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Pyroelectric electron emission from nanometer-thick films of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$

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We report pyroelectric emission from $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) thin films on nanometer-sharp tips. The epitaxial PZT films are 30 nm thick and grown directly on single-crystal silicon tips. Pyroelectric emission occurs for heating rates of $\geq 50^\circ\text{C}/\text{min}$ in a $20\text{ V}/\mu\text{m}$ external field. The emission current is a maximum of 240 nA when the heating rate is $100^\circ\text{C}/\text{min}$ and the electric field strength is $\geq 6.7\text{ V}/\mu\text{m}$. The emitted charge is $\sim 7\%$ of that expected for a perfect thin film emitter of epitaxial $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$. We calculate that pyroelectric emission can occur without an applied field if the heating rate exceeds $4.0 \times 10^7^\circ\text{C}/\text{min}$. © 2013 AIP Publishing LLC.
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Electron emission is critical in many modern devices including microscopy instruments, medical imaging tools, and consumer displays. Conventional electron sources generate electrons using the thermionic effect, which is power inefficient, or using the field emission effect, which requires high voltages. Alternatively, the pyroelectric effect can be used to generate electrons in polar crystal materials.^{1–5} Compared to thermionic or field emitters, pyroelectric emitters operate with a temperature variation of only a few degrees, emit high energy electrons with no acceleration, and produce large current densities.³ Previous studies of pyroelectric emission have been limited to pyroelectric materials with thicknesses greater than $50\mu\text{m}$,^{1,6–10} and this large thickness generally limits the integration and use of pyroelectric emission in many modern semiconductor devices. Consequently, there is a need to develop thin pyroelectric films for electron emission that can be integrated into semiconductor devices and microelectromechanical systems (MEMS).

Pyroelectric emission is a special case of field emission, where the energy necessary for electrons to tunnel into vacuum is provided by internally bound charges rather than an external electric field. The pyroelectric effect occurs when the temperature-dependent spontaneous polarization of the pyroelectric deviates from an equilibrium state during a change in temperature, which can eject electrons from a polar crystal face into vacuum. Thus, pyroelectric emission is not dependent upon the absolute temperature of the pyroelectric material, but rather the rate of change of the temperature of the pyroelectric material when operated below the pyroelectric phase transition temperature. To maintain the heating rates necessary for electron emission from semiconductor and MEMS devices with integrated heaters, the emitter films that are thermally coupled to the heaters must have very small heat capacities.

Electron emission from a pyroelectric crystal requires an electric field strength of $10^2\text{--}10^4\text{ V}/\mu\text{m}$.^{3,7,11} This electric

field can be provided by an applied external field or an internal pyroelectric effect. Both electric fields can be locally enhanced at the geometric apex of a sharp asperity, so that the threshold external or internal electric field for electron ejection is reduced by a field enhancement factor.^{12,13} For example, consider a $1\mu\text{m}$ thick pyroelectric crystal with a pyroelectric coefficient of $-250 \times 10^{-6}\text{ C}/\text{m}^2\text{ K}$ and a bulk conductivity of $10^{-8}\text{ S}/\text{m}$ whose emission surface is $150\mu\text{m}$ from the collection anode. The voltage required for emission using an applied field is 15 kV, while the same field can be generated by a temperature rate of change of $3.6 \times 10^7^\circ\text{C}/\text{min}$ using the pyroelectric effect. However, if the emission surface is a $10\mu\text{m}$ tall tip with a tip radius of $1\mu\text{m}$, the field enhancement factor is 12 which reduces the conditions necessary for emission to 1.25 kV or $3 \times 10^6^\circ\text{C}/\text{min}$. Previous studies have measured pyroelectric emission from crystals that were 0.05–10 mm thick.^{6,9,10,14} Pyroelectric films of 0.2–2 mm thick can emit electrons with heating rates less than $3^\circ\text{C}/\text{min}$,^{7,13} whereas films of 0.02–200 μm thick that can be integrated with modern semiconductor devices require much higher heating rates of up to $10^9^\circ\text{C}/\text{min}$ to overcome other electric compensation mechanisms and emit electrons. Previous publications have suggested that pyroelectric electron emission is not possible from a film having a thickness less than $1\mu\text{m}$ due to a size effect that reduces the critical electric field necessary for ejecting electrons from the crystal face.^{3,5}

This letter describes pyroelectric electron emission from a microfabricated cathode having an integrated 30 nm thick film of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT). We present experimental evidence of pyroelectric emission from nanometer-sharp tip arrays coated with films of epitaxial PZT for heating rates of $10\text{--}120^\circ\text{C}/\text{min}$ in combination with an external electric field. The measured emission charge is about 7.3% of the hypothetical maximum for this material and experimental parameters.

