NANOMETER-THICK OXIDE FILMS FOR PYROELECTRIC ENERGY CONVERSION

BY

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DISSERTATION

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Abstract

Pyroelectric energy conversion utilizes the temperature dependence of spontaneous polarization in crystalline materials to convert waste heat into electricity. High-power-density thermal-to-electrical energy conversion is possible using pyroelectric thin films which allow fast thermal cycling and high electric fields. Published studies, however, have not investigated pyroelectric energy conversion in nanometer-thick films. In addition, there is a lack of suitable techniques for characterization of pyroelectric and other related temperature-dependent properties of thin films. This work develops and implements techniques for temperature-dependent piezoelectric and pyroelectric characterization of nanometer-thick films, and investigates pyroelectric energy conversion using high-frequency thermal-electrical cycles.

Phase-sensitive techniques measured high-temperature electromechanical and pyroelectric response in ~100 nm thick PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films deposited using pulsed laser deposition. Piezoresponse force microscopy (PFM), an atomic force microscopy (AFM) based technique, measured the electromechanical response while a doped-silicon resistive micro-heater provided local temperature control up to 400 °C. Three techniques characterized the pyroelectric response using temperature oscillations generated by a hotplate, a microfabricated heater, or a modulated laser. The pyroelectric current was measured from a microelectrode fabricated onto the film over a heating frequency range 0.02 Hz – 1.3 MHz.

This work investigated pyroelectric energy conversion in ~200 nm thick epitaxial BaTiO$_3$ films using a microfabricated platform that allowed simultaneous thermal and electrical control. The low thermal mass of the active material and precise thermal-electrical control enabled
pyroelectric cycles up to 3 kHz frequency and maximum power density of 30 W/cm³. In comparison, earlier studies were typically limited to cycle frequencies less than 1 Hz and the highest reported power density was 0.11 W/cm³. In addition to studying high frequency thermal-electrical cycles, this dissertation also examined the effect of variations in temperature and electric field with microsecond temporal resolution. This work will facilitate the design and operation of pyroelectric cycles with high energy and power densities.

This dissertation reports advancements in piezoelectric and pyroelectric characterization of thin films, and presents high-power-density solid-state pyroelectric energy conversion which could be useful for future waste heat harvesting applications.
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Chapter 1
Introduction

The phenomenon of pyroelectricity characterizes the thermal-electrical interaction in crystalline materials. Pyroelectric materials are important for applications in sensing, actuation, and energy harvesting. Recent developments in nanometer-thick ferroelectric films have led to significant advances in primarily non-volatile memory applications. These thin films offer distinct advantages for thermal-to-electrical energy conversion. But waste heat harvesting has not been investigated in nanometer-thick pyroelectric films. In addition, there is a lack of suitable techniques for characterization of pyroelectric and other related temperature-dependent properties of thin films. Using nanometer-thick pyroelectric films can lead to a commercially-viable solid-state waste heat harvesting technology, complementary to thermoelectrics.

1.1 Pyroelectric Effect

Pyroelectricity is defined as the temperature dependence of spontaneous polarization of crystalline materials [1]. All crystalline materials can be classified in 32 classes [2]. Of these 32 crystal classes, 11 have centrosymmetry and are non-polar. Of the remaining 21 classes, 20 are piezoelectric i.e. exhibit electrical polarity when subjected to stress. And 10 of the 20
piezoelectric crystal classes are typically pyroelectric i.e. have a unique polar axis and magnitude of the spontaneous polarization, $P_S$, which decreases with increase in temperature. A change in the polarization is followed by a motion of compensating charges which induces an electric current in the external circuit as shown in Figure 1.1. The pyroelectric crystals that have two or more stable orientations which can be shifted from one to another by application of an electric field are said to be ferroelectric. Furthermore, ferroelectrics have a characteristic Curie temperature $T_C$ above which the material is non-polar. The polarization of ferroelectric materials is thus temperature as well as electric field dependent.

When an electric field, $E$, is applied to a polar material the total electric displacement is given by $D = \varepsilon E + P_S$. Here $\varepsilon = \left(\frac{dD}{dE}\right)_T$ is the electric permittivity and the generalized pyroelectric coefficient is defined as rate of electric displacement change with temperature $T$ at a constant electric field, $p = \left(\frac{dD}{dT}\right)_E = E\left(\frac{d\varepsilon}{dT}\right)_E + \left(\frac{dP_S}{dT}\right)_E$. While the intrinsic $\left(\frac{dP_S}{dT}\right)_E$ contribution exists only in polar materials, the $E\left(\frac{d\varepsilon}{dT}\right)_E$ contribution can occur in all dielectrics. In addition, since pyroelectric materials are polar and piezoelectric, strain resulting from thermal expansion results in additional temperature-dependent contribution to the electric displacement change.

Applications of pyroelectric materials in thermal imaging, radiometry, gas analysis and energy harvesting have so far relied on bulk ferroelectrics [3-5]. However, thin films have distinct advantage over bulk samples. Thin films are compatible with standard microfabrication processes necessary for microelectronic applications. In addition, it is possible to achieve high electric fields with low operating voltages with nanometer-thick films. Furthermore, thin-film
epitaxy has enabled tuning material properties by controlling the composition, epitaxial strain and thickness of the films [6-8]. Thus, recent advances in our understanding of thin film ferroelectrics and their fabrication have paved the way for its future applications in nanoscale electronics and energy conversion applications. The research on nanometer-thick films has primarily focused on electrical properties for memory and transistor applications [9-11]. Pyroelectric and other temperature dependent properties of thin films, on the other hand, are vastly understudied due to lack of precise spatiotemporal thermal control and will be the focus of this thesis.

![Mechanism of pyroelectricity](image)

**Figure 1.1** Mechanism of pyroelectricity. The intrinsic electric displacement of a pyroelectric crystal reduces in magnitude with increase in temperature. This change in electric displacement causes a flow of compensating charges which results in an electric current in the external circuit. [1]
1.2 Material Characterization

Electric displacement of a pyroelectric material varies with temperature, mechanical stress as well as electric field. Figure 1.2 shows the interactions between thermal, electrical and mechanical properties of pyroelectric materials [12]. In the thermal-electrical regime, the pyroelectric effect converts fluctuations in temperature ($T$) to an electric displacement ($D$) change. Conversely, electrocaloric effect produces an entropy ($S$) change from an electric field ($E$) variation. In the electro-mechanical regime, the piezoelectric effect causes a stress ($\sigma$) induced electric displacement change. And converse piezoelectric effect is responsible for electric field driven strain ($\varepsilon$) changes in the material. Traditionally these effects have been measured using techniques that are suitable for bulk samples. These conventional methods are, however, inadequate for nanometer-thick films in which the responses are often small and thus challenging to measure reliably. In addition, thin films have a greater density of trapped charges and pinholes than single crystal samples, which further complicates material characterization. These problems have particularly prevented temperature dependent characterization of electrical and mechanical properties. The goal of this work was to develop platforms and techniques to enable accurate measurements of pyroelectric and other temperature dependent properties of nanometer-thick films which are essential for energy harvesting applications.

Measuring the piezoelectric response of thin films is important for understanding ferroelectric phenomena such as switching kinetics and polarization dynamics [13]. Characterizing the electromechanical response is also critical for sensing, transduction and energy harvesting applications [4,11]. Piezoresponse force microscopy (PFM) is an atomic force microscope (AFM) based technique for quantitative measurement of ferroelectric properties in thin films with high spatial resolution [14,15]. A metal-coated microcantilever with a sharp tip at
its end is used to apply a local electrical field to the sample and the resulting deflection is measured using the AFM detection system. PFM allows accurate measurement of picometer-scale electromechanical responses with a nanometer-scale spatial resolution. However, investigating temperature-dependent properties using PFM is challenging due issues with noise and compatibility with AFM systems. In particular, very few local ferroelectric measurements have been reported at elevated temperatures [13,16,17].

Pyroelectric characterization of materials involves measuring the electrical response resulting from a thermal excitation. Traditional techniques for measuring the pyroelectric response typically use conventional heat sources such as hotplates and ovens to generate temporal temperature fluctuations [18-20]. These methods work reasonably well for bulk samples which have a large thermal mass and require slow temperature changes. However, they have achieved limited success with thin films which have a large density of defects and pin-holes [21]. Bulk heating of thin films releases trapped charges and induces spurious signals that are difficult to distinguish from the pyroelectric response [22-24]. Laser-based methods have partially solved this problem by using high frequency temperature fluctuations, but they are expensive and the estimation of the temperature field is not straightforward [25-27]. Thus, new techniques to enable accurate pyroelectric characterization of thin films are needed.
1.3 Pyroelectric Energy Conversion

Pyroelectric materials can convert temperature fluctuations into usable electrical energy. The simplest approach, referred to as direct pyroelectric energy conversion, uses an electrical load connected in a circuit with a pyroelectric capacitor [28-30]. Alternating electrical current flows across the load as the pyroelectric material heats and cools in succession due to the temperature-driven change in electric displacement. This simple setup can be improved by using a constant poling voltage and a rectifier circuit [31-33]. The other, more popular approach utilizes thermodynamic cycles that involve simultaneous thermal and electrical cycling of pyroelectric materials for generating electrical energy. Such pyroelectric cycles have reported electrical energy output up to a 100 times greater than direct pyroelectric energy.
conversion [34,35]. Even though the applied electrical field does no work in an ideal system with no resistive losses and constant material properties, thermal-electrical cycles improve energy conversion performance in two ways. First, applied poling bias enhances the pyroelectric response which increases the energy output. And second, electric field control of electric displacement enables thermodynamic processes not achievable by thermal cycling alone which helps attain higher energy densities. Thus, active control and syncing the electric field with the temperature change can enhance electrical energy generation.

So far, energy conversion using pyroelectric cycles has been investigated primarily in bulk samples and micron-thick polymer films. The thickness of the single crystal and polycrystalline ceramic samples generally varied between 0.1 and 1 mm [4,36]. In comparison, the polymer films were thinner, with 5 µm being the thickness of the thinnest film reported [37]. Most studies used bulk samples belonging to the PbZrxTi1-xO3 or (1-x)Pb((Mn/Zn)1/3Nb2/3)-xPbTiO3 family of materials and P(VDF-TrFE) polymer films because of their high pyroelectric coefficients [34,38-43]. These bulk samples and thick films have high thermal mass which inhibit operation of pyroelectric cycles at high frequencies. Few studies have demonstrated direct pyroelectric energy conversion in low dimensional systems such as ZnO and KNbO3 nanowires, but pyroelectric cycles were not studied [44,45].

Realization of pyroelectric cycles for energy conversion requires a thermal subsystem for controlling heating and cooling of the pyroelectric material and an electrical subsystem which controls the electric field across the pyroelectric material and monitors the progress of the energy harvesting cycle. Figure 1.3 shows a schematic of commonly used thermal and electrical subsystems [4]. Temperature oscillations were generated by pumping oil across the pyroelectric ceramic stack at high temperature. The electric field was controlled using a voltage source and
the charge on the ferroelectric material was monitored by a Sawyer-Tower circuit (not shown in the figure) [46]. Other techniques used for temperature control include manually moving samples between variable temperature oil or water baths or bringing them in mechanical contact with hot and cold metal blocks [4,47,48]. One recent study used liquid-based thermal interfaces that could change the thermal conductance between the pyroelectric material and the heat source/sink [37]. However the maximum cycle frequency in published literature was 10 Hz, [39] and was typically less than 1 Hz [32,37,49]. The low cycling rates can be attributed to bulk heating methods and mechanical motion used to generate temperature oscillations. Electric field control, typically achieved using an external voltage source and electrical switches, was relatively straightforward. However, applied voltages up to a few kV were required to reach the desired electric field in bulk samples [39,41]. Use of such high voltage is dangerous due to the risk of arcing and is not suitable for portable applications. Majority of the work so far focused on identifying pyroelectric materials suitable for energy conversion; little attention was given to the instrumentation required for thermal-electrical cycles in comparison.

Despite the recent advances, pyroelectric energy conversion is still far from commercial viability due to low energy and power densities, and difficulty of implementation in real-world systems. The maximum reported energy density is 1 J/cm$^3$, power density is 0.11 W/cm$^3$, and efficiency is 5% of the Carnot limit [36-38]. The energy density and efficiency are limited by the low pyroelectric coefficients and high heat capacities of available materials. Majority of thermal energy input contributes towards lattice heating and only a small fraction is available for changing the electric displacement which is harvested as electrical energy. The power density, on the other hand, is primarily limited by the frequency of the temperature oscillation source and can be improved by selecting a suitable target application and/or careful engineering design.
Thermal-electrical cycles can be used for waste heat harvesting in systems with natural temperature fluctuations such as internal combustion engines, power electronics, modern semiconductor devices, and gas turbines [50-53]. The temperature variations can be as high as 200 °C, and the oscillation frequency can vary from a few mHz to several kHz depending on the application. In addition, electrical energy can be generated using pyroelectric thin films by converting spatial gradients into temporal fluctuations, for example using a heat pipe, without significantly affecting the energy conversion efficiency [34,44,54].

