### Study of harsh environment operation of flexible ferroelectric memory integrated with PZT and silicon fabric

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<td>Authors</td>
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Novel high temperature multilayer electrode-barrier structure for high-density ferroelectric memories
Study of harsh environment operation of flexible ferroelectric memory integrated with PZT and silicon fabric

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Flexible memory can enable industrial, automobile, space, and smart grid centered harsh/extreme environment focused electronics application(s) for enhanced operation, safety, and monitoring where bent or complex shaped infrastructures are common and state-of-the-art rigid electronics cannot be deployed. Therefore, we report on the physical-mechanical-electrical characteristics of a flexible ferroelectric memory based on lead zirconium titanate as a key memory material and flexible version of bulk mono-crystalline silicon (100). The experimented devices show a bending radius down to 1.25 cm corresponding to 0.16% nominal strain (high pressure of ~260 MPa), and full functionality up to 225 °C high temperature in ambient gas composition (21% oxygen and 55% relative humidity). The devices showed unaltered data retention and fatigue properties under harsh conditions, still the reduced memory window (20% difference between switching and non-switching currents at 225 °C) requires sensitive sense circuitry for proper functionality and is the limiting factor preventing operation at higher temperatures. © 2015 AIP Publishing LLC.

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Recently, the potential application of lead zirconium titanate (PZT) in high-temperature harsh environments has gained interest. Owing to the material’s high Curie temperature ($T_C \sim 390°C$), lead Pb$^{2+}$ and actuators are desirable in petrochemical deep oil well drilling, automotive fuel injectors, and aerospace monitoring of deep space probes applications. Actual PZT sensors suitable for high-temperature high-pressure environments have already been reported. Although PZT exhibits ferroelectric as well as piezoelectric properties, utilizing its ferroelectric properties in high temperature applications has not been equally explored. Various PZT thin film optimizations and scaling down of device dimensions have already been studied as PZT is the most widely used material in today’s commercial FeRAM. Previous studies have been done on the reliability of PZT based ferroelectric memories under high temperatures up to 350 K ($177°C$). Today, harsh environments require electronics that can collectively function above 200°C, withstand high pressures, and fight corrosive environments ($O_2$, and $H_2O$ vapor rich). It has been reported that PZT (52/48—PbZr$_{0.52}$Ti$_{0.48}$O$_3$) loses up to 45% of its polarization on applying 1.5 GPa mechanical compression, whereas PZT (95/5—PbZr$_{0.95}$Ti$_{0.05}$O$_3$) can get totally depolarized (dysfunctional). This necessitates the study of the combined effect of high-temperature and high-pressure combined, if the devices are to be functioning in such harsh environments. Moreover, there is an increased demand for automation and deployment of robotic systems in harsh environments such as off-shore oil and gas rigs which can heavily benefit from the introduction of a flexible high density memory module. A fully flexible electronic system that affix and conform to any non-planar surface needs an integrated flexible memory for several critical functions, such as programming and data storage. Exciting progress has been achieved in flexible electronics and ferroelectric flexible memories with organic materials research due to the natural flexibility of the material systems. Nonetheless, key fundamental challenges exist with organic electronics related to their limited thermal budget and operation stability. Another challenge is their ultra-large-scale-integration potential where memory devices must be ultra-scaled for ultra-high-density memory. On the other hand, Zuo et al. demonstrated flexible PZT ferroelectric capacitors on platinum (Pt) foil, in 2012, using transfer transfer technique to harness the advantages of PZT in flexible ferroelectric memory. However, the platinum substrate is not suitable for monolithic integration, and the reported devices were not tested for harsh environment conditions including bending stress as the focus of the work was the effect of releasing the devices on Pt thin membranes on ferroelectric properties. In that regard, silicon based inorganic electronics (90% of today’s electronics are made on silicon) enjoy unique advantage thanks to the maturity of state-of-the-art complementary metal oxide semiconductor (CMOS) technology. Finally, the inherent low mobility of organic/polymeric materials (record mobilities are much lower than silicon) hinders their implementation in high performance applications. Each memory cell has one storage element and an access/select transistor. Because memory components need to be ultra-dense, the number of access transistors is the highest in any given chip area. Utilizing the fundamental inverse proportionality between the flexural modulus ($E_{flexural}$) and the thickness ($t$) of a material ($E_{flexural} \propto 1/t^3$), we show that transforming the high-performance silicon electronics into ultra-thin flexible ones can be an efficient route for achieving...
flexible memory devices. Since silicon has higher thermal stability than that of polymer/organic materials, the transformed flexible devices can be potentially leveraged for high-temperature operation needed for harsh/extreme environment applications. Using a completely CMOS compatible process, we transformed an array (1000 devices of various square areas from 100 to 250 μm a side) of PZT based ferroelectric memory fabricated on standard bulk monocrystalline silicon (100) into an ultra-thin flexible silicon based memory. Then, we studied its high-temperature (up to 225 °C) characteristics related to changes in remnant polarization ($P_r$), coercive electric fields, capacitances, memory window, fatigue, and retention properties. All tests were carried out at 1.25 cm bending radius state (bending upward) under ambient conditions (a gas mixture of 78% nitrogen, 21% oxygen, and ~1% argon). This is a critical milestone towards the possibility of pushing a non-volatile flexible memory into key applications that was not possible otherwise due to the lack of flexibility in rigid high performance electronics and the limited performance and thermal instability of flexible organic electronics. The key fabrication steps of the ferroelectric memory devices fabricated on bulk silicon, then, transformed using our transfer-less etch back process by sequential reactive ion etching$^{25}$ process into flexible fabric are depicted in Figure 1. Fabrication details can be found in the supplementary material (Fig. S1).$^{26}$

