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Ferroelectric Tunnel Junctions based on Ferroelectric-Dielectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3$ Capacitor Stacks

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Abstract—We report on a two-layer based ferroelectric tunnel junction with hafnium zirconium oxide (HZO) as the ferroelectric layer and aluminum oxide as the tunneling layer. The experimental results focus on optimizing the thicknesses of the layer stack. The device operation relies on the polarization reversal of the HZO layer, while electron tunneling occurs through the dielectric layer. The ferroelectric response of the HZO shows high remanent polarization values and good endurance with only weak wake-up and fatigue behavior. Adding the additional dielectric tunneling layer, the device becomes operational as a ferroelectric tunnel junction in the nanoampere current range. It shows good on/off ratios and promising retention behavior, paving the way for future applications as a polarization-based resistive memory device.

Keywords—ferroelectric tunnel junction, $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$, memory

I. INTRODUCTION

Due to the approaching scaling limit of charge-based memories such as DRAM, new types of data storage mechanisms are needed. In the last years, ferroelectric materials have gathered an increased interest in their application as memories and various other technologies due to their promising attributes such as low power consumption, high

Fig. 1 Schematic view of the $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3/\text{TiN}$ capacitor structure. V_{bias} denotes the externally applied voltage across the device.

Fig. 2 Cross-section TEM image of a $\text{TiN}/8\text{nm } \text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/4\text{nm } \text{Al}_2\text{O}_3/\text{TiN}$ capacitor.

switching speeds and non-volatility. Hafnium oxide and its derivatives have been found to show ferroelectric behavior [1,2]. Due to its excellent ferroelectric properties, CMOS compatible deposition processes and lead-free composition, $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ (HZO) can pave the way to new emerging polarization-based memories. Besides capacitor based ferroelectric random access memory (FeRAM) and ferroelectric field effect transistors (FeFET), ferroelectric tunnel junctions (FTJ) offer a possibility to store data in a non-volatile way and allow a non-destructive read-out scheme [3]. The scalability of FTJs is not limited by the amount of stored polarization charge and therefore allows a higher scalability into denser memory arrays [4]. The concept of tunnel junctions was first proposed by Esaki in 1971 [5], but experimental results only became available in the recent decade due to the possibility of reliable thin film growth techniques [6]. FTJs utilize a thin ferroelectric layer sandwiched between two (different) electrodes, which allows electron tunneling through the oxide layer (tunneling electroresistance; TER). The two different polarization states are used to alter the potential landscape and therefore change the tunneling transmission coefficient, giving the possibility to store binary data [7]. Due to the limited thickness scaling of HZO without loss of its ferroelectric properties [8], pure metal-ferroelectric-metal

Fig. 3 Simulated band diagrams of the TiN/Hf_{0.5}Zr_{0.5}O₂/Al₂O₃/TiN capacitor revealing the working mechanism of an FTJ based on the two polarization states: a) downwards polarization P_{down}, where no tunneling current through the barrier is expected, b) upwards polarization P_{up}, where a larger tunneling current through the Al₂O₃ layer can be achieved.

stacks are harder to realize for this kind of device, although there have been reports that utilize this setup [9]. Instead, we incorporate an additional dielectric aluminum oxide layer into the capacitor which will serve as the tunneling barrier, while the hafnium zirconium oxide functions as the polarization reversal layer, resulting in a metal-ferroelectric-dielectric-metal (MFIM) stack with symmetric titanium nitride electrodes. Fujii *et al.* have recently shown that these two-layer stacks can exhibit the typical characteristics of a ferroelectric tunnel junction [10].

II. EXPERIMENTAL

MFIM capacitor structures were deposited directly on a p-doped silicon wafer with a native SiO₂. The 12 nm thick TiN top and bottom electrodes were reactively sputtered at room temperature in a BESTEC physical vapor deposition (PVD) tool. Hafnium zirconium oxide and aluminum oxide were deposited without vacuum break in an Oxford OpAL atomic layer deposition (ALD) tool, using TEMA-Hf, TEMA-Zr and TMA as precursors and water as the oxygen source. HZO (with a ratio of hafnium/zirconium 50:50) and Al₂O₃ films were deposited at a temperature of 260°C, with varying thicknesses that can be controlled by the number of ALD cycles. Two different thicknesses for the HZO layer (8 nm and 12 nm) and seven different thicknesses for the Al₂O₃ layer (0.5/1/1.5/2/2.5/3/4 nm) were utilized. After completion of the stack, a post-deposition annealing step for crystallization was carried out at 600 °C for 20 s in a nitrogen atmosphere. The capacitor area was defined by evaporating 10 nm titanium and 30 nm platinum as circular contact metal pads through a shadow mask with a diameter of 200 μm and subsequent structuring of the TiN top electrode by wet etching with an SC1 clean. Fig. 1 depicts the schematic setup of the MFIM capacitor structure. In Fig. 2 a transmission electron

