Characterization of the interface electronic structure of ultra-thin ferroelectric $HfZrO_2$ films for low power, CMOS-compatible, non-volatile memories

The fast growing Internet of Things (IoT) requires intelligent, fast and energy efficient handling of sensory, inhomogeneous data that goes beyond current storage and data processing capabilities. Edge computing requires that the data are processed at the source that is the IoT sensor node, away from central processors imposing stringent requirements on the IoT devices.

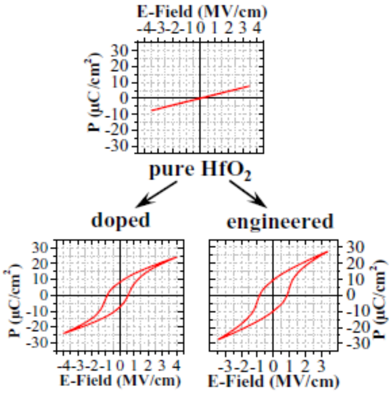
In this context, optimal usage of the constrained resources such as memory, bandwidth, processor, and most importantly power of IoT devices is necessary for sustainable and long-life IoT deployments.

The microcontroller unit (MCU) with embedded non-volatile memory (eNVM) is at the heart of IoT devices, hierarchically placed between the sensor nodes and the host microprocessor with the task of pre-computing the data to reduce heavy loading of the host processor. Most of the power is consumed during the time the MCU is inactive so eNVM can be used to realize a “normally off” MCU drastically cutting power consumption.

NV memory elements could be embedded in an advanced CMOS platform and distributed near the logic circuits to store contents locally and essentially make logic circuits non-volatile At present, eFlash is a standard NVM used in MCUs because it is high density, manufacturable and low cost technology. However, it suffers from low write speed, high power, low endurance and vulnerability to radiation.

Therefore, a new, more robust eNVM with higher speeds, lower power and high endurance is required to replace eFlash in (normally-off) MCUs.

Several NVM candidates with high speed/low power characteristics have emerged. FeRAM has the highest endurance among all NVM candidates, low energy per bit and power consumption which could make it a potentially good candidate to replace Flash in embedded applications. However, the current embedded FeRAM with perovskite FE has serious problems with regard to memory cell scaling, compatibility with Si processing, manufacturability and cost that inhibit development as a mainstream solution. New materials which overcome the shortcomings of present day FeRAM are needed.



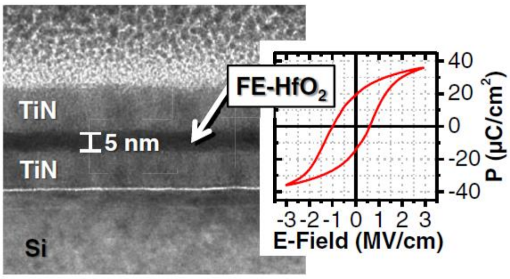


Figure 1: (left) FE HfO_2 may be obtained by doping and by strain engineering.[1] (right) 5 nm HZO capacitor

Within the framework of the H2020 European project 3εFERRO, led by the CEA, we will use FE HfO_2-based materials to develop a competitive and versatile FeRAM technology for eNVM solutions. The high-k HfO_2 gate dielectric is already key for modern nanoelectronics since it is compatible with Si technology allowing scaling of advanced CMOS. The recent discovery[2] of ferroelectricity in HfO_2 creates the prospect that this material may impact other areas such as embedded memory by allowing scaling of FeRAM cells. FE HfO_2 could also be integrated into transistor gates for 1T FeFET memory cells with non-destructive read, integrated in the FEOL with CMOS. Finally, FE HfO_2 integrated in the gate of transistor could also produce negative capacitance FETs (NCFETs)[3], functioning as low power steep slope switches to further boost low power/high performance operation.

Therefore, the functionality and versatility of ferroelectric HfO_2 could have a significant impact on embedded NVM solutions, tightly integrated with logic to increase the energy efficiency of computation.

We aim to achieve **for the first time** HfO_2-based ferroelectric phases at relatively low temperatures compatible with back end of the line processing and integrate **for the first time** HfO_2-based FeRAM arrays with CMOS to make embedded NVM using the new ferroelectric HfO_2 material. The PhD work therefore focuses on the optimization and characterization of the HfO_2-based material properties. Amongst the challenges requiring materials optimization are the remanent polarization, switching speed, reliability (wake-up, fatigue, endurance, time to breakdown), retention and coercive field.

