Electrode-Dependent Oxygen Vacancy Dynamics and Fluid Imprint Behavior in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) Capacitors

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Ferroelectric random-access memory (FeRAM) has attracted considerable attention as a next-generation memory technology that enables low-power, high-speed, and nonvolatile data storage through the switchable polarization of ferroelectric capacitors. [1-2] However, one of the key reliability concerns that can degrade long-term device stability is the imprint phenomenon, in which the coercive field gradually shifts under electrical stress. [3] In particular, fluid imprint arises under sub-switching or alternating stress conditions and induces time-dependent asymmetry in the polarization switching characteristics. [4-5] This effect can reduce the sensing margin and cause read/write errors, making it essential to understand and control for FeRAM applications.

While prior studies have primarily focused on the composition, crystal phase, thickness, and other intrinsic properties of ferroelectric films, the influence of electrode materials on fluid imprint has been relatively underexplored. Electrodes not only provide electrical boundary conditions but also directly affect oxygen vacancy generation or suppression in the ferroelectric layer, depending on their work function and chemical oxygen affinity. For example, tungsten (W) is chemically stable with low oxygen affinity, which suppresses oxygen vacancy formation, whereas titanium nitride (TiN), despite being compatible with ALD processing, exhibits strong oxygen scavenging behavior, increasing the interfacial oxygen vacancy concentration and making it more vulnerable to imprint. Such electrode-dependent oxygen vacancy dynamics act as a key factor in determining the magnitude and direction of coercive field shifts, directly impacting capacitor reliability.

In this work, we present a physics-based model to quantitatively analyze the effect of electrode properties on fluid imprint behavior. The model incorporates oxygen vacancy formation energy, interfacial redox reactivity, and field-driven defect migration to elucidate the correlation between electrode-dependent vacancy dynamics and coercive field shifts. Based on this framework, we demonstrate that optimizing the electronic and chemical properties of electrodes can effectively mitigate fluid imprint and guide the design of ferroelectric devices with enhanced long-term stability. In particular, conductive oxide electrodes such as LSMO(lanthanum strontium manganite, $La_{1-x}Sr_xMnO_3$), with high oxygen vacancy formation energy and oxygen storage capability, are shown to suppress defect generation and offer a promising route toward improved memory reliability. [6]

References

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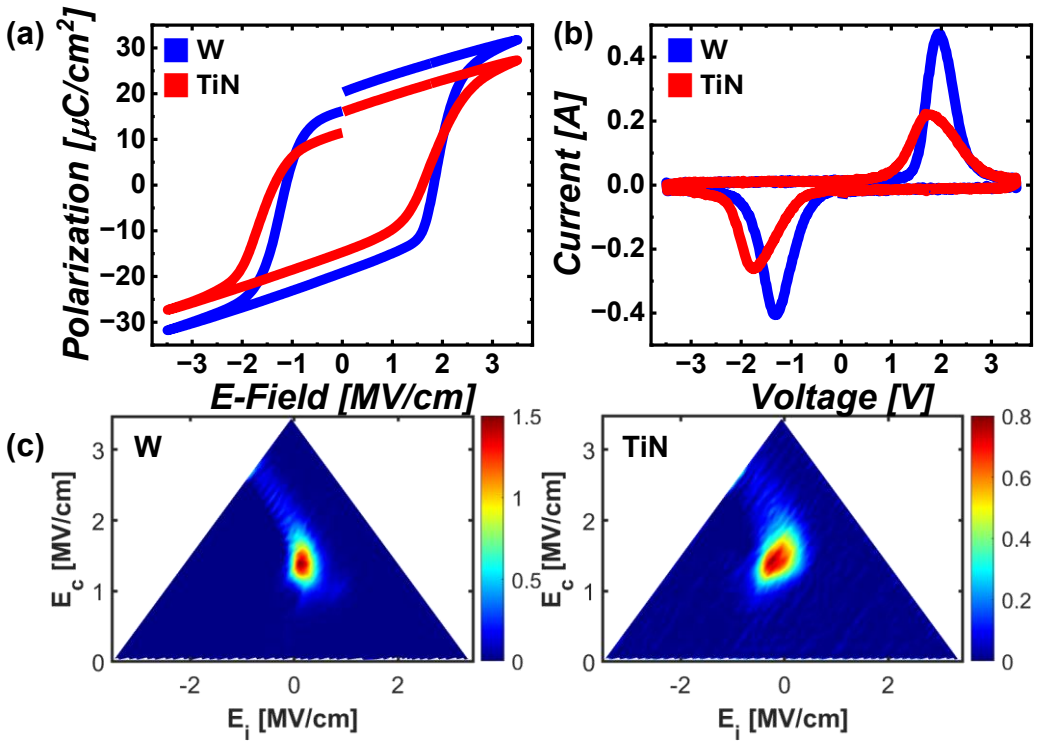

Figure 1. (a) Polarization–electric field (P–E) hysteresis loops of HZO capacitors with W (blue) and TiN (red) electrodes, showing that TiN exhibits a lower remanent polarization (P_r) and a larger coercive field (E_c) compared to W. (b) Current–voltage (I–V) characteristics, where the TiN electrode also demonstrates a larger E_c. (c) First-order reversal curve (FORC) diagrams revealing that TiN has a broader switching field distribution than W, indicating greater variability in domain switching behavior.