Figure 1 shows an array of microfabricated tips used for pyroelectric emission. The tips are $1\mu\text{m}$ tall and have a tip radius of 30 nm. We batch fabricate PZT emitter tips in a close-packed array with a $6\mu\text{m}$ pitch on a 100 mm silicon

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FIG. 1. Experimental setup for pyroelectric electron emission. Tip emitter samples were tested in a vacuum chamber at 10^{-6} – 10^{-7} Torr. The samples were secured to an alumina plate using silver paint and separated from the anode using Kapton tape of 150 μm thick. A ceramic heater heated the samples from the bottom while the anode generated a macroscopic electric field using a positive voltage bias. (Inset) A SEM micrograph of a microfabricated tip emitter array coated with a 30 nm thick epitaxial pyroelectric film. The tips have a mean tip radius of 30 nm.

wafer. The emitter tips are first sharpened using an oxidation sharpening process to form silicon tips with a radius of 10 nm,¹⁵ followed by epitaxial growth of PZT directly on silicon using pulsed-laser deposition. Further information on the emitter fabrication is reported elsewhere.¹⁶ We deposited 30 nm thick films of either $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT 20:80) or $\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ (PZT 80:20) on the silicon tip arrays and fully characterized the pyroelectric films using x-ray diffraction, atomic force microscopy, and electronic measurements. The resulting PZT films were (001)-oriented and the average pyroelectric coefficient value, as measured on sister films on varying substrates, was $-250 \times 10^{-6} \text{ C/m}^2 \text{ K}$.^{16–18}

Figure 1 also shows the experimental setup for measuring the cathode electron emission characteristics. We characterized emission by varying the background electric field and cathode temperature while measuring the emitter current. The externally applied electric field was controlled by a metal anode, and the macroscopic field strength was calculated as the anode-cathode voltage difference divided by their separation distance of 150 μm . The local electric field strength near the tip apex will be discussed later, but it was certainly higher than the calculated macroscopic field strength. A strip of Kapton tape with a circular hole in the center was used as an electrode spacer. The 5.5 mm diameter circular hole exposed an area of 23.76 mm^2 containing about 7.6×10^5 emitter tips. The cathode temperature was managed by a closed-loop electrical heater with a maximum heating rate of 120 $^\circ\text{C}/\text{min}$, but passively cooled. We measured emitter current with a low-noise current amplifier and preamplifier, in that order, electrically connected to the back of the cathode chip with a combined gain of 10^6 . The preamplifier low-pass filter removed 60 Hz noise. The tip array was placed in vacuum at 5×10^{-7} Torr and baked at 200 $^\circ\text{C}$ for 20 min to remove any residual water. Before emission experiments, the pyroelectric films were poled to orient the crystal Z^+ polar faces towards the anode by applying a -2.5 kV bias on the anode while heating the cathode to

200 $^\circ\text{C}$, holding for 15 min, and then cooling to room temperature. Refer to the supplementary material for field emission I-V measurements at elevated steady-state temperatures using 30 nm PZT films.¹⁹

The goal of the experiments was to investigate how electron emission from the 30 nm PZT films depended upon an applied electric field strength and heating rate. For the experiments that varied the applied electric field, the temperature was ramped twice from 50 $^\circ\text{C}$ to 150 $^\circ\text{C}$ while the applied field was controlled over the range from 1 to 20 $\text{V}/\mu\text{m}$ between runs. For experiments that varied the heating rate, the applied electric field strength was maintained at 20 $\text{V}/\mu\text{m}$ while the heating rate was changed from 10 to 120 $^\circ\text{C}/\text{min}$ between runs.

Figure 2 shows pyroelectric emission current as a function of external electric field strength from emitter tips coated with PZT (20:80). For an applied electric field strength of less than 6.7 $\text{V}/\mu\text{m}$, heating the pyroelectric film at 100 $^\circ\text{C}/\text{min}$ had no effect on the emission current. Similarly, a control sample of bare silicon emitter tips that were not coated with PZT showed no effect on the emission current when the heating rate was 100 $^\circ\text{C}/\text{min}$ and the applied electric field was 1–20 $\text{V}/\mu\text{m}$. In contrast, when the applied electric field exceeded 6.7 $\text{V}/\mu\text{m}$, heating the emitter tips coated with PZT (20:80) at 100 $^\circ\text{C}/\text{min}$ induced an increase in emission current of 60–120 nA, or 2.0%–14.0% above the steady state field emission current. There was a time lag between the start of heating and pyroelectric emission due to the finite heat capacity of the heater-cathode assembly. When the pyroelectric film cooled and reached thermal equilibrium, the emission current would return to the

