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Retention Characteristics of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ -based Ferroelectric Tunnel Junctions

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Abstract - We report on the retention properties of double-layer hafnium zirconium oxide ($\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$; HZO) based ferroelectric tunnel junctions (FTJ). Utilizing HZO as the ferroelectric layer and aluminum oxide (Al_2O_3) as the tunneling barrier a scalable FTJ memory operation with good endurance and an on/off ratio of about 10 was achieved. Due to inherent depolarization fields from the double layer structure, the device suffers from strong retention loss over time. An extrapolation to 10 years at room temperature shows vanishing differences between the on and off state currents. We propose a way to avert this retention loss by using a constant bias that can be built-in by a work function difference from the metal electrode. This leads to more stable on-current retention and only small off-current increase, giving rise to an improved retention behavior of the FTJ.

Keywords - ferroelectric tunnel junction, $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, memory, retention

I. INTRODUCTION

$\text{HfO}_2/\text{ZrO}_2$ -based (anti-)ferroelectric memories have become a strong research focus in the memory landscape over the last years [1-3]. The most prominent candidates are 1T ferroelectric field effect transistors (FeFET) or 1T1C ferroelectric random access memory (FeRAM) cells, while other applications are also being investigated, such as negative capacitance [4], logic-in-memory [5] or neuromorphic computing [6]. All memories show fast switching speed, low power consumption and utilize already

established CMOS-compatible processes. Ferroelectric tunnel junctions (FTJ) based on $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) can overcome some limitations from ferroelectric memories, e.g. by having a non-destructive read-out. A ferroelectric tunnel junction in its simplest form is a two-terminal device with a ferroelectric layer sandwiched between two metal electrodes [7]. The read-out is done by sensing the tunneling resistance of the stack rather than measuring the polarization switching current, which makes the refresh of the cell unneeded after the read operation. The write operation is done by applying high electric fields which enables switching of the remanent polarization of the ferroelectric layer into two different states, $+P_r$ and $-P_r$. The change of polarization leads to a modulation of the barrier width and height of the whole stack, which in turn changes the total resistance between the metal electrodes. In nominally symmetrical metal-ferroelectric-metal (MFM) stacks, the change in the potential landscape can be explained due to a finite screening length in the metal electrodes and asymmetric interfaces from different process conditions, which lead to a de-facto asymmetry [8]. Another approach is the deposition of an additional dielectric layer (e.g. a thin Al_2O_3 film) that serves as the tunneling barrier [9]. This metal-ferroelectric-insulator-metal (MFIM) capacitor induces an inherent asymmetry in the whole structure for increased operation efficiency, circumventing the problems of nominally symmetric stacks. Additionally it overcomes the difficulty to scale the ferroelectric down to a thickness that makes tunneling

Figure 1. a) Ferroelectric polarization-voltage hysteresis of a $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{TiN}$ capacitor with 2 different HZO thicknesses, b) grazing-incidence X-ray diffraction (GIXRD) pattern of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ layer, c) band diagrams of the $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3/\text{TiN}$ ferroelectric tunnel junction structure for the two different remanent polarization states P_{up} and P_{down} , d) current-voltage response of the ferroelectric tunnel junction corresponding to P_{up} and P_{down} .

possible, which is a difficult task for HfO_2 based ferroelectrics [10]. The working principle of this 2-layer stack is illustrated in the band diagrams in Fig. 1c. The two different remanent polarization states of the HZO (assumed P_r -value of $20 \mu\text{C}/\text{cm}^2$, 50:50 ratio of Hf:Zr) layer lead to different tunneling currents through the dielectric film.

II. EXPERIMENTAL DETAILS

Our $\text{TiN}/\text{HZO}/\text{Al}_2\text{O}_3/\text{TiN}$ MFIM samples were deposited directly on a p-doped silicon wafer. The TiN bottom electrode of 12 nm thickness was sputtered using a PVD process at room temperature. $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (1:1 ratio of hafnia and zirconia) and Al_2O_3 layers were fabricated in an Oxford ALD tool at 260°C without vacuum break. TEMA-Hf, TEMA-Zr and TMA were used as precursors with water as the oxygen source. The TiN top electrode (12 nm) was sputtered on top using the same process conditions as for the bottom electrode. Afterwards a post-metallization anneal at 600°C for 20 s was done to crystallize the HZO into the ferroelectric phase. Circular capacitor structures were formed by Ti/Pt evaporation through a shadowmask (diameter $200 \mu\text{m}$) and subsequent SC1 etching of the underlying TiN top electrode. Polarization-voltage measurements were performed on an Aixacot TF3000 Analyzer, using triangular voltage pulses with a frequency of 10 kHz. Grazing-incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) measurements were carried out on a Bruker D8. The current-voltage response of the FTJ was analyzed with a Keithley 4200 SCS on a semi-automatic Cascade probe station with pulsed measurement units for voltage and current sensing.

