

Multilevel Data Storage Memory Using Deterministic Polarization Control

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Ferroelectric random access memory (FeRAM) uses two oppositely oriented spontaneous polarizations whose directions can be switched by applying external electric fields.^[1,2] Although FeRAM would be an ideal non-volatile memory because of its high endurance,^[3] fast read/write time,^[4] and low power consumption,^[5] the technology is still struggling with a challenging scalability problem.^[6] Here, to overcome this scalability issue, we create a general framework for realizing the reliable multilevel polarization (MLP) states, not depending on a specific ferroelectric system. We use the displacement current for the precise quantitative control of polarization switching. We demonstrate eight stable polarization states for 3-bit data storage, satisfying both good retention and state reproducibility, in two distinctly different ferroelectric systems, i.e., Pb(Zr,Ti)O₃ and BiFeO₃ thin films. This illustrates that our approach has the potential of being an efficient means of enhancing polarization-based electronic functions^[7–12] as well as scaling up the storage density of FeRAM.

A fevered search for a single universal memory that combines the speed of static RAM (SRAM), the non-volatility of flash, and the high density of dynamic RAM (DRAM) has resulted in a number of emerging memory technologies such as FeRAM, phase-change RAM (PRAM),^[13] magnetic RAM (MRAM),^[14] and resistive RAM (RRAM).^[15] Of these, the most mature is the FeRAM technology, but it has still struggled with high cost and difficulty in obtaining high storage density. Due to the depolarization field and leakage current problems, it is quite challenging to reduce the feature size of the ferroelectric

memory compared to other universal memory candidates. As a result, despite its high potential as a universal memory, FeRAM is now commercially available with relatively low densities.^[5,6] A possible breakthrough for addressing these critical issues of cost and low density in FeRAM might be made through a multilevel operation.

Ferroelectrics have an internal degree of freedom that allows arbitrary control of the MLP states. In principle, we can obtain any intermediate polarization value between two saturated values (i.e., $+P_S$ or $-P_S$) by adjusting the ratio of up-polarization ($+P_S$) and down-polarization ($-P_S$) domains, as shown in **Figure 1a**. However, obtaining an intermediate state with the desired polarization value is challenging due to the stochastic and complex nature of polarization switching.^[16,17] Therefore, ferroelectric applications have been restricted to just the two saturated values, with little effort having been expended to use the MLP states. Here, we introduce a simple approach for achieving ferroelectric MLP states and then demonstrate its applicability to real systems. If realized, MLP states could increase the storage density of FeRAM without requiring difficult technological solutions, such as reduction in feature size, and would be making true progress towards a universal memory with a significant reduction in cost-per-bit.

The extension of bistable ferroelectric polarization states to MLP states is possible by controlling the current generated during polarization switching. This switching process is always accompanied by a displacement current density J_D . J_D , first introduced by Maxwell in 1861 in his electromagnetism theory, is defined as the rate of change of electric polarization and/or the electric field:^[18]

$$J_D = \frac{\partial P}{\partial t} + \epsilon_0 \frac{\partial E}{\partial t} \quad (1)$$

where ϵ_0 is the vacuum dielectric permittivity. The introduction of J_D completed the Maxwell's equation and predicted the existence of electromagnetic waves, making J_D one of the most important physical quantities in any electromagnetism textbook. However, to date, it had not been noted that J_D could be used as a practical tuning parameter in controlling physical processes such as polarization switching.

We propose that J_D can play a central role in realizing MLP states in an insulating ferroelectric capacitor. Conventionally, ferroelectric polarization is totally switched from $-P_S$ to $+P_S$ by applying an electrical pulse higher than the coercive field to a ferroelectric capacitor. During the polarization switching process, J_D appears between the plates of the capacitor, with a

