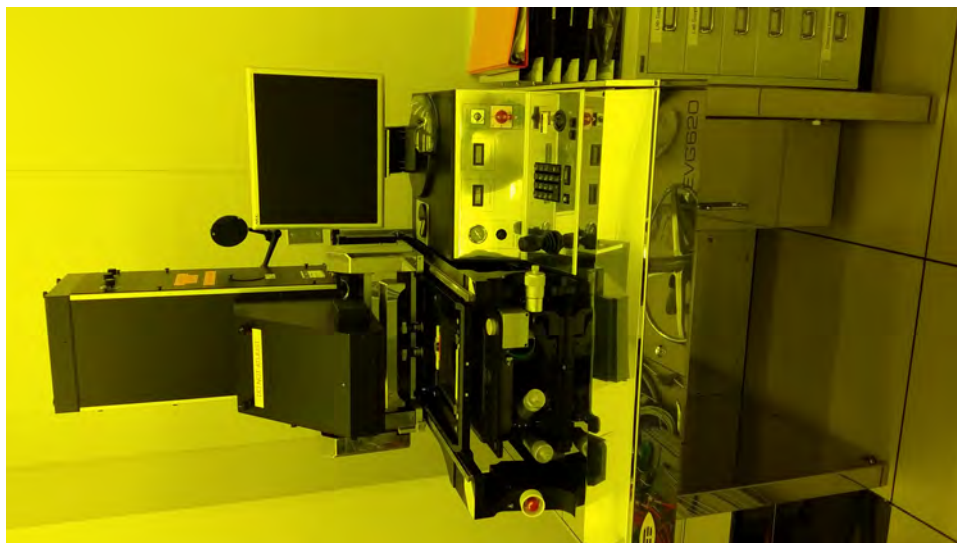


Figure B-2. EVG photolithography tool used in device fabrication



Figure B-3. PECVD tool used in device fabrication



Figure B-4. Profilometer tool used in device analysis



Figure B-5. TRION RIE tool used in device fabrication



Figure B-6

Appendix C. L-Edit Masks

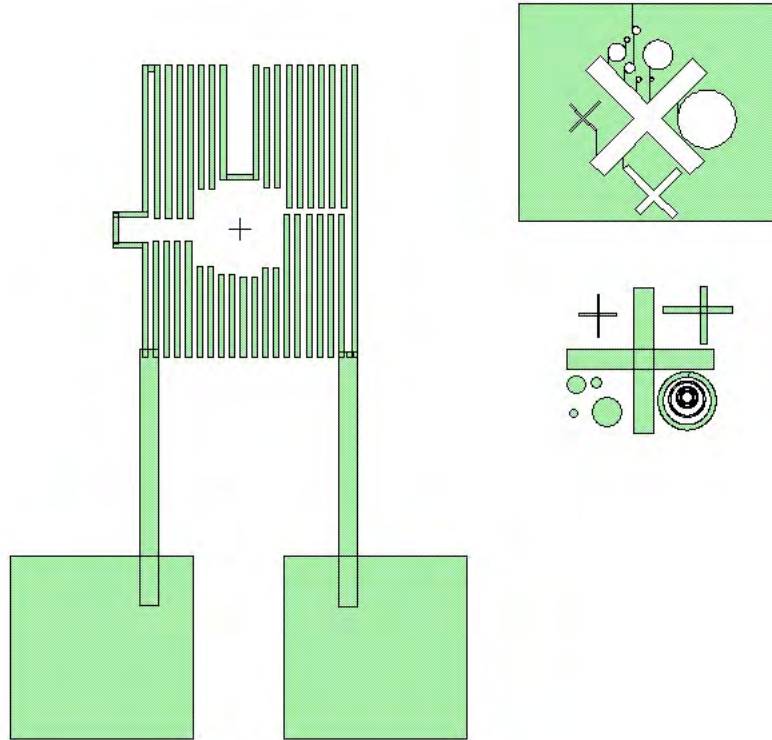


Figure C-1. Heating layer mask pattern of energy harvesting device

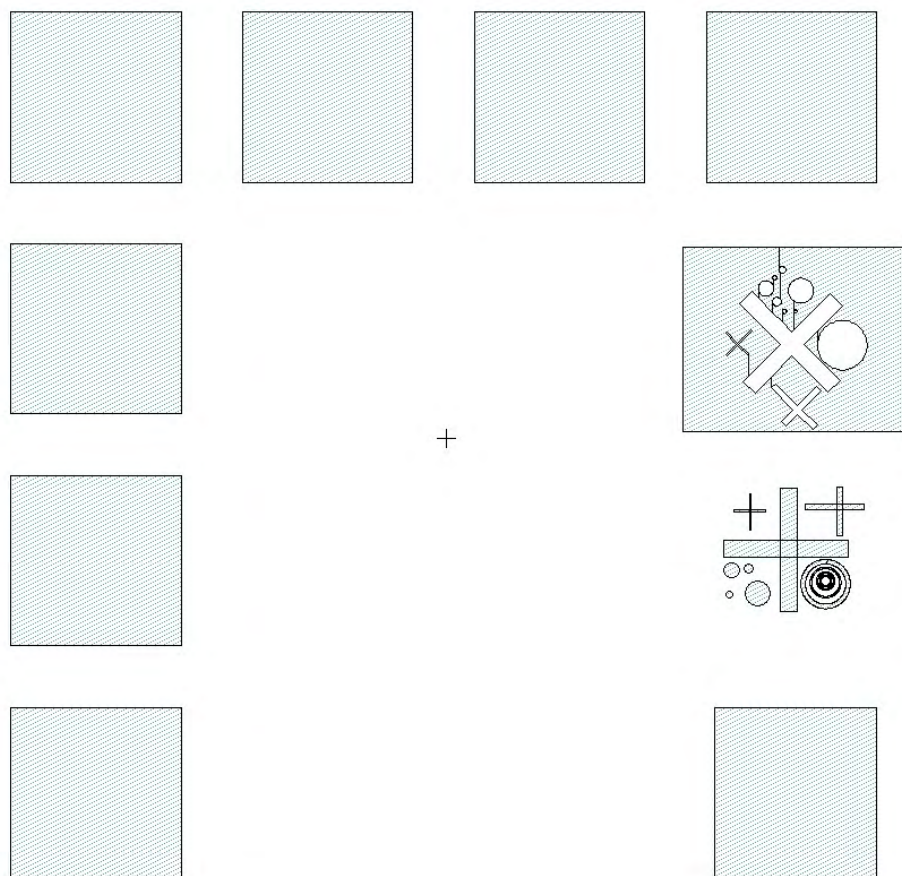


Figure C-2. Insulation layer mask pattern of energy harvesting device

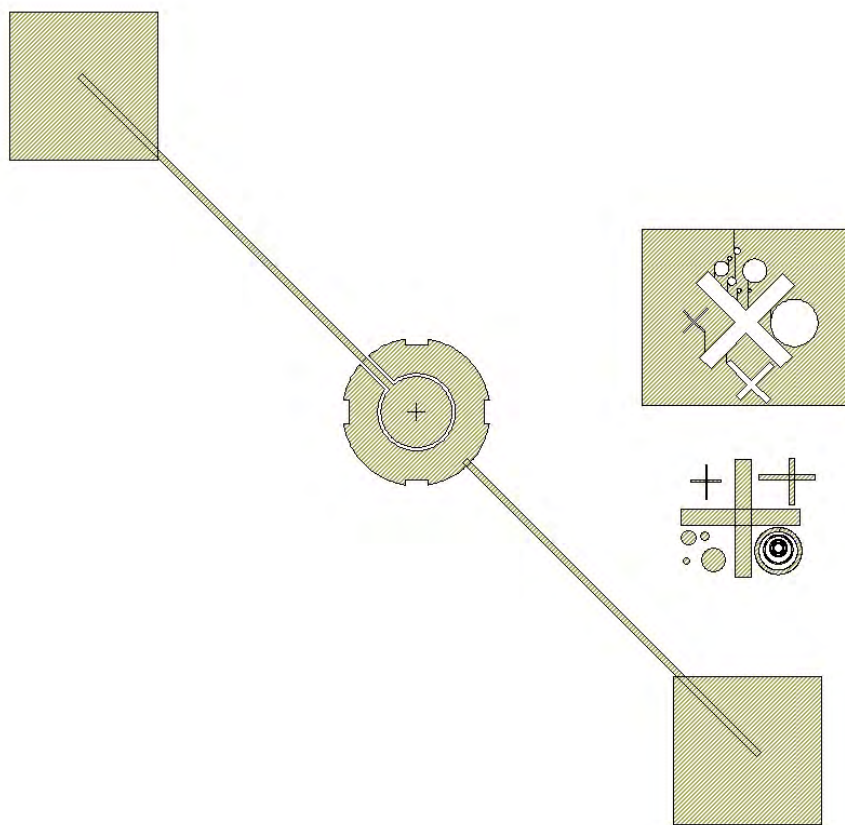


Figure C-3. Lower electrode layer mask pattern of energy harvesting device

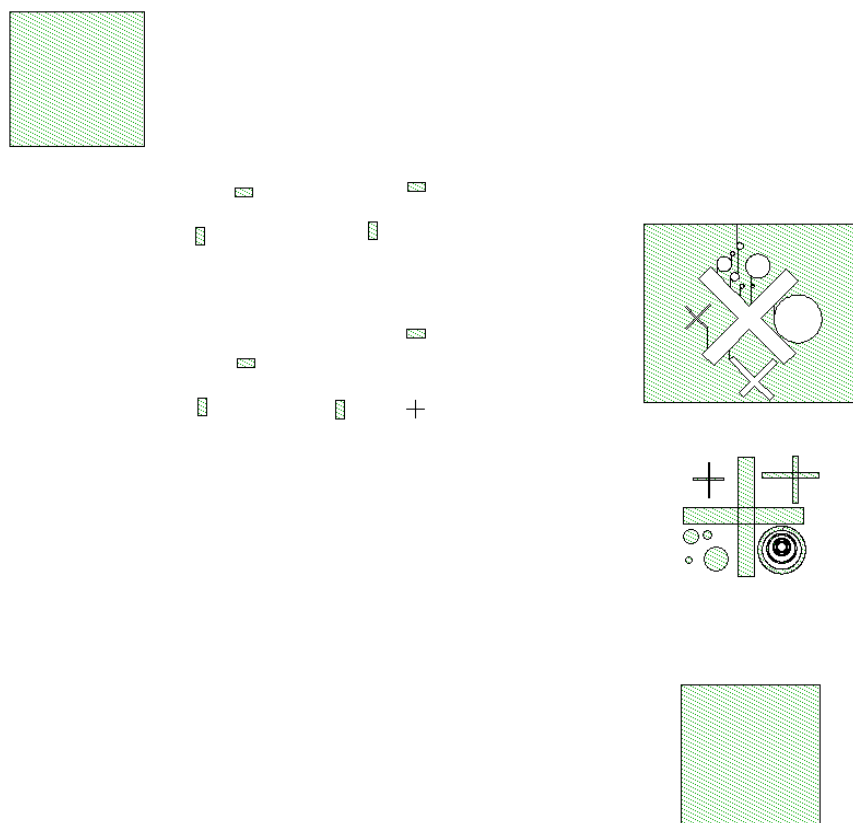


Figure C-4. PZT etch mask pattern of energy harvesting device

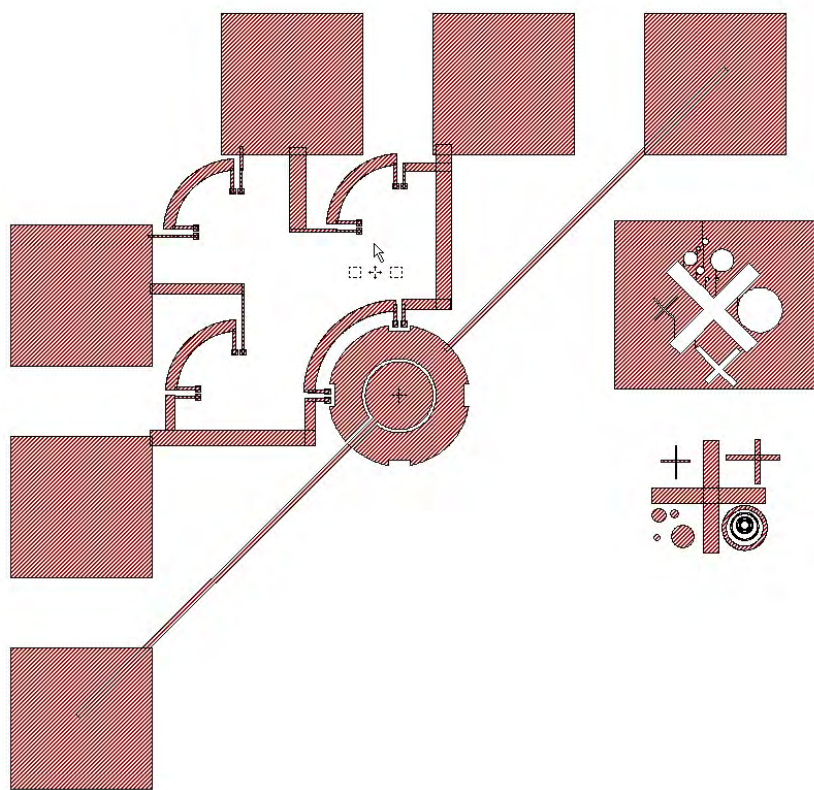


Figure C-5

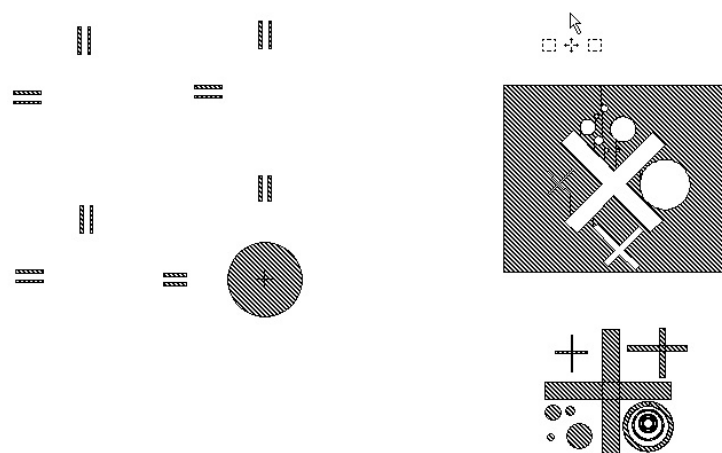


Figure C-6. Upper electrode layer mask pattern of energy harvesting device

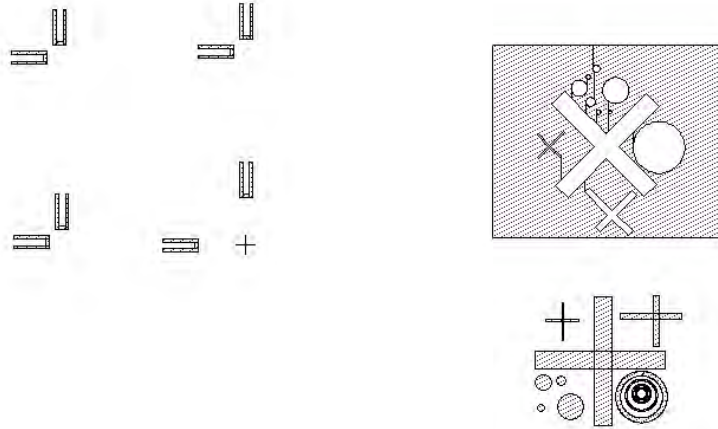


Figure C-7. Aluminum layer mask pattern of energy harvesting device

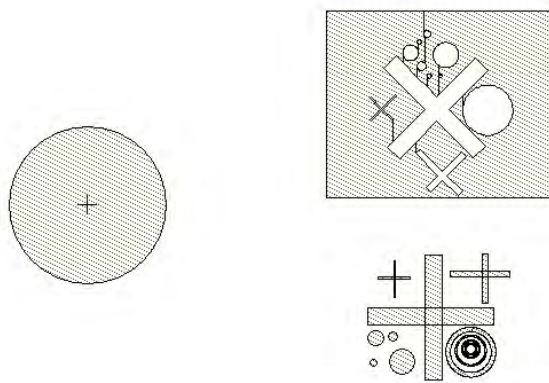


Figure C-8. Piezoresistive layer mask pattern of energy harvesting device

Appendix D. Python Code

```
# For this script named Steady_State_analysis.py
# import to the Console using: import Steady_State_analysis and run with: Steady_St
from memcad.project import MemcadProject
from memcad.gui.utils import *
from com.coventor.JDBSI import *
from java.io import File

# A function that creates an analysis.
def Steady_State_analysis_MemMech(analysisName,modelName,restart,scalechoice,scalefac
    myAnalysis = Analysis(analysisName,modelName,"MemMech")
    # Get the solver settings for this solver.
    myMemMechSettings = myAnalysis.getSolverSettings()
    # Solver Settings and Boundary Conditions

    # Command for solver settings m_advanced.
    myMemMechSettings.setSolverSetting("linearBricks","none")
    # Command for solver settings m_analysis.
    myMemMechSettings.setSolverSetting("Analysis","PiezoElectric")
