

# Deposition of doped and undoped HfO<sub>2</sub> for fast and low energy consumption ferroelectric devices

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## 1) Context / Study motivation

IoT sensor node requires edge computing which means processing data at the source. These systems need highly energy efficient microprocessor units (MCU) using embedded non-volatile memories (eNVM). However eFLASH technology is limited by low write speed, high power and low endurance. Alternative fast, low power and high endurance eNVM could greatly enhance energy efficiency. FeRAM has the highest endurance of all emerging NVMs. However perovskite based eFeRAM is incompatible with Si CMOS, it does not easily scale and has manufacturability and cost issues.

Recently discovered doped HfO<sub>2</sub> [1] is a promising candidate to solve these problems. HfO<sub>2</sub> processes are already integrated in Si CMOS industry and in theory its ferroelectric properties allow us to use oxide layer thinner than 10nm. Nevertheless the endurance properties should be improved for industrial applications and the nucleation and stabilization of the ferroelectric phase (f-phase) is not well understood [2].

The f-phase in doped HfO<sub>2</sub> is attributed to the polar orthorhombic phase (o-III phase), but other phases are present inside the oxide after the growth.

Metal/Ferroelectric/Metal(MFM) capacitor is the elementary “brick” for FeRAM in the 1Transistor-1Capacitor (1T-1C) model. Consequently the stack TiN/Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/TiN has been particularly studied as Zr-doped HfO<sub>2</sub> exhibits quite good endurance and retention properties [3-5].

Consequently, the stack TiN/Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/TiN seems to be adapted for new fast and low energy consumption FeRAM, but more studies on the phase transition conditions are required.

## 2) Description of approach and techniques

In this work, we study different materials in order to build MFM capacitors. We have

deposited TiN by reactive sputtering in different conditions. We have deposited (Hf,Zr)O<sub>2</sub> solid solution, HfO<sub>2</sub> and ZrO<sub>2</sub> made by magnetron reactive sputtering respectively from an alloy target of Hf/Zr, from a Hf and Zr target, and also HfO<sub>2</sub> by non-reactive sputtering from a HfO<sub>2</sub> target as insulator oxides on Pt and TiN as electrodes. We compare (Hf,Zr)O<sub>2</sub> solid solution behaviour with undoped HfO<sub>2</sub> and undoped ZrO<sub>2</sub> behaviour. X-rays Diffraction (XRD) are proceeded to characterize structural properties. I(V) and C(V) characterization are performed for Pt/(Hf,Zr)O<sub>2</sub>/Pt stacks and we measure the resistivities of all electrodes.

## 3) Results / Conclusions / Perspectives

In order to reduce the thermal budget we use low temperature in-situ annealing. XRD reveals a very similar monoclinic phase for (Hf,Zr)O<sub>2</sub>, HfO<sub>2</sub> and ZrO<sub>2</sub> on Pt and TiN at 350°C which seems not to be related to the thickness. This material could be used for other high-K applications.

We observed that the HfO<sub>2</sub>, ZrO<sub>2</sub> and (Hf,Zr)O<sub>2</sub> behaviours are not the same if we proceed by in-situ annealing inside the sputtering machine or if we proceed by post-annealing process. One origin of this difference can be attributed to a difference in annealing duration.

In order to stabilize the ferroelectric phase, complementary experiments are needed, particularly deposition at higher temperature.

For the electrodes, TiN was deposited on different substrates. Different crystalline orientations were observed with the same thickness depending on the used substrate.

These preliminary results could find other applications but also could lead us to find a pathway and a better understanding of the stabilization of the ferroelectric phase as we are completing the experimental phase diagram of Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>.

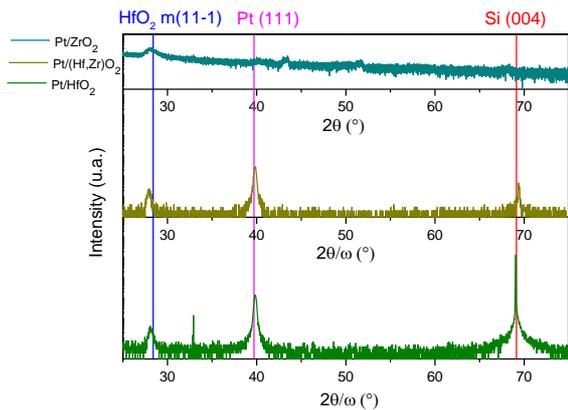


Figure 1. X-rays diffraction patterns of  $\text{HfO}_2$ ,  $\text{ZrO}_2$  and  $(\text{Hf,Zr})\text{O}_2$  solid solution at  $350^\circ\text{C}$  from respectively a Hf target, a Zr target and an alloy target of Hf/Zr with 56% of Hf and 44% of Zr by reactive sputtering on Pt. The three patterns show the nucleation of a monoclinic phase.

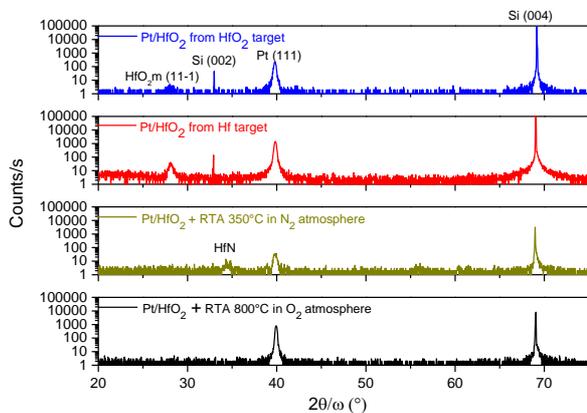


Figure 2. X-rays diffraction patterns of  $\text{HfO}_2$  grown from Hf or  $\text{HfO}_2$  targets by sputtering on Pt and annealed by different technics.

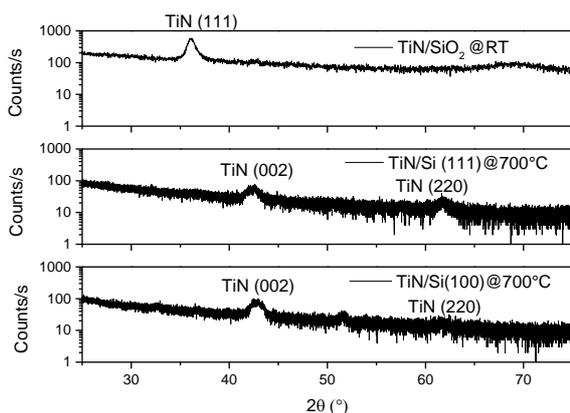


Figure 3. X-rays diffraction pattern for the growth of TiN on Si and  $\text{SiO}_2$  in the same conditions by reactive sputtering.

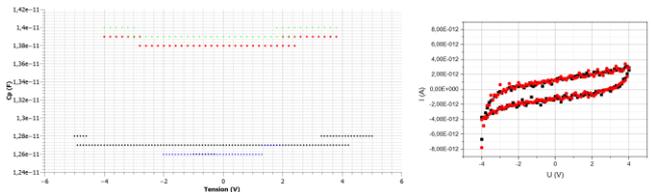


Figure 4.  $C(V)$  and  $I(V)$  characteristics for a  $\text{Pt}/(\text{Hf,Zr})\text{O}_2/\text{Pt}$  sample showing no ferroelectric behavior.

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