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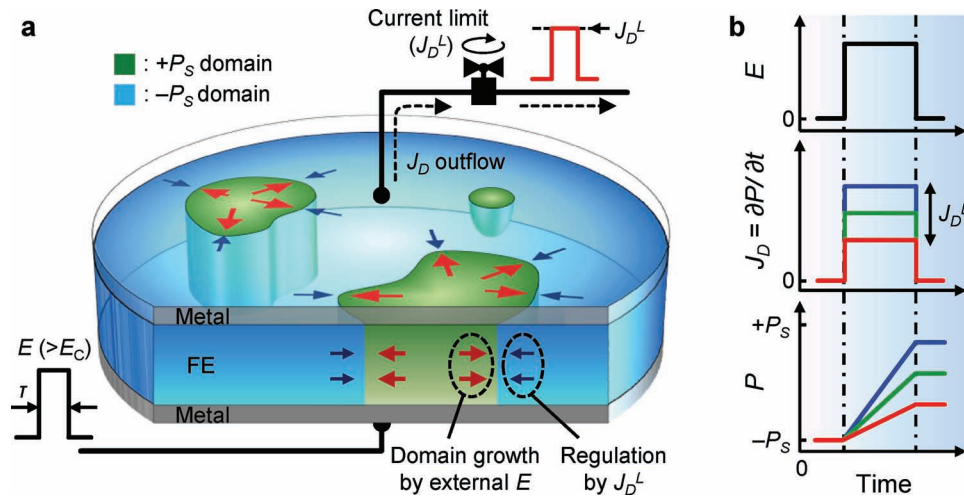


Figure 1. a) By limiting the J_D outflow to J_D^L , we can control the speed of domain growth and polarization switching. b) The speed of polarization switching is tuned precisely by setting a current flow upper limit (i.e., J_D^L), where we can also determine the amount of switched polarization simply by calculating $\Delta P = J_D^L \tau$, where τ is the width of the applied electric pulse.

magnitude equal to that of the conduction current in the wires leading to and from the capacitor, as shown in Figure 1a. The key concept in our approach for obtaining MLP states is tuning of the speed of polarization switching by limiting the current outflow generated from J_D . If we set an upper limit on the current outflow to J_D^L , the speed of polarization switching can be exactly controlled as J_D^L . As a result, as shown in Figure 1b,

the amount of the switched polarization can be determined simply as $J_D^L \tau$, where τ is the width of the applied electrical pulse. Thus, by limiting the J_D response, we can control both the speed and amount of the polarization switching, allowing us to create MLP states with any polarization value.

Figure 2a shows J_D during the polarization switching of a tetragonal $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) (001) epitaxial thin film^[19] as a

