Top Electrode Engineering for Freedom in Design and Implementation of Ferroelectric Tunnel Junctions Based on Hf$_{1-x}$Zr$_x$O$_2$

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ABSTRACT: Ferroelectric tunnel junctions (FTJs) based on ultra-thin HfO$_2$ have great potential as a fast and energy-efficient memory technology compatible with complementary metal oxide semiconductors. FTJs consist of a ferroelectric film sandwiched between two distinct electrodes, the properties of which are intricately linked to the electrical properties of the FTJs. Here we utilize a W crystallization electrode (CE) to achieve a high and reproducible remanent polarization, combined with a metal replacement process in which the W is carefully removed and replaced by another top electrode (TE). In this way we separate the ferroelectric film properties from the device design and can thereby evaluate the effect of the TE work function (WF) and conduction band electron density ($n_e$) on the tunneling electroresistance (TER) and device reliability. We compare FTJs designed with a TiN bottom electrode and W, Cr, or Ni TE and find that the use of high electron density metals such as Ni or Cr as TE allows for an improved TER, albeit at the cost of reliability due to a large built-in electric field. To bypass this effect, a bilayer Cr/Ni TE is implemented, which allows for a high TER and minimal built-in field, leading to excellent retention and endurance beyond $10^8$ cycles. The results presented here thus highlight a process flow for reliable design and implementation of FTJs.

KEYWORDS: hafnium oxide, tunneling electroresistance, ferroelectric tunnel junction, thin films, work function

INTRODUCTION

Current memory technologies cannot keep up with the exponential growth of Internet traffic and online services, requiring huge data storage and bandwidth; hence, new solutions are required. As data centers are projected to exceed 20% of the global electricity demand in 2030, power efficiency will be a key factor for any new memory technology. Ferroelectric tunnel junctions (FTJs) based on HfO$_2$ have emerged as promising complementary metal oxide semiconductor (CMOS) compatible devices for non-volatile memory technologies and neuromorphic computing hardware. The FTJ is two-terminal voltage-controlled resistive memory, consisting of a ferroelectric insulating barrier sandwiched between two metal electrodes. Because of asymmetric screening of the polarization charge at the interface to the two metal electrodes, this leads to different barrier heights depending on the direction of polarization (Figure 1a). This in turn affects the electronic transmission through the barrier, resulting in a low resistance state (LRS) and high resistance state (HRS). The charge screening length at these interfaces is dependent on the free electron density ($n_e$) of the electrodes. The operation of FTJs can be highly energy efficient (<1 fJ/bit) and be operated as memristive elements, granting their use as analog memories and in neuromorphic

Figure 1. (a) Schematic of band bending due to asymmetric screening lengths in the top and bottom electrodes and (b) impact of WF differences between the top and bottom electrode on the built-in field, here shown without band bending due to polarization charge for clarity.

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FTJs are a relatively young device technology, first realized by Zhuravlev et al.\(^1\) and popularized by Chanthbouala et al., who demonstrated multilevel resistive switching in a BaTiO\(_3\)-based FTJ.\(^{7,10}\) There have since been studies demonstrating an excellent ratio between resistances in the two polarization states, called tunneling electroresistance (TER), and also demonstration of synaptic functionality.\(^{11}\) However, perovskite-based FTJs unfortunately suffer poor compatibility with CMOS technology. Therefore, as Böscke et al. demonstrated ferroelectricity in thin-film HfO\(_2\)\(^{12}\) a material already integrated in CMOS, research on FTJs picked up steam and there are now many examples of HfO\(_2\)-based FTJs in the literature.\(^{2,3,13-17}\) Nevertheless, the performance of HfO\(_2\)-based FTJs is still inferior to that of the perovskite-based device; with lower read currents, endurance, limited retention and small TER still restricting the technology.\(^{16-20}\) Moreover, the diminishing ferroelectric behavior for films below 5 nm\(^{21,22}\) is posing a challenge in improving the low read current of these devices. This has been attributed to a strongly increasing energy barrier for crystallization in ultrathin HfO\(_2\)/ZrO\(_2\) films.\(^{25}\) However, recent results indicate a stable polarization in Hf\(_{1-x}\)Zr\(_x\)O\(_2\) films down to 1 nm using a W top electrode,\(^{23}\) which provides a beneficial strain for crystallization into the ferroelectric orthorhombic crystal phase.\(^{24}\) However, being always confined to a W top electrode would be prohibitive for designing an FTJ with improved performance. In this work we propose the use of a W electrode during crystallization (crystallization electrode, CE), which is removed after crystallization and replaced by another metal of choice (a metal replacement process). This method was previously used by Kobayashi et al. to realize HfO\(_2\)-based FTJs\(^{15}\) and allows assessment of device stacks with comparable Hf\(_{1-x}\)Zr\(_x\)O\(_2\) properties and superior freedom and control in the FTJ design, as it enables one to separately optimize the ferroelectricity in the Hf\(_{1-x}\)Zr\(_x\)O\(_2\) and the electronic properties of the top electrode suitable for a high-performing FTJ.