    if ( restart == 1 ) : myMemMechSettings.setSolverSetting("StartFrom","Restart")
    # Commands for table SurfaceBCs from m_theBCs

    mySurfaceBCsConditions = myMemMechSettings.getConditions("SurfaceBCs",9)
    mySurfaceBCsCondition7 = mySurfaceBCsConditions.getCondition(7)
    if method == 1 : mySurfaceBCsCondition7.setCondition("FixType","Potential")
    if method == 1 : mySurfaceBCsCondition7.setCondition("Patch1","pztOutTop")
    if method == 1 : mySurfaceBCsCondition7.setCondition("LoadValue","Scalar " + str(me
    if method == 1 : mySurfaceBCsCondition6 = mySurfaceBCsConditions.getCondition(6)
    if method == 1 : mySurfaceBCsCondition6.setCondition("Patch1","pztInTop")
    if method == 1 : mySurfaceBCsCondition6.setCondition("LoadValue","Scalar -" + str(m
    if method == 1 : mySurfaceBCsCondition6.setCondition("FixType","Potential")
    if method == 2 : mySurfaceBCsCondition5 = mySurfaceBCsConditions.getCondition(5)
    if method == 2 : mySurfaceBCsCondition5.setCondition("Patch1","pztInTop")
    if method == 2 : mySurfaceBCsCondition5.setCondition("LoadValue","Scalar " + str(me
    if method == 2 : mySurfaceBCsCondition5.setCondition("FixType","Temperature")
    if method == 2 : mySurfaceBCsCondition2 = mySurfaceBCsConditions.getCondition(2)
    if method == 2 : mySurfaceBCsCondition2.setCondition("FixType","LoadPatch")
    if method == 2 : mySurfaceBCsCondition2.setCondition("Patch1","oxideBottom")
    if method == 2 : mySurfaceBCsCondition2.setCondition("LoadValue","Scalar .01" + " "
    mySurfaceBCsCondition4 = mySurfaceBCsConditions.getCondition(4)
    mySurfaceBCsCondition4.setCondition("FixType","Temperature")
    mySurfaceBCsCondition4.setCondition("Patch1","edge")
    mySurfaceBCsCondition4.setCondition("LoadValue","Scalar 300 ")
```

```

mySurfaceBCsCondition3 = mySurfaceBCsConditions.getCondition(3)
mySurfaceBCsCondition3.setCondition("FixType","Potential")
mySurfaceBCsCondition3.setCondition("Patch1","siliconInTop")