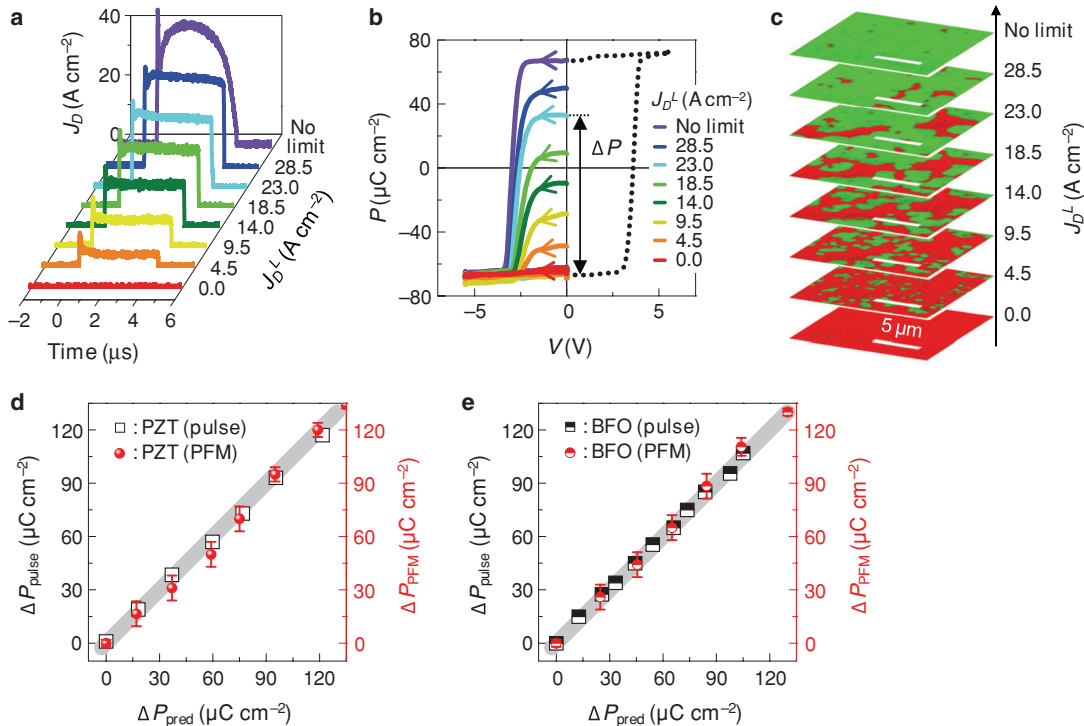


Figure 2. a) Plots of outflowing current generated from J_D under an applied voltage pulse of +7 V (4.1 μs) to a $\text{Pb}(\text{Zr,Ti})\text{O}_3$ capacitor. We can predict ΔP_{pred} simply by calculating $J_D^L \tau$. b) Pulse-measured polarization hysteresis loops, from which we can measure the switched polarization ΔP . c) Domain evolutions imaged by PFM, as a function of J_D^L . d) Predicted and measured ΔP values show good agreement with each other for $\text{Pb}(\text{Zr,Ti})\text{O}_3$ capacitors. ΔP_{pulse} and ΔP_{PFM} indicate ΔP , obtained by pulse-measured hysteresis and PFM imaging, respectively. The solid gray guideline indicates the case when $\Delta P_{\text{pred}} = \Delta P_{\text{pulse}}$ or $\Delta P_{\text{pred}} = \Delta P_{\text{PFM}}$. e) Predicted and measured ΔP values for BiFeO_3 capacitors also show good agreement with each other.

function of chosen J_D^L values. Using our PZT films, we initially set the capacitor in the $-P_S$ state, and then we applied a voltage pulse of +7 V, which is greater than the coercive voltage. During the polarization switching, we set the current limit as J_D^L and monitored J_D by measuring the current outflow response. For limiting the J_D flow, we used a transistor-based current limiter that can be compatible with a conventional FeRAM structure; see Supporting Information, Figure S1. As shown in Figure 2a, there was no J_D response when we did not permit current outflow (i.e., for $J_D^L = 0$). Without limiting the current outflow, a conventional nonlinear J_D response was observed from the full switching to the $+P_S$ state. With J_D^L values between 4.5 and 28.5 A cm⁻², the J_D responses showed a rectangular-like behavior, as expected and shown in Figure 1b. The spike-like feature of the J_D data near $t = 0$ is due to the $\epsilon_0(\partial E/\partial t)$ contribution to J_D , which is not related to the polarization switching, and thus can be neglected. From Figure 2a, we found that the height of the rectangular-shaped J_D response was nearly the same as the J_D^L value. This demonstrates that we could control the speed of polarization switching by the J_D^L value. Furthermore, owing to the constant speed of the polarization change, the amount of the switched polarization of the MLP states is simply predicted to be $\Delta P_{\text{pred}} = J_D^L \tau$.

We verified the controllable switching for obtaining MLP states by showing that the actually switched polarization ΔP was the same as ΔP_{pred} . To measure ΔP , we performed pulse measurements (Supporting Information, Figure S2).^[19] As shown in Figure 2b, the pulse measurements provided us with polarization–voltage (P – V) hysteresis loops in the negative V region. The remnant polarization value at $V = 0$ determined ΔP for each MLP state. Even though we applied the same voltage pulse (i.e., +7 V) for the polarization switchings, the measured ΔP values showed a systematic increase with increasing J_D^L . Furthermore, as shown in Figure 2d, the ΔP values were the same as ΔP_{pred} within our measurement error. This result suggests that J_D is actually a critical control parameter for tuning polarization states in ferroelectrics and other related physical properties, such as domain configurations.

We visualized the correlation between the systematic evolution of ΔP and the ferroelectric domain configuration of PZT films using piezoelectric force microscopy (PFM).^[20–22] Figure 2c clearly shows that the domain pattern evolved systematically with increasing J_D^L . From the domain images, we could also estimate ΔP by summing the piezoelectric signals over the scanned area and normalizing it accordingly. Figure 2d shows that the estimated ΔP values from the PFM images were also in good agreement with ΔP_{pred} , confirming the precise controllability of the polarization switching and domain configuration using J_D .