We evaluate the impact of the choice of TE in terms of WF and \(n_\text{F}^\prime\) on the ratio of HRS to LRS, called tunneling electroresistance (TER), and on the reliability of Hf\(_{1-x}\)Zr\(_x\)O\(_2\)-based FTJs. We specifically study W, Cr, and Ni as TE, because of their interesting relative properties, and find that W, Cr, and Ni lead to gradually increasing built-in electric fields due to the WF difference compared to the BE (TiN) (Figure 1b). W has a similar WF as TiN, providing a small built-in field, while Ni with its higher WF gives the largest built-in field. Moreover, both Cr and Ni have higher \(n_\text{F}^\prime\) compared to W, where \(n_\text{F}^\prime\) = 6.3 × 10\(^{28}\) m\(^{-3}\), \(n_\text{F}^\prime\)\(^\text{Ni}\) = 9.1 × 10\(^{28}\) m\(^{-3}\), and \(n_\text{F}^\prime\)\(^\text{Cr}\) = 8.3 × 10\(^{28}\) m\(^{-3}\) \(^{[\text{page S1 of the Supporting Information (SI)}]}\). The carrier density is the main parameter to influence the polarization-dependent electric field across the potential barrier, induced by incomplete Thomas–Fermi screening of the polarization charge.\(^{25}\) The TER is thus solely dependent on the relative carrier densities in the electrodes.\(^{26}\) Finally, a bimetal electrode consisting of Ni with a thin interfacial layer of Cr is introduced to tune the WF while keeping \(n_\text{F}^\prime\) high, providing yet another level of design freedom.

### EXPERIMENTAL SECTION

Ferroelectric metal–insulator–metal (MIM) structures consisting of TE/Hf\(_{1-x}\)Zr\(_x\)O\(_2\)/TiN were fabricated on Si(100) substrates. The fabrication commenced by deposition of a 10 nm thick TiN bottom electrode (BE) by RF magnetron sputtering in an AJA Orion system equipped with a quartz microbalance thickness meter. Subsequently, 45 cycles (~4.5 nm) of Hf\(_{1-x}\)Zr\(_x\)O\(_2\) were grown by alternating cycles (1:1) of TEMA(Zr) and TDMA(Hf) precursors by thermal atomic layer deposition (ALD) in a Picosun Sunale R-100 system at 200 °C. Following ALD, 50 nm of W was deposited as a crystallization electrode (CE) through DC magnetron sputtering at 100 W in the AJA Orion. All samples were annealed by rapid thermal processing (RTP) at 540 °C for 30 s in a nitrogen environment to crystallize the Hf\(_{1-x}\)Zr\(_x\)O\(_2\). As it is the immediate interface between the Hf\(_{1-x}\)Zr\(_x\)O\(_2\) and TE that determines the screening of polarization charge, and thus the behavior of the FTJ, a meticulous removal of the CE is paramount. The CE is first removed through wet etching by H\(_2\)O\(_2\) at 60 °C for 1 min. However, X-ray photoemission spectroscopy (XPS) performed at the FlexPES beamline at the MAX IV synchrotron facility reveals a thin WO\(_3\) layer remaining on the sample (Figure S1, SI), which must be removed before the deposition of the replacement top electrode. Likely, the WO\(_3\) forms during the deposition step or in the annealing process, by oxygen scavenging from the Hf\(_{1-x}\)Zr\(_x\)O\(_2\) to produce a thin WO\(_3\) layer at the W/Hf\(_{1-x}\)Zr\(_x\)O\(_2\) interface. Failure to remove this oxide leads to devices with low TER and minimal influence by the choice of TE. The WO\(_3\) interfacial layer is removed using heated NH\(_4\)OH at a temperature of 60 °C for 60 s. Finally, devices were defined by patterning of the top electrodes (TE) using optical lithography and electron-beam evaporation (Ni and Cr) or DC magnetron sputtering (W), followed by a lift-off process. For brevity, the samples will now be referred to as “Ni-”, “Cr-” and “W-sample”.