mySurfaceBCsCondition3.setCondition("Patch2","siliconOutTop")
if method == 3 : mySurfaceBCsCondition2 = mySurfaceBCsConditions.getCondition(2)
if method == 3 : mySurfaceBCsCondition2.setCondition("FixType","LoadPatch")
if method == 3 : mySurfaceBCsCondition2.setCondition("Patch1","oxideBottom")
if method == 3 : mySurfaceBCsCondition2.setCondition("LoadValue","Scalar " + str(me
mySurfaceBCsCondition1 = mySurfaceBCsConditions.getCondition(1)
mySurfaceBCsCondition1.setCondition("Patch1","edge")
mySurfaceBCsCondition1.setCondition("FixType","fixAll")
mySurfaceBCsCondition8 = mySurfaceBCsConditions.getCondition(8)
mySurfaceBCsCondition8.setCondition("Patch1","sym1")
mySurfaceBCsCondition8.setCondition("FixType","SymmetryPlane")
mySurfaceBCsCondition9 = mySurfaceBCsConditions.getCondition(9)
mySurfaceBCsCondition9.setCondition("Patch1","sym2")
mySurfaceBCsCondition9.setCondition("FixType","SymmetryPlane")

# Commands for table VolumeBCs from m_thePartBCs
#myVolumeBCsConditions = myMemMechSettings.getConditions("VolumeBCs",1)
#myVolumeBCsCondition1 = myVolumeBCsConditions.getCondition(1)
#myVolumeBCsCondition1.setCondition("Part","ALL")
#myVolumeBCsCondition1.setCondition("LoadValue","Scalar 300 ")
#myVolumeBCsCondition1.setCondition("BCType","T-Initial")
# Commands for table GeometryTransforms from tt_geometry
if scalechoice == 1:
    myGeometryTransformsConditions = myMemMechSettings.getConditions("GeometryTransfo
    myGeometryTransformsCondition1 = myGeometryTransformsConditions.getCondition(1)
    myGeometryTransformsCondition1.setCondition("Part","ThinSi PZTouter PZT ")
    myGeometryTransformsCondition1.setCondition("Transform","Scale 0.0 0.0 "+str(scal
if scalechoice == 2:
    myGeometryTransformsConditions = myMemMechSettings.getConditions("GeometryTransfo
    myGeometryTransformsCondition1 = myGeometryTransformsConditions.getCondition(1)
    myGeometryTransformsCondition1.setCondition("Part","PZTouter PZT ")
    myGeometryTransformsCondition1.setCondition("Transform","Scale 0.0 0.0 "+str(scal
