### Title
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# PYROELECTRIC ELECTRON EMISSION FROM A THIN FILM OF $PbZr_xTi_{1-x}O_3$ ON A NANOFABRICATED CATHODE

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## ABSTRACT

We report pyroelectric emission from thin films of crystalline $PbZr_{0.8}Ti_{0.2}O_3$ (PZT) on nanometer-sharp tips. The epitaxial PZT films are 30 nm thick and grown directly on batch fabricated single-crystal silicon tips. Pyroelectric emission occurs for heating rates ≥ 50 °C/min in a 20 V/μm external field, and for electric field strengths ≥ 6.7 V/μm when heated at 100 °C/min. The emitted electric charge is reasonable when compared to the theoretical maximum charge for this PZT film and these testing parameters. We calculate that a heating rate of $4.0\times10^7$ °C/min is necessary for unassisted pyroelectric emission.

## KEYWORDS

Pyroelectric, PZT, electron emission, tip array.

## INTRODUCTION

Electron emission is used for research, medical, and consumer applications in devices such as electron microscopes, X-ray sources, and field emission displays. Conventional electron emitters generate electrons using the thermionic effect, which is power inefficient and requires bulky cooling equipment, or using the field emission effect, which necessitates high-voltage electrostatic fields and often leads to emitter damage from vacuum breakdown. Pyroelectric electron emitters leverage the pyroelectric effect in polar crystal materials to emit electrons during a change in temperature. The change in temperature forces electric compensation of the crystal's internal spontaneous polarization; if the resulting electric field is larger than $10^2$–$10^4$ V/μm, surface electrons are ejected into vacuum [1].

While there are many published reports of pyroelectric emission from large crystal cathodes [2-4], there are a lack of publications on electron emission from miniature cathodes smaller than 1 mm that operate based on the pyroelectric effect. Here we report pyroelectric emission from nanofabricated cathode tips with integrated 30 nm thick films of $PbZr_{0.8}Ti_{0.2}O_3$ (PZT). Emission occurs for heating rates ≥ 50 °C/min and electric fields ≥ 6.7 V/μm.

## FABRICATION

The surface electric field generated by the pyroelectric effect is geometrically enhanced at sharp tips [5]. Figure 1(a) shows an array of nanofabricated pyroelectric emitter tips, which are about 1 μm tall and have a tip radius of 30 nm. Figure 1(b) shows a single pyroemitter coated with a 30 nm thick film of epitaxial PZT. We fabricated the tips on a 100 mm silicon wafer in a close-packed array with a 6 μm pitch. After the wafer is diced into 10 mm × 10 mm chips, each chip has approximately $3.2\times10^6$ tips.

To fabricate the pyroelectric emitter array, we began with a silicon wafer and anisotropically etched the wafer using deep reactive-ion etching to form circular silicon pillars 2.7 μm in diameter and 2 μm tall. The circular pillars were then partially sharpened in an isotropic wet etch containing hydrofluoric, nitric, and acetic acid, which reduced the pillar terminus diameter to 0.5 μm while maintaining a pillar base diameter of 2.5 μm. The tips were further sharpened using an iterative oxidation sharpening process [6] to a tip radius of about 10 nm, height of 1 μm, and base diameter of 2 μm. Finally, we deposited a 30 nm thick epitaxial pyroelectric film of $PbZr_{0.8}Ti_{0.2}O_3$ directly on the silicon tips with no buffer layer. The PZT film was grown using pulsed-laser deposition at 650°C in oxygen at a pressure of 200 mTorr.

We characterized the quality of the pyroelectric film using X-ray diffraction, atomic force microscopy, and other electronic measurements [7]. The resulting PZT film was (00*l*)-oriented on tips with an average radius of 30 nm, and the average pyroelectric coefficient was $250\times10^{-6}$ C/m$^2$K from measurements on sister films on a range of substrates.

