**Tunneling electroresistance effect in a Pt/Hf$_{0.5}$Zr$_{0.5}$O$_2$/Pt structure**

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The present work reports the fabrication of a ferroelectric tunnel junction based on a CMOS compatible 2.8 nm-thick Hf$_{0.5}$Zr$_{0.5}$O$_2$ tunnel barrier. It presents a comprehensive study of the electronic properties of the Pt/Hf$_{0.5}$Zr$_{0.5}$O$_2$/Pt system by X-ray photoelectron and UV-Visible spectroscopies. Furthermore, two different scanning probe techniques (Piezoresponse Force Microscopy and conductive-AFM) were used to demonstrate the ferroelectric behavior of the ultrathin Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer as well as the typical current-voltage characteristic of a ferroelectric tunnel junction device. Finally, a direct tunneling model across symmetric barriers was used to correlate electronic and electric transport properties of the ferroelectric tunnel junction system, demonstrating a large tunnel electroresistance effect with a tunneling electroresistance effect ratio of 20.

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Modern electronic devices rely on the development of high-density, high-speed, and low power consumption semiconductor memories. Although a wide variety of memory types is available, the market is mainly dominated by Dynamic Random Access Memory (DRAM). However, DRAM has gradually reached its physical scalability limits and new types of memory based on different physical approaches are now attracting attention. One such alternative is the ferroelectric tunnel junction (FTJ) memory, which besides good scalability offers advantages such as low operating energy, high operation speed, high endurance, non-volatility, and a simple structure.

The physical concept of FTJs was proposed by Esaki in 1971. However, the demonstration of this idea was challenging because of the difficulty of producing ferroelectric ultrathin films compatible with quantum-mechanical electron tunneling. Indeed, experimental investigations on FTJs have only just begun due to recent improvements in nanoscale fabrication and characterization techniques. An FTJ is composed of an ultrathin ferroelectric film sandwiched between two electrodes. The polarization reversal of the tunnel barrier is used to modulate the tunnel transmission coefficient, giving rise to two different electrical resistance states. This effect is known as the tunneling electroresistance effect (TER).

Selection of the ferroelectric barrier material is important for CMOS compatibility of the FTJ fabrication process. In recent years, TER effects have been reported for FTJs based on perovskite materials such as BaTiO$_3$, PbTiO$_3$, and BiFeO$_3$. Unfortunately, these perovskite materials suffer from lack of CMOS compatibility due to poor interfacing with silicon, an elevated crystallization temperature, and electrical degradation under forming gas treatment. In comparison to perovskites, Hf$_{0.5}$Zr$_{0.5}$O$_2$ films offer many advantages including: (i) moderate crystallization temperature ($T \sim 450^\circ$C), (ii) excellent ferroelectric properties (their ferroelectricity starts to exist at a thickness below ~10 nm), and (iii) CMOS compatibility. Also, their precursors (hafnium and zirconium oxide films) can be routinely grown directly on silicon substrates.

Due to the importance of Hf$_{0.5}$Zr$_{0.5}$O$_2$ films in the semiconductor industry, the present communication reports the fabrication of a FTJ consisting of a 2.8 nm-thick Hf$_{0.5}$Zr$_{0.5}$O$_2$ tunnel barrier sandwiched between Platinum (Pt) electrodes. The TER effect of the FTJ was verified by fitting the experimental data with a direct tunneling model across a potential profile with a rectangular shape. A high quality Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer was deposited on a (111)-oriented polycrystalline Pt substrate. Before deposition, the substrate was ultrasonically rinsed with acetone and methanol, followed by one annealing at 650°C to stabilize the Pt microstructure. The Pt/Hf$_{0.5}$Zr$_{0.5}$O$_2$ (2.8 nm) hetero-structure was grown via on-axis radio-frequency (RF) magnetron sputtering at 450°C, using a deposition pressure of 5 mTorr (2 sccm O$_2$ and 2 sccm Ar) for an RF power of 20 W on a 1-in. target.