if scalechoice == 3:
    myGeometryTransformsConditions = myMemMechSettings.getConditions("GeometryTransfo
    myGeometryTransformsCondition1 = myGeometryTransformsConditions.getCondition(1)

```

```

        myGeometryTransformsCondition1.setCondition("Part","oxide ")
        myGeometryTransformsCondition1.setCondition("Transform","Scale 0.0 0.0 "+str(scalefactor))
    if scalechoice == 4:
        myGeometryTransformsConditions = myMemMechSettings.getConditions("GeometryTransformsConditions")
        myGeometryTransformsCondition1 = myGeometryTransformsConditions.getCondition(1)
        myGeometryTransformsCondition1.setCondition("Part","oxide PZTouter PZT ThinSi ")
        myGeometryTransformsCondition1.setCondition("Transform","Scale "+str(scalefactor))

    return myAnalysis

# Main program to run the analysis defined by the function above.
def main2(analysisName,restart,scalechoice,scalefactor,method, methodfactor):
    # Create an analysis.

    myAnalysis = Steady_State_analysis_MemMech(analysisName,"OxideSiPZT251Nocuts_8symet")
    # Run the analysis and wait for completion.
    myAnalysis.run()
    # Queue the analysis.
    #myAnalysis.queue()
    return

def main():
    # Create an analysis.
    for num in range(6,11):
        for num2 in range(1,5):
            if num2 == 1 : analysisName = "PZTandSiScale"
            if num2 == 2 : analysisName = "PZTScale"
            if num2 == 3 : analysisName = "OxideScale"
            if num2 == 4 : analysisName = "ThreeAxisScale"
            main2(analysisName + str(num) + "_pressure_Apr5",0,num2,num/10.0,3, .01)
            main2(analysisName + str(num) + "_steady_high_Apr5",1,num2,num/10.0,3, .0001)
            main2(analysisName + str(num) + "_voltage_Apr5",1,num2,num/10.0,1, .1)
            main2(analysisName + str(num) + "_steady_low_Apr5",1,num2,num/10.0,3, .0000)
            main2(analysisName + str(num) + "_prssureheat_Apr5",0,num2,num/10.0,2, 350)

    # Run the analysis and wait for completion.