## EXPERIMENT

Figure 2 shows the experimental setup for measuring pyroelectric emission. We studied pyroelectric emission from the cathode by varying the background electric field and cathode temperature while measuring the emitter current. The pyroemitter chip was mounted on an alumina plate and separated from a stainless-steel anode by 150 μm thick Kapton tape. The electrically insulating Kapton

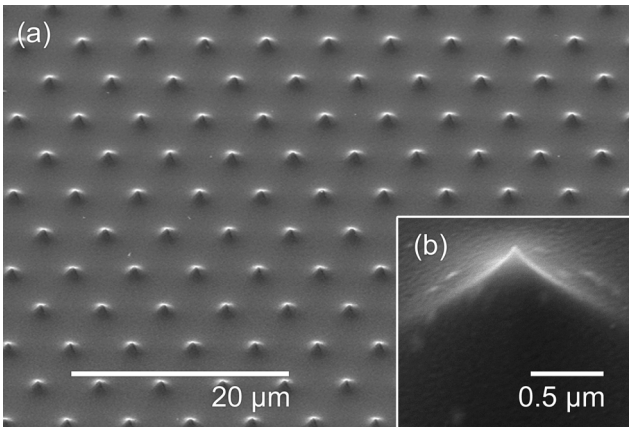


*Figure 1: Micrographs of the nanofabricated cathode emitter (a) array and (b) single emitter. The pyroelectric emitters are coated with a 30 nm thick $PbZr_{0.8}Ti_{0.2}O_3$ film.*

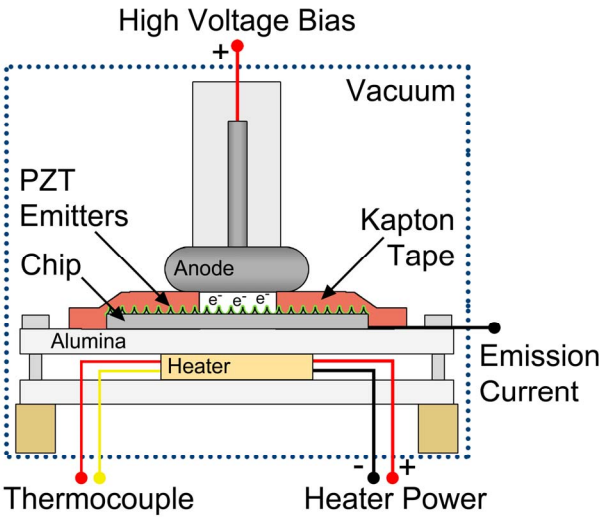


*Figure 2: Experimental setup for measuring pyroelectric electron emission. The cathode-anode separation is 150 μm from the Kapton tape thickness and the emitter chip temperature is controlled by a closed-loop heater.*

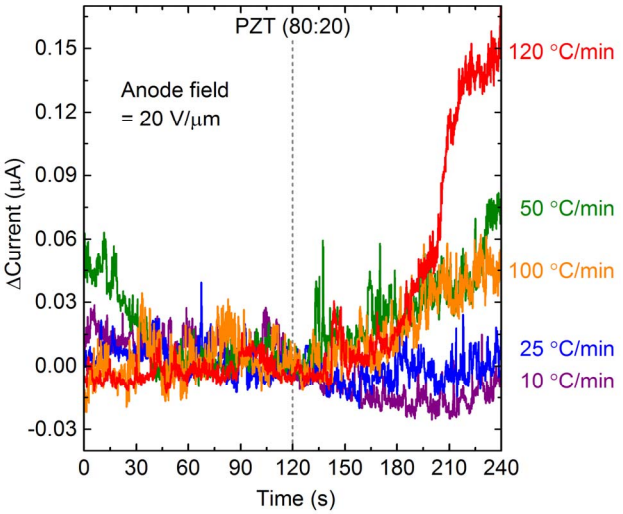


*Figure 3: Pyroelectric emission from $PbZr_{0.8}Ti_{0.2}O_3$ with varying heating rates. The background electric field strength was 20 V/μm. The emission current was offset to be zero at t = 120 sec.*

tape had a circular opening in the middle to expose an area of 23.76 $mm^2$ of the tip array, or about $7.6\times10^5$ tips, and thereby acted as a way to repeatedly control the emitter-anode separation distance and macroscopic emission area. We controlled the emitter chip temperature using a closed-loop electrical heater and we controlled the external electric field in the vicinity of the emitter tips by applying a voltage to the anode. The electric field strength was calculated as the voltage difference between the emitter chip and anode divided by their separation distance of 150 μm. We measured emitter current with a low-noise current amplifier electrically connected to the back of the emitter chip. The tip array was placed in vacuum at $5\times10^{-7}$ Torr and baked at 200 °C for 20 minutes to remove any residual water. To orient the pyroelectric $Z^+$ polar faces towards the anode before the emission experiments, the emitter chips were heated to 200 °C and subsequently cooled to room temperature while applying a −2.5 kV bias on the anode.