![Diagram of the thermal and electrical subsystems used by Olsen et al [4] to investigate energy conversion using pyroelectric cycles.](image)

**Figure 1.3** Diagram of the thermal and electrical subsystems used by Olsen et al [4] to investigate energy conversion using pyroelectric cycles.
1.4 Dissertation Overview

Investigation of pyroelectric, piezoelectric and other temperature-dependent properties of different material systems will promote better scientific understanding and also enable applications in sensing, transduction and energy conversion. This dissertation reports advancements in techniques for characterization of piezoelectric and pyroelectric properties of nanometer scale thin films. Microfabricated platforms were developed specifically to study the temperature and electric field dependent properties, and investigate pyroelectric energy conversion using thermal-electrical cycles. Chapter 2 describes high temperature nanometer scale piezoelectric characterization of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films using an atomic force microscope. Chapter 3 presents three techniques for pyroelectric characterization of thin films and compares them with the widely used bulk characterization method. Chapter 4 reports high power density thermal to electrical energy conversion from BaTiO$_3$ thin films due to simultaneous temperature and electric field oscillations. Finally, Chapter 5 describes how temporal variations in temperature and electric field affect pyroelectric energy conversion performance. Combining material advances with optimal device design and operating conditions can facilitate the use of pyroelectric thin films in waste heat harvesting applications.
1.5 References


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Chapter 2
High-Temperature Piezoresponse Force Microscopy

2.1 Introduction

The extensive use of ferroelectric thin films in sensors, actuators and non-volatile memory applications [1] requires the understanding of local ferroelectric properties. Ferroelectric phenomena such as switching kinetics and polarization dynamics depend upon temperature [2], and the temperature-dependence of ferroelectric properties is of particular interest for energy conversion applications [3]. However there is a lack of high temperature measurements of ferroelectric thin films. This chapter describes scanning probe-based measurements of a ferroelectric thin film at high temperature.

Lead zirconate titanate (PZT) is one of the most extensively studied ferroelectric materials due to its excellent ferroelectric, piezoelectric, and pyroelectric properties [1,4,5]. There have been few published measurements of local ferroelectric switching and phase transitions at high temperature. Traditional dielectric and ferroelectric measurements using capacitor structures have been limited by a lack of high-temperature stable electrical contacts and substantial increases in leakage currents in the material at high temperatures. This has led
researchers to focus on non-contact techniques such as second harmonic generation (SHG) [6,7] and X-ray diffraction (XRD) [7,8], to probe the nature of order in such thin film samples. Unfortunately, it is hard to obtain quantitative measures of response from such techniques and to probe at the same spatial resolution as with scanning probe measurements. Many articles report local measurements of ferroelectric materials using scanning probe-based techniques [9,10], but only a few have considered ferroelectric response above room temperature [10-13].

Piezoresponse force microscopy (PFM) is an atomic force microscopy (AFM) based technique in which an electrically biased conductive AFM tip is used to detect the converse piezoelectric response of the surface at the first harmonic component of the bias-induced tip deflection. It has become the primary tool to study local static and dynamic properties of ferroelectric thin films [11]. There is, however, limited work on the electromechanical response of thin ferroelectric films at elevated temperatures, since high temperature characterization is challenging in conventional AFM. Most AFM-compatible heater stages are not capable of reaching temperatures above about 200 °C, due to thermal drift, noise, and the general inability of AFM systems to withstand high temperature. Variable temperature PFM has been reported, but at relatively low temperatures [10,12-14].

This work presents high temperature piezoresponse measurements of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films using a microfabricated heated platform inside a commercial AFM system. The PZT film thickness is 100 nm and the temperature range is 25-400 °C.
2.2 Heater fabrication and Characterization

Figure 2.1 shows the heater fabrication process. We fabricated the heating platform on a 100-mm SOI wafer with a handle layer thickness of 500 µm, a silicon dioxide buried oxide (BOX) layer of thickness 2 µm and device layer thickness of 500 nm with a resistivity of 14-22 Ω-cm, doped with boron. First, the device layer was patterned and etched to form the “hour-glass” shaped heater structure. The heating line is a 500 µm long and 30 µm wide strip of silicon at the “neck” of the hour-glass. Next, a 10 µm wide channel in the heater line was defined using ion implantation of phosphorus and subsequent diffusion at 1000 °C [15]. This doping step defined the high resistance heater line with an estimated resistivity of 0.001 Ω-cm. Another phosphorus implantation and diffusion step was used to highly dope the conductive electrical traces on either end of the heater line to a target resistivity of 0.00017 Ω-cm. A Shipley 1827 photoresist mask was used for both the implantation steps. Finally, we fabricated electrical contacts on the high-doped ends of the microfabricated heater with a 10 nm chromium adhesion layer beneath 200 nm sputtered gold.
The silicon heater temperature was calibrated using Raman spectroscopy \cite{15}. The device was operated with dc voltage and the Raman microscope laser spot was focused near the center of the heater line. Figure 2.2 shows a plot of the heater temperature as a function of input power.

**Figure 2.1** Summary of heater fabrication. (a) Fabrication was done on an SOI wafer with B-doped device layer. First, we formed the heater structure on the device layer of the SOI wafer using an ICP-DRIE etch. (b) Next, we performed low-dosage phosphorus implantation and diffusion to define the heater line. (c) A high dose phosphorus doping step defined the conductive traces running to the heater line. (d) Finally, gold electrode pads were sputtered and patterned.
The heater temperature increases almost linearly with heater power. The temperature-dependence of the heater electrical resistance allows the temperature to be precisely controlled.

![Graph of heater temperature vs. heater power](image)

**Figure 2.2** Heater temperature as a function of heater power, measured using Raman spectroscopy.

### 2.3 PZT film deposition

A 100 nm thick PbZr$_{0.2}$Ti$_{0.8}$O$_3$ layer was deposited on the heater device by pulsed laser deposition from a Pb$_{1.1}$Zr$_{0.2}$Ti$_{0.8}$O$_3$ ceramic target (Praxair Inc.). The PZT layer was deposited at 600 °C in an oxygen background pressure of 200 mTorr with a laser fluence of 1.75 J/cm$^2$ at a laser repetition rate of 10 Hz. After growth, the samples were cooled in a 700 mTorr oxygen environment at 5 °C/min to room temperature. Figure 2.3 shows X-ray diffraction and AFM topography, indicating single phase (00l)-oriented PZT films with RMS roughness < 6 nm.
2.4 Experimental Setup

Figure 2.4 shows the experimental setup, consisting of the PZT thin film synthesized onto the microfabricated heating platform and mounted in our AFM system. The heating platform consisted of a heating line at the center having electrical resistance of 1 kΩ and diverging silicon traces of electrical resistance 0.1 kΩ. Device design and doping concentrations were chosen to achieve a uniform temperature in the heater line and negligible heating elsewhere. The silicon dioxide layer reduces heat flow into the substrate and allows high temperature operation. The temperature-dependence of the heater electrical resistance allows the temperature to be controlled in the AFM.

Figure 2.3 X-ray diffraction data of PZT film on silicon. The PZT 002 peak indicates a preferential out-of-plane polarization. Inset: AFM topography image of the PZT film on heater device.
The samples were measured in our Asylum Cypher AFM. The PFM measurement applied a periodic voltage to the tip, $V_{ac}$, carried by a steady voltage $V_{dc}$ that steps in magnitude in time [16]. Between each voltage step, $V_{dc}$ was set to 0 V with the AC bias still applied to determine the bias-induced remnant piezoresponse [17]. We used a Pt-coated tip with resonant frequency $\sim 320$ kHz, and spring constant $\sim 42$ N/m to minimize electrostatic contribution in the PFM signal [18]. A probing signal ($V_{ac}$) with an amplitude of 1 V and a frequency close to the contact resonance peak ($\sim 1.4$ MHz) of the tip-sample contact was used to achieve an optimal signal-to-noise ratio [16]. While the operating frequency was close to the contact resonance frequency, the operating frequency was at least 20 kHz away from the peak resonance, to prevent resonance-induced phase shift. The AFM feedback loop was enabled to keep the cantilever deflection constant during the hysteresis loops.

Figure 2.4 Schematic of the experimental setup. PZT thin film is deposited on the microfabricated heater structure which can be resistively heated. The voltage waveform applied to the conductive AFM tip for local hysteresis measurements is shown.
The doped silicon heater line used for heating also serves as the bottom electrode, which in a typical piezoresponse force spectroscopy setup is grounded. To induce heating, the heater line was supplied with a DC voltage of $V_H$. To ensure that the voltage applied to the heater does not interfere with the hysteresis loop measurement, we placed the AFM tip such that it is at a location where the heater strip voltage is 0 V. $+V_H/2$ voltage was applied at one end of the heater and $-V_H/2$ voltage at the other end; the center of the heating line was at 0 V. Thus we placed the AFM tip as near to the center of the heating line as possible. Figure 2.5 shows an optical image of the AFM cantilever placed on the heater, ready for measurement. The dark region on the left of the image is the chip of the cantilever and the white spot on the cantilever is the laser spot of the AFM. The Pt-coated AFM cantilever was oriented orthogonal to the narrow heater line to minimize electrostatic and non-local interactions between the tip and sample [19]. Before each measurement, we checked the position of the tip over the heater by engaging the tip to the surface and performing a contact resonance tune (mapping the cantilever deflection as a function of the frequency of electrical excitation on the tip) with heating bias applied. The tune was
compared with the contact resonance tune when both ends of the heater were grounded. If there was any non-zero voltage on the heater line just below the tip, the cantilever deflection increased drastically and the contact resonance peak was amplified. In case any electrostatic effects were observed in the tune, rather than repositioning the tip, voltages at the ends of the heater were changed slightly such that the absolute value of their difference still remained $V_H$ but voltages at either end deviated slightly from $+V_H/2$ and $-V_H/2$. The precise cantilever placement and heater voltage control helped in ruling out electrostatics from the heating circuit and we were able to tune the heating voltage to within ±0.5 V.

In addition to the PZT-coated sample, we performed the same measurements on a SiO$_2$ sample to establish a baseline response, which was near zero in all cases. At least five measurements were taken on three different samples to verify reproducibility.

### 2.5 Results and Discussion

Figure 2.6 shows amplitude and phase measured for the remnant piezoelectric hysteresis loops at 350 °C. Hysteretic behavior is evident from the characteristic “butterfly” amplitude loops and 180° phase switching corresponding to out-of-plane domain switching. The presence of significant electrostatic interactions between the tip and sample can usually be pointed out by a reduction in observable hysteresis and a linear scaling of the amplitude with tip bias. No such trends are seen in our data, which confirms that electrostatic interference is minimized.
Figure 2.7(a) shows the measured piezoresponse hysteresis loops for different heater temperatures. The remnant piezoresponse was measured as the deflection of the calibrated AFM tip at the probing bias frequency when the tip DC bias was stepped to zero after each voltage pulse [16]. At a fixed coercive voltage, the overall piezoresponse increased with increasing temperature, up to 400 °C. Figure 2.7(b) shows the remnant PFM amplitude at zero DC offset at different heater temperatures. The piezoresponse response increases drastically at 350 °C and

**Figure 2.6** High temperature remnant hysteresis loops. (a) Amplitude and (b) phase for the local hysteresis loop at high temperature (350 °C).
drops to zero at 400 °C. We propose that this corresponds to the ferroelectric-paraelectric phase transition of the film.

**Figure 2.7** Piezoresponse as a function of temperature. (a) Local hysteresis loops are shown for different heater temperatures. (b) PFM amplitude at 0 V tip DC offset is plotted as a function of the heater temperature. The temperature dependence of piezo-coefficient $d_{33}$ is also shown (solid line). Piezoresponse increases with temperature, as expected from the PFM electromechanical response, until it diminishes at 400 °C indicating a ferroelectric-paraelectric transition.

The well-behaved hysteresis loops of Figures 2.6 and 2.7 are consistent with the AFM tip following the sample electromechanical response. For the field induced in the 100 nm thick PZT films, we expect the piezoresponse to indicate the inverse piezoelectric coefficient $d_{33}$ [20]. It is
thus possible to infer the temperature-dependence of $d_{33}$ from the measured piezoresponse. The solid line of Figure 2.7(b) is the qualitative $d_{33}$ which is proportional to $(T_c-T)^{1/2}$. This $d_{33}$ temperature-dependence is expected from previous measurements of LiTaO$_3$ crystals [21] and also from phenomenological models [2]. In previous high-temperature PFM measurements on triglycine sulfate single crystals [9], the piezoresponse followed the temperature-dependence of spontaneous polarization and did not indicate the temperature-dependence of $d_{33}$. This observation was attributed to electrostatic forces that arose from unscreened polarization-bound charge, which induce cantilever deflections that can be comparable to or larger than the electromechanical response [13,22]. The thin film geometry of the present study allows for a more uniform electrical field to be induced in the sample compared to previous measurements on bulk crystals. Moreover, the experimental setup investigated here allows minimal electrostatic and non-local interactions between the tip and the sample through the use of stiff cantilevers and a configuration that minimizes the cantilever-sample overlap region.