```

Bibliography

1. C. R. Bowen, J. Taylor, E. LeBoulbar, D. Zabek, a. Chauhan, and R. Vaish, “Pyroelectric materials and devices for energy harvesting applications,” *Energy & Environmental Science*, vol. 00, no. 12, pp. 1–21, 2014.
2. F. Cottone, L. Gammaitoni, and H. Vocca, “Nonlinear energy harvesting,” , no. October, 2008.
3. S R Anton and H A Sodano, “A review of power harvesting using piezoelectric materials (2003-2006),” *Smart Materials & Structures*, vol. 16, no. 3, pp. R1–R21, 2007.
4. Ashcon Navid, Damien Vanderpool, Abubakarr Bah, and Laurent Pilon, “Towards optimization of a pyroelectric energy converter for harvesting waste heat,” *International Journal of Heat and Mass Transfer*, vol. 53, no. 19-20, pp. 4060–4070, 2010.
5. Simone Dalola, Vittorio Ferrari, and Daniele Marioli, “Pyroelectric effect in PZT thick films for thermal energy harvesting in low-power sensors,” *Procedia Engineering*, vol. 5, pp. 685–688, 2010.
6. B A Strukov and A P Levaniuk, *Ferroelectric Phenomena in Crystals: Physical Foundations*, Springer, 1998.
7. K Uchino, “1 - The development of piezoelectric materials and the new perspective,” in *Advanced Piezoelectric Materials*, Kenji Uchino, Ed., Woodhead Publishing Series in Electronic and Optical Materials, pp. 1–85. Woodhead Publishing, 2010.
8. T Ikeda, *Fundamentals of Piezoelectricity*, Oxford science publications. Oxford University Press, 1996.
9. Vinod Wadhawan, *Introduction to Ferroic Materials*, 2000.
10. M E Lines and A M Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Oxford University Press, Oxford, 2001.
11. T Mitsui, *An introduction to the physics of ferroelectrics*, 1976.
12. Markys G Cain, *Characterisation of ferroelectric bulk materials and thin films*, 2014.
13. Sidney B Lang, “Pyroelectricity : From Ancient Changes in the net dipole moment of certain materials form,” *Physics Today* , no. August, pp. 31–36, 2005.

14. A. L. Kholkin, N. A. Pertsev, and A. V. Goltsev, "Piezoelectricity and crystal symmetry," *Piezoelectric and Acoustic Materials for Transducer Applications*, pp. 17–38, 2008.
15. K a Cook-Chennault, N Thambi, and a M Sastry, "Powering MEMS portable devicesa review of non-regenerative and regenerative power supply systems with special emphasis on piezoelectric energy harvesting systems," *Smart Materials and Structures*, vol. 17, no. 4, pp. 043001, 2008.
16. C. R. Bowen, H. a. Kim, P. M. Weaver, and S. Dunn, "Piezoelectric and ferroelectric materials and structures for energy harvesting applications," *Energy & Environmental Science*, vol. 7, no. 1, pp. 25, 2014.
17. Adam A. Heitmann and George A. Rossetti, "Thermodynamics of ferroelectric solid solutions with morphotropic phase boundaries," *Journal of the American Ceramic Society*, vol. 97, no. 6, pp. 1661–1685, 2014.
18. R Bouregba, G Poullain, B Vilquin, and H Murray, "Orientation control of textured PZT thin films sputtered on silicon substrate with TiO_x seeding," *Materials Research Bulletin*, vol. 35, pp. 1381–1390, 2000.
19. T Haccart, E Cattani, and D Remiens, "Dielectric, ferroelectric and piezoelectric properties of sputtered PZT thin films on Si substrates: influence of film thickness and orientation," *Semiconductor Physics, Quantum Electronics & Optoelectronics*, vol. 5, pp. 78–88, 2002.
20. a.a. Heitmann and G.a. Rossetti, "Thermodynamics of polar anisotropy in morphotropic ferroelectric solid solutions," *Philosophical Magazine*, vol. 90, no. April 2012, pp. 71–87, 2010.
21. X. Q. Ke, D. Wang, X. Ren, and Y. Wang, "Formation of monoclinic nanodomains at the morphotropic phase boundary of ferroelectric systems," *Physical Review B - Condensed Matter and Materials Physics*, vol. 88, no. 21, pp. 1–6, 2013.
22. Paul Muralt and Associate Member, "PZT Thin Films for Microsensors and Actuators : Where Do We Stand ?," vol. 47, no. 4, pp. 903–915, 2000.
23. Sergey Prosandeev, Dawei Wang, A R Akbarzadeh, and L Bellaiche, "First-principles-based effective Hamiltonian simulations of bulks and films made of lead-free Ba(Zr,Ti)O₃ relaxor ferroelectrics," *J. Phys.: Condens. Matter Journal of Physics: Condensed Matter J. Phys.: Condens. Matter*, vol. 27, no. 27, pp. 223202–16, 2015.
24. G Markys, *Springer Series in Measurement Science and Technology Characterisation of Ferroelectric Bulk Materials and Thin Films*, 2014.

25. R E Kirk and D F Othmer, *Kirk-Othmer encyclopedia of chemical technology: FerroElectrics to Fluorine Compounds*, Encyclopedia of Chemical Technology. Wiley, 1980.
26. Aditya Chauhan, Satyanarayan Patel, Gaurav Vats, and Rahul Vaish, "Enhanced Thermal Energy Harvesting Using Li, K-Doped Bi 0.5 Na 0.5 TiO 3 Lead-Free Ferroelectric Ceramics," *Energy Technology*, vol. 2, no. 2, pp. 205–209, 2014.
27. Gaurav Vats, Aditya Chauhan, and Rahul Vaish, "Thermal energy harvesting using bulk lead-free ferroelectric ceramics," *International Journal of Applied Ceramic Technology*, vol. 12, no. S1, pp. E49–E54, 2015.
28. R. E. Newnham, D. P. Skinner, and L. E. Cross, "Connectivity and piezoelectric-pyroelectric composites," *Materials Research Bulletin*, vol. 13, no. 5, pp. 525–536, 1978.
29. K. Wasa, T. Matsushima, H. Adachi, T. Matsunaga, T. Yanagitani, and T. Yamamoto, "High-Tc/high-coupling relaxed PZT-based single crystal thin films," *Journal of Applied Physics*, vol. 117, no. 12, pp. 124106, 2015.
30. S Tadigadapa and K Mateti, "Piezoelectric MEMS sensors: state-of-the-art and perspectives," *Measurement Science and Technology*, vol. 20, no. 9, pp. 092001, 9 2009.
31. S Tadigadapa and K Mateti, "Piezoelectric MEMS sensors: state-of-the-art and perspectives," *Measurement Science and Technology*, vol. 20, no. 9, pp. 92001, 2009.
32. Devashish Lingam, Ankit R. Parikh, Jiacheng Huang, Ankur Jain, and Majid Minary-Jolandan, "Nano/microscale pyroelectric energy harvesting: challenges and opportunities," *International Journal of Smart and Nano Materials*, vol. 4, no. 4, pp. 229–245, 2013.
33. S. Pamir Alpay, Joseph Mantese, Susan Trolier-McKinstry, Qiming Zhang, and Roger W. Whatmore, "Next-generation electrocaloric and pyroelectric materials for solid-state electrothermal energy interconversion," *MRS Bulletin*, vol. 39, no. 12, pp. 1099–1111, 2014.
34. Gael Sebald, Daniel Guyomar, and Amen Agbossou, "On thermoelectric and pyroelectric energy harvesting," *Smart Materials and Structures*, vol. 18, no. 12, pp. 125006, 2009.
35. JiangYu Li, "Exchange coupling in P(VDF-TrFE) copolymer based all-organic composites with giant electrostriction.," *Physical review letters*, vol. 90, no. JUNE 2003, pp. 217601, 2003.