Electrical characterization was performed using a Keysight B1500A parameter analyzer equipped with a B1530A waveform generator fast measurement unit for pulsed measurements. For current–voltage measurements high-resolution source measurement units (HRSMUs) coupled with a ES288A Atto-sense unit was used. The electrical characterization was performed on circular capacitors with an area of 2000 μm\(^2\). The conventional positive-up–negative-down (PUND) technique was utilized to measure the polarization vs electric field (P–E) characteristics. Rectangular voltage pulses were used for wake-up cycling and endurance at a frequency of 100 kHz. All polarization measurements were performed at 10 kHz.

### RESULTS

The P–E curves for representative devices from the W-, Cr- and Ni-samples are shown in Figure 2a–c. To avoid polarization reversal in between the P-U and N-D pulses during the PUND measurement the “zero bias” level was modified accordingly for the Ni- and Cr-samples. The polarization of all the devices is strikingly similar, independent of the TE used, with remanent polarization (\(P_r\)) of all devices in the range of 15–17 μC/cm\(^2\), in line with typical results published for ferroelectric Hf\(_{1-x}\)Zr\(_x\)O\(_2\).\(^{27}\) The center of the P–E curve, \(E_{0.5}\), is also indicated, and a pronounced shift toward the right is observed, in particular for the Cr- and Ni-samples. As discussed above, the WF difference between the TE and BE will give rise to a built-in electric field that shifts the coercive fields at which the polarization switches. This effect has been utilized successfully for antiferroelectric tunnel junctions to attain nonvolatile properties in an otherwise volatile material.\(^{28}\)

The elemental metals W, Cr, and Ni used as TE, all have well-established tabulated WF values, of 4.5, 4.5, and 5.1 eV, respectively.\(^{29}\) The WF of the BE TiN can be tuned by process conditions in the range of 4.25–4.55 eV.\(^{27}\) By quantifying the shift \(E_{0.5}\) in the polarization–electric field (P–E) an estimation of the TiN WF can be obtained. The use of W as TE provides
a quite symmetrical PE curve (Figure 2c) with \( E_0 = (E^+ + E^-)/2 = 0.25 \text{ MV/cm} \), indicating that the WF of the used TiN appears only slightly smaller than the 4.5 eV expected of W.\(^{29}\) Assuming a voltage drop only across the Hf\(_{1-x}\)Zr\(_x\)O\(_2\) film, the observed built-in field would correspond to a TiN WF of 4.4 eV, which appears reasonable. However, due to the fluid imprint phenomenon present in hafnia-based ferroelectrics, the absolute value of the extracted field depends on the measurement history and must therefore be interpreted with caution.\(^{31}\) With the use of Cr and Ni (Figure 2a,b) as TE, clear shifts are observed in the PE characteristics with \( E_0 = 0.7 \text{ MV/cm} \) and \( E_0 = 1 \text{ MV/cm} \), respectively. The use of Ni with a tabulated WF of 5.1 eV\(^{29}\) shifts the PE curve toward more positive bias, as expected, while the use of Cr also induces a relatively strong shift (0.7 MV/cm) toward positive fields, although Cr is expected to have a WF similar to that of W.\(^{29}\) The observed built-in electric field and relative electron densities \( n_{\text{TE}}/n_{\text{TiN}} \) are summarized for all samples in Figure 2d), where \( n_{\text{TiN}} = 5.5 \times 10^{28} \text{ m}^{-3} \).\(^{32}\) These results indicate the excellent design possibilities, enabled by the metal replacement process, and allows for tuning of the switching bias while decoupling the ferroelectric properties, which is similar in all three samples.