There are two important issues to be addressed as to the reliability of the obtained MLP states. First, every intermediate polarization state should be stable and retain its value with minimal relaxation for a long time. In principle, as the depolarization energy for the multidomain state is smaller than the single domain state, the multidomain state should be stable.^[1] To address this retention issue, we monitored the time-dependent evolution of the domain structure at a microscopic scale with a spatial resolution of ≈ 50 nm by performing PFM measurements just after switching (Figure 3a) and two days after

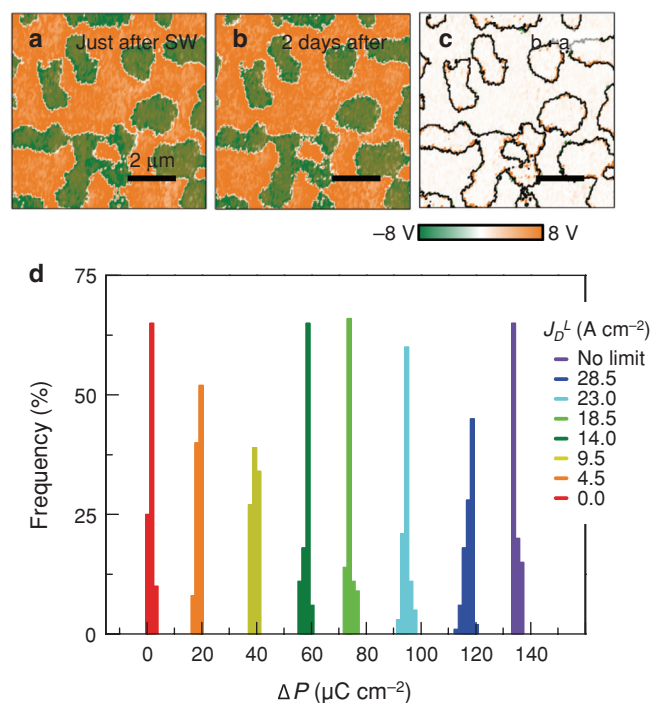


Figure 3. Microscopic domain images a) just after switching and b) two days after switching. c) Difference between the two domain states, obtained by subtracting the piezoelectric signal of (a) from (b). The black solid lines represent the original domain boundaries of (a). d) Plot of frequency versus measured ΔP for each polarization state as obtained from 100 pulse measurements.

switching (Figure 3b). Figure 3c demonstrates that only a negligibly small amount of relaxation occurred after two days, even on the microscopic scale. This suggests that the multidomain structure of the MLP states is highly stable and robust.

The second concern is the reproducibility of every MLP state. Specifically, each state must be well separated with a given value of polarization during repeated write/read processes. To address this issue, we performed a cycling test of the writing process. We wrote eight MLP states by adjusting J_D , and then measured the ΔP values by a pulse measurement of the hysteresis, as shown in Figure 2b. The writings and pulse measurements of ΔP were repeated 100 times for each MLP state. Figure 3d shows that for all states, the measured ΔP values had a narrow distribution with a standard deviation of less than 1.5 $\mu\text{C cm}^{-2}$. Because of this precise control, every state is very reproducible and also well separated from its neighboring states with a margin of about 15 $\mu\text{C cm}^{-2}$, which is large enough to avoid the possibility of reading errors. Based on the retention and reproducibility test, we conclude that our concept of using J_D can serve as a method of achieving MLP states for applications in ferroelectric-based electronics.

It is important to note that realization of MLP states using our concept does not greatly depend on the complex nature of the polarization switching process. Polarization switching usually depends on the material of the system and is affected by complicated factors in ferroelectric materials.^[1,16,17] A conventional method of making an intermediate polarization between $-P_S$ and $+P_S$ is to adjust the strength (e.g., the amplitude and/

or the width) of an applied electrical pulse. However, that method does not reliably enable MLP applications, since the inevitable variation of defect distribution and/or fatigue in materials can induce a large variation in ΔP , even with applied electrical pulses of the same strength (Supporting Information, Figure S3). Our method is completely different as the outflow of J_D , i.e., the speed of polarization switching, is directly controlled; it yields a general framework with which to obtain reproducibly any polarization value between $-P_S$ and $+P_S$, independent of the system material.