microscope (TEM) cross-section image of the device is shown. Polarization-voltage measurements (P-V) were carried out using an aixACCT TF Analyzer 3000 by applying triangular pulses with a frequency of 10 kHz and measuring the current response, which is integrated over time to obtain the polarization charge. Device operation and retention was measured on a semi-automatic probe station using a Keithley 4200 SCS with pulse measurement units for voltage and current detection.

III. DEVICE CONCEPT AND OPTIMIZATION

The simplest form of a ferroelectric tunnel junction consists of two metal electrodes where a thin ferroelectric film is sandwiched in between (metal-ferroelectric-metal; MFM). When using the same electrodes and a homogeneously deposited ferroelectric layer, no difference in the tunneling coefficient is expected for the two different polarization states due to the (ideal) complete symmetry of the stack in both configurations. Nonetheless, different tunneling resistances have been achieved in nominally symmetric stacks, which is attributed to different interface states due to the experimental deposition procedure [11]. Additionally, the different electron screening length of the metal electrodes can alter the potential landscape for the two polarization states, resulting in two different tunneling resistances. When using this simple approach of MFM stacks, a very thin ferroelectric layer is needed due to the exponential decrease of the direct tunneling current with increasing tunnel layer thickness. However, achieving layer thicknesses down to the single nanometer range while maintaining sufficient ferroelectric behavior might turn out to be difficult depending on the material that is used [12,13].

Another approach has been theoretically investigated [14,15]: the combination of a ferroelectric layer and a dielectric layer between the metal electrodes. Due to the asymmetry, the inner potential of this asymmetric 2-layer structure can be changed into a potential barrier or a potential well by switching between the two polarization states. This resulting difference in the barrier height and tunneling length is responsible for the two different tunneling resistances. The band diagram in Fig. 3 shows this schematic device operation for our metal-ferroelectric-dielectric-metal (MIFM) capacitor. It shows the simulated band diagrams of the stack with two opposite

Fig. 4 Electrical polarization hysteresis measurement of a reference TiN/Hf_{0.5}Zr_{0.5}O₂/TiN sample, showing good ferroelectric properties: a) polarization hysteresis with a remanent polarization P_r = 20 μC/cm², b) endurance plot showing only a weak wake-up and fatigue behavior up to 10⁷

Fig. 5 a) Experimental I-V curve for a TiN/Hf_{0.5}Zr_{0.5}O₂/Al₂O₃/TiN device with 12 nm ferroelectric and 2.5 nm dielectric layer, b) prepolarization pulses to set the polarization state into the up and down orientation.

polarization states in the HZO layer (P_{up} and P_{down}) and an additional bias at the bottom TiN electrode. Significant tunneling through the dielectric layer only occurs for the P_{up} state, while in the P_{down} state a much smaller tunneling current is expected.

IV. RESULTS AND DISCUSSION

In Fig. 4, the polarization hysteresis and the endurance behaviour of a TiN/HZO/TiN reference sample (produced with same deposition parameters as described in section II.) is shown. The reference samples with a 12 nm thick HZO ferroelectric layer without the dielectric layer shows a very good ferroelectric response (as seen in Fig. 4a). The detailed optimization conditions for these layers can be found elsewhere [8]. The maximum remanent polarization P_r is found to be $20 \mu\text{C}/\text{cm}^2$. In the endurance plot (Fig. 4b) only a weak wake-up and fatigue behavior is detected. The wake-up effect is attributed to internal bias fields from inhomogeneously distributed defects which can be moved by cycling of the sample. Continuous cycling of the ferroelectric layer leads to a homogeneous distribution of defects that reduces the internal bias fields and opens up the hysteresis [16]. This leads to a higher amount of switching domains and an increase of the P_r value [17]. In our samples the wake-up is negligible. The pure HZO sample can be cycled up to 10^7 times before reaching a hard breakdown without major loss of ferroelectric properties. This ensures the necessary high quality of the ferroelectric film to warrant that the characterization results of the MFIM structures are not limited by the ferroelectric layer.