The top electrode’s impact on the tunneling current density \((J)\) will now be investigated more closely. The \(J−V\) characteristics of the three samples are shown in Figure 3a). The arrows and numbers indicate the sweep direction and sequence of the measurement. Starting at 0 V and sweeping the bias above that corresponding to the positive coercive field \( E^+ \) (solid, 1), thereby switching the polarization of the ferroelectric, and then back down to 0 V (dashed, 2) the tunneling current at low field through the device increases and a counterclockwise hysteresis is observed, indicating a hysteresis caused by polarization charge.\(^{25}\) Sweeping the bias from 0 V to negative polarity, beyond the voltage corresponding to the negative coercive field \( E^- \), a high current is measured (solid, 3) followed by a lower current on the returning sweep (dashed, 4). Once again, a counterclockwise hysteresis is observed. The described characteristics are similar for all three samples independent of the TE, but the values switching voltages are

![Figure 2](https://pubs.acs.org/acsaelm/article-figures/2021/acsaelm.1c01181/Figure2.jpg)

Figure 2. Polarization–electric field of samples with selected top electrodes. (a–c) \(P−E\) curves of device with Ni, Cr, and W top electrode, respectively, where \( E_0 \) indicates the built-in field. (d) The relative free electron density between the top and bottom electrode and extracted built-in electric field is shown.

![Figure 3](https://pubs.acs.org/acsaelm/article-figures/2021/acsaelm.1c01181/Figure3.jpg)

Figure 3. Measured electrical data of FTJs with Ni (black), Cr (red), and W (green) top electrodes. (a) \(J−V\) characteristics when swept from 0 V to above the coercive field to switch the polarization and memory state. (b) the corresponding TER extracted from the ratio of the solid and dashed sweeps in part a. (c–e) The retention characteristics of devices where the solid line is an extrapolation. The black vertical dashed line indicates 10 years. (f) Schematics of the band diagram under (i) zero, (ii) positive, and (iii) negative applied electric field. Injection into oxide trap states is indicated by the solid arrows.
shifted in accordance with the $E_{c}^+$ and $E_{c}^-$ values observed in the $P$–$E$ diagrams (Figure 2a–c), leading to a negligible memory window for Cr and Ni devices at negative biases. Interestingly, the off-state current density at positive polarity of both the Ni and Cr devices is lower compared to W, particularly for the Ni-sample. We attribute this to the large built-in electric field in the Ni and Cr devices for which asymmetric charge injection is present. \[35,36\] The electronic transmission through HfO$_2$ and ZrO$_2$ films have previously been carefully examined and shown to be dominated by Poole–Frenkel (PF) and trap-assisted tunneling (TAT) mechanisms depending on the applied field. \[35,36\] The dominating trap energy ($E_{trap}$) in these materials is reported to be 1.82 eV below the conduction band edge, \[37\] thus requiring thermal activation for injection from the TE Fermi level. Analysis of the temperature-dependent $J$–$V$ characteristics of the devices in this work (pages S2–S7, SI) is consistent with the literature, concluding that the transport is limited by TAT via a trap state located 1.77 eV below the Fermi energy ($\Phi_F$), raising the injection energy barrier ($\Phi_s$) to be 1.82 eV below the conduction band edge, \[37\] thus limiting the conduction, causing a lower current level in devices with Cr and Ni TEs. \[35\]