The vertical shift of the hysteresis loops along the response axis can be explained by the asymmetric electrode structure and the widely observed process of imprint [23,24]. Such imprint phenomenon is observed at all temperatures and unlike macroscopic measurements, which generally manifest imprint as a shift of the hysteresis loop along the horizontal voltage axis, the displacement measured in any piezoelectric-based method results in a vertical shift of the data. Such shifts of the piezoelectric hysteresis loop can be associated with non-switched or relaxed regions and the presence of preferred polarization state (i.e., imprint). This is especially evident in remnant loops such as those studied here. Domain pinning at free lateral surfaces and the ferroelectric-electrode interface can also result in such shifts [25]. Some of the measured hysteresis loops show a small deviation from an ideal loop shape. The measured hysteresis loops
were repeatable over many experiments and samples. Similar deviations from ideal loop shapes have been reported by others [16,25] and have been attributed to the interaction of the forming domain with the ferroelectric film topography and microstructure [26,27].

2.6 Conclusion

In summary, we have performed piezoresponse force microscopy on a 100 nm film of PZT over the temperature range 25-400 °C. The piezoresponse increases with temperature but decreases at about 400 °C, which we believe corresponds to the PZT Curie temperature. This work opens possibilities for nanoelectromechanical measurements at temperature well above the heating temperature of commercial AFM heater stages.
2.7 References


Chapter 3

Pyroelectric Current Measurements on PbZr$_{0.2}$Ti$_{0.8}$O$_3$ Epitaxial Layers

3.1 Introduction

Pyroelectricity, the temperature dependence of spontaneous polarization [1], enables a variety of devices [2-4] that utilize the pyroelectric current generated by temperature fluctuations. Pyroelectric materials are used in applications such as thermal imaging, radiometry, environmental monitoring, and gas analysis, all of which rely on bulk ferroelectric materials. However, future nanoscale electronic and energy conversion devices will increasingly require thin films. Challenges facing thin film ferroelectrics include their susceptibility to size- and strain-induced effects. Over the last few decades, thin-film epitaxy has developed dramatically and it is now possible to synthesize ferroelectric thin films with control over film composition, epitaxial strain, electrical boundary conditions, and thickness [5-7]. These synthesis capabilities have been instrumental in developing an understanding of the dielectric, piezoelectric, and ferroelectric responses of thin film materials. However, understanding the pyroelectric response of thin films remains a challenge, owing to pinhole defects and trapped charges in these films [8]. The lack of understanding of pyroelectric properties in thin films has limited the development of
pyroelectric materials and new devices based on these materials. Techniques to measure pyroelectric currents and the pyroelectric coefficient of thin films are thus urgently needed in order to enable new applications of pyroelectric thin films [8-10].

Conventional techniques to characterize pyroelectric response are based on heating by a laser [11] or simply placing the material on a hotplate or in a furnace [12]. These techniques were developed for bulk ceramics or single crystals, and are adequate for large samples. The techniques using bulk sample heating have had limited success in their application to thin films due to defects in the thin films as well as thermally activated trapped charges [8,13-15]. It is possible to achieve higher rates of temperature change using, for example, laser heating. Dynamic techniques that rapidly modulate the sample temperature allow for the measurement of continuous pyroelectric current [16,17]. When the temperature change is due to continuous temperature oscillations at a single frequency, the pyroelectric current measurement accuracy can be higher than for temperature changes that are step changes, pulses, or ramps, since a periodic current can be conveniently measured using phase-sensitive detection with high signal-to-noise [8,18]. When the sample is periodically heated by a hotplate or thermoelectric element, the rate of temperature change is typically limited to ~1 K/sec. When the sample is periodically heated using laser intensity modulation, the temperature can oscillate in the range $10^3 - 10^6$ K/sec [19,20]. However there is a lack of publications showing frequency-domain pyroelectric current measurements in the range $1 - 10^3$ K/sec [21]. Furthermore, there has been little work to compare pyroelectric properties across different measurement techniques. Comparison of pyroelectric measurements using independent techniques allow validation of the experimental results in the absence of any baseline measurements of thin film pyroelectric properties. It can be difficult, however, to compare pyroelectric property measurements across different techniques,
since this comparison requires accurate measurements of the thermal properties of the pyroelectric thin film, which are in general not independently measured. Thus there remains significant unmet needs for pyroelectric property measurements on solid state thin films.

Here we present frequency-domain measurements of pyroelectric currents from thin films of PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} (PZT). 150 nm thick PZT films were grown on DyScO\textsubscript{3} (DSO) (110) single crystal substrates with 20 nm SrRuO\textsubscript{3} (SRO) bottom electrodes via pulsed-laser deposition (see Figure 3.1 for X-ray diffraction and atomic force microscopy image of the as-grown films) [22]. We independently measure the thermal properties of the pyroelectric thin films using time domain thermoreflectance, [23] allowing accurate estimates of the temperature distribution within the sample. The thermal properties of the pyroelectric thin films allows us to estimate the temperature distribution within the film. The pyroelectric current measurements use either bulk heating for low frequency periodic (LFP) measurements; microfabricated resistive heaters for 2ω measurements; or a chopped laser beam for laser intensity modulation (LIM) measurements. We measure the pyroelectric coefficient of the thin-film samples in three different frequency regimes: less than 1 Hz (LFP), from 10 Hz to 1 kHz (2ω), and above 100 kHz (LIM). We compare these techniques to each other and to the widely used direct method [12] for pyroelectric current measurement.
Figure 3.1 (a) X-ray diffraction pattern showing (00$l$) oriented films. (b) Atomic force microscopy image of a 150 nm thick PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film on SrRuO$_3$/DyScO$_3$ (110). The RMS roughness of the film was 0.3 nm. Film growth temperature was 630 °C.
3.2 Direct and Low Frequency Periodic Measurements

Figure 3.2 illustrates pyroelectric measurement using the direct [12] and LFP methods [16,17]. The sample consisted of 100 µm diameter axisymmetric capacitors with a 80 nm SRO / 150 nm PZT / 20 nm SRO device structure produced via a MgO hard-mask process (Figure 3.2a) [24]. A current amplifier mounted close to the sample measured the current from the top SRO electrode during heating, while the sample was mounted in a dark faraday cage to reduce environmental noise. Figure 3.2b shows the direct measurement temperature and current profiles. We increased the temperature at a constant rate from 300 to 350 K in 300 s, and then held the temperature at 350 K for 100 s before the heater was turned off such that the sample could cool. A linear temperature ramp should result in a constant, non-zero pyroelectric current \( i_p = pA\frac{dT}{dt} \), where \( p \) is the pyroelectric coefficient, \( A \) is the area of the electrode and \( dT/dt \) is the rate of change of temperature with time, in this case 0.16 K/sec. The measured current is however not constant with a constant temperature rate, and there is non-zero current when the temperature is constant. This data illustrates the difficulty in measuring pyroelectric response using conventional direct measurement techniques. Although some of the current is pyroelectric, there are non-pyroelectric currents, most likely resulting from thermally-stimulated currents that result from temperature-induced releasing of trapped charges [13-16,25]. This effect is a particular problem for thin films, where the density of trapped charges can be larger than in bulk samples.

Figure 3.2c shows the temperature and current for pyroelectric measurement using the LFP method. A sinusoidal temperature oscillation with a background temperature of 320 K (\( T_b \)) and 1.25 K (\( T_0 \)) amplitude, was applied to the sample at 0.02 Hz (\( \omega = 0.125 \) rad/sec). The sample temperature is \( T = T_b + T_0\sin(\omega t) \) and the theoretical pyroelectric current is \( i_p = pAT_0\omega\cos(\omega t) \).
Thus, the pyroelectric current should be phase-shifted from the temperature oscillations by 90°. The measured pyroelectric current was fitted to a sine function, $i_0 \sin(\omega t + \phi)$, to extract the magnitude, $i_0$, and phase of the pyroelectric current with respect to the temperature oscillation, $\phi$. The pyroelectric coefficient was then obtained by considering the out-of-phase component of the measured current as $p = i_0 \sin(\phi)/AT_0\omega$. While the LFP technique works reasonably well for this thin film, precise control of the sample temperature is difficult and the measurement must be performed at low heating frequencies to ensure thermal equilibrium, which results in a low pyroelectric current and signal-to-noise ratio. One advantage of these direct measurements is that the sample is in thermal equilibrium, and so the temperature can be estimated without detailed knowledge of the pyroelectric thin film thermal properties.
Figure 3.2 (a) Setup for pyroelectric measurement using the (b) direct and (c) low frequency periodic (LFP) method. The direct method uses a linear temperature ramp. The LFP method uses low frequency sinusoidal temperature oscillation. Resulting pyroelectric current is shown. The direct measurement showed contribution from non-pyroelectric current. The LFP measurement used an oscillatory temperature with ≈1.25 K amplitude and 0.02 Hz frequency. Amplitude of resulting pyroelectric current was less than 1 pA.
3.3 2ω Method

The 2ω method utilized periodic heating of a metal line heater to generate temperature fluctuations in the pyroelectric film. The heater was integrated with the pyroelectric film in a microfabricated platform that allowed sinusoidal temperature oscillations via joule heating and pyroelectric current measurement.

3.3.1 Device design and fabrication

The device design, shown in Figure 3.3, includes a 20 µm wide, 1.4 mm long Pt line heater line. The heater line sits atop a SiO$_2$ layer over the pyroelectric thin film. The SRO bottom electrode and pyroelectric layers underneath the contact pads are removed to prevent capacitive coupling between top and bottom electrodes. The low dielectric constant SiO$_2$ series capacitance between the metal line and pyroelectric film minimizes voltage-induced higher order effects that interfere with the pyroelectric signal.

Devices with 150 nm thick PZT were fabricated on DSO substrates. First, e-beam evaporated MgO was selectively deposited, in the regions that fall under the contact pads, using a lift-off process. Next, the 150 nm thick PZT / 20 nm SRO heterostructure was deposited using pulsed-laser deposition. The PZT/SRO layer was then lifted off by etching the underlying MgO in phosphoric acid. Next, an 80 nm thick blanket layer of plasma enhanced chemical vapor deposition (PECVD) SiO$_2$ was deposited. The lift-off mask for the heater structure with contact pads was defined using photolithography. We used 150 nm sputtered platinum, with 10 nm chromium adhesion layer, for the metallization step.
The sample was secured in a ceramic electronic package. Connections to the contact pads were made via wire-bonds. Silver paint was used to contact the SRO bottom electrode after scratching the top layers.

Figure 3.3 (a) Schematic of the device for pyroelectric measurements using the $2\omega$ method. (b) Optical image of a fabricated sample with five devices.
3.3.2 2ω Measurement

Figure 3.4a shows the measurement setup for pyroelectric measurement using the 2ω method. Periodic electrical excitation of a 20 µm wide platinum strip with chromium adhesion layer at frequency \( \omega \) produces a temperature oscillation at a frequency 2\( \omega \) [26]. This temperature oscillation generates a pyroelectric current that is measured using the current input (10^6 V/A gain) of a lock-in amplifier [27]. The SiO\(_2\) layer deposited on the pyroelectric film ensures that the external electric field across the pyroelectric film is negligible and does not interfere with the pyroelectric response of the thin film. We verified that the resulting signal was due to periodic heating of the metal strip and not a voltage-based artifact by comparing the 2\( \omega \) current measured at different strip biases but with the same heating power using a series resistor before or after the metal strip.