III. RESULTS AND DISCUSSION

In order to achieve a stable operation of the FTJ, the ferroelectric layer should not limit the overall memory properties of the device. We are therefore using an optimized $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ layer. The remanent polarization of this HZO film is shown in Fig. 1a for thicknesses of 8 nm and 12 nm. The maximum P_r value of the layer is about $22 \mu\text{C}/\text{cm}^2$ and the coercive field E_c is about $1.2 \text{ MV}/\text{cm}$, while only showing a small wake-up and

Figure 2. Retention characteristics measured at room temperature of a $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3/\text{TiN}$ ferroelectric tunnel junction for different HZO and Al_2O_3 thicknesses.

Figure 3. Theoretical depolarization field E_{dep} normalized to the coercive field E_c in dependence of the Al_2O_3 thickness for different HZO thicknesses.

fatigue behavior. This is in good agreement with literature and previous reports on ferroelectric $\text{HfO}_2/\text{ZrO}_2$ [11]. The GIXRD pattern in Fig. 1b indicates that the polycrystalline HZO film consists of a mixture of the paraelectric tetragonal and the ferroelectric orthorhombic phase as well as a small monoclinic phase fraction. When adding the dielectric Al_2O_3 layer, the operation of the FTJ is enabled. For both polarization states of the ferroelectric HZO layer (P_{up} and P_{down}), a typical I-V response of the MIFM stack can be seen in Fig. 1d. Two clearly separable tunneling currents at a readout voltage of 2 V can be measured, depending on the previously set polarization state. When the polarization is pointing upwards towards the top electrode, a higher tunneling of about 2.5 nA can be achieved, while the tunneling current in the opposing polarization (pointing downwards towards the bottom electrode) is much lower at 0.22 nA. Therefore, the resulting on/off ratio of our device is about 10. We have shown before that operation of this HZO/ Al_2O_3 -based FTJ memory is only possible in a certain thickness window for both the ferroelectric and the dielectric layer [9]. Thickness variation of the HZO layer is limited by the requirement of comparable optimized ferroelectric properties, and Al_2O_3 thickness deviation either leads to premature ferroelectric switching or decrease in tunneling current for low and high Al_2O_3 thickness, respectively. All following results (if not noted differently) are shown for an HZO thickness of 12 nm and an Al_2O_3 thickness of 2 nm.

It is known that these kind of double-layer stacks – which can also be found in a similar way in ferroelectric field effect transistors (channel/gate oxide–ferroelectric layer–metal electrode) – suffer from depolarization fields and charge trapping effects, which can limit endurance and retention of these devices. In this work, we are focusing on the retention properties of these double-layer FTJ's under different bias/operation conditions and propose mechanisms to enhance retention stability. In Fig. 2 the retention at room temperature measured up to 7 days is shown for different HZO and Al_2O_3 thicknesses. After applying a high voltage for setting the polarization in the ferroelectric layer, the current was read out at a voltage V_{read} of 2 V as a rectangular voltage bias with fast measuring and integration time (ns/ μs range). This was done to prevent charge trapping into the device during read-out which occurs when a comparably slow voltage sweep up to 2 V is applied. The difference in the on-current between the 8 nm and

12 nm samples can be understood from the different band diagrams for both thicknesses. The samples with 8 nm HZO thickness have a higher band bending in both the ferroelectric and dielectric layer compared to the sample with 12 nm thick HZO. This leads to a slightly higher tunneling current through the Al_2O_3 layer when applying the readout voltage at the bottom electrode. While there is no significant change over time in the off-state currents independent of the HZO/ Al_2O_3 thickness, the measured on-current decreases rapidly in the first minutes for the 8 nm HZO samples. After about 1 h, the current loss is similar for both HZO thicknesses and follows the trend of retention loss that has been reported before in literature for similar structures [12]. An extrapolation to 10 years shows that the memory window disappears. The loss is even stronger when measuring the retention at higher temperatures. The driving force for the retention loss is the depolarization field associated to the double layer structure. In a perfect MIM structure, the polarization charges are completely compensated at the metal/ferroelectric interface, resulting in a perfectly screened ferroelectric layer, hence no internal field is present. When adding another dielectric layer, the whole structure consists of 2 capacitors in series, where the uncompensated polarization charges at the ferroelectric/dielectric interface lead to a finite field in the ferroelectric, which is antiparallel to the polarization direction. This depolarization field can suppress the stability of the ferroelectric properties and leads to a loss of remanent polarization. When the depolarization field is higher than the coercive field, the polarization will start to decrease, which in turn then lowers the polarization field. The depolarization field E_{dep} can be calculated from assuming ideal layers (with no fixed interface charges) according to:

$$E_{\text{dep}} = - \frac{P_r}{\epsilon_0 \cdot \epsilon_{r,FE} \left(1 + \frac{\epsilon_{r,DE} \cdot d_{FE}}{\epsilon_{r,FE} \cdot d_{DE}} \right)} \quad (1)$$

where P_r is the remanent polarization in the ferroelectric layer, ϵ_0 is the vacuum permittivity, $\epsilon_{r,FE}$ and $\epsilon_{r,DE}$ are the relative permittivities of the ferroelectric and the dielectric layer, and $d_{r,FE}$ and $d_{r,DE}$ are the thicknesses of the ferroelectric and the dielectric layer, respectively. The theoretically calculated depolarization field normalized to E_c for 8 and 12 nm thick

Figure 4. Current-voltage response of the TiN/Hf_{0.5}Zr_{0.5}O₂/Al₂O₃/TiN FTJ structure measured at different times after the initial set operation corresponding to a P_r loss due to an existing depolarization field.