The measured resistance in the HRS and LRS, giving the resistance ratio $R_{HRS}/R_{LRS}$ corresponding to the TER is presented in Figure 3b). For all three samples the TER has a clear peak at a certain applied bias, 0.2, 0.4, and 1 V for W, Cr, and Ni TEs, respectively. The peak TER of the W-sample reaches a value of $\Delta E$ lower than for the Cr- and Ni-samples, which achieve peaks of TER = 7 and 12, respectively. We thus observe a clear correlation between a high peak TER and a high relative $n_i$ of the TE compared to the TiN (Figure 2d). We attribute the increase in TER for the Ni- and Cr-samples to a larger modulation of the potential barrier, as the depolarization field induced by incomplete polarization screening is directly impacted by the electron concentration asymmetry of the electrodes. \[35,36\] Furthermore, the shift in bias position of the peak TER is consistent with the increasing built-in field in the samples. Importantly, for the Ni- and Cr-samples the peak TER lies far from zero bias and there is almost no measurable TER at negative bias polarity.

The ability for a FTJ device to keep a programmed state is essential for practical use as a nonvolatile memory. With the strong induced shifts of the $P$–$E$ curves, particularly in the Cr- and Ni-samples, it is critical to evaluate the state retention properties of the devices. The retention is assessed by programming the device into a predefined state by applying a positive set pulse above $E_{c}^+$, which switches the device into the positive polarization state (LRS). The state is read at increasing time intervals using an $I$–$V$ sweep between 0 and 0.3 V, where the resistance is extracted at a read bias of +0.3 V, much below $E_{c}^+$, to not disturb the programmed state. Corresponding measurements are performed for the opposite resistance state as well. In Figure 3c–e the retention data measured at room temperature is shown for the Ni-, Cr-, and W-sample, respectively. For both the W and Cr-samples good retention with a distinct separation between the HRS (diamonds) and LRS (circles) is observed, even when extrapolated to 10 years, as indicated by the dashed black line. However, for the sample with a Ni TE the HRS is unstable, and we observe read disturbance during the measurements. Although the volatile property demonstrated in the Ni-sample is detrimental for memory applications, it becomes an attractive trait to emulate artificial neurons in hardware neural networks. \[39\]

The second aspect of memory reliability is in terms of its state cycling endurance. The evolution in $P$–$E$ characteristics, $P_{m}$ and TER with cycling is critical for the system level application of the FTJ. Thus, the endurance of these metrics was evaluated and is presented in Figure 4. To compare the endurance between samples in a fair way, all cycling was performed with the same absolute electric field amplitude $\Delta E$ from the flat band field $E_{0}$ extracted from Figure 2d). The change in $P$, when cycling with $\Delta E = 3.3$ MV/cm is displayed in Figure 4a), where the Ni-sample (black) exhibits a hard breakdown (HBD) after $1 \times 10^5$ cycles, indicated with open circles. The Cr-sample (red) also has a rather limited endurance with HBD after $2 \times 10^4$ cycles, while the W-sample (green) completes $1 \times 10^8$ cycles without experiencing HBD, although the polarization gradually degrades after $1 \times 10^5$ cycles. This observed polarization fatigue is a common phenomenon in hafnia-based ferroelectrics and is attributed to domain wall pinning caused by charged defects gradually building up in the oxide. \[40\] The worse endurance of the Ni- and Cr-samples compared to the W-sample is somewhat unexpected, since the effective potential drop across the oxide is similar in all samples. It is worth noting that despite the early HBD no fatigue is observed with cycling as in the W-sample; instead, HBD occurs directly following the wake-up phase. Noteworthy, a major difference for these samples in comparison with the W-sample is the much more asymmetric charge injection, as discussed previously (Figure 3f), which could lead to a quicker buildup of defects at the higher-injection electrode (TiN). However, the full investigation of
Figure 5. Electrical characterization of a ferroelectric tunnel junction device with a WF tuned top electrode of 1/200 nm Cr/Ni. (a) the $P-E$ characteristics are shown. (b) the $P_r$ endurance with $\Delta E = 3.3$ MV/cm is presented up to 100 million cycles. (c) the $J-V$ characteristics when swept above the coercive field are shown with the extracted TER in part d. (e) The endurance of the TER with cycling at $\Delta E$ between 3.3 and 1.7 MV/cm and (f) the retention of the HRS (diamonds) and LRS (circles).

this phenomena would require additional experiments and analysis beyond the scope of this work.