The goal of the experiments was to investigate how electron emission from the 30 nm PZT films depended upon the applied electric field strength and film heating rate. For experiments that varied the heating rate, the applied electric field strength was maintained at 20 V/μm while the heating rate was changed from 10–120 °C/min between runs. For the experiments that varied the applied electric field, the temperature was ramped twice from 50 °C to 150 °C and allowed to cool passively in the vacuum chamber while the applied field was controlled over the range from 1–20 V/μm between runs.

## RESULTS AND DISCUSSION

Figure 3 shows the emission current as a function of the PZT film heating rate. The emission currents have been offset to be zero at the onset of heating, $t$ = 120 sec. In our measurement system, electrons emitted from the PZT film towards the anode increase the current, while electrons flowing in the opposite direction from the anode to the PZT film cause a drop in the current. Therefore, an increase in the emission current during a heating cycle indicates pyroelectric emission. The PZT emitters demonstrate pyroelectric emission for heating rates greater than 50 °C/min with a background field of 20 V/μm. There is no observed change in emission current for heating rates less than 50 °C/min. The maximum increase in emission current from pyroelectric emission was 150 nA when the heating rate was 120 °C/min. There is a phase lag between the start of heating and pyroelectric emission because the heater is thermally separated from the emitter chip. Pyroelectric emission from the PZT film during variable heating rate experiments was reliable and repeatable.

Figure 4 shows the emission current as a function of the external electric field strength. We observed pyroelectric emission from the PZT film for external electric fields greater than 6.7 V/μm when the heating rate was 100 °C/min. In comparison to other PZT film chemistries, emission from this PZT stoichiometry was noisy and characterized by sporadic bursts of current. These bursts of current happen when gas molecules ionize between the anode and PZT film, which allows electrons to flow from the anode to the PZT film and recharge the PZT film surface [8].

We quantified the emitted charge during a heating cycle by integrating the measured current during a heating cycle over time. Table 1 lists the emitted charge for a given external field strength. The theoretical maximum emitted charge for a pyroelectric crystal is

$$Q_{max} = \pi \times \Delta T \times A = 594\ \mu C \qquad (1)$$

where $\pi = 250\times10^{-6}$ $C/m^2K$ is the pyroelectric coefficient, $\Delta T$ = 100 K is the change in temperature, and $A$ = 23.76 $mm^2$ is the emission area. For this calculation, we use the exposed macroscopic emission area rather than the sum of the local emission areas near the apex of the emitter tips, which is not quantitatively known. The average PZT emitted charge was about 8% of the theoretical maximum

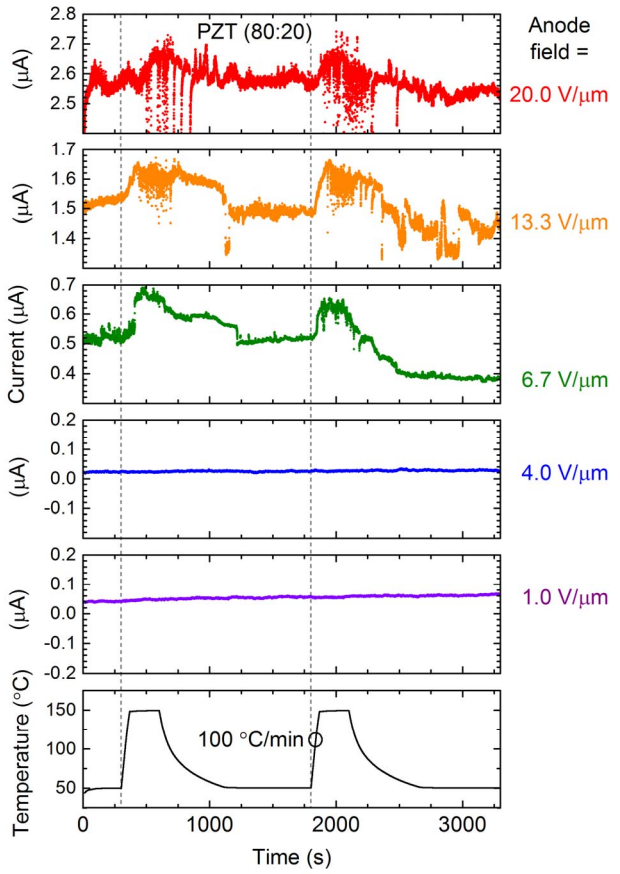


*Figure 4: Pyroelectric emission from $PbZr_{0.8}Ti_{0.2}O_3$ with varying electric field strengths. The sample was actively heated at 100 °C/min but passively cooled for two cycles. The current noise is surface flashover events and discharge from the anode to the pyroemitters.*