The atomic percentage of Hf, Zr, and O in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ films was determined by X-ray photoelectron spectroscopy (XPS, VG Escalab 220i XL) with a monochromatic Al K$_\alpha$ X-ray source. All high resolution spectra were collected in the constant pass energy (20 eV) mode. The binding energy scale was calibrated using a pure gold standard sample and setting Au 4f$_{7/2}$ at a binding energy of 84 eV. The energies and intensities of the photoelectron peaks were analyzed with the CasaXPS processing software. The thickness, surface roughness, and density of the film were determined by X-ray reflectivity (XRR) using a Philips X’Pert materials research diffractometer and the Gen-X software. Ferroelectric switching of the films was studied by Piezoresponse Force Microscopy (PFM) using an AIST-NT SPM instrument. Conductive Pt-Ir coated silicon cantilever
tips (radius of ~30 nm) were used for PFM imaging and polarization studies.

The band gap energy \( (E_g) \) of a 47 nm-thick Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) layer grown on quartz (0001) was calculated from a Tauc plot method using the transmission spectra obtained from a Perkin-Elmer UV/VIS spectrometer. To determine the band alignment of Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) with Pt, crystalline Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films with thicknesses of 2.8 nm (ultrathin) and 15 nm (bulk) were deposited on Pt substrates. XPS was employed to measure the shallow core level, valence band maxima, and Fermi energies.

Nanoscale electrical measurements were performed by conductive-AFM (C-AFM). For the electrical characterization, a Pt top electrode was deposited using DC sputtering through a shadow mask consisting of an array of 300 \( \mu \)m diameter holes. Local \( I-V \) characteristics were measured by positioning a conductive Pt–Ir coated silicon tip at a given point on the top electrode surface.

In a FTJ, the tunneling current that flows through the ferroelectric barrier depends highly on the barrier thickness. Therefore, it is crucial to determine the layer thickness of our films. In the present work, the layer thicknesses were found to be 2.8 nm for the film used in fabrication of the FTJ and 15 nm for those used to analyze the chemical composition (Fig. 1(a)). The presence of multiple oscillations in both XRR curves indicates a smooth surface (rms ~0.8 nm). The densities of 8.40 g/cm\(^3\) and 8.73 g/cm\(^3\) were obtained for the 2.8 nm and 15 nm thick films, respectively. These values are comparable with those reported in the literature (8.34 g/cm\(^3\)).

To investigate the chemical stoichiometry of the Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films on Pt substrates, an XPS analysis was performed. Fig. 1(b) shows a survey scan, which revealed the presence of Hf, Zr, O, and C on the sample surface. Additional, high resolution scans were performed in the selected binding energy ranges for Hf, Zr, and O to determine the elemental composition of the deposited film. As can be seen from Fig. 1(c), Zr3d consists of two wide peaks, Zr3d\(_{5/2} \) (~180.5 eV) and Zr3d\(_{3/2} \) (~182.8 eV), due to the Zr–O bonds. In Fig. 1(d), the two peaks, at ~17.3 eV and ~18.80 eV, are due to Hf4f\(_{7/2} \) and Hf4f\(_{5/2} \), respectively, and correspond to the Hf–O bonds. The peak at 530 eV in Fig. 1(b) is attributed to the main peak of O1s in the orthorhombic lattice of Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\). The relative atomic concentrations were determined based on the peak areas and the relative sensitivity factors. Films grown at 450 °C had a stoichiometry of ~0.5:0.5:2 (Hf:Zr:O).

Contrary to conventional ferroelectric memories (Fe-RAMs), the scalability of the FTJs is not limited by its readout process, since the tunneling conductance in an FTJ does not depend on the amount of the stored charges and can be probed in a non-destructive way, allowing the fabrication of denser semiconductor memories. However, one of the main challenges is to achieve a stable polarization in the ultrathin barrier layer. In that sense, ferroelectric characterization is crucial for ultrathin films. In this work, the ferroelectric properties of the Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) film were investigated by PFM. The local piezoresponse was measured at room temperature on the bare surface of the 2.8 nm-thick Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) films. A clear hysteresis was observed in both phase and amplitude signals (Figs. 2(a) and 2(b)). Both signals were acquired away from the contact resonance frequency of the cantilever (\( f_{\text{PFM}} = 51 \) kHz, \( f_{\text{Cantiliver}} = 600 \) kHz) as a function of voltage, which was applied to the conductive tip while the bottom electrode (BE) remained grounded. The ferroelectric behavior presented in Fig. 2 is attributed to the formation of the non-centrosymmetric orthorhombic phase (Pbc\(_{21}\)). For a thickness below 10 nm, this ferroelectric phase is induced by tensile strain from the coalescence of the nucleating grains. The values of the coercive voltages creating the downward and upward polarizations are +1.9 V and −1.9 V, respectively.
Different regions of the Hf$_{0.5}$Zr$_{0.5}$O$_2$ film were poled by a constant voltage to the tip while scanning the film’s surface. The resulting PFM phase image, presented in Fig. 2(c), shows a phase contrast of $\sim 180^\circ$ between the square domains written at $+3 \, \text{V}$ and $-3 \, \text{V}$; qualitatively, this demonstrates the appearance of the downward and upward polarization states, respectively. The unpoled region outside the larger domains corresponds to the sample virgin state, which exhibits a spontaneous upward polarization. The amplitude image (Fig. 2(d)) reveals narrow dark lines, which are attributed to domain walls. The PFM measurements presented here attest to the stable polarization in the ultrathin Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer and therefore fulfill a crucial requirement for quantum-mechanical tunneling in a FTJ memory.