For a FTJ device, the $P_r$ endurance does not provide a complete insight, as generation of charged defects can screen the $P_r$ and limit its effect on the band structure, even when a large $P_r$ is still measurable. Figure 4b–d shows the TER endurance for $\Delta E$ in the range 1.7–3.3 MV/cm and directly assesses the reliability of the FTJs in a practically important device metric. The TER endurance was measured by cycling rectangular voltage waves with a frequency of 100 kHz at altering field amplitudes with reference to $E_0$ for a set number of cycles, followed by a $J-V$ sweep from zero bias to the positive applied cycling field amplitude and back down to zero, before continuing cycling. The TER was then assessed at the bias position of the peak TER that was extracted from Figure 3b). No effort was made to dynamically adjust this bias position to account for shifts in the peak TER. The measurement scheme is completely detailed in Figure S9 (SI) and the measured HRS and LRS currents are presented in Figure S10 (SI) from which it is clear that the TER degradation is mainly due to an increase in leakage current in the HRS. From these measurements it becomes evident that the $P_r$ endurance behavior is not necessarily reflected in the TER endurance. For instance, the Ni-sample exhibits an increasing $P_r$ in the first 1000 cycles (Figure 4a). Yet, for the same field amplitude (3.3 MV/cm) the TER sets out at its maximum value and quickly degrades as cycling begins, reducing the TER from 12 to 6 in the first 100 cycles and all the way down to 4 before experiencing HBD (Figure 4b). Even for a reduced field of 2.7 MV/cm, TER degradation is observed as cycling is initiated, and further reduction of the field is no longer sufficient to switch the polarization, resulting in a TER of 1 independent of cycling. Similarly, the Cr-sample (Figure 4c) is also experiencing a rather quick TER degradation for the highest fields of 3.3 and 2.7 MV/cm, where the TER is substantially decreased with cycling. However, reducing the applied field to 2.2 MV/cm, a lower TER of roughly 4 is achieved and retained after 2 $\times$ 10$^5$ cycles. The peak TER of the W-sample is smaller than that for the Ni- and Cr-samples, as presented earlier in Figure 3b due to the lower $n_0$ relative to that of TiN. However, the ability to retain the TER for many cycles is much improved in these devices. Even for the highest field of 3.3 MV/cm, only minor deterioration of the TER is observed in the range investigated. In addition, reducing the field to 1.7 and 2.2 MV/cm still yields a TER of 2, which shows no deterioration with cycling. Although, both Ni and Cr achieve a much-improved peak TER in comparison to the W-sample they also experience a faster rate of decline with cycling. It is thus clear that the TER value is not predominately determined by the absolute value of the $P_r$, which is still in the wake up phase as TER degrades. Instead, it is believed that the decay of the TER can be explained again by asymmetric carrier injection, which quickly leads to a significant number of captured charges at defect states close to the TiN interface that effectively screens the polarization charge and reduces TER.41 No effort was made to dynamically optimize the read bias to the peak TER, and a slight shift of the peak TER position is observed with cycling, as shown in Figure S11(SI). Dynamically changing the read bias with cycling would somewhat counteract the observed TER fatigue in the samples. A faster fatigue rate with increased applied electric field has been reported in other works as well and was attributed to increased oxygen vacancy generation and aggregation with switching.42 The growth of a dead-layer was also observed in that case, which in our case does not seem likely, as we do not observe an increase of $E_c$ with cycling. Contrary to our improved fatigue performance at lower switching fields, Li et al. present an increased rate of fatigue
for nonsaturated switching of the ferroelectric, a characteristic not observed in this study. To summarize, a successful FTJ design should consider and balance both the difference of \( n_p \) and \( WF \) for a high TER, good endurance, and retention.