FIG. 2. Pyroelectric emission from $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ with varying electric field strengths. Phase lag between the onset of heating and pyroelectric emission is caused by the thermal separation between the heater and pyro-emitters. (Bottom) The sample was actively heated at 100 $^\circ\text{C}/\text{min}$ but passively cooled for two cycles.

approximate steady state value measured before the commencement of heating.

During the heating phase, the crystal Z^+ polar faces become progressively less positive, causing ejection of uncompensated electrons from the pyroelectric crystals. In our experimental setup, electrons flowing from the cathode crystal to the anode during pyroelectric emission caused a positive current, which is plotted in Fig. 2 as an increase in the current from steady state. During the cooling phase, the crystal Z^+ polar faces become increasingly positive, which causes electrons to travel from the anode to the crystal surfaces. Electrons flowing from the anode to the cathode crystal caused a negative current, which is represented by a decrease in the current from steady state in Fig. 2. This “recharge” phase is commonly observed and often characterized by sporadic bursts of current, known as surface flashovers. Surface flashovers happen when the anode surface field exceeds the breakdown electric field and gas molecules between the anode and cathode ionize.^{1,3}

Figure 3 shows pyroelectric emission current as a function of applied electric field strength from emitter tips coated with PZT (80:20). Again, a minimum external field of $6.7 \text{ V}/\mu\text{m}$ was required for pyroelectric emission with a heating rate of $100^\circ\text{C}/\text{min}$. Emission current from PZT (80:20) was much noisier and had larger contributions from pyroelectric emission than PZT (20:80); emission current increased 80–240 nA, or 3.1%–40.8% above the steady state field emission current. Surface flashover events, large positive or negative instantaneous changes in current, were much more visible during the heating and cooling thermal phases than for the PZT (20:80) emitter tips.

FIG. 3. Pyroelectric emission from $\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ with varying electric field strengths. The noise is surface flashover events and discharge from the anode to the pyroemitters. (Bottom) The sample was actively heated at $100^\circ\text{C}/\text{min}$ but passively cooled for two cycles.

We quantified the pyroelectric emitted charge for each electric field strength condition by integrating the measured current over time. Table I lists the emitted charge for both PZT films. Surprisingly, the largest emitted charge for both PZT stoichiometric variations was for an electric field of $13.3 \text{ V}/\mu\text{m}$ and not the maximum field of $20 \text{ V}/\mu\text{m}$. This may be a result of the increase in occurrence and severity of surface flashover events at the maximum applied field of $20 \text{ V}/\mu\text{m}$.

The hypothetical maximum emitted charge for a pyroelectric crystal is

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

where $\pi = -250 \times 10^{-6} \text{ C}/\text{m}^2 \text{ K}$ is the pyroelectric coefficient, $\Delta T = 100 \text{ K}$ is the change in temperature, and $A = 23.76 \text{ mm}^2$ is the emission area. For this calculation, we use the exposed macroscopic emission area rather than the unknown sum of the local emission areas near the apex of the emitter tips. The largest emitted charge was 9.5% of the hypothetical maximum for PZT (20:80) and 10.7% for PZT (80:20). The disparity between the measured emitted charge and the hypothetical maximum charge is likely caused by electronic compensation mechanisms other than electron emission that can occur in pyroelectric materials. Possible sources of compensation current include polarization switching of bound charges, bulk conduction, and screening charges which depend on the experimental setup, the pyroelectric bulk conductivity, and the interface conditions.³ Nevertheless, the observed emission current is of the expected order of magnitude for pyroelectric emission.

Figure 4 shows pyroelectric emission current as a function of heating rate for PZT (20:80), shown in the top panel, and for PZT (80:20), shown in the center panel. The emission currents have been offset to be zero at the onset of heating, when $t = 120 \text{ s}$. In the presence of a $20 \text{ V}/\mu\text{m}$ electric field, both PZT (20:80) and PZT (80:20) films demonstrated pyroelectric emission with heating rates greater than $50^\circ\text{C}/\text{min}$. For heating rates less than $50^\circ\text{C}/\text{min}$, we did not observe a change in the field emission current. The thermal phase lag between the start of heating and emission was more noticeable on this shorter timescale. As observed previously, the measured emission current from PZT (80:20) was much noisier than current from PZT (20:80). Heating the PZT (80:20) film induced reliable pyroelectric emission from the cathode emitters to the anode, whereas the decrease in emission current from PZT (20:80) indicated some surface flashover events or field emission from the anode to the cathode crystal. This may indicate that the PZT (80:20) crystal polar faces were more

TABLE I. Emitted charge calculated by integrating current in Figs. 3 and 4.