The ultra-thin flexible ferroelectric memory array was bent on a 2.5 cm diameter metallic cylinder stub brought in contact with a thermal chuck (inset of Figure 2(a)). All measurements were taken using aixACCT TF Analyzer 2000E utilizing the feedback virtual ground method in which connection cables’ capacitances are electrically inactive. The temperature was varied gradually using an aixACCT temperature controller at an initial heating up rate of 18 °C/min, then the rate slows down as the temperature increases to avoid overheating. Measurements were taken in steps of 50 °C (~12 min total ramping time) from room temperature at 25 °C up to 225 °C under ambient conditions. This wide temperature range covers the targeted harsh/extreme environment applications: (i) oil and gas industry’s deep well drilling temperature requirements are similar to inside a combustion engine in hot weather ~200 °C$^{3,27,28}$ (ii) a space craft on a mission to Mercury’s temperature requirements is 175 °C and NASA’s extreme temperature electronics program has testing facilities for up to 250 °C$^{29}$ and (iii) silicon is limited in electronic performance to below 250 °C (thermal insulating packaging techniques can let devices survive higher external temperatures).$^{30}$ The bent devices experienced a constant high-pressure of 260 MPa (operation pressure in deep wells ~20 000 psi$^3$ which is equivalent to 138 MPa), resulting from the tensile stress due to bending the ferroelectric memory devices at 1.25 cm bending radius throughout the measurements. Although the substrate’s mechanical flexibility allowed a bending radius down to even 0.5 cm,$^{28}$ the anomaly in retention behavior at this radius at room temperature did not allow for a lower curvature measurement. The tests were carried out under ambient conditions with typical humidity (55%) level in Saudi Arabia (it is to be noted that harsh environments have humidity levels ranging from 10% to 100%).$^{28}$ Figure 2 shows the cycle-to-cycle variation of polarization vs. voltage bias (a) and capacitance vs. voltage bias (b) for 10 consecutive cycles, at 1 kHz frequency. The error bars represent standard deviation (~2.5% for polarization values between $P_r$ and saturation polarization ($P_{max}$) and ~1.7% for capacitance values). Hence, same device is characterized at different temperatures except for retention and fatigue tests at 25 °C and 225 °C due to the destructive nature of the measurement.

The flexible PZT ferroelectric capacitors function as the storage element in FeRAM, where the two possible polarization states of the devices correspond to a binary value (“0” or “1”). Therefore, it is critical to have two distinguishable polarization states with sufficient charges. Figure 3 shows the polarization vs. applied voltage (Figure 3(a)) for the same device, the change in $P_{r+}/P_{r-}$ and $V_{c+}/V_{c-}$ (Figure 3(b)) for five different devices with error bars representing standard deviation, and the change in $P_{max}/P_{max-}$ (Figure 3(c)) with variation of coefficient of less than 1% at different temperatures. One of the most critical reliability aspects of FeRAM is imprint, which is the device preference to stick to specific memory state and is worsened by high temperatures. The imprint property is usually manifested as a shift in the coercive voltages shifting the hysteresis plot laterally and increasing one of the polarization state at the expense of the other.$^{31}$ However, the plots show that although $V_{c+}$ decreased with temperature; $V_{c-}$ did not increase with an equivalent amount. In addition, there is a similar decrease in $P_{r+}$ and $P_{r-}$ values which in case of imprint should have compensated each other. Finally, the reduction in $P_{max}$

![Image](https://via.placeholder.com/150)

**FIG. 2.** Cycle-to-cycle variation in polarization of the memory devices (a), inset showing the physical setup utilizing a 2.5 cm diameter metallic stub, and capacitance (b) behavior of flexible ferroelectric PZT memory capacitors.