The equivalent circuit shown in the top-right of Figure 3.4a relates the measured 2\( \omega \) current to the pyroelectric current. The pyroelectric layer is modeled as a current source in parallel with a dielectric, which is a resistor and capacitor in parallel [28,29]. The SiO\(_2\) passivation layer is represented by an equivalent resistance and capacitance. The pyroelectric current, \( i_{p,2\omega} \), is evaluated from the measured 2\( \omega \) current, \( i_{2\omega} \), as

\[
i_{p,2\omega} = i_{2\omega} \left( \frac{Z_p}{Z_p + Z_d} \right)^{-1},
\]

where \( Z_p = \frac{R_p}{1 + j(2\omega)R_pC_p} \) and \( Z_d = \frac{R_d}{1 + j(2\omega)R_dC_d} \). The resistance (R), capacitance (C) and electrical impedance (Z) of the pyroelectric (PZT) and dielectric (SiO\(_2\)) films are indicated by the subscripts \( p \) and \( d \), respectively. The resistivity and dielectric constant of the PZT and SiO\(_2\) films were measured independently to evaluate intrinsic resistance and capacitance.
Since the heating frequency is low (<2 kHz) and the thermal penetration depth is much larger than the film thicknesses, the heat diffusion is one-dimensional in the radial direction. We use this model to relate electrical power input with the resulting temperature oscillations as in the $3\omega$ method [30,31]. The frequency-dependent temperature oscillations of the semi-infinite substrate due to the line heat source of width $2b$ and length $l$ is given by [32]

$$
\Delta T_s = \frac{P}{l\pi \Lambda_s} \int_0^{\infty} \frac{\sin^2(kb)}{(kb)^2(k^2 + q^{-1})^{3/2}} dk ,
$$

(3.2)

where $q^{-1} = (D/2\omega)^{1/2}$ is the thermal penetration depth, $j = \sqrt{-1}$, $P$ is the input power, $D$ is the thermal diffusivity, and $\Lambda_s$ is the substrate thermal conductivity. The thin films between the metal line and substrate each add a frequency-independent temperature oscillation given by [33]

$$
\Delta T_f = \frac{P}{l\Lambda_f} t ,
$$

(3.3)

where $t$ is the film thickness and $\Lambda_f$ is the film thermal conductivity, which was measured using time domain thermoreflectance [23]. The temperature oscillation of the PZT film can then be evaluated by adding the contributions from the substrate, SRO layer and half the PZT layer, $\Delta T = \Delta T_s + \Delta T_{f(SRO)} + \frac{1}{2} \Delta T_{f(PZT)}$. The pyroelectric current, $i_p = pA(dT/dt)$, can thus be written as a function of temperature oscillation $\Delta T$ at a frequency $2\omega$ as

$$
i_{p,2\omega} = jpA(2\omega)\Delta T .
$$

(3.4)

Figure 3.4b shows the amplitude of the temperature oscillation and the magnitude of measured pyroelectric current measured as a function of heating frequency for an input heating power of 4.26 W per unit length (m). The solid lines show the predicted amplitude of the temperature oscillation (Eqs. 3.2 and 3.3) and the magnitude of the pyroelectric current (Eq. 3.4). The symbols show the pyroelectric current obtained from the $2\omega$ current measurement (Eq. 3.1).
The pyroelectric coefficient is the only free parameter and is obtained by fitting the model to the measured data. Pyroelectric current magnitude of >1 nA was measured in comparison to <1 pA for the LFP method.

Figure 3.4 (a) Setup for pyroelectric measurement using the $2\omega$ method. A lock-in amplifier measures the pyroelectric current at frequency $2\omega$ generated due to a temperature oscillation caused by electrical excitation at frequency $\omega$. The pyroelectric layer is modeled as a current source with intrinsic resistance and capacitance as shown in the equivalent circuit (top-right). (b) Magnitude of pyroelectric current and temperature oscillation amplitude plotted as a function of heating frequency. A constant pyroelectric coefficient was used to fit the theoretical model and experiment. Data is shown for 4.26 W/m input power per unit heating length.
3.3.3 Pyroelectric current versus $\Delta T$

Figure 3.5 shows the magnitude of the pyroelectric current versus the amplitude of the temperature oscillation estimated by the theoretical model. Results obtained for three heating frequencies - 20 Hz, 200 Hz and 2 kHz, are shown. For each heating frequency, four sets of $\Delta T$ correspond to four different input powers. Measured pyroelectric current varies linearly with heating frequency, as expected from Equation 3.4. It is challenging to achieve temperature oscillation amplitudes less than $\sim$1 K using a traditional heating setup, as in the direct and LFP techniques. Temperature oscillation amplitudes less than 0.01 K were achieved for the $2\omega$ measurement. In addition, pyroelectric current <1 pA is expected for the low heating frequencies achievable using hotplates and ovens, which is difficult to measure precisely. We measure pyroelectric current greater than 10 nA in magnitude for 2 kHz heating frequency.
Figure 3.6 shows the phase of the pyroelectric current and temperature oscillation as a function of heating frequency for the $2\omega$ method. The symbols represent the phase of the pyroelectric current measured through a lock-in amplifier. The solid lines show the predicted phase of temperature oscillation (Eqs. 3.2 and 3.3) and pyroelectric current (Eq. 3.4). The phase is calculated with reference to the power input into the heater line. The difference in phase of the pyroelectric current and temperature oscillation should be $90^\circ$. This is observed in results from the $2\omega$ method shown for 4.26 W/m input power per unit heating length.

### 3.3.4 Pyroelectric current and $\Delta T$ phase

Figure 3.5 shows the magnitude of the pyroelectric current plotted as a function of temperature oscillation amplitude for three specific heating frequency values. The four data points in each series correspond to the heating power amplitudes 0.07, 0.27, 1.07 and 4.26 W per unit heating length (m) (from left to right). An increase in the heating frequency by a decade corresponds to a decade increase in the magnitude of pyroelectric current.
3.3.5 Property values for modeling

Table 3.1 shows the thermal and electrical property values used in theoretical models. The thermal conductivities of PZT, SRO thin films and DSO substrates were measured using time-domain thermoreflectance. The heat capacity of the DSO substrate was assumed equal to that of SrTiO$_3$ single crystalline substrate. Thermal conductivities of SiO$_2$, PZT, and SRO thin films are used to evaluate their respective temperature oscillation contributions (Eq. 3.3).

The intrinsic capacitance and resistance of SiO$_2$ and PZT layers were evaluated from their dielectric constant and resistivity values. A test sample for electrical characterization of PECVD SiO$_2$ consisted of 80 nm thick SiO$_2$ circular capacitors. Electrical characterization of PZT was performed on a sample identical to the $2\omega$ pyroelectric measurement device, but without the SiO$_2$ layer between platinum and PZT. Dielectric constant calibration was done using

\[ \text{Figure 3.6} \] Phase of the $2\omega$ pyroelectric current and temperature oscillation as a function of heating frequency. Corresponding amplitudes of pyroelectric current and temperature oscillation are shown in Figure 3.4b. Solid lines show the results from the theoretical model.
capacitance-voltage measurements with maximum ac-drive amplitude of 0.2 V at 1 kHz. Current-voltage measurements were performed in the 0 – 1 V\textsubscript{RMS} range, using a lock-in amplifier, to characterize SiO\textsubscript{2} and PZT electrical resistivity. Capacitance and resistance of individual layers were used estimate the pyroelectric current from the measured 2\omega current based on the equivalent circuit shown in Figure 3.4a (Eq. 3.1).

<table>
<thead>
<tr>
<th></th>
<th>PECVD SiO\textsubscript{2}</th>
<th>PZT</th>
<th>SRO</th>
<th>DSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
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<td>1.5</td>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>Heat Capacity (J/m\textsuperscript{3}-K)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7 \times 10\textsuperscript{6}*</td>
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<tr>
<td>Dielectric Constant</td>
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<td>-</td>
</tr>
<tr>
<td>Resistivity (\Omega-m)</td>
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<td>2.47 \times 10\textsuperscript{7}</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.1** Thermal and electrical property values used for modeling.

### 3.4 Laser Intensity Modulation Measurements

Pyroelectric characterization at an even higher frequency range is possible using laser diagnostics. Figure 3.7a shows the measurement setup used for pyroelectric measurement using a modulated laser as a local heat source. Previous publications reported the pyroelectric response of thin-films using laser intensity modulation but lacked accurate thermal property values required to fully analyze the data [11,19,20]. Improvements in laser-based diagnostics now enable more accurate measurements [23]. Our LIM method probes the pyroelectric response of the thin film using a Ti:sapphire laser oscillator with a repetition rate of 80 MHz. Using an
electro-optical modulator, the laser beam was modulated from 100 kHz – 1.3 MHz and the pyroelectric response was probed with a spatial resolution of <10 µm. Measurements were done on capacitors consisting of 180 nm thick PZT, with SRO bottom electrode and 20 µm wide, 1.4 mm long platinum top electrodes with a chromium adhesion layer. The platinum top electrode (optical absorption coefficient = 0.29, at a wavelength of 785 nm) absorbed the laser power to raise the temperature. The periodic modulation of the laser beam causes periodic temperature oscillation within the film. This temperature oscillation generates a pyroelectric current at the modulation frequency which is measured using a lock-in amplifier. For a heating frequency >100 kHz, the thermal penetration depth is small compared to the $1/e^2$ radius of the laser beam ($w_0 = 4.7 \, \mu m$). Hence, the temperature oscillation amplitude of the substrate is given by a one-dimensional heat flow model with a uniform heat flux $P/(\pi w_0^2)$ [23],

$$\Delta T_s = \frac{P}{\pi w_0^2 \sqrt{j\omega \Lambda_s C_s}}, \quad (3.5)$$

where $C_s$ is the volumetric heat capacity of the substrate. The temperature oscillation of the PZT film can be evaluated by including the contributions from the SRO layer and half the PZT layer using Equation (3), $\Delta T = \Delta T_s + \Delta T_{f(SRO)} + \frac{1}{2} \Delta T_{f(PZT)}$. The resulting pyroelectric current is

$$i_p = j\rho (\pi w_0^3) \omega \Delta T. \quad (3.6)$$

Figure 3.7b shows the amplitude of temperature oscillation and pyroelectric current as a function of the laser modulation frequency. The laser power absorbed by the sample was 1.3 mW. Temperature oscillation amplitude was estimated using Equations 3.3 and 3.5. The model (Eq. 3.6) was fitted to the measured pyroelectric current to estimate the pyroelectric coefficient of the PZT thin film. One value of the pyroelectric coefficient was used in the model for fitting across the entire heating frequency range. At high frequencies, the capacitive reactance of the sample
decreases significantly. Since the model does not account for the sample capacitance, we observe a mismatch between the measured and predicted pyroelectric current at high heating frequencies. This LIM method allowed quantitative characterization of sub-micron epitaxial pyroelectric layers at high frequency with a spatial resolution < 10 µm.
Figure 3.7 (a) Setup for laser intensity modulation (LIM) based pyroelectric measurement. The laser power absorbed by the sample was 1.3 mW and the $1/e^2$ radius of the beam was 4.7 µm. An RF lock-in amplifier measures the pyroelectric current at the laser modulation frequency. (b) Magnitude of pyroelectric current and temperature oscillation amplitude as a function of modulation frequency. A constant pyroelectric coefficient was used to fit the theoretical model and experiment.
3.5 Results and Discussion

Our measurements span heating frequencies from 0.02 Hz to 1.3 MHz. Figure 3.8a shows the magnitude of the pyroelectric current per unit heating area as a function of time rate of change of temperature for each of the three methods. The error bars correspond to standard deviation from measurements done on multiple devices across different samples. Pyroelectric current density is directly proportional to the rate of change of temperature with time $\frac{dT}{dt}$. The pyroelectric current density increases by eight orders of magnitude as the time rate of change of temperature varies from 0.018 K/sec for the LFP method to $3.1 \times 10^6$ K/sec using the LIM method.

Figure 3.8b compares the phase difference between the measured pyroelectric current and estimated temperature oscillation as a function of rate of heating for the three methods. The phase difference for the LFP method is calculated from the time traces of the temperature and current oscillations. Since the phase of the pyroelectric current was not known explicitly with reference to the (laser) power input for the LIM method, the pyroelectric current phase was obtained by subtracting the phase of the measured current from the reference phase measured in the absence of any sample.

The true pyroelectric current is phase-shifted from the temperature oscillations by 90° [16]. However, a non-90° phase-shift is commonly observed due to thermally stimulated current and other artifacts. Our measurements show that the phase difference is nearly 90° for the $2\omega$ method, whereas a noticeable deviation is observed for the LFP measurements. We believe that this deviation in phase difference is due to the release of trapped charges due to bulk heating of the sample in the LFP technique that occurs in phase with the temperature change. For the LIM method, sample capacitance causes a phase shift between the phase of heating (laser...
modulation) and the phase of the measured pyroelectric current. This is not accounted for in our simplified model and hence the discrepancy in the phase data at high heating frequencies.

Figure 3.9 shows the measured pyroelectric coefficients of PZT 20/80 thin films on DSO substrate as a function of heating rate. The figure shows results from the LFP, 2ω, and LIM measurements, but it was not possible to estimate the pyroelectric coefficient using the direct method because of the significant thermally stimulated current contribution. Unlike the model results shown in Figure 3.4b and 3.7b, where a single pyroelectric coefficient was used in the model across the entire heating frequency range, pyroelectric coefficients were estimated by fitting the theoretical model to the measured pyroelectric current at each heating frequency. The measured pyroelectric coefficient is nearly constant at \(-200 \, \mu\text{C/m}^2\text{K}\) across a large range of heating rates, which is close to \(-180 \, \mu\text{C/m}^2\text{K}\) reported for poled PZT 20/80 films deposited via spin coating [34]. The pyroelectric response is essentially unchanged up to 1 MHz, which is consistent with other frequency-dependent measurements reported in the literature [35,36]. The observed reduction in the pyroelectric coefficient magnitude near 1 MHz heating frequency can be attributed to capacitive effects not included in the modeling. While there may be thermomechanical-induced strains in the pyroelectric layer, any currents generated by these strains are small relative to the pyroelectric currents observed here.
Figure 3.8 (a) Magnitude of pyroelectric current density and (b) phase difference between pyroelectric current and temperature oscillation plotted as a function of rate of temperature change for LFP, $2\omega$ and LIM measurements.
3.6 Conclusion

We have demonstrated three frequency-domain techniques for measuring pyroelectric currents from PZT thin films using temperature oscillations over the range 0.02 Hz to 1.3 MHz. Measurements using low frequency 1.25 K temperature oscillations produce pyroelectric current less than 1 pA which is below the noise floor of most measurement setups. Developed specifically for thin films, the $2\omega$ method, proved more robust as it produced easily measurable pyroelectric current greater than 1 nA between 20 Hz - 2 kHz heating frequencies. An even higher heating frequency regime was made accessible by using a laser-based method that resulted in pyroelectric currents of ~100 nA. These techniques enable the study of pyroelectric
thin films, which could improve future nanoscale electronics and energy conversion devices using these films.
3.7 References


Chapter 4
High Power Density Pyroelectric Energy Conversion from BaTiO$_3$ Thin Films

4.1 Introduction
Pyroelectric energy conversion relies upon the temperature dependence of electric displacement in order to convert temperature fluctuations into electrical energy [1]. Unlike thermoelectric energy conversion which has been extensively investigated, [2,3] pyroelectric energy conversion has received considerably less attention, due to low energy and power densities [4,5]. The energy output can be improved significantly by using modern approaches to pyroelectric energy conversion that rely on thermal-electrical cycles in comparison with direct pyroelectric effect which utilizes only thermal cycles [6].