Field ($\text{V}/\mu\text{m}$)	PZT (20:80)		PZT (80:20)	
	$\int I \cdot dt$ (μC)	% of max ^a	$\int I \cdot dt$ (μC)	% of max ^a
20.0	26.39	4.4	27.77	4.7
13.3	56.47	9.5	63.59	10.7
6.7	31.52	5.3	55.69	9.4
1.0	~ 0	0	~ 0	0

^aThe hypothetical maximum is $\pi \times \Delta T \times A = 594 \mu\text{C}$.

FIG. 4. Pyroelectric emission from (top) $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ and (center) $\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ with (bottom) varying heating rates. The emission current was offset to be zero at $t = 120$ s. The background electric field strength was $20 \text{ V}/\mu\text{m}$ for all cases. Pyroelectric emission, signified by a deviation of the current from zero after the onset of heating, occurs at heating rates greater than $50^\circ\text{C}/\text{min}$ for this electric field strength.

uniformly poled in the Z^+ direction, while the PZT (20:80) polar faces had a larger percentage of faces poled in the Z^- direction. An alternative explanation for PZT (80:20) emission reliability is that more charge must be emitted since PZT (80:20) is generally more electrically insulating than PZT (20:80) and therefore dissipates proportionally less charge from bulk conduction.²⁰

This work demonstrates pyroelectric electron emission from films of PZT only 30 nm thick in the presence of an external electric field. We propose that it is possible to achieve heating rates for pyroelectric emission from these same films with no external electric field. The minimum threshold electric field required for electrons to tunnel from the cathode surface into vacuum is about $10^2 \text{ V}/\mu\text{m}$.^{3,7,11} The electric field may be a combination of the field generated by the anode-cathode potential and the pyroelectric field from the pyroelectric effect, both of which can be amplified at tip asperities by geometric field enhancement. The condition required for unassisted pyroelectric electron emission from a flat film is

$$10^2 \text{ V}/\mu\text{m} \leq \frac{\pi \alpha d_s}{\sigma_s d_g}, \quad (2)$$

where $\alpha = dT/dt$ is the temperature change rate, $d_s = 30 \text{ nm}$ is the pyroelectric film thickness, $\sigma_s = 10^{-8} \text{ S/m}$ is the pyroelectric bulk conductivity, and $d_g = 150 \mu\text{m}$ is the vacuum gap height.⁷ To satisfy this condition, a flat film heating rate α must be greater than $1.2 \times 10^9^\circ\text{C}/\text{min}$. However, the local electric field at a tip apex can be much higher than the applied electric field through geometric enhancement.^{12,13,21}

The ratio of the local field to the macroscopic field, called the field enhancement factor, is

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

where $h = 1 \mu\text{m}$ is the tip height and $\rho = 30 \text{ nm}$ is the tip radius.¹³ The calculated field enhancement factor γ for our tip emitters is 30.1, which reduces the required applied electric field to $3.32 \text{ V}/\mu\text{m}$ and the required heating rate α for unassisted pyroelectric emission to $4.0 \times 10^7^\circ\text{C}/\text{min}$. Refer to the supplementary material for an experimental determination of the field enhancement factor using Fowler-Nordheim plots of field emission from tip emitters.¹⁹

Equation (2) assumes no bulk electric conduction through the pyroelectric film, which is valid when the heating time is much less than the charge relaxation time in the film. The film relaxation time is

$$\tau = \frac{\epsilon_s \epsilon_o}{\sigma_s}, \quad (4)$$

where $\epsilon_o = 8.854 \times 10^{-12} \text{ F/m}$ is the vacuum permittivity and $\epsilon_s = 500$ is the pyroelectric relative permittivity. The relaxation time under these conditions is 443 ms, which is considerably greater than the $1.5 \mu\text{s}$ it would take to heat the pyroelectric film 1°C at a rate of $4.0 \times 10^7^\circ\text{C}/\text{min}$ for unassisted pyroelectric emission. For the work in this letter, the minimum time to heat the film 1°C at a rate of $120^\circ\text{C}/\text{min}$ was 500 ms, which is comparable to the charge relaxation time of 443 ms. Thus, much of our potential emission current may have been screened by bulk conductive current. This is consistent with the observed emitted charge that is somewhat less than the hypothetical maximum. Higher heating rates could facilitate pyroelectric emission with little or no background electric field.