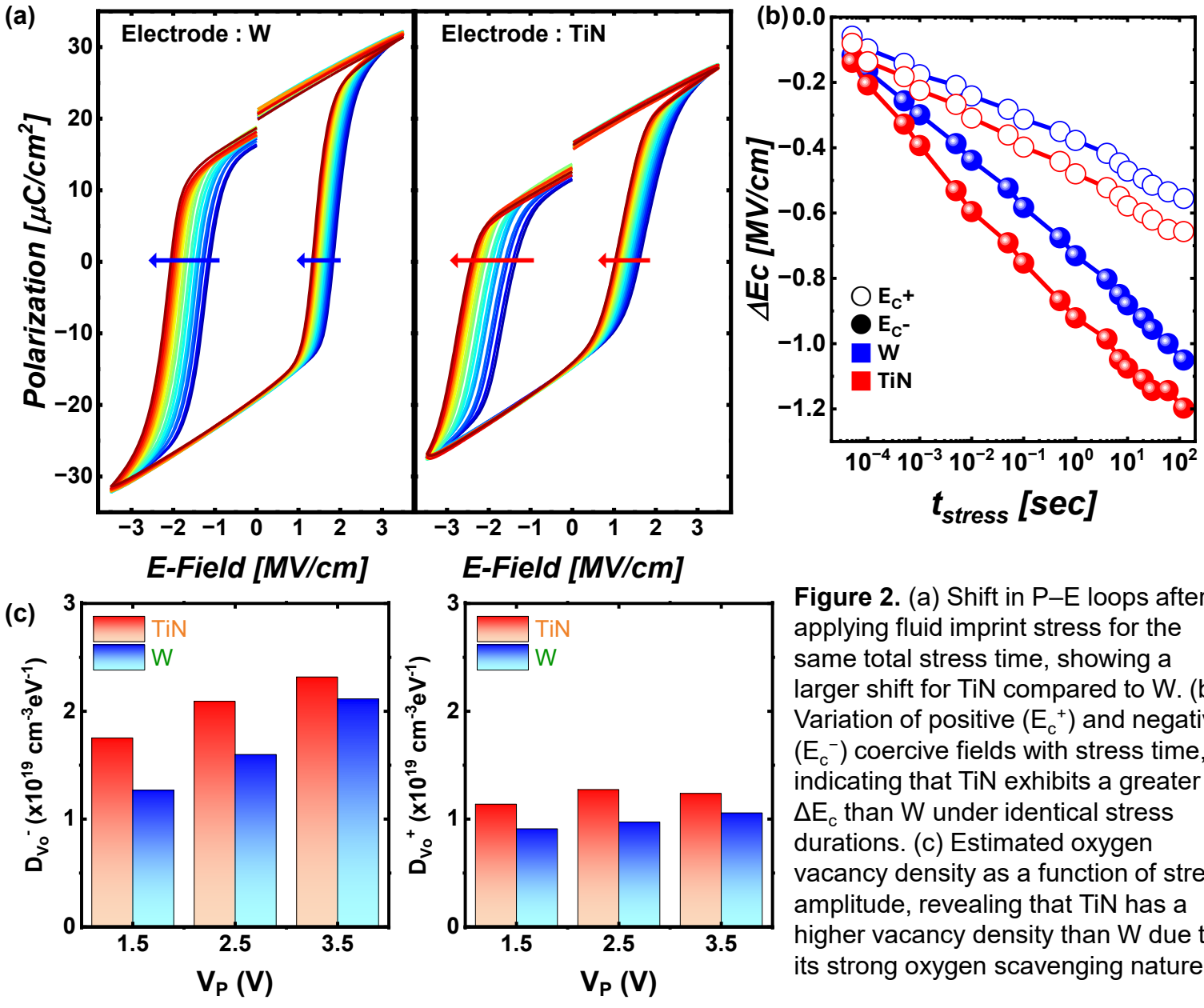

Figure 2. (a) Shift in P–E loops after applying fluid imprint stress for the same total stress time, showing a larger shift for TiN compared to W. (b) Variation of positive (E_c^+) and negative (E_c^-) coercive fields with stress time, indicating that TiN exhibits a greater ΔE_c than W under identical stress durations. (c) Estimated oxygen vacancy density as a function of stress amplitude, revealing that TiN has a higher vacancy density than W due to its strong oxygen scavenging nature.