To verify if Hf$_{0.5}$Zr$_{0.5}$O$_2$ films are suitable for FTJ devices, the optimized potential barrier profile has to be studied. For this purpose, optical characterization by UV/visible transmission spectroscopy and XPS band structure analysis were found complementary in identifying a suitable ferroelectric material. To gain quantitative information on the material’s electronic properties, we characterized the band line-up at the Pt/Hf$_{0.5}$Zr$_{0.5}$O$_2$ interface using a Kraut procedure. In this method, XPS spectra of both (core levels and valence bands) were simultaneously recorded and used to determine the valence band offset (VBO) first. The valence band maximum (VBM) of Hf$_{0.5}$Zr$_{0.5}$O$_2$ and the Fermi level ($E_F$) of Pt were determined by extrapolating the leading edge to the baseline and finding the intersection point. The binding energy difference between the shallow core peaks (Pt4f and Hf4f), $E_F$, and the VBM were measured and referenced with core level binding energies of ultrathin heterostructures in order to calculate the valence band offset (VBO), according to:

$$VBO = (E_{\text{Pt}4f} - E_F)_{\text{Pt}} - (E_{\text{Hf}4f} - \text{VBM})_{\text{HZO}} - (E_{\text{Pt}4f} - E_{\text{Hf}4f})_{\text{HZO}/\text{Pt}}.$$  

The energy separation between the Pt4f centroid and the leading $E_F$ was estimated to be $70.5 \pm 0.05 \, \text{eV}$ for a clean, thick Pt layer, as shown in Fig. 3. Similarly, the energy difference between the Hf4f centroid and the VBM for the Hf$_{0.5}$Zr$_{0.5}$O$_2$ thick film was estimated to be $14.3 \pm 0.05 \, \text{eV}$. The binding energy difference between Pt4f and Hf4f core levels was calculated to be $53.5 \pm 0.05 \, \text{eV}$ for a XPS spectrum measured on the Hf$_{0.5}$Zr$_{0.5}$O$_2$ (2.8 nm)/Pt heterostructure. Substituting these values in Eq. (1), a VBO of $2.70 \pm 0.05 \, \text{eV}$ was obtained.

Knowing $E_g$ values from the UV/visible measurements ($5.37 \, \text{eV}$, Fig. S1, supplementary material) and the VBO from the XPS analysis ($2.70 \, \text{eV}$), we estimated the conduction band offset or potential step height ($\phi$) using:

$$\phi_{1(2)} = E_g - \text{VBO}_{\text{Pt}/\text{HZO}}.$$  

A value of $2.67 \pm 0.07 \, \text{eV}$ was obtained. The electronic band diagram of Fig. 4 corresponds to the Pt/Hf$_{0.5}$Zr$_{0.5}$O$_2$/Pt heterostructure for a voltage equal to zero (rectangular shape). From the above PFM analysis, it is known that the obtained potential step height corresponds to a ferroelectric film with a spontaneous upward polarization.