HZO in dependence of the Al_2O_3 thickness is shown in Fig. 3. For a given Al_2O_3 thickness the depolarization field is stronger when the HZO thickness is lower (for a given Al_2O_3 thickness). This explains the stronger retention loss at the beginning for our samples with 8 nm HZO. Since the calculated depolarization field is significantly higher than the coercive field for the relevant Al_2O_3 thickness, more domains will switch after a short amount of time. Equation (1) shows that the depolarization field is reduced when the polarization decreases, so at one point the depolarization field goes below the coercive field ($E_{\text{dep}} < E_c$) and it will take much longer times to switch the low- E_c domains into the opposite state. This leads to the observed continuous loss of the memory window over time. Further evidence for this behavior can be found when looking at the I-V measurements from the polarization hysteresis analysis in Fig. 4. When setting the ferroelectric layer into the high P_r state (noted as “initial set operation”), the switching current can be measured. In the ideal case this is the result of all switchable domains in the ferroelectric layer. In our case, the measurement curve shows a broad switching peak which originates from the distribution of the coercive field due to the polycrystalline structure of the film. When measuring two set operations directly after each other, no switching current is measured for the second sweep (see “directly after set operation”). Due to the depolarization after some time, a significant switching current can be measured when setting the state again. This can be seen from the I-V curves which were measured at similar time stamps as the ones used in the retention measurements (Fig. 2). Note that this procedure was done after the retention analysis on the same devices since the necessary high voltage sweep sets the device into its high remanent polarization state.

The depolarization field is a fundamental problem when dealing with more than one layer in a ferroelectric device [13]. One idea to circumvent or weaken this problem is to override the depolarization field with a constant external voltage or with a built-in field from a work function difference from the metal

Figure 5. Retention characteristics at room temperature of the TiN/Hf_{0.5}Zr_{0.5}O₂/Al₂O₃/TiN ferroelectric tunnel junction under different bias conditions.

electrodes. Here we investigated how the retention behavior changes when a constant bias is applied. The results are shown in Fig. 5. The external voltage was applied to the bottom electrode of the whole MIFM stack. When applying a constant negative voltage of -1 V or -2 V, the off-state - corresponding to the polarization state P_{down} - is stabilized and the off-current stays at the same level. On the other hand, it leads to a fast and strong degradation of the on-state current since back-switching from P_{up} into the downwards polarization state is promoted. This leads to a very fast closure of the memory window. By applying a constant positive voltage of +1 V or +2 V one can stabilize the on-state current and compensate the depolarization field. This enables a stable on-state over a period of about 100 minutes. Since the constant positive bias stimulates switching into the upwards polarization, an increase of the off-current is expected. Due to the k -value mismatch in the stack, a large part of the external voltage drops over the Al_2O_3 layer. Consequently, only a small portion of the domains in the ferroelectric layer will switch and therefore only a small current increase occurs. Since the polarization hysteresis for the MIFM structure is slightly shifted towards the right (not shown here), the effect of a constant bias leading to an unwanted switching process in the ferroelectric layer is more prominent for the negative bias values. Additionally, fixed negative charges at the ferroelectric/dielectric interface can reduce E_{dep} for the P_{down} state, while increasing it for the P_{up} state [4].

For improving the retention of the FTJ to be adopted in a NVM memory, instead of a constant external voltage we propose to use different work functions of the metal electrodes to induce a built-in bias field to counteract the depolarization field. By using a metal with a lower work function than TiN (~ 4.6 eV) as the top electrode (or vice versa with a higher work function as the bottom electrode), e.g. Ti (4.1 eV) or Al (4.2 eV), one could achieve similar behavior as we have shown in Fig. 5, while also increasing the overall current density of the device. Built-in fields from work function differences have also been used in other ferroelectric devices, utilizing a similar effect [14]. Another way to make the retention characteristics more symmetric, would be to control the amount of fixed charges at the ferroelectric/dielectric interface, which directly affect the depolarization fields in opposite ways.

IV. CONCLUSIONS

We have investigated the retention properties of $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3/\text{TiN}$ ferroelectric tunnel junctions. By utilizing this double capacitor structure, the ferroelectric HZO layer serves as memory layer where the binary information is stored as the remanent polarization states, while the dielectric aluminum oxide layer serves as the tunneling layer. This allows for a non-destructive readout. Inherently, these double layer stacks suffer from depolarization fields, which leads to a loss of memory window over time. The main on-current decrease already happens shortly after setting the polarization state due to back-switching of ferroelectric domains (the depolarization

field is higher than the coercive field). By applying a constant external voltage, the on-current is stabilized over time with only a small increase of the off-current. The voltage can also be built-in by incorporating a work function differences from different metal electrodes in the stack or by fixed charges at the interface. This leads to a longer retention of the ferroelectric tunnel junction.

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