36. Q. M. Zhang, "Giant Electrostriction and Relaxor Ferroelectric Behavior in Electron-Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer," *Science*, vol. 280, no. 5372, pp. 2101–2104, 6 1998.
37. A. M. Glazer, "Simple ways of determining perovskite structures," *Acta Crystallographica Section A*, vol. 31, no. 6, pp. 756–762, 1975.
38. Karin M. Rabe, Matthew Dawber, Cline Lichtensteiger, Charles H. Ahn, and Jean Marc Triscone, "Modern physics of ferroelectrics: Essential background," *Topics in Applied Physics*, vol. 105, no. 2007, pp. 1–30, 2007.
39. Kiyotaka Wasa, Tomoaki Matsushima, Hideaki Adachi, Isaku Kanno, and Hidetoshi Kotera, "Thin-film piezoelectric materials for a better energy harvesting MEMS," *Journal of Microelectromechanical Systems*, vol. 21, no. 2, pp. 451–457, 2012.
40. K. Kanda, Y. Iga, T. Hashimoto, T. Fujita, K. Higuchi, and K. Maenaka, "Microfabrication and Application of Series-Connected PZT Elements," *Procedia Chemistry*, vol. 1, no. 1, pp. 808–811, 2009.
41. Zhenxing Bi, Zhisheng Zhang, and Panfeng Fan, "Characterization of PZT Ferroelectric Thin Films by RF-magnetron Sputtering," *Journal of Physics: Conference Series*, vol. 61, pp. 120–124, 2007.
42. B S Lee, S C Lin, W J Wu, X Y Wang, P Z Chang, and C K Lee, "Piezoelectric MEMS generators fabricated with an aerosol deposition PZT thin film," *Journal of Micromechanics and Microengineering*, vol. 19, pp. 065014, 2009.
43. S Tadigadapa and K Mateti, "Piezoelectric MEMS sensors: state-of-the-art and perspectives," *Measurement Science and Technology*, vol. 20, no. 9, pp. 092001, 2009.
44. Kelu Zheng, Jian Lu, and Jiaru Chu, "A novel wet etching process of Pb(Zr,Ti)O₃ thin films for applications in microelectromechanical system," *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers*, vol. 43, no. 6 B, pp. 3934–3937, 2004.
45. Li Wang, Ruihong Liang, Chaoliang Mao, Gang Du, Genshui Wang, and Xianlin Dong, "Effect of PMN content on the phase structure and electrical properties of PMN-PZT ceramics," *Ceramics International*, vol. 39, no. 7, pp. 8571–8574, 2013.
46. Satyanarayan Patel, Aditya Chauhan, and Rahul Vaish, "Enhanced energy harvesting in commercial ferroelectric materials," *Materials Research Express*, vol. 1, no. 2, pp. 025504, 2014.

47. Dragan Damjanovic, "Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics," *Reports on Progress in Physics*, vol. 61, no. 9, pp. 1267–1324, 1998.
48. Satyanarayan Patel, Aditya Chauhan, and Rahul Vaish, "Analysis of High-Field Energy Harvesting using Ferroelectric Materials," *Energy Technology*, vol. 2, no. 5, pp. 480–485, 2014.
49. T R Shrout, S J Zhang, R Eitel, C Stringer, and C A Randall, "High Performance , High Temperature Perovskite Piezoelectrics," vol. 00, no. 814, pp. 126–129, 2004.
50. Cheol Woo Ahn, Jong Jin Choi, Jungho Ryu, Woon Ha Yoon, Byung Dong Hahn, Jong Woo Kim, Joon Hwan Choi, and Dong Soo Park, "Composition design rule for energy harvesting devices in piezoelectric perovskite ceramics," *Materials Letters*, vol. 141, pp. 323–326, 2015.
51. Andrea Mazzalai, Martin Kratzer, Ramin Matloub, Cosmin Sandu, and Paul Muralt, "Nanostructural tuning of the texture of PZT pervoskite thin films grown by RF sputtering for piezoelectric MEMS," *MRS Proceedings*, vol. 1674, pp. 14–1674, 2014.
52. Ali Koochekzadeh, Eskandar Keshavarz Alamdari, Abod-al-ghafar Barzegar, and Ali A Salardini, "Thermal Effects of Platinum Bottom Electrodes on PZT Sputtered Thin Films Used in MEMS Devices," vol. 437, pp. 598–602, 2010.
53. Austin J. Fox, Bill Drawl, Glen R. Fox, Brady J. Gibbons, and Susan Trolier-Mckinstry, "Control of crystallographic texture and surface morphology of Pt/-Tio2 templates for enhanced PZT thin film texture," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 62, no. 1, pp. 56–61, 2015.
54. R. Bouregba, G. Poullain, B. Vilquin, and H. Murray, "Orientation control of textured PZT thin films sputtered on silicon substrate with TiOx seeding," *Materials Research Bulletin*, vol. 35, no. 9, pp. 1381–1390, 2000.
55. W. C. Roentgen, "No Title," *Ann. Phys. Chem*, vol. 11, pp. 771–786, 1880.
56. Hiep Nguyen, Ashcon Navid, and Laurent Pilon, "Pyroelectric energy converter using co-polymer P(VDF-TrFE) and Olsen cycle for waste heat energy harvesting," *Applied Thermal Engineering*, vol. 30, no. 14-15, pp. 2127–2137, 2010.
57. Felix Y. Lee, Ashcon Navid, and Laurent Pilon, "Pyroelectric waste heat energy harvesting using heat conduction," *Applied Thermal Engineering*, vol. 37, pp. 30–37, 2012.