Optimization considers atomic and electronic structural quality and physical quantities relevant for device characteristics (e.g. remanent polarization, endurance, imprint, fatigue). Films will be grown on the selected substrates by different techniques: mainly atomic layer deposition (ALD), chemical vapour deposition (CVD) and molecular beam epitaxy or deposition (MBE) with pulsed laser deposition (PLD) a possible alternative.
One partner, NaMLab (Dresden, Germany) will provide basic capacitor structures including ALD growth of doped HfO_2 and $Hf_xZr_{1-x}O_2$ and PVD deposition of various electrode materials. A second partner, NCSRD (Athens, Greece) will grow MBE HZO on several substrates including Ge.

The formation of an interface layer (IL) can be of crucial important to ultimate device performance. Control of the IL, in a capacitance or transistor structure is probably one of the major challenges for materials engineering of FE HfO_2. When used as a high k gate oxide HfO_2 is usually amorphous whereas the FE phase must be crystallized in the orthorhombic structure. It is therefore necessary to find a working compromise between thermal budget and crystallization temperature. For this reason, in addition to doped HfO_2, HZO will also be optimized, since the crystallization can be as low as 400°C[4].

Thus, in addition to the standard electrical characterization, advanced characterization tools, including HR-TEM and both soft and hard X-ray photoemission will describe the IL formation and its effect on for example band line-up and leakage. Synchrotron radiation induced

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[1] Muller et al., Ferroelectric Hafnium Oxide Based Materials and Devices: Assessment of Current Status and Future, *ECS J. Sol. St. Sci. & Technol*. **4**, N30 (2015)

[2] Contribution by members of 3eFERRO (NaMlab & collaborators): J. Muller, et al., “Ferroelectricity in simple binary ZrO_2 and HfO_2”, *NanoLett.* **12**, 4318 (12); Also: Progress Report: M.H. Park, et al., “Ferroelectricity and Antiferroelectricity of doped thin HfO_2-based films” *Adv. Mater.* **27** , 1811 (15);

[3] S. Salahuddin, S. Datta, *NanoLett.* **8** , 405 (08)

[4] Zarubin, Appl. Phys. Lett. **109**, 192903 (2016)

photoemission using both soft and hard X-rays will be carried out. Structural defects induce energy levels in the band gap, specific techniques for investigation of electrically active defects will be employed to extract information on defect activation energy, concentration and trapping cross sections. Combining results of structural, chemistry and trap investigations will further understanding of how the defects and ILs affect the material parameters and device characteristics.

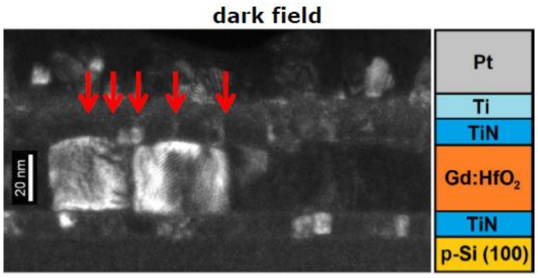

Figure 2: ~ 30 nm granularity in HfO_2 MIM structure on silicon[5]

A special effort will be dedicated to imaging FE domains in doped HfO_2 and $HfZrO_2$. Static PFM, C-AFM and Low energy and photoemission electron microscopy (LEEM and PEEM) will be employed to study domain configuration and to investigate the ferroelectricity and leakage at nanoscale. Understanding domain kinetics is essential for switching polarization and may affect the write/read speed of the memory devices. Domain switching may be also influenced by ILs or other structural defects, thus results regarding domains will be correlated with those from material and interface advanced characterization.

The thesis work will require close collaboration with the CEA partners in the 3εFERRO project. The successful candidate will participate actively in regular project meetings. The candidate will also carry out the synchrotron radiation campaigns at, for example, Soleil (Saint Aubin), Elettra (Trieste), Petra-3 (Hambourg).

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[5] Hoffmann et al., Direct Observation of Negative Capacitance in Polycrystalline Ferroelectric HfO_2, *Adv. Func. Mat.* **26** 8643 (2016)