In conclusion, we report pyroelectric electron emission from $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ films only 30 nm thick on microfabricated cathode tips. The nanometer-sharp tip emitters are batch fabricated out of silicon and epitaxially coated with crystalline PZT with no buffer layer. Pyroelectric emission occurs when the PZT tip emitters are heated at $100^\circ\text{C}/\text{min}$ in the presence of an electric field $\geq 6.7 \text{ V}/\mu\text{m}$, or when the heating rate is $\geq 50^\circ\text{C}/\text{min}$ in the presence of a $20 \text{ V}/\mu\text{m}$ electric field. The development of nanometer-thick pyroelectric films capable of thermally induced electron emission will facilitate batch microfabrication of emitters in micrometer-scale form factors. Several applications would benefit from a low-voltage, power efficient electron beam source, especially X-ray emitters, field emission displays, and electron microscopes.

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¹B. Rosenblum, P. Bräunlich, and J. P. Carrico, *Appl. Phys. Lett.* **25**, 17 (1974).

²J. D. Brownridge, *Nature* **358**, 287 (1992).

- ³G. Rosenman, D. Shur, Y. E. Krasik, and A. Dunaevsky, *J. Appl. Phys.* **88**, 6109 (2000).
- ⁴D. W. Kim, E. M. Bourim, S. H. Jeong, and I. K. Yoo, *Physica B* **352**, 200 (2004).
- ⁵J. F. Scott, *Science* **315**, 954 (2007).
- ⁶G. Rosenman, *Ferroelectrics* **133**, 235 (1992).
- ⁷D. Shur and G. Rosenman, *J. Appl. Phys.* **80**, 3445 (1996).
- ⁸J. D. Brownridge and S. M. Shafroth, *Appl. Phys. Lett.* **79**, 3364 (2001).
- ⁹E. Bourim, D. W. Kim, V. S. Kin, C. W. Moon, and I. K. Yoo, *J. Electroceram.* **13**, 293 (2004).
- ¹⁰M. Klopfer, T. Wolowiec, V. Satchouk, Y. Alivov, and S. Molloy, *Nucl. Instrum. Methods Phys. Res. A* **689**, 47 (2012).
- ¹¹G. Rosenman and I. Rez, *J. Appl. Phys.* **73**, 1904 (1993).
- ¹²R. G. Forbes, C. J. Edgcombe, and U. Valdre, *Ultramicroscopy* **95**, 57 (2003).
- ¹³E. G. Pogorelov, Y.-C. Chang, A. I. Zhbanov, and Y.-G. Lee, *J. Appl. Phys.* **108**, 044502 (2010).
- ¹⁴H. Mizota, Y. Nakanishi, H. Oohashi, Y. Ito, T. Tochio, S. Yoshikado, and T. Tanaka, *Radiat. Phys. Chem.* **75**, 1626 (2006).
- ¹⁵R. B. Marcus, T. S. Ravi, T. Gmitter, K. Chin, D. Liu, W. J. Orvis, D. R. Ciarlo, C. E. Hunt, and J. Trujillo, *Appl. Phys. Lett.* **56**, 236 (1990).
- ¹⁶P. C. Fletcher, V. K. R. Mangalam, L. W. Martin, and W. P. King, *J. Vac. Sci. Technol. B* **31**, 021805 (2013).
- ¹⁷J. Karthik, J. C. Agar, A. R. Damodaran, and L. W. Martin, *Phys. Rev. Lett.* **109**, 257602 (2012).
- ¹⁸B. Bhatia, J. Karthik, T. Tong, D. G. Cahill, L. W. Martin, and W. P. King, *J. Appl. Phys.* **112**, 104106 (2012).
- ¹⁹See supplementary material at <http://dx.doi.org/10.1063/1.4806973> for I-V measurements at elevated steady state temperatures, Fowler-Nordheim plots of field emission from PZT films, and an estimate of the field enhancement factor from experiment.
- ²⁰R. V. Mangalam, J. Karthik, A. R. Damodaran, J. C. Agar, and L. W. Martin, *Adv. Mater.* **25**, 1761 (2013).
- ²¹C. J. Edgcombe and U. Valdrè, *Solid-State Electron.* **45**, 857 (2001).