A pyroelectric energy conversion cycle generates electrical work from the temperature ($T$) and electric field ($E$) driven changes in the electric displacement ($D$) of the pyroelectric material. The first theoretical studies of pyroelectric energy conversion claimed that pyroelectric energy conversion has unacceptably poor performance, with maximum possible energy conversion efficiency below 1% [7,8]. Subsequent experiments showed that thermal-electrical cycles can
achieve power density \(0.11 \text{ W/cm}^3\), energy density \(1 \text{ J/cm}^3\), and efficiency of \(\sim 5\%\) of the Carnot limit [9-11]. The key to this improved performance was the utilization of thermal-electrical cycles operating close to the ferroelectric phase transition at high electric fields. Table 4.1 shows a representative list of experimental studies of pyroelectric energy conversion using thermodynamic cycles. Most publications have focused on pyroelectric energy conversion in bulk samples [6,10,12-14] and thick polymer films [15-17] with thermal cycling rates typically slower than 1 Hz [9,13,18]. There has been a lack of research on pyroelectric energy conversion at high cycle rates.

In this chapter we report high power pyroelectric energy conversion from 200 nm thick films of BaTiO\(_3\) using the pyroelectric Ericsson cycle. The power density is as high as \(30 \text{ W/cm}^3\), more than 100 times larger than previously reported for pyroelectric cycles, and comparable to that of bulk thermoelectrics [19]. In bulk pyroelectric materials, the power density is fundamentally limited by the rate of heat transfer through the pyroelectric material, as well as practical limits on the maximum applied electric field [20]. The nanometer-scale pyroelectric film allows us to overcome these limitations, with thermal and electrical cycling as fast as 3 kHz, combined with applied electric field as high as 125 kV/cm. Under these conditions, the power density of pyroelectric energy conversion is not governed by heat transfer or electric field, but rather by dielectric losses.
<table>
<thead>
<tr>
<th>Pyroelectric Material</th>
<th>Thermal cycling method</th>
<th>Temperature range (°C)</th>
<th>E-field range (kV/cm)</th>
<th>$dT/dt$ range (°C/sec)</th>
<th>Energy density (J/cm$^3$)</th>
<th>Power density (W/cm$^3$)</th>
<th>$\eta_T/\eta_C$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZST single crystal</td>
<td>Pumping hot/cold fluid</td>
<td>146 – 159</td>
<td>0 – 28</td>
<td>1.76</td>
<td>0.1</td>
<td>0.014</td>
<td>-</td>
<td>[12]</td>
</tr>
<tr>
<td>P(VDF-TrFE) film</td>
<td>Hot and cold water baths</td>
<td>40 – 97</td>
<td>70 – 348</td>
<td>-</td>
<td>0.279</td>
<td>-</td>
<td>37.5%</td>
<td>[21]</td>
</tr>
<tr>
<td>PZN-PT single crystal</td>
<td>Hot and cold oil baths</td>
<td>100 – 130</td>
<td>0 – 20</td>
<td>30</td>
<td>0.106</td>
<td>0.106</td>
<td>-</td>
<td>[13]</td>
</tr>
<tr>
<td>P(VDF-TrFE) film</td>
<td>Pumping hot/cold fluid</td>
<td>70 – 87</td>
<td>202 – 739</td>
<td>3.66</td>
<td>0.13</td>
<td>0.011</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>P(VDF-TrFE) film</td>
<td>Hot and cold metal blocks</td>
<td>25 – 110</td>
<td>200 – 350</td>
<td>5.61</td>
<td>0.155</td>
<td>0.01</td>
<td>-</td>
<td>[22]</td>
</tr>
<tr>
<td>P(VDF-TrFE) film</td>
<td>Switchable liquid interfaces</td>
<td>40 – 100</td>
<td>100 – 400</td>
<td>36</td>
<td>0.25</td>
<td>0.11</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>PLZT ceramic</td>
<td>Hot and cold oil baths</td>
<td>30 – 200</td>
<td>2 – 70</td>
<td>10.2</td>
<td>1.014</td>
<td>0.048</td>
<td>-</td>
<td>[10]</td>
</tr>
<tr>
<td>BaTiO$_3$ thin film</td>
<td>Microfabricated heater</td>
<td>20 – 120</td>
<td>100 – 125</td>
<td>300,000</td>
<td>0.01</td>
<td>30</td>
<td>0.03%</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 4.1 Representative list of energy conversion measurements using the pyroelectric Ericsson cycle.
4.2 Pyroelectric Ericsson Cycle

Figure 4.1 shows the pyroelectric Ericsson cycle consisting of two isothermal and two isoelectric processes [6,12]. The cycle is completed by first applying an electric field aligned with the polar axis of the BaTiO$_3$ film such that the electrical displacement is increased at a constant temperature (A-B). Next, the temperature is increased at constant electric field (B-C) thereby decreasing the electric displacement. From here the electric field is decreased (C-D), again lowering the electric displacement. And finally, the film is cooled back to the starting temperature and recovers the initial electric displacement (D-A). Each displacement change results in a current in the external circuit. Table 4.2 shows the analytical expressions for the electric displacement, entropy, electric energy and heat for the four-step pyroelectric Ericsson cycle. The net electric work includes the pyroelectric contribution

$$E_{BC} \int_{T_s}^{T_c} p_{BC} dT + E_{DM} \int_{T_d}^{T_s} p_{DM} dT$$

and the dielectric contribution

$$\int_{E_s}^{E_q} e_{AB} EdE + \int_{E_c}^{E_q} e_{CD} EdE$$

where $p = \left(\frac{dD}{dT}\right)_E$ is the pyroelectric coefficient and $e = \left(\frac{dD}{dT}\right)_T$ is the dielectric permittivity. The heat input includes the energy required to change the electric displacement

$$T_{AB} \int_{T_s}^{T_c} p_{AB} dE + T_{CD} \int_{T_c}^{T_d} p_{CD} dE$$

and that required to heat the lattice

$$\int_{T_s}^{T_c} c_{BC} dT + \int_{T_d}^{T_s} c_{DA} dT$$

where $c = \left(\frac{dU}{dT}\right)_E$ is the heat capacity and $U$ is the internal energy. The thermodynamic efficiency is the net work out divided by the heat in and is limited by the large irreversible lattice heat contribution [23].
Table 4.2 Thermodynamic quantities for the pyroelectric Ericsson cycle. [6]

<table>
<thead>
<tr>
<th></th>
<th>AB</th>
<th>BC</th>
<th>CD</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric displacement</td>
<td>( \int_{E_A}^{E_B} \varepsilon_{T,ab} dE )</td>
<td>( \int_{T_B}^{T_C} p_{E,BC} dT )</td>
<td>( \int_{E_C}^{E_D} \varepsilon_{T,CD} dE )</td>
<td>( \int_{T_D}^{T_2} p_{E,DA} dT )</td>
</tr>
<tr>
<td>Entropy</td>
<td>( \int_{E_A}^{E_B} p_{T,ab} dE )</td>
<td>( \int_{T_B}^{T_C} c_{E,BC} \frac{dT}{T} )</td>
<td>( \int_{E_C}^{E_D} p_{T,CD} dE )</td>
<td>( \int_{T_D}^{T_2} c_{E,DA} \frac{dT}{T} )</td>
</tr>
<tr>
<td>Electric energy</td>
<td>( \int_{E_A}^{E_B} \varepsilon_{T,ab} E dE )</td>
<td>( \int_{T_B}^{T_C} p_{E,BC} dT )</td>
<td>( \int_{E_C}^{E_D} \varepsilon_{T,CD} E dE )</td>
<td>( \int_{T_D}^{T_2} p_{E,DA} dT )</td>
</tr>
<tr>
<td>Heat</td>
<td>( \int_{E_A}^{E_B} T_{AB} p_{T,ab} dE )</td>
<td>( \int_{T_B}^{T_C} c_{E,BC} dT )</td>
<td>( \int_{T_D}^{T_{CD}} T_{CD} p_{T,CD} dE )</td>
<td>( \int_{T_D}^{T_2} c_{E,DA} dT )</td>
</tr>
</tbody>
</table>
4.3 Measurement Platform

Pyroelectric energy conversion requires synchronized temperature and electrical cycles, with faster cycle rates leading to higher power output. Figure 4.2 shows a microfabricated platform that allows rapid switching of the temperature and electric fields. The device consists of a BaTiO$_3$ thin-film capacitor of area $500 \times 20 \, \mu$m$^2$, with epitaxial top and bottom SrRuO$_3$ electrodes, fabricated via pulsed-laser deposition on a GdScO$_3$ (110) single crystal substrate. A blanket layer of SiO$_2$ covers the pyroelectric capacitor with windows to access the top and bottom SrRuO$_3$ electrodes. A 15 µm wide, 440 µm long platinum line sits atop the electrically insulating SiO$_2$ layer and serves as the heater.

The 50 nm SrRuO$_3$ / 200 nm BaTiO$_3$ / 50 nm SrRuO$_3$ heterostructures were deposited on GdScO$_3$ substrates by pulsed-laser deposition employing a KrF excimer laser (wavelength = 248nm) using BaTiO$_3$ and SrRuO$_3$ ceramic targets (Praxair Inc.). The BaTiO$_3$ layer was deposited at 600 °C in 20 mTorr of oxygen, at laser repetition rates of 2 Hz and a laser fluence of 1.6 J/cm$^2$. The SrRuO$_3$ layer was deposited at 630 °C in 100 mTorr of oxygen, at laser repetition

![Figure 4.2 Schematic of the microfabricated device and setup used to implement the Ericsson cycle on a 200 nm thick BaTiO$_3$ film.](image)
rates of 12 Hz and laser fluence of 1.8 J/cm². Following growth, films were cooled to room temperature at an oxygen pressure of 760 Torr. X-ray diffraction of the as-grown films indicates single phase (00l) oriented films (Figure 4.3a). Figure 4.3b shows the atomic force microscope (AFM) topography of the deposited BaTiO₃ film before the top SrRuO₃ electrode deposition. The RMS roughness of the film was 1.1 nm.

![Figure 4.3](image)

**Figure 4.3** (a) X-ray diffraction pattern of a 150 nm thick BaTiO₃ film on SrRuO₃/GdScO₃. (b) 5 µm×5 µm AFM height image of the BaTiO₃ film.

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4.4 Energy Conversion Measurements

The pyroelectric Ericsson cycle was realized by controlling the time-dependent temperature and external electric field across the BaTiO$_3$ film. A periodic voltage applied to the platinum heater causes resistive heating, which results in a periodic temperature oscillation (Figure 4.4). The temperature amplitude was estimated from the solution of the heat diffusion equation (see Chapter 5 for details) [24]. A periodic electric field, phase-synced with the heating, applied across the film thickness completes the cycle. The film electric displacement changes in response to variations in temperature (pyroelectric contribution) as well as electric field (dielectric contribution). This electric displacement change is calculated in real time by integrating the current measured from the bottom SrRuO$_3$ electrode. Figure 4.5 shows the Ericsson cycle between 20 and 100 °C at a 1 kHz cycle frequency and the corresponding isothermal ferroelectric hysteresis loops. The ferroelectric hysteresis loops progress in a counterclockwise fashion, which represents electricity dissipation as heat [25]. The Ericsson cycle, however, progresses in a clockwise fashion and represents electricity generation from heat.