![Image](https://via.placeholder.com/150)

**FIG. 1.** Patterned ferroelectric capacitor structures after all thin film deposition steps (a). Flip-chip (turning upside down) of the thin film stack and etching back the bulk silicon using reactive ion etching in sequential manner (b). Digital image (c) shows the flexible silicon fabric with PZT based ferroelectric memory devices (top), scanning electron microscope (SEM) image shows 40 μm thick flexible silicon fabric with the memory devices (bottom left), and SEM zoomed-in image showing the marked up layers (bottom right).
The decrease in $V_c$ with temperature indicates that these traps have a net negative polarity, possibly due to adsorbed water or hydrogenous species. For the same reason (more charges/traps are able to respond to high frequency alternating small signals; hence, they do not contribute anymore to the hysteric behavior of the devices.) This explains the observed anomaly in the behavior of coercive electric fields: initially, the devices had interfacial traps concentrated at the interface between the top Pt electrode and the PZT thin film due to the exposure of PZT to ambient during the transfer from the RTP to the sputtering step. This also happens after sputtering the bottom Pt electrode and before spinning PZT but Pt, as an inert metal, is much more durable and resistant to contaminants than PZT. For instance, it has been reported that the interface at the PZT/top electrode has significant traps and defects introduced during the process compared to the bottom electrode/PZT interface. The decrease in $V_{c+}$ with temperature indicates that these traps have a net negative polarity, possibly due to adsorbed water or hydrogenous species. For the same reason (more charges/traps are able to respond to the varying AC small signal), capacitance increases as temperature increases (Figures 4(a) and 4(b)). The increase in relative permittivity ($\varepsilon_r$) at low electric fields (coercive field) with temperature for PZT below the Curie temperature has already been reported up to $85\,^\circ C$. Here, we extend this regime up to $225\,^\circ C$, noting that $\varepsilon_r$ starts to saturate as the sample approached $T_C$. Table I summarizes the anomalies in basic performance metrics of the flexible ferroelectric devices at maximum temperature, and constant tensile high pressure. The results show that the memory devices can still function properly when the maximum percentile change is a decrease in $V_{c+}$ which means that when the devices operate at high temperatures, the required electric field to switch the polarization decreases (lower power operation). Since circuit designers tolerate behavior variation within 10% of electronic components, these memories should be used for a specific operation temperature as in the wide range ($25$–$225\,^\circ C$), the change is less than 10%. Nevertheless, if the devices are designed for the high coercive switching fields at lower temperature, they would still function in the dynamic range up to higher temperatures as required switching fields is lower, and the requirement is satisfied. The caveat would be making sure that the read voltage does not switch the device causing erroneous readout, which is an optimization issue. The other most affected parameter is the 45% decrease in remnant polarization (from 14 to $7.5\, \mu C/cm^2$). Although this is a significant degradation; it should not affect the functionality. Actually, most of the reported functional polymer based flexible FeRAMs over the past five years fall within the 7–8 $\mu C/cm^2$ $P_r$ range at room temperature. Figure 4(c) depicts the reduction in memory window as a function of increased temperature. In supplementary Figure S2, we have shown representative memory window extraction plots at various temperatures. The memory window is defined as the ratio of switching current ($I_{sw}$) and non-switching current ($I_{nsw}$). For the reported devices, peak switching and non-switching currents were 2 mA and 1 mA, respectively. For memory array operations, the resulting currents due to switching/non-switching is passed to a sense resistor, converted into a voltage level, and passed to a comparator circuitry to determine if the read state is a “0” or a “1” bit. Although the shrinkage in memory window is severe, still 20% higher switching currents at $225\,^\circ C$ can