While it is commonly accepted that in order to have a sizable TER effect, it is mandatory to have asymmetric FTJs (junction that involves different electrodes); however,
recent theoretical\textsuperscript{22} and experimental\textsuperscript{21} results showed a large TER effect in symmetric FTJs (Junction that involves similar electrodes). Moreover, some drawbacks concerning retention time, switching, and polarization imprint in asymmetric FTJs were reported.\textsuperscript{22} Thus, we focused this work on a FTJ fabricated by covering with a Pt top electrode the 2.8 nm-thick Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} film deposited on the Pt layer. The resulting FTJ was characterized by measuring its hysteretic I–V curve. Voltage sweeps were applied to the top electrode via a conductive AFM tip. The bottom electrode was grounded and a compliance current of 100 nA was set during the measurements to avoid soft dielectric breakdown was grounded and a compliance current of 100 nA was set during the measurements to avoid soft dielectric breakdown of the junctions (Fig. 5(a) inset). A typical I–V curve is shown in Fig. 5(a). It displays a hysteretic behavior characterized by two different resistance states: an initial high-resistance state and a low-resistance state. The existence of two clearly defined resistance states suggests a TER effect.\textsuperscript{20}

To confirm that the electric switching observed by C-AFM is due to the TER effect rather than another resistive switching mechanism, we correlated the electronic structure depicted in Fig. 4 with the transport properties of the Pt/Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/Pt tunnel junction,\textsuperscript{23} assuming direct tunneling across a rectangular shaped electronic profile.\textsuperscript{16} This model, known as the Simmons model,\textsuperscript{16} is based on Fermi-Dirac statistics and WKB approximation, assuming a low voltage (V) and a barrier width (s). The tunneling current density (J) through a barrier at low voltage range is given by

\begin{equation}
J = \left[ \frac{3(2m\varphi)^2}{2s} \right] \left( \frac{e}{\hbar} \right)^2 V \times \exp \left[ \frac{-4(4s\varphi)}{\hbar} \frac{(2m\varphi)^2}{C_0} \right],
\end{equation}

where “m” is the effective electron mass, “\varphi” is the electronic potential barrier height, “\hbar” is the Plank constant, and “e” is the electron charge. The experimental I–V curve for the “OFF” state (upward polarization) was fitted using the experimentally determined parameters such as electronic potential barrier height (\varphi = 2.67 eV), barrier width (s = 2.8 nm), and adding only the scaling factor, which was assumed to be the same for both states, following the method described in the literature.\textsuperscript{20,24} Then, using the same scaling factor, the same barrier width (s = 2.8 nm), and Eq. (3), the I–V curve for the “ON” state was fitted to obtain the potential step barrier height for that state (\varphi = 2.33 eV). The change in the barrier height is (\Delta \varphi) \approx 13\%. The TER effect in our FTJ was quantified by the TER ratio (J\textsubscript{OFF} – J\textsubscript{ON}/J\textsubscript{ON}), resulting in a ratio of 20; this value is in the typical range of TER ratios (10 > TER ratio > 100).\textsuperscript{6}

In the Pt/Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/Pt configuration, the nominal symmetry is in fact incompatible with the large TER effect observed and the effects invoked by Bilc et al.\textsuperscript{22} for an FTJ with symmetric electrodes cannot account for the values we observe. We attribute the \textit{de facto} asymmetry to the presence of different interface states as our experimental procedure required the breaking of the vacuum for the top electrode deposition through a contact mask. Owing to the TER effect, an FTJ’s electrical resistance depends on the polarization orientation.\textsuperscript{18} The low resistance state of our FTJ occurs when the ferroelectric polarization of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} points to the Pt bottom electrode (BE), it bends down the conduction band and lowers the potential barrier height (Fig. 5(b)), due to the build up of negative screening charges near the Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/Pt (BE) interface.\textsuperscript{5,6,18} Inversely, when the ferroelectric polarization of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} points to the Pt top electrode, positive screening charges will build up at the Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}/Pt (BE) interface bending upward the conduction band, and creating an insulating region at the bottom interface, resulting in a high-resistance state of the device.\textsuperscript{5,6,18}

In summary, we fabricated a FTJ consisting of Pt top and bottom electrodes and a 2.8 nm-thick Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} tunnel barrier. A large change in electrical resistance was observed on this FTJ with a TER ratio of 20. This change was comparable to those reported FTJs.\textsuperscript{20} The observed TER effect was described by a direct tunneling model based on a rectangular shaped potential profile. This study attests to the potential of Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} as a FTJ CMOS compatible material to replace the current DRAM technologies.

See supplementary material for the complete optical characterization by transmission UV/visible spectroscopy.

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