The practical implementation of energy conversion cycles required synchronous heating and electric field. The low temperature for all cycles was 20 °C. The temperature oscillation amplitude at a particular heating frequency was varied between 50 – 100 °C by varying the input sinusoidal heating voltage across the platinum strip. A step voltage, phase-synced with the heating bias, was applied to the top SrRuO$_3$ electrode. The Ericsson cycle upper voltage across the 200 nm film was maintained at 2.5 V and the lower voltage was varied from 2.25 to 1.25 V. The voltage across the film thickness was switched between the high and low limits at the estimated temperature maxima and minima. The slew rate for the voltage step at 1 kHz cycle frequency was 6.85 kV/s. The electric displacement of the pyroelectric film was estimated by
numerical integration of the ac current measured from the bottom SrRuO$_3$ electrode using a current-to-voltage converter. The heating bias, external voltage across the film thickness and the current from the bottom electrode were acquired using an oscilloscope. The area of the resulting electric displacement-applied electric field loop was used to estimate the electric energy density.

Figure 4.4 Estimated film temperature, applied electric field, resulting current and electric displacement change versus time.
4.5 Results and Discussion

The pyroelectric Ericsson cycle can produce either a net positive or a net negative electrical work out, depending upon the operating conditions. Figure 4.6 shows the pyroelectric Ericsson cycle realized in our device for a range of applied electric fields (ΔE), temperature oscillation amplitudes (ΔT), and cycle frequencies. Figure 4.6a shows Ericsson cycles with a maximum electric field of 125 kV/cm and different minimum electric fields. Larger values of ΔE generate counterclockwise cycles that correspond to net work in (heat dissipation), while smaller values of ΔE generate clockwise cycles that correspond to net work out (electricity generation). The sign of the work, net in or out, depends upon the competition between the pyroelectric contribution and the counteracting dielectric loss originating from different dielectric constants at 20 °C and 100 °C. Similar crossing-over of the Ericsson cycles at large ΔE were reported for a

Figure 4.5 Measured Ericsson cycle shown on a D-E plot alongside hysteresis loops (inset) at low and high temperatures.
bulk single crystal ferroelectric operating near the morphotropic phase boundary or operating at a cycle rate faster than the thermal time constant [13,14]. In our system, the dielectric loss can be attributed to large $\Delta E$ and relatively low resistivity ($\sim 10^8 \, \Omega$-cm). The net electrical work out also depends upon $\Delta T$ (Figure 4.6b) and cycle frequency (Figure 4.6c). Increasing the $\Delta T$, while maintaining the same $\Delta E$ and fixing the low temperature at 20 °C, results in an increase in electric displacement change due to the pyroelectric effect. However changing the cycle frequency, for a given $\Delta E$ and $\Delta T$, results in no significant change in the pyroelectric and dielectric response of the material [26].

The energy density and power density of the pyroelectric Ericsson cycle depends upon the operating conditions. Figure 4.7a shows the measured energy density as a function of $\Delta T$, which can be positive or negative, depending upon $\Delta E$ as discussed above. Figure 4.7b shows the measured energy density as a function of the cycle frequency. The energy density is about the same for 300 Hz and 1 kHz, and is negative for the highest and lowest frequencies. At 100 Hz, the negative energy density is likely due to electrical losses in the pyroelectric film. At 10 kHz, the negative energy density is due to operation faster than the device thermal time constant. The thermal penetration depth is larger than the BaTiO$_3$ film thickness, resulting in a near uniform temperature field in the device, for all but the highest operating frequencies [27]. Figure 4.7c shows the power density as a function of cycle frequency, calculated by multiplying the energy density per cycle with the number of cycles per unit time. The power density is directly proportional to the cycle frequency until the apparent drop at high frequency.

A maximum power density of 30 W/cm$^3$ was measured at 3 kHz cycle frequency for a temperature range of 20 – 120 °C and an electric field range of 100 – 125 kV/cm. This power density is significantly greater than the maximum previously reported for pyroelectric cycles of...
0.11 W/cm$^3$ [9]. However, the corresponding energy density was only $\sim$0.01 J/cm$^3$ and the efficiency was $\sim$0.03% of Carnot. This energy density is less than has been reported for low cycle frequencies [10]. The low energy density and conversion efficiency was due to the relatively low pyroelectric coefficient of the BaTiO$_3$ film and large dielectric losses. The finite resistivity of the BaTiO$_3$ film also contributed to the electrical loss via leakage currents [21]. While the leakage current limited the net electricity generation, Joule heating in the film was very small relative to the heat input.

By shrinking our pyroelectric material to the nanometer-scale, and operating the pyroelectric cycle at high field strength and high cycle frequency, we find an operating regime where the pyroelectric energy conversion is not limited by heat transfer through the pyroelectric material. This is in stark contrast to the published literature on pyroelectric energy conversion, where energy conversion in thick films and bulk samples is limited by heat transfer in the pyroelectric material [6,12-17]. Instead, at the nanometer scale, pyroelectric energy conversion is limited by dielectric loses, which are due to the high electric fields achieved in the thin films. The significant improvement in the power density was achieved despite no significant change in the pyroelectric properties of these nanometer-thick films from its bulk values [26]. Even higher power densities are possible by using films with higher pyroelectric coefficients and engineering materials with less electrical losses and, for example, by increasing the film resistance via cation co-doping [28,29]. While further optimization is possible by matching the ferroelectric-paraelectric phase transition temperature with a particular heat source, the change in power output due to operation near the transition temperature is not significant due to the broad second order phase transition characteristic of ferroelectric thin films.
Figure 4.6 Electric displacement versus electric field. The pyroelectric Ericsson cycles are shown for different (a) $\Delta E$, (b) $\Delta T$ and (c) cycle frequencies. The clockwise cycles shown in blue represent energy generation and the counterclockwise cycles shown in red represent energy dissipation. A maximum electric field of 125 kV/cm and low temperature of 20 °C was used for all cycles.
Figure 4.7 Electric energy and power densities. (a) Measured energy density as a function of $\Delta T$ for different electric field ranges. Measured energy density (b) and power density (c) as a function of cycle frequency for different $\Delta T$. A maximum electric field of 125 kV/cm and low temperature of 20 °C was used for all cycles. The error bars for energy density were obtained using data from four cycles.
4.6 Conclusion

In conclusion, we investigated pyroelectric energy conversion in a 200 nm thick BaTiO$_3$ film using a microfabricated platform that allows synchronous thermal and electrical cycles. We achieved power densities as high as 30 W/cm$^3$, but the corresponding energy densities and thermodynamic efficiencies were only 0.01 J/cm$^3$ and 0.03% of the Carnot limit. The high power density is due to the rapid thermal cycling, enabled by the thin film and microscale thermal-electrical control. The figure of merit for any energy conversion technology depends upon its application. Here, we focus on power density, a key limitation for miniature devices and a long standing challenge for pyroelectric materials. Other figures of merit could include engineering calculations of cost per watt of generated electricity. For energy harvesting, the heat is freely available, and the cost is driven by materials and installation. The pyroelectric materials reported in our paper could be used for power generation in systems with temperature fluctuations, for example internal combustion engines, power electronics, and modern semiconductor devices [30-32].
4.7 References


[18] I. M. McKinley, R. Kandilian, and L. Pilon, "Waste heat energy harvesting using the Olsen cycle on 0.945Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-0.055PbTiO\(_3\) single crystals", *Smart Materials and Structures*, vol. 21, no. 3, p. 035015, 2012.


Chapter 5
High-Frequency Thermal-Electrical Cycles for Pyroelectric Energy Conversion

5.1 Introduction

Waste heat accounts for more than half the energy produced in the world [1]. A significant fraction of this rejected energy is at low temperature which is difficult to harvest efficiently. Thermoelectric devices that convert spatial temperature variations into electrical energy are one solution to this problem [2]. However, the relatively low efficiencies of thermoelectric materials, along with constraints on operating environments have prevented widespread adoption [3]. Other solutions include heat exchangers that convert thermal energy into useful work using a liquid or gas based thermodynamic cycle [4]. The moving parts and fluid flows required in these systems, however, cannot be easily scaled to small sizes or rapid cycle rates.

Pyroelectric energy conversion utilizes the temperature dependence of electric displacement of polar materials to convert temperature fluctuations into electrical energy [5,6]. Initial first principle studies predicted electricity generation from heat using pyroelectric
materials to be unfeasible due to energy conversion efficiencies less than 1% [7,8]. More recent studies have, however, found energy densities up to 1 J/cm³ and efficiencies as high as 5.4% of the Carnot limit using thermodynamic cycles that utilize temperature as well as electric field dependence of the electric displacement of pyroelectric materials [9,10]. The four-step pyroelectric Ericsson cycle is one such thermodynamic cycle that consists of two isothermal and two isoelectric processes [10,11]. Pyroelectric energy conversion using such thermal-electrical cycles can be particularly attractive for systems with temperature fluctuations such as internal combustion engines and power electronics that produce low-quality, low-temperature waste heat [12,13].

Investigation of pyroelectric energy conversion using thermal-electrical cycles requires a setup that can simultaneously vary the temperature and electric field across the pyroelectric material in time. Published research on pyroelectric energy conversion commonly used oil baths or pumping fluid to generate temperature oscillations in bulk samples, typically at frequencies less than 1 Hz [9,11,14-17]. Other methods of temperature control used thermal contact with hot and cold metal blocks or switchable liquid interfaces [18,19]. Desired electric fields required application of voltages as high as a few kV across the thick samples which are impractical for most applications [15,20]. Use of bulk samples with large thermal mass and coarse thermal and electrical control limited the investigation of pyroelectric energy conversion to slow changes in temperature and electric field. While some published studies have investigated the effect of temperature oscillation amplitude, electric field range and cycle frequency on pyroelectric energy conversion, very few have examined the effect of temporal variations in temperature and applied electric field [9,21,22].
This chapter presents an analysis of the transient thermal and electrical operation of pyroelectric energy conversion cycles with the goal of maximizing the output electrical energy density. We developed a microfabricated platform consisting of a 150 nm thick BaTiO$_3$ film that allows simultaneous, high-frequency thermal and electrical cycling. The device enables investigation of the energy conversion process in the pyroelectric film in response to arbitrary variations in temperature and electric field with microsecond temporal control. We studied the effect of phase shifts between heating and electric field at a cycle frequency of 1 kHz, electric field change rates between $1.42 \times 10^5$ kV/cm-s and $11.33 \times 10^5$ kV/cm-s, and temperature change rates around $6 \times 10^5$ K/s on the pyroelectric energy conversion process. Thermal-electrical cycles obtained using different temperature and electric field profiles are compared with the pyroelectric Ericsson cycle.

5.2 Pyroelectric Energy Conversion Test Platform

Figure 5.1 shows the construction and thermal-electrical operation of the pyroelectric energy conversion test platform [22]. The device consists of a BaTiO$_3$ thin-film capacitor with electrical access to top and bottom electrodes. A gold strip placed above the pyroelectric capacitor serves as the resistive heater. A high resistivity SiO$_2$ layer, sandwiched between the top electrode and heater strip, electrically insulates the pyroelectric film and minimizes interference from the heating voltage.

The pyroelectric film was integrated in the test platform using standard microfabrication techniques. Figure 5.1a shows the schematic of the device which was fabricated on a 5 mm × 5 mm × 0.5 mm GdScO$_3$ (110) substrate and the 40 nm SrRuO$_3$ and 150 nm BaTiO$_3$ films were
deposited using pulsed laser deposition [23]. The BaTiO$_3$ layer was deposited at 600 °C in 20 mTorr of oxygen at laser repetition rates of 2 Hz and a laser fluence of 1.5 J/cm$^2$. The SrRuO$_3$ layer was deposited at 640 °C in 100 mTorr of oxygen at laser repetition rates of 15 Hz and laser fluence of 1.4 J/cm$^2$. Figure 5.2a shows the x-ray diffraction and atomic force microscopy image of the as-grown films. The SrRuO$_3$ and BaTiO$_3$ layers were selectively etched by ion milling using a hard-baked photoresist mask to define the bottom electrode and active material of the ferroelectric capacitor. Next, a sacrificial MgO mask was deposited using photoresist lift-off and e-beam evaporation to define the top electrode [24]. The 80 nm thick top SrRuO$_3$ electrode was fabricated using pulsed laser deposition followed by an MgO lift-off step in phosphoric acid. Then, a 150 nm thick layer of SiO$_2$ was deposited over the 500 µm × 20 µm ferroelectric capacitor using plasma enhanced chemical vapor deposition. Freon reactive ion etching of the SiO$_2$ layer and manual scratching of the BaTiO$_3$ layer was used to access the top and bottom electrodes of the capacitor. Finally, we fabricated the 10 µm wide, 440 µm long heater strip and contact pads over the SiO$_2$ layer using sputter deposition of 10 nm Cr / 100 nm Au followed by a photoresist lift-off process.

Figure 5.1b shows the setup used to monitor the pyroelectric cycles. The BaTiO$_3$ film is represented as a dielectric capacitor in parallel with a temperature-change-rate dependent current source. The electric displacement ($D$) of the pyroelectric film varies with changes in external electric field ($E$) as well as temperature ($T$), which causes an electric current to flow in the external circuit. The pyroelectric film electric displacement change was found by numerically integrating the electric current measured from the bottom SrRuO$_3$ electrode using a current-to-voltage converter as in the virtual ground method [25]. The top SrRuO$_3$ electrode was either
grounded or maintained at a fixed voltage to decouple the heating circuit from the current measurement circuit.

