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Deposition of doped and undoped HfO₂ for fast and low energy consumption ferroelectric devices

Jordan Bouaziz^{1,2}

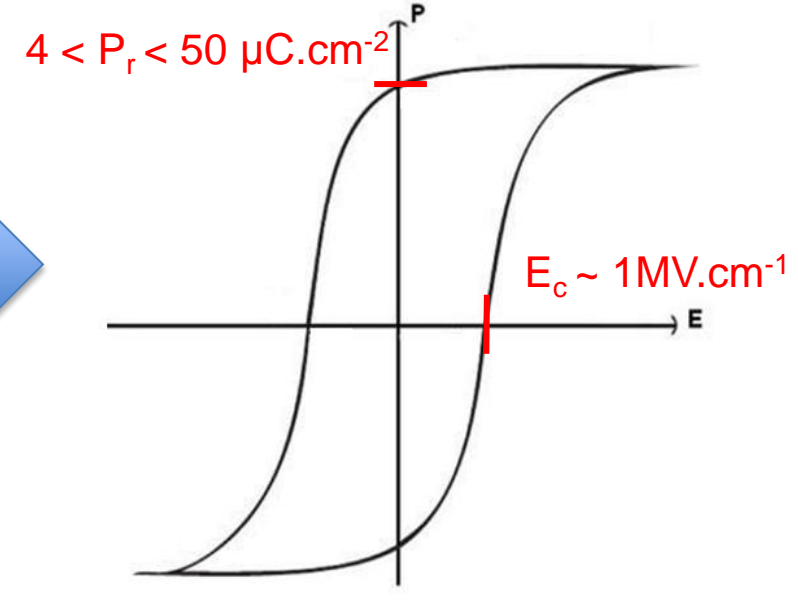