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<th>Performance metric</th>
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<th>Value at 225 °C and 260 MPa</th>
<th>% Change at 225 °C and 260 MPa</th>
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<td>Remnant polarization ($P_{r+}$)</td>
<td>$13.91$ $\mu C/cm^2$</td>
<td>$7.66$ $\mu C/cm^2$</td>
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<tr>
<td>Remnant polarization ($P_{r-}$)</td>
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<td>$-8.34$ $\mu C/cm^2$</td>
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<tr>
<td>Coercive voltage ($V_{c+}$)</td>
<td>$2.04$ V</td>
<td>$1.06$ V</td>
<td>$48$</td>
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<tr>
<td>Coercive voltage ($V_{c-}$)</td>
<td>$-1.20$ V</td>
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<td>$8$</td>
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<tr>
<td>Saturation polarization ($P_{max+}$)</td>
<td>$\pm 40.84$ $\mu C/cm^2$</td>
<td>$\pm 34.67$ $\mu C/cm^2$</td>
<td>$15$</td>
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<tr>
<td>Maximum capacitance</td>
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<tr>
<td>Relative permittivity</td>
<td>$1304$</td>
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FIG. 3. Polarization hysteresis plots vs. voltage bias (a), change in coercive voltage and remnant polarization (b), and decrease in saturation polarization (c) at wide range of temperatures.
be distinguished with a sensitive sense circuitry. Based on the above results, memory window proves the limiting case for higher temperature operations because once the switching and non-switching current are non-distinguishable to the sense circuitry, the memory device functionality fails. Figure 5(a) shows the data retention ability for the memory devices uncompromised at highest temperature. The retention ability indicates how long (without consuming power) the storage memory cell can retain the stored data (bit) accurately. Reported values for FeRAM and industry standard for non-volatile memories are 10 years. Retention measurement was executed by applying $15 \text{ V}$ write/read pulse, pulse duration is $50 \mu\text{s}$, and read frequency is 1 kHz. Another important memory property is fatigue. Fatigue measurements indicate how many switching cycles (read/write cycles) can a memory cell undertake before it fatigues. An acceptable indication of the functional number of cycles is when $P_{r+/r-}$ values lose 50% of their initial values. Figure 5(b) shows the fatigue behaviour at 1 MHz disturbance signals (common operation frequency for commercially available FeRAM) of the bent memory devices at 25°C and 225°C indicating its ability to switch up to $10^9$ cycles at elevated temperatures. Similar fatigue behavior improvement for bent devices has been previously reported. On the other hand, at an elevated temperature of 225°C, the devices showed fatigue resistance and degradation were insignificant even at 1 kHz. Both fatigue improvement and degradation have been reported with increased temperature. This can be attributed to the composition of the PZT, and deposition and crystallization conditions. For instance, James et al. reported that thermal healing is responsible for recovering the piezoelectric properties of PZT after physical tensile cycling fatigue tests. Furthermore, Genenko et al. reported on improvements in fatigue properties of soft ceramic PZT and degradations in hot-pressed PZT with increased temperature. In addition to the flexible PZT memory’s ability to retain more than 50% of its basic properties and an uncompromised fatigue and retention behavior under high-temperature and high-pressure conditions, PZT ferroelectric non-volatile memories are intrinsically radiation hard. It has been previously reported that PZT thin film non-volatile memory can withstand up to $10^{15}$ neutron/cm$^2$ dose while retaining 90% of their initial switching charge. Furthermore, PZT non-volatile memories are not the factor limiting hardness level in CMOS electronics but rather silicon. Therefore, PZT based non-volatile memories have an intrinsic edge for applications inside nuclear reactors, inter and extra space missions, and nuclear warfare applications. We have reported the physical-mechanical-electrical characteristics of a flexible version of PZT ferroelectric non-volatile memory initially fabricated on a bulk monocrystalline silicon (100) for high-temperature (up to 225°C) focusing on harsh/extreme environments related to...
industrial/automobile/space/smart grid/nuclear applications. The combined effect of 225°C, 260 MPa tensile stress due to bending at 1.25 cm radius, and 55% humidity under ambient conditions (21% oxygen), led to a maximum 48% reduction in switching coercive fields, 45% reduction in remnant polarization, and an expected increase of 22% in relative permittivity and normalized capacitance. Although the devices showed uncompromised data retention and fatigue properties under harsh conditions, the reduced memory window (20% difference between switching and non-switching currents at 225°C) requires sensitive sense circuitry for proper functionality and is the limiting factor preventing operation at higher temperatures. Finally, the inherent radiation hardening property of PZT along with the aforementioned results make flexible PZT ferroelectric memory devices suitable for high-temperature, high-pressure, humid, as well as radioactive (harsh) environments.

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26See supplementary material at http://dx.doi.org/10.1063/1.4927913 for detailed description on fabrication details and memory window calculation.