Pyroelectric energy conversion cycles rely upon thermal as well as electrical response of the electric displacement. Figure 5.1c shows an illustration of the pyroelectric Ericsson cycle A-B-C-D alongside the corresponding isothermal D-E loops at the maximum and minimum temperatures. A pyroelectric Ericsson cycle comprises of two isothermal processes, A→B and C→D, and two isoelectric processes, B→C and D→A. Starting from A, the out-of-plane electric field is first increased at low temperature, increasing the electric displacement. Then, the temperature is increased while the electric field is held constant at a high value, resulting in a decrease in the electric displacement. Next, the electric field is reduced to its low value at high temperature, again decreasing the electric displacement. Finally, the clockwise cycle is completed by lowering the temperature to its original value at a constant low electric field. The area of the cycle A-B-C-D represents the total electrical energy density output from the pyroelectric cycle.
Figure 5.1 (a) Schematic of the microfabricated device consisting of a 150 nm thick BaTiO$_3$ film and (b) the setup used to implement pyroelectric thermal-electrical cycles. (c) Illustration of the four-step pyroelectric Ericsson cycle on an electric displacement versus electric field plot superimposed on $D$-$E$ loops shown at the extreme temperatures.
Figure 5.2 (a) X-ray diffraction pattern showing single phase (00l) oriented films. Inset: 5 μm × 5 μm atomic force microscope image of the 150 nm thick BaTiO$_3$ film on SrRuO$_3$/GdScO$_3$ (110). The RMS roughness of the film was 0.67 nm. (b) Film dielectric constant and tanδ measured as a function of temperature with excitation amplitude of 5 mV at 1 kHz.
5.2.1 Electrical characterization

The field-dependence of the BaTiO$_3$ film electric displacement was characterized using room temperature displacement-electric field ($D$-$E$) loops shown in Figure 5.3a. A 1 kHz triangular voltage waveform was applied to the top SrRuO$_3$ electrode. The resulting current was measured from the bottom SrRuO$_3$ electrode and the film electric displacement change was determined using the virtual ground method [25]. The Curie temperature of the ferroelectric film is about 400 °C (see temperature dependence of the BaTiO$_3$ film dielectric constant shown in Figure 5.2b). All measurements were performed below the Curie temperature where the film electric displacement decreases with increase in temperature as shown in Figure 5.1c.

We characterized the temperature dependence of ferroelectric electric displacement by measuring the pyroelectric current from the device generated due to sinusoidal heating of the thin film [26]. Figure 5.3b shows the pyroelectric coefficient of the BaTiO$_3$ film measured as a function of out-of-plane electric field using a lock-in amplifier based 2ω method [26]. A sinusoidal voltage at 1 kHz applied to the heater strip causes a temperature oscillation in the BaTiO$_3$ film at 2 kHz. The temperature fluctuation generates pyroelectric current which was measured from the bottom electrode. The voltage on the top electrode was simultaneously varied with the heating bias at 0.1 Hz to obtain the field-dependence of the pyroelectric response. Measurements were performed at constant background temperatures of 20 and 100 °C, controlled using a bulk heating stage. The pyroelectric coefficient was calculated by dividing the pyroelectric current, measured at the temperature oscillation frequency, with the capacitor area and the time rate of change of temperature. The measured pyroelectric coefficient shown in
Figure 5.3b increases as the background temperature increases from 20 to 100 °C, as is expected for a ferroelectric below the Curie temperature.

**Figure 5.3** (a) Displacement-Electric field loops measured at 1 kHz excitation frequency and (b) pyroelectric loops measured using the BaTiO$_3$ device at 2 kHz heating frequency, at temperatures 20 °C and 100 °C.
5.2.2 Pyroelectric film temperature

This section describes the calculation of amplitude of temperature change induced by resistive heating of the gold strip and variation of film temperature with time. For pyroelectric characterization of the BaTiO$_3$ film discussed in Section 5.2.1, we estimated the amplitude of sinusoidal temperature oscillation using a one-dimensional heat diffusion equation in radial coordinates. The gold strip is modeled as a line-heat source carrying electrical current at frequency $\omega$, over a semi-infinite volume. This current causes a temperature oscillation in the sample at a frequency $2\omega$ due to resistive heating of the metal strip. The frequency-dependent temperature oscillation amplitude of the semi-infinite substrate due to the line heat source of width $2b$ and length $l$ is given by [27]

$$
\Delta T_s = \frac{P}{l\pi\Lambda_s} \int_0^\infty \frac{\sin^2(kb)}{(kb)^2 (k^2 + q^2)^{1/2}} \, dk ,
$$

where $q^1 = (D/2\omega)^{1/2}$ is the thermal penetration depth, $j = \sqrt{-1}$, $P$ is the input electrical power, $D$ is the substrate thermal diffusivity, and $\Lambda_s$ is the substrate thermal conductivity. The thin films between the metal strip and substrate each add a frequency-independent temperature oscillation given by [28]

$$
\Delta T_f = \frac{P}{l\Lambda_f} \frac{t}{2b} ,
$$

where $t$ is the film thickness and $\Lambda_f$ is the film thermal conductivity. The temperature oscillation amplitude of the BaTiO$_3$ film was calculated as $\Delta T = \Delta T_s + \Delta T_{f,\text{SrRuO}_3} + \frac{1}{2} \Delta T_{f,\text{BaTiO}_3}$. The contribution to $\Delta T$ from thin films was significantly smaller than the substrate contribution since the films were only ~100 nm thick. Table 5.1 shows the thermal property values used for these
calculations [29]. The 3ω method was used to measure the room temperature thermal conductivity of the GdScO$_3$ substrate [27]. The volumetric heat capacity of the substrate was assumed equal to that of the SrTiO$_3$ single crystalline substrate [30].

We measured the change in BaTiO$_3$ film temperature with time using the temporal pyroelectric response of the film under no applied bias. Figure 5.4 shows $\Delta T$ profiles for different heating voltage waveforms presented in this chapter. The pyroelectric current from the BaTiO$_3$ film was measured from the bottom SrRuO$_3$ electrode, while the top SrRuO$_3$ electrode was grounded. The pyroelectric current depends upon the rate of change of temperature with time ($t$) and is given by $i_p = pA(\frac{dT}{dt})$, where $p$ is the pyroelectric coefficient and $A$ is the area of the capacitor. We used a constant $p = -20 \ \mu$C/m$^2$K to evaluate the average $\Delta T(t)$ of the pyroelectric film by integrating $i_p$ with respect to time. The magnitude of $\Delta T$ thus obtained was implicitly calculated from the heat diffusion model described above; variation of $\Delta T$ in time was measured from the pyroelectric response of the thin film.
5.3 Results and Discussion

We used the microfabricated platform to control the temperature and electric field, and monitored the energy conversion cycles by measuring the displacement changes induced due to

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity (W/m-K)</th>
<th>Heat capacity (J/m$^3$-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEVCD SiO$_2$</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>4.8</td>
<td>-</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>GdScO$_3$</td>
<td>2.4</td>
<td>$2.7 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 5.1 Material properties used for thermal modeling.

Figure 5.4 Measured pyroelectric current and estimated temperature rise for different heating voltage profiles. The arrows point toward data with increasing heating rates.
the pyroelectric and dielectric response of the BaTiO$_3$ thin film. All measurements reported in this section were done at a background temperature of 20 °C and the cycle frequency was 1 kHz. Results presented here show how the rates of temperature change, electric field switching and phase lag between thermal and electrical cycles affect the electrical energy density. The phase shift between $\Delta T$ and $\Delta E$ waveforms determines the film displacement at which the isothermal process ends and isoelectric process begins. Different temperature and electric field change rates, on the other hand, may lead to processes that are no longer isothermal or isoelectric. In addition, varying $\Delta T$ and $\Delta E$ rates also influences the heat transfer through the sample and dielectric response of the pyroelectric film which affects energy conversion.

5.3.1 $\Delta T$-$\Delta E$ phase difference

Energy conversion using pyroelectric cycles depends upon the synchrony between thermal and electrical cycles. Figure 5.5 shows the time-varying heating voltage, temperature change of the BaTiO$_3$ film, three phase-shifted out-of-plane electric field profiles, measured electric current and the resulting film electric displacement change. In a traditional pyroelectric Ericsson cycle, the electric field switches at the maximum and minimum temperatures to obtain the highest electric displacement change and energy density. The temperature is held constant while the electric field changes. In the measurements shown in Figure 5.5, identical heating bias waveforms were used to obtain the same $\Delta T$ variation in the pyroelectric film with time. The electric field switches between 200 and 183 kV/cm at a $5.67\times10^5$ kV/cm-s ramp rate. The high electric field ramp rate ensures that the temperature is nearly constant. However, unlike the Ericsson cycle, the electric field does not necessarily switch at the highest and lowest
temperatures, and depends on the phase of the electric field profile relative to the heating bias profile. Results are shown for phase angles -42°, 0° and 42°, where zero-phase corresponds to the case when the electric field switches at the mid-point of the heating bias maxima and minima. For -42° phase angle, the electric field switches (at \( t = 0.1 \text{ ms} \)) before the corresponding temperature extreme is reached. The 0° electric field profile switches at the heating bias extremes which do not coincide with the temperature extremes as shown by the \( \Delta T \) profile. For the profile with 42° phase angle, the electric field changes from high to low (at \( t = 0.3 \text{ ms} \)) near the maximum temperature and from low to high (at \( t = 0.8 \text{ ms} \)) before the minimum temperature is reached.

Different thermal-electrical cycles shown in Figure 5.6a for different phase angles are a result of staggered electric field waveforms, and dissimilar heating and cooling profiles. For negative phase angles (shown in blue), the temperature first increases and then decreases at constant low electric field which results in a corresponding decrease followed by an increase in the electric displacement that does not contribute to electrical work out. Maximum electrical energy might be expected for the case when the electric field switches near the highest and lowest temperatures, as is the case for electric field profile phase-shifted by 42° (shown in red). Instead, the maximum energy density is observed for phase angles 0° or 21°, as shown in Figure 5.6b, where the electric field decreases before the maximum temperature is reached. This counterintuitive result is a consequence of the competition between decrease in displacement due to a decrease in electric field and increase in displacement as the temperature decreases for the 42° phase profile. The finite dielectric response time, which depends on the electric field ramp rate, causes the field-driven reduction in displacement to coincide with the counteracting
pyroelectric response during the initial cooling phase during which the temperature decreases at the fastest rate and the pyroelectric contribution to electric displacement is highest.

**Figure 5.5** Applied heating bias, estimated temperature change, out-of-plane electric field, measured current and electric displacement change versus time for electric field switching at phase angles $-42^\circ$, $0^\circ$ and $42^\circ$. Zero-phase corresponds to the case when electric field switches at the mid-point of the heating bias extrema. A vertical offset is added to the $\Delta D$ plots for clarity. The arrows point toward data corresponding to increasing E-field switching phase.
5.3.2 Electric field ramp rate

The electric field ramp rates determine the change in film temperature while the electric field varies since the temperature of the pyroelectric film changes continuously in our setup. Electric field switches nearly instantaneously at high ramp rates and the process is nearly isothermal, but the temperature-change-driven pyroelectric contribution can be significant for...
low electric field change rates when the process is no longer isothermal. Figure 5.7 shows the
time-varying heating voltage, estimated $\Delta T$, applied electric field with different ramp rates,
measured electric current, and the resulting film displacement change. The electric field
transitions from high to low at the mid-point of the heating bias maxima corresponding to $0^\circ$
phase angle for all measurements. The $\Delta D$ increase due to a rise in electric field (at $t = 0.7$ ms) is
about the same for all cases but the decrease in $\Delta D$ (at $t = 1.2$ ms) is different for different ramp
rates. While the dielectric contribution to the displacement change is about the same for an
increase or decrease in electric field, the pyroelectric contribution changes depending on the rate
of change of temperature. When the electric field increases, the temperature is decaying slowly
as heat is lost to the environment and the pyroelectric contribution is negligible. But when the
electric field decreases, the temperature is increasing rapidly with the rising heating power,
producing a significant pyroelectric-effect-induced displacement change.

Figure 5.8 shows the thermal-electrical cycles and measured energy densities for different
electric field ramp rates. The isothermal condition is valid for the low temperature top branch of
the clockwise cycles as the electric field increases from 183 kV/cm to 200 kV/cm irrespective of
the electric field change rate since the accompanying reduction in film temperature is not
significant. But the duration over which electric field decreases affects the bottom branch of the
cycles as the temperature is changing simultaneously. For the slowest rate of $1.42 \times 10^5$ kV/cm-s
(shown in blue), a decrease in electric field is initially accompanied by a rapid increase in
temperature which results in a sharp drop in the electric displacement near 200 kV/cm. However
as the electric field approaches 183 kV/cm the temperature begins to decrease which increases
the electric displacement. The temperature-driven increase in $\Delta D$ counteracts the field-driven
decrease in electric displacement that eventually increases the total $\Delta D$. The overall energy
density, however, is nearly independent of the field change rate since the total temperature change is the same resulting in an identical pyroelectric response superimposed over the dielectric response which does not produce any electrical work by itself.