58. C. R. Bowen, J. Taylor, E. Le Boulbar, D. Zabek, and V. Yu Topolov, "A modified figure of merit for pyroelectric energy harvesting," *Materials Letters*, vol. 138, pp. 243–246, 2015.
59. Rahul Vaish, "Piezoelectric and pyroelectric materials selection," *International Journal of Applied Ceramic Technology*, vol. 10, no. 4, pp. 682–689, 2013.
60. Xiangwen Zhang, Fei Yue Wang, and Li Li, "Optimal selection of piezoelectric substrates and crystal cuts for SAW-based pressure and temperature sensors," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 54, no. 6, pp. 1207–1215, 2007.
61. Gael Sebald, Elie Lefeuvre, and Daniel Guyomar, "Pyroelectric energy conversion: Optimization principles," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 55, no. 3, pp. 538–551, 2008.
62. M J Madou, *Manufacturing Techniques for Microfabrication and Nanotechnology*, Fundamentals of Microfabrication and Nanotechnology. Taylor & Francis, 2011.
63. S. Kal, S. Das, D. K. Maurya, K. Biswas, A. Ravi Sankar, and S. K. Lahiri, "CMOS compatible bulk micromachined silicon piezoresistive accelerometer with low off-axis sensitivity," *Microelectronics Journal*, vol. 37, no. 1, pp. 22–30, 2006.
64. "combdribe," .
65. "summit," .
66. S Franssila, *Introduction to Microfabrication*, Wiley, 2004.
67. Erno H. Klaassen, Kurt Petersen, J.Mark Noworolski, John Logan, Nadim I. Maluf, Joe Brown, Christopher Storment, Wendell McCulley, and Gregory T.A. Kovacs, "Silicon fusion bonding and deep reactive ion etching: a new technology for microstructures," *Sensors and Actuators A: Physical*, vol. 52, no. 1-3, pp. 132–139, 1996.
68. "drie," .
69. Jinxing Liang, Fusao Kohsaka, Takahiro Matsuo, Xuefeng Li, and Toshitsugu Ueda, "Improved bi-layer lift-off process for MEMS applications," *Microelectronic Engineering*, vol. 85, no. 5-6, pp. 1000–1003, 2008.
70. D. Zhuang and J. H. Edgar, "Wet etching of GaN, AlN, and SiC: A review," *Materials Science and Engineering R: Reports*, vol. 48, no. 1, pp. 1–46, 2005.

71. P a Köllensperger, W J Karl, M M Ahmad, W T Pike, and M Green, "Patterning of platinum (Pt) thin films by chemical wet etching in Aqua Regia," *Journal of Micromechanics and Microengineering*, vol. 22, no. 6, pp. 067001, 2012.
72. Chii Rong Yang, Po Ying Chen, Yuang Cherng Chiou, and Rong Tsong Lee, "Effects of mechanical agitation and surfactant additive on silicon anisotropic etching in alkaline KOH solution," *Sensors and Actuators, A: Physical*, vol. 119, no. 1, pp. 263–270, 2005.
73. "silicon_etching," .
74. "anisotropic_etch_profile," .
75. Benjamin S. Williams, Sushil Kumar, Hans Callebaut, Qing Hu, and John L. Reno, "Terahertz quantum-cascade laser at $\lambda = 100 \mu\text{m}$ using metal waveguide for mode confinement," *Applied Physics Letters*, vol. 83, no. 11, pp. 2124–2126, 2003.
76. K B Lee, *Principles of Microelectromechanical Systems*, Wiley, 2011.
77. "Schematic-diagram-of-e-Beam-evaporation," .
78. G. Bräuer, B. Szyszka, M. Vergöhl, and R. Bandorf, "Magnetron sputtering - Milestones of 30 years," *Vacuum*, vol. 84, no. 12, pp. 1354–1359, 2010.
79. "SputterDeposition," .
80. a Stoffel, A Kovács, W Kronast, and B Müller, "LPCVD against PECVD for micromechanical applications," *Journal of Micromechanics and Microengineering*, vol. 6, no. 1, pp. 1–13, 1999.
81. S A Campbell, *Fabrication Engineering at the Micro- and Nanoscale*, Oxford series in electrical and computer engineering. Oxford University Press, 2013.
82. Ankita Bose and Monjoy Sreemany, "Influence of processing conditions on the structure, composition and ferroelectric properties of sputtered PZT thin films on Ti-substrates," *Applied Surface Science*, vol. 289, pp. 551–559, 2014.
83. "litho_fig1," .
84. Liming Yu, Francis E H Tay, Guolin Xu, Bangtao Chen, Marioara Avram, and Ciprian Iliescu, "Adhesive bonding with SU-8 at wafer level for microfluidic devices," *Journal of Physics: Conference Series*, vol. 34, no. 1, pp. 776–781, 2006.
85. Rajesh Luharuka and Peter J. Hesketh, "Design of fully compliant, in-plane rotary, bistable micromechanisms for MEMS applications," *Sensors and Actuators A: Physical*, vol. 134, no. 1, pp. 231–238, 2 2007.