*Table 1: Emitted charge calculated by integrating current in Figure 4. Theoretical max is $\pi \times \Delta T \times A$ = 594 μC.*

| Field (V/μm) | ∫ I*dt (μC) | % of theoretical max |
|---|---|---|
| 20.0 | 27.77 | 4.7% |
| 13.3 | 63.59 | 10.7% |
| 6.7 | 55.69 | 9.4% |
| 4.0 | ~ 0 | 0% |
| 1.0 | ~ 0 | 0% |

charge and reached a maximum of 10.7% at an electric field strength of 13.3 V/μm.

While this work demonstrates assisted pyroelectric electron emission from a film of $PbZr_{0.8}Ti_{0.2}O_3$ only 30 nm thick, it is useful to try and estimate what heating rates would be required for unassisted emission from the same film with no external electric field. The minimum threshold electric field necessary for electron emission is about $10^2$ V/μm [1]. The source of the electric field can be some combination of the field generated by the anode voltage potential or the pyroelectric charge, and both of these fields are geometrically enhanced near a tip apex.

The condition required for unassisted pyroelectric electron emission from a flat film is

$$10^2 \text{ V/μm} \le \frac{\pi \alpha d_s}{\sigma_s d_g} \tag{2}$$

where $\pi = 250\times10^{-6}$ C/m$^2$K is the pyroelectric coefficient, $\alpha = dT/dt$ is the temperature change rate, $d_s$ = 30 nm is the pyroelectric film thickness, $\sigma_s = 10^{-8}$ S/m is the pyroelectric bulk conductivity, and $d_g$ = 150 μm is the vacuum gap height [9]. To satisfy this condition, a flat film heating rate $\alpha$ must be greater than $1.2\times10^9$ °C/min for unassisted pyroelectric emission. However, the electric field at a tip apex can be much higher than the macroscopic electric field on the surface of a flat film. The ratio of the local field to the macroscopic field, called the field enhancement factor, is

$$\gamma = 1.2\left(\frac{h}{\rho} + 2.5\right)^{0.9} \tag{3}$$

where $h$ = 1 μm is the tip height and $\rho$ = 30 nm is the tip radius [5]. The calculated field enhancement factor $\gamma$ for our tip emitters is 30.1, which reduces the required electric field for emission to 3.32 V/μm and the required heating rate $\alpha$ for unassisted pyroelectric emission to $4.0\times10^7$ °C/min.

Equation (2) assumes no compensation of the pyroelectric charge by bulk electric conduction through the pyroelectric film. This assumption is valid when the heating time is much less than the charge relaxation time in the pyroelectric film. The charge relaxation time is

$$\tau = \frac{\varepsilon_s \varepsilon_o}{\sigma_s} \tag{3}$$

where $\varepsilon_o = 8.854\times10^{-12}$ F/m is the vacuum permittivity and $\varepsilon_s$ = 500 is the pyroelectric relative permittivity. The relaxation time for the pyroelectric film is 443 ms, which is considerably greater than the 1.5 μs it would take to heat the pyroelectric emitter tips 1 °C at a rate of $4.0\times10^7$ °C/min for unassisted pyroelectric emission. For the work reported in this paper, the minimum time to heat the film 1 °C at the maximum heating rate of 120 °C/min was 500 ms. This heating time is comparable to the calculated charge relaxation time of 443 ms. Therefore, much of the charge generated by the pyroelectric effect was screened by bulk electric conduction through the PZT film. This is consistent with the observation that the measured emitted charge was notably less than the theoretical maximum.

The analysis suggests that higher heating rates will facilitate pyroelectric emission from nanometer-thick films with little or no background electric field. We plan to integrate these pyroelectric emitter tips on semiconductor heaters that have heating rates greater than $10^8$ °C/min for unassisted pyroelectric emission.

## CONCLUSIONS

We have demonstrated pyroelectric emission from $PbZr_{0.8}Ti_{0.2}O_3$ films only 30 nm thick on nanofabricated silicon tips. Pyroelectric emission occurs when the PZT tip emitters are heated at 100 °C/min in the presence of an

electric field ≥ 6.7 V/μm, or when the heating rate is ≥ 50 °C/min in the presence of a 20 V/μm electric field. These electron sources could be used in miniature electron microscopes or energy-efficient X-ray sources.

## ACKNOWLEDGEMENTS

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