We verified the generality of our concept using another ferroelectric material: a BiFeO₃ (BFO) (001) epitaxial thin film. The BFO thin films have a small monoclinic distortion, and their polarization direction is oriented along the [111] crystalline direction. These cause unusual polarization switching path and domain configuration in BFO,^[23,24] which are quite different from those of PZT (001) thin films with tetragonal structure and the [001]-oriented polarization. Despite these large differences, our results with BFO thin films also showed, as with PZT thin films, good agreement between the predicted and measured ΔP values in every MLP state, as shown in Figure 2e (Supporting Information, Figure S4). Also, we found that our concept worked well in polycrystalline PZT films, closer to a real application (Supporting Information, Figure S5,S6). This confirms the generality of our concept and its independence from a specific material and/or polarization switching nature.

In summary, we demonstrated the deterministic control of ferroelectric polarization for high-density multilevel memory devices. This is the first demonstration of multilevel states in ferroelectric systems, satisfying both good retention and state reproducibility that are the basic requirements in universal-memory candidates such as FeRAM, MRAM, PRAM, and RRAM. Although fabrication limits come into play in those candidates, our MLP states are able to triple or quadruple the density, even at existing feature scales. In addition, these multilevel polarization states can be used to enhance the functionality of a wide range of ferroelectric phenomena that are commonly based on polarization and domain configuration, such as tunable transistor/diode,^[7–9] ferroelectric tunnel junctions,^[10] switchable photovoltaics,^[11,12] and magnetoelectric-coupling device.^[25,26]

Experimental Section

Sample Fabrication: 400-nm-thick Pb(Zr_{0.2}Ti_{0.8})O₃ (PZT) epitaxial thin films were grown sandwiched between a Pt top electrode and a single-crystal SrRuO₃ bottom electrode by pulsed laser deposition on SrTiO₃ (001) single-crystal substrates.^[19] For the lattice-matched bottom electrodes on the SrTiO₃ substrates, atomically flat, epitaxially strained SrRuO₃ films were used. PZT capacitors were fabricated by patterning sputtered Pt top electrodes with a typical area of $7.5 \times 10^3 \mu\text{m}^2$.

400-nm-thick BiFeO₃ (BFO) epitaxial thin films were grown sandwiched between a Pt top electrode and a single-crystal SrRuO₃ bottom electrode by sputtering onto SrTiO₃ (001) single-crystal substrates with a 4° miscut toward the [100] direction.^[26] A SrRuO₃ layer (100-nm thick) was deposited as a bottom electrode on a SrTiO₃ substrate by 90° off-axis sputtering at 550 °C. The BiFeO₃ thin film was grown on top of the SrRuO₃ bottom electrode by fast-rate off-axis sputtering at 690 °C. A mixture of Ar and O₂ gas with a 3:1 ratio was used at a total pressure of 400 mTorr. The BiFeO₃ sputtering target had a 5% excess of Bi₂O₃ to

compensate for the volatile Bi element. Pt (40-nm thick) was deposited as the top electrode at room temperature by on-axis sputtering and patterned by photolithography. The diameter of the Pt top electrodes was 50–200 μm .

Ferroelectric Domain Imaging: A piezoelectric force microscope (PFM; XE-100, Park Systems) was used to investigate the ferroelectric domain pattern of the MLP state. In this experiment, a separate needle probe was adopted to obtain reliable electric contact with the top electrode. Since the PFM cantilever only detects piezoelectric vibration, reliable domain images of a large area of the ferroelectric capacitors could be obtained. The amplitude, R , and phase, θ , of the piezoelectric signals were measured with a lock-in amplifier (SR830, Stanford Research Systems). From our domain images, ΔP could also be determined. In the setup, the amount of switched polarization near a particular position should be proportional to $R\cos\theta$, as $R\cos\theta \propto d_{33} = 2Q_{33}\epsilon\epsilon_0P$, where d_{33} is the piezoelectric constant, Q_{33} is the electrostriction coefficient, and ϵ is the dielectric constant of the ferroelectric layer. ΔP was estimated by summing the $R\cos\theta$ signals over the scanned area and properly normalizing it.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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