With this in mind, we designed a device utilizing the attractive high \( n_p \) of Ni and Cr coupled with a more balanced \( WF \) to yield high endurance and retention. The use of bilayer metals is common in CMOS technology to tune the \( WF \) and alter the flat band voltage of a transistor. The bilayer TE was deposited using electron beam evaporation with a thin interface layer of 10 Å of Cr followed by 200 nm of Ni. Figure 5 displays the electrical data measured for the sample with the Cr/Ni TE. From the PE characteristics of the Cr/Ni sample shown in Figure 5a, a PE hysteresis is observed with \( P_r = 13 \mu \text{C/cm}^2 \). The \( P−E \) curve is close to symmetrical around zero field with a modest built-in field of \( E_0 = 0.27 \text{ MV/cm} \), similar to the W-sample. The low built-in field allows for an excellent \( P_r \) endurance, as demonstrated in Figure 5b) with the sample still being functional after \( 1 \times 10^8 \) cycles, although some fatigue is observed, as for the W-sample. Furthermore, the \( J−V \) data in Figure 5c) shows an anticlockwise hysteresis with a difference between the HRS and LRS for both polarities of the read bias. An extraction of the TER reveals an almost symmetrical dependency on the read bias with a peak TER = 8 at \( V_{\text{read}} = 200 \text{ mV} \), comparable to that of the pure Cr-sample. Moreover, the reliability of the Cr/Ni device was investigated, measuring the TER endurance and retention properties as shown in Figure 5ef, respectively. An improved TER endurance is observed, with limited degradation for the highest fields of 3.3 and 2.7 MV/cm when compared with the pure Ni- and Cr-samples. The TER evolution with cycling is similar to that of the W-sample, but with the key exception of an overall higher TER. Although some degradation of the TER occurs with cycling at fields of 3.3 and 2.7 MV/cm, the TER is stable and even slightly increasing with cycling for 2.2 and 1.7 MV/cm, possibly reflecting the visible \( P \), wake-up effect in Figure 5b). Together with the improved TER endurance, excellent retention at room temperature with a clear separation of the HRS and LRS is observed. Extrapolation to 10 years, as indicated by the black dashed line, suggests a high \( n_p \) and symmetrical \( WF \) can be achieved and ultimately provide superior performance to a single-metal TE. In combination with the CE replacement process, a bimetal TE offers a superior degree of freedom in FTJ device design.

**CONCLUSION**

This work describes use of a crystallization electrode (CE) and a replacement TE process to separate the ferroelectric properties in ferroelectric Hf\(_{1−x}\)Zr\(_x\)O\(_2\) from the aspects of FTJ device design. This allows for optimization of the FTJ electrostatics and enables the design of FTJs with high TER and endurance and excellent retention. We emphasize the correlation between the built-in field and TE electron density on the FTJ performance and reliability and point out that the target should be a large asymmetry in electron density for high TER with a minimal built-in-bias for high endurance and retention. In conclusion, bilayer TE is implemented to minimize the built-in bias field while still achieving a high TER. With this method a Hf\(_{1−x}\)Zr\(_x\)O\(_2\)-based FTJ with a Cr/Ni bilayer TE is fabricated, showcasing a peak TER = 8 with stable endurance and nonvolatile retention at room temperature extrapolated to 10 years.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.1c01181.

Calculation of free electron densities; deconvolution of the measured XPS spectra and relative peak components of a reference Hf\(_{1−x}\)Zr\(_x\)O\(_2\) and postannealing with the W CE; evaluation of dominating conduction mechanism by \( I−V \) data analysis; measured \( P−E \) characteristics of the Ni\(_2\), Cr\(_2\), and W-samples during endurance measurements; schematic illustration of the measurement scheme used to extract the presented TER endurance data; evolution of the HRS and LRS current densities with cycling (PDF)

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**Notes**

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