86. Jason Felder, Eugene Lee, Don L Devoe, and Senior Member, "Zipper Microstage Actuators," vol. 24, no. 4, pp. 896–903, 2015.
87. Shai Shmulevich and David Elata, "Dynamically Balanced Folded-Beam Suspensions for Resonators," *Journal of Microelectromechanical Systems*, vol. PP, no. 99, pp. 1–1, 2015.
88. "wafer-encapsulation-schematic0," .
89. Robert A. Lake, Kyle K. Ziegler, and Ronald A. Coutu, "Thermal tuning of MEMS buckled membrane actuator stiffness," *Procedia Engineering*, vol. 87, pp. 1382–1385, 2014.
90. R Arya, M M Rashid, D Howard, S D Collins, and R L Smith, "Thermally actuated, bistable, oxide/silicon/metal membranes," *Journal of Micromechanics and Microengineering*, vol. 16, no. 1, pp. 40–47, 2006.
91. S Boisseau, G Despesse, S Monfray, O Puscasu, and T Skotnicki, "Semi-flexible bimetal-based thermal energy harvesters," *Smart Materials and Structures*, vol. 22, no. 2, pp. 025021, 2 2013.
92. Onoriu Puscasu, Stphane Monfray, Frdric Boeuf, Guillaume Savelli, Frdric Gailard, Daniel Guyomar, and Thomas Skotnicki, "Scale laws for enhanced power for MEMS based heat energy harvesting," *Silicon Nanoelectronics Workshop, IEEE*, pp. 1–2, 2012.
93. Chun Ching Hsiao, An Shen Siao, and Jing Chih Ciou, "Improvement of pyroelectric cells for thermal energy harvesting," *Sensors*, vol. 12, no. 1, pp. 534–548, 2012.
94. Richard C. Jaeger, Jeffrey C. Suhling, Ramanathan Ramani, Arthur T. Bradley, and Jianping Xu, "CMOS stress sensors on (100) silicon," *IEEE Journal of Solid-State Circuits*, vol. 35, no. 1, pp. 85–95, 2000.
95. Heng Chung Chang, Hsieh Shen Hsieh, Sung Cheng Lo, Chih Fan Hu, and Weileun Fang, "Piezoresistive pressure sensor with Ladder shape design of piezoresistor," *Proceedings of IEEE Sensors*, vol. 1, 2012.
96. Scott R. Hunter, Nickolay V. Lavrik, Thirumalesh Bannuru, Salwa Mostafa, Slo Rajic, and Panos G. Datskos, "Development of MEMS based pyroelectric thermal energy harvesters," *Energy harvesting and storage*, vol. 8035, no. March, pp. 80350V–80350V–12, 2011.
97. Scott R. Hunter, Nickolay V. Lavrik, Salwa Mostafa, Slo Rajic, and Panos G. Datskos, "Review of pyroelectric thermal energy harvesting and new MEMS-based resonant energy conversion techniques," *Proceedings of the Society of Photo-Optical Instrumentation Engineers*, vol. 8377, no. March 2016, pp. 1–83770, 2012.

98. S. K. T. Ravindran, T. Huesgen, M. Kroener, and P. Woias, "A self-sustaining micro thermomechanic-pyroelectric generator," *Applied Physics Letters*, vol. 99, no. 10, pp. 104102, 9 2011.
99. Jian Zhao, Renjing Gao, Shutian Liu, and Yu Huang, "A new sensitivity-improving method for piezoelectric resonance mass sensors through cantilever cross-section modification," *IEEE Transactions on Industrial Electronics*, vol. 61, no. 3, pp. 1612–1621, 2014.
100. Harald Steiner, Franz Keplinger, Johannes Schalko, Wilfried Hortschitz, and Michael Stifter, "Highly Efficient Passive Thermal Micro-Actuator," vol. 24, no. 6, pp. 1981–1988, 2015.
101. O. Puscasu, S. Monfray, C. Maître, P.J. Cottinet, D. Rapisarda, G. Savelli, F. Gaillard, G. Ricotti, P. Ancey, F. Boeuf, D. Guyomar, and T. Skotnicki, "A disruptive technology for thermal to electrical energy conversion," *Microelectronics Journal*, vol. 45, no. 5, pp. 554–558, 5 2014.
102. Daniel a Porter and Thomas a Berfield, "A bi-stable buckled energy harvesting device actuated via torque arms," *Smart Materials and Structures*, vol. 23, no. 7, pp. 075003, 2014.
103. Helios Vocca, Igor Neri, Flavio Travasso, and Luca Gammaitoni, "Kinetic energy harvesting with bistable oscillators," *Applied Energy*, vol. 97, pp. 771–776, 9 2012.
104. J.P. Carmo, L.M. Gonçalves, and J.H. Correia, "Thermoelectric micro converter for energy harvesting systems," *IEEE Transactions on Industrial Electronics*, vol. 57, no. 3, pp. 861, 2010.
105. Krishna Veni Selvan and Mohamed Sultan Mohamed Ali, "Micro-scale energy harvesting devices: Review of methodological performances in the last decade," *Renewable and Sustainable Energy Reviews*, vol. 54, pp. 1035–1047, 2 2016.
106. J C Wyant, "White light interferometry," *Proceedings of the SPIE - The International Society for Optical Engineering*, vol. 4737, no. 2002, pp. 98–107, 2002.
107. a. L. Kholkin, Ch Wüthrich, D. V. Taylor, Nava Setter, and Ch. Wutchrich, "Interferometric measurements of electric field-induced displacements in piezoelectric thin films," *Review of Scientific Instruments*, vol. 67, no. 5, pp. 1935, 1996.
108. Hiroyuki Fujiwara, *Spectroscopic Ellipsometry Principles and Applications*, vol. 53, 1989.
109. J Tang and A C Albrecht, *Raman Spectroscopy*, 1970.

110. Wei Hua Xu, Dexin Lu, and Tong Yi Zhang, “Determination of residual stresses in $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ thin films with Raman spectroscopy,” *Applied Physics Letters*, vol. 79, no. 25, pp. 4112–4114, 2001.

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14. ABSTRACT The consumption of energy is one of the largest single expenses across the US armed forces. A device that harvests waste heat into usable electrical power would increase overall power efficiency and reduce costs. Traditional combustion engines and moving fluid systems are too bulky and expensive to be placed in many conventional systems or places. Ferroelectric materials can generate electrical charge, but only if moved from a cold sink to a hot source using a mechanical device. MEMS devices are mechanical devices made with specialized techniques with feature sizes on the micrometer scale. A MEMS device that moves in response to heat was fabricated, and is used as a mechanical base for a ferroelectric energy harvesting material. A micron scaled device for harvesting electrical power from a spatial thermal gradient was fabricated.					
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