The electric measurement results described in the following are derived on a fixed HZO layer thickness (12 nm) and varying Al₂O₃ dielectric layer thicknesses. Fig. 5 shows a typical I-V curve measured on the MIFM samples together with the pre-polarization pulse waveform that was used to set the two different polarization states. A triangular pulse with a frequency of 10 kHz with a varying voltage amplitude, depending on the thickness of the aluminum oxide layer was used to set the ferroelectric state (see Fig. 5b). The switching field of the HZO layer is expected to stay constant, so when increasing the Al₂O₃ thickness the external voltage must be increased accordingly to achieve the same voltage drop across the ferroelectric layer. For example, when adding 0.5 nm of aluminum oxide nearly the same external bias as for the reference samples (amplitude of 4 V) is needed for switching

Fig. 6 a) Dependence of the current on/off ratio on the thickness of the Al₂O₃ dielectric layer (for a fixed 12 nm HZO thickness) showing where device operation is possible, b) retention measurements at room temperature.

between the polarization states. However, when the dielectric layer thickness increases to 4 nm the external voltage has to be increased to 7.5 V to achieve the polarization switching. The pre-polarization pulse always consists of both negative and positive amplitude regions (or vice versa) to guarantee complete switching of the ferroelectric layer. To achieve the I-V curves in Fig. 5a, the bias was applied to the bottom TiN electrode while grounding the top TiN electrode. Depending on the previously set polarization the device shows two different current levels. When the polarization is pointing towards the bottom electrode, a current of 1.4 nA is measured at 2 V bias. For the opposite case (polarization pointing towards the top electrode) at 2 V bias a much smaller current of only 0.1 nA is measured. The existence of these clearly separate resistance states is compelling evidence for a TER effect.

In Fig. 6a the dependence of the on/off-ratio on the different thicknesses of the aluminum oxide is shown. The current to determine this ratio was taken at the read voltage of 2 V, pre-polarization was carried out as described before. The influence of the dielectric thickness is crucial for the device operation. For smaller thicknesses higher tunneling currents are expected. During readout operation the internal electric field in the ferroelectric layer has to be below the coercive field in order not to disturb the stored state. However, from the band diagrams similar to the ones shown in Fig. 3 it becomes clear that for too thin aluminum oxide layers the potential of the top electrode cannot exceed the conduction band of the ferroelectric. Hence the tunneling coefficient becomes very small independently of the polarization state of the HZO layer. In this case of a very thin aluminum oxide thickness, the read voltage of 2 V is already enough to switch the polarization. Therefore disturb free readout is not possible for this stack configuration. When measuring the I-V curves for the samples with a 2.5 nm and 3 nm aluminum oxide layer, no disturbance of the stack is measured when applying the read voltage for the current readout. Therefore, a significant current difference for the two device states is found. Only in this range for the dielectric thickness the device is working and can be operated as a memory. When further increasing the aluminum oxide thickness the tunneling coefficient becomes very low due to the high width of the dielectric barrier, rendering the device inoperational again. This gives a limited range for the dielectric thickness where functionality of the FTJ is ensured. In addition,

retention measurements were examined on these devices. In Fig. 7b the retention of the device with a 12 nm HZO ferroelectric and a 2.5 nm Al_2O_3 dielectric layer is shown up to 2 days. Extrapolation to 10 years gives a residual on/off ratio of 3. The drop in the higher current state over time is caused by the depolarization field that is induced by the uncompensated polarization charge at the ferroelectric/dielectric interface [18]. The incomplete screening of the ferroelectric charges through the second capacitor in series (dielectric Al_2O_3 layer) is responsible for a constant electric field across the HZO layer, which eventually might result in back-switching of the polarization and charge trapping effects and therefore impacts the tunneling current of the device. Further optimizations of the layers in regards to permittivity and thickness as well as the optimization of the different interfaces should be able to reduce the depolarization fields and therefore improve the retention for longer times also at higher temperatures.

V. CONCLUSION

In summary we fabricated metal-ferroelectric-dielectric-metal capacitor devices that can function as novel ferroelectric tunnel junctions compatible with standard semiconductor fabrication processes. The $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3/\text{TiN}$ stack benefits from the stable ferroelectric switching in the hafnium zirconium oxide layer while the aluminum oxide dielectric serves as the tunneling barrier. This way stable writing and read-out operation can be achieved by having two distinct layers with different purpose in the stack. A large tunneling electroresistance effect can be achieved with a TER ratio of about 14. The tunneling effect through the aluminum oxide barrier is strongly dependent on the thickness of this layer, giving a certain range for a stable operation of the device. Retention measurements show the potential that these CMOS-compatible devices have for application in non-volatile FTJ memory devices. Therefore, encouraging results with an optimized thickness ratio of the ferroelectric and tunneling layer are achieved. Further optimization will target at increasing the read current and lowering the depolarization field to achieve even better retention.

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