**Figure 5.7** (a) Applied heating bias, estimated temperature change, out-of-plane electric field, measured current and electric displacement change versus time for electric field change rates of $1.42 \times 10^5$, $2.83 \times 10^5$, $5.67 \times 10^5$ and $11.33 \times 10^5$ kV/cm-s. The arrows point toward data with increasing electric field ramp rates.
5.3.3 Temperature change ramp rate

We controlled the duration and rate of heating and cooling of the BaTiO$_3$ film by changing the slope of the heating bias versus time. Figure 5.9 shows five heating voltage profiles with different ramp rates, corresponding $\Delta T$, applied electric field, measured electric current, and

Figure 5.8 (a) Pyroelectric Ericsson cycles shown on a $D$-$E$ plot with increasing electric field ramp rates (represented by the direction of the arrow). (b) Measured energy density plotted as a function of electric field change rate.
resulting film electric displacement change. The heating bias was increased linearly from 0 V to 2.5 V at varying rates, held constant at 2.5 V for 0.12 ms, and then decreased to 0 V. There is no temperature change when the voltage along the length of gold heater strip is zero. As the heating voltage \( V \) increases linearly, the temperature increases in proportion with the input heating power which scales as \( V^2 \). The temperature continues to increase when the heating bias is held constant due to the sample heat capacity. The maximum temperature is reached just as heating voltage begins to decrease (at \( t = 0.6 \) ms). Thereafter, the sample is convectively cooled but the cooling rate is less than the heating rate and is dependent on the rate of heat transfer to the environment. A steeper heating voltage profile corresponds to a shorter heating period which results in a lower average temperature of the film due to non-uniform heating [22]. The electric field changes isothermally since the ramp rate is quite high at \( 5.67 \times 10^5 \) kV/cm-s, and with phase angle of 0° relative to the heating bias. The displacement change due to a change in electric field is about the same for all heating profiles, but higher heating bias ramp rates result in smaller \( \Delta D \) due to lower \( \Delta T \) amplitudes as it decreases the pyroelectric contribution.

Figure 5.10 shows the thermal-electrical cycles and corresponding energy densities for different heating voltage ramp rates. The average temperature change ramp rate was calculated for each heating profile by dividing the maximum \( \Delta T \) with the duration of temperature increase. Steeper heating voltage profiles resulted in lower \( \Delta T \) which reduced the magnitude of displacement change due to the pyroelectric effect but did not alter the temperature change rates significantly. The lower average film \( \Delta T \) reduced the total displacement change and electrical energy density. We also tried to achieve the same \( \Delta T \) for the five heating voltage profiles shown here by varying the maximum applied heating bias to the extent possible, but did not observe any noticeable temperature-change-rate dependence of the output electrical energy density. This
observation is consistent with previous studies which reported no significant dependence of the pyroelectric coefficient on the heating frequency [26]. While we did not observe a dependence of output energy density on the temperature-change-rate itself, we did notice the effect of heat transfer rate on $\Delta T$ and the generated electrical energy. These results highlight the importance of using thin films with small thermal mass and its placement near the heat source with rapid temperature fluctuations. In addition, design of the energy conversion platform should enhance conduction heat transfer within the platform as well as rapid convective cooling from the environment.
Figure 5.9 (a) Applied heating bias, estimated temperature change, out-of-plane electric field, measured current and electric displacement change versus time for temperature change rates of $4.99 \times 10^5$, $5.36 \times 10^5$, $5.76 \times 10^5$, $6.27 \times 10^5$ and $7.06 \times 10^5$ K/s. The arrows point toward data with increasing heating rates.
In summary, we investigated the effect of temporal variations in temperature and electric field on pyroelectric energy conversion using a microfabricated platform consisting of a 150 nm thick dielectric layer.

**Figure 5.10** (a) Pyroelectric Ericsson cycles shown on a $D$-$E$ plot with increasing heating rates (represented by the direction of the arrow). (b) Measured energy density plotted as a function of average temperature change rate and the corresponding $\Delta T$.

### 5.4 Conclusion

In summary, we investigated the effect of temporal variations in temperature and electric field on pyroelectric energy conversion using a microfabricated platform consisting of a 150 nm thick dielectric layer.
thick BaTiO$_3$ film. The platform allowed microsecond control of the temperature and electric field which enabled thermal-electrical cycles at a 1 kHz frequency. With the temperature and electric field profiles for the pyroelectric Ericsson cycle as the starting point, we studied the effect of three parameters – (1) the phase between $\Delta T$ and $\Delta E$ waveforms, (2) $\Delta E$ change rate, and (3) $\Delta T$ change rate. Maximum energy density was obtained when the electric field is switched from its maximum to minimum value before the highest temperature is reached rather than exactly at the $\Delta T$ maxima owing to the finite response time of the dielectric material. The electric field and $\Delta T$ change rates had no direct effect on the energy density, but higher $\Delta T$ change rates cause non-uniform heating of the pyroelectric film which reduced the measured energy density. We measured an energy density of around 3 mJ/cm$^3$ and power density of 3 W/cm$^3$ at representative electric field change rate of $5.67 \times 10^5$ kV/cm-s and $\Delta T$ change rate of $6.27 \times 10^5$ K/s from the BaTiO$_3$ films.

This work represents a significant improvement over earlier studies that were typically limited to pyroelectric cycles at frequencies less than 1 Hz due to a lack of precise electro-thermal control and large thermal mass of the pyroelectric materials used. Using the approach outlined in this chapter, it should be possible to replicate temperature variations in real-world systems and design thermal-electrical cycles to maximize electrical energy output. The results presented provide a framework for optimizing the energy conversion performance of pyroelectric cycles in systems with high frequency temperature fluctuations such as internal combustion engines and power electronics. We hope that this work will enable the use of pyroelectric materials for future waste heat harvesting applications.
5.5 References


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Chapter 6
Conclusions and Future Work

6.1 Conclusions
This dissertation introduces a framework for investigating thermal-to-electrical energy conversion in pyroelectric thin films. This work developed microfabricated platforms and implemented techniques for temperature-dependent piezoelectric and pyroelectric characterization of nanometer-thick films. The phase-sensitive methods presented in this thesis allow accurate characterization of pyroelectric thin films which was not possible using bulk characterization techniques employed earlier. Additionally, the present work investigates pyroelectric energy conversion in thin films using thermal-electrical cycles with microsecond temporal resolution. Fast thermal cycling and high electric fields allowed high-power-density energy conversion from the nanometer-thick pyroelectric films.

High-temperature local piezoelectric characterization of thin films was achieved using an atomic force microscope (AFM) compatible doped silicon micro-heater. Piezoresponse force microscopy was used to measure the electromechanical response from 100 nm thick PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} films between room temperature and 400 °C. The measured piezoresponse
response shows characteristic hysteresis loops with applied bias and increases with increasing temperature. The piezoresponse diverged between 350 and 400 °C which corresponds to the ferroelectric-paraelectric phase transition for the \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) thin films. This approach allows high temperature nanoelectromechanical measurements in thin films using an AFM.

The present work measured the pyroelectric response of 150 nm thick \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) films using three phase-sensitive techniques in different frequency regimes. The low frequency periodic method measured the pyroelectric current generated in response to sinusoidal heating at 0.2 Hz from a hotplate. The \( 2\omega \) method used a current-carrying gold strip micro-heater to generate temperature oscillations in the frequency range 20 Hz – 2 kHz. The laser intensity modulation method measured the pyroelectric response due to high-frequency heating in the 100 kHz to 1 MHz range. All three techniques reported \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) film pyroelectric coefficient values around \(-200 \mu\text{C/m}^2\text{K}\). We also compared results obtained using the widely used direct method and highlighted the challenges for pyroelectric characterization in nanometer-thick films. The techniques presented in this work will enable accurate pyroelectric characterization of nanometer-thick films.

This dissertation investigated pyroelectric energy conversion in a 200 nm thick \( \text{BaTiO}_3 \) film using a microfabricated platform that allowed simultaneous thermal and electrical cycling. While earlier studies were typically limited to cycle frequencies less than 1 Hz, we were able to achieve cycle frequencies up to 3 kHz due to the low thermal mass of the active material and precise thermal-electrical control. A maximum power density of 30 W/cm\(^3\) was measured from pyroelectric Ericsson cycles at 3 kHz frequency, 20 – 120 °C temperature range and 100 – 125 kV/cm electric field range. The measured power density is a significant improvement over the previous highest value of 0.11 W/cm\(^3\) reported for pyroelectric cycles [1].
In order to understand the effect of temporal fluctuations in temperature and electric field on pyroelectric energy conversion, this work subjected a 150 nm thick BaTiO$_3$ film to rapid electric field changes as high as $11 \times 10^5$ kV/cm-s, and temperature change rates as high as $6 \times 10^5$ K/s. We investigated the effect of phase difference between electric field and temperature cycles, and electric field and temperature change rates on the electrical energy generated from thermal-electrical cycles based on the pyroelectric Ericsson cycle. The energy density varies appreciably with phase shifts between temperature and electric field waveforms, but no noticeable effect of temperature and electric field change rates was observed. This work will facilitate the design and operation of pyroelectric cycles with high energy and power densities.

6.2 Future Work

This dissertation opens possibilities for further development of methods for characterizing and optimizing pyroelectric energy conversion using thin films. We used well understood material systems to demonstrate key ideas for harvesting waste heat using nanometer-thick pyroelectric films. However, the energy density was only 0.01 J/cm$^3$ and the thermodynamic efficiency was less than 0.1% of the Carnot limit due to non-optimal material properties. The next step is to examine materials with higher pyroelectric coefficients and electrical resistivity such as Pb$_{1-x}$La$_x$(Zr$_{1-y}$Ti$_{1+y}$)$_{1-x/4}$O$_3$ and (1-x)Pb(Z$_{1/3}$Nb$_{2/3}$)$_x$PbTiO$_3$ which have reported energy densities as high as 1 J/cm$^3$ and efficiencies up to 5% of the Carnot limit [2,3]. Further improvements in energy density are possible by operating near a phase transition where the pyroelectric response is highest [2]. Higher energy conversion efficiencies are also possible.
by engineering platforms that combine piezoelectric and pyroelectric energy conversion and minimize heat loss to the surrounding environment.

6.2.1 Effect of operating temperature on pyroelectric energy conversion

Highest energy conversion efficiencies are reported for pyroelectric cycles operating near a phase transition [2,4]. A significant increase in the pyroelectric response is observed near the ferroelectric-to-paraelectric phase transition. However the counteracting thermodielectric response, from the temperature-dependent electrical permittivity, also increases just below the Curie temperature and can reduce the total electrical energy produced. But the thermodielectric effect can be used to convert thermal energy into electrical energy above the ferroelectric Curie temperature where the temperature-dependence of electrical permittivity reverses sign [5]. By appropriately choosing the operating temperature range of pyroelectric cycles, it might be possible to improve thermal-to-electrical energy conversion by combining the pyroelectric and thermodielectric effects.

6.2.2 Hybrid pyroelectric-piezoelectric energy conversion

It is possible to improve the overall energy conversion efficiency by generating electricity from temperature- as well strain-induced changes in the electric displacement. Simultaneous harvesting of thermal and mechanical energies can be achieved by actively controlling the strain change in the pyroelectric material in addition to temperature, perhaps using a flexible platform [6]. Another approach to realize hybrid pyroelectric-piezoelectric energy conversion could involve thermally biased mechanical energy conversion cycles [7]. Large mechanical
deformations may be obtained in thin films presented in this work by using thinner substrates or back-side etching of the substrate after film deposition.

6.2.3 Direct electrocaloric measurement

The techniques presented in this work can potentially be adapted to directly measure electrocaloric temperature change in thin films. Recent publications have reported large electrical field induced entropy changes in nanometer-thick films, which are attractive for refrigeration applications [8,9]. However, nearly all these studies used indirect methods for estimating the electrocaloric temperature change. The pyroelectric energy conversion device presented in this dissertation can likely measure the electrocaloric temperature change by employing the metal strip as a resistance thermometer. The temperature change originating from electrical cycling of the thin film can be sensed by simultaneously measuring the resistance change of the electrically isolated metal strip.

6.2.4 Thermal fatigue in pyroelectric thin films

We frequently observed partial depolarization of the pyroelectric films after repeated thermal cycling. While electrical fatigue is well documented in published literature, hardly any studies have reported the effect of thermal cycling on the polarization in ferroelectric thin films [10]. Only a few studies have reported the effect of thermal shock and thermal fatigue using pulsed laser heating [11]. Thermal fatigue is particularly a problem for pyroelectric energy conversion. The diagnostic platform presented in this work can be used to study thermal fatigue.
by exposing ferroelectric films to continuous temperature fluctuations, while simultaneously examining the changes in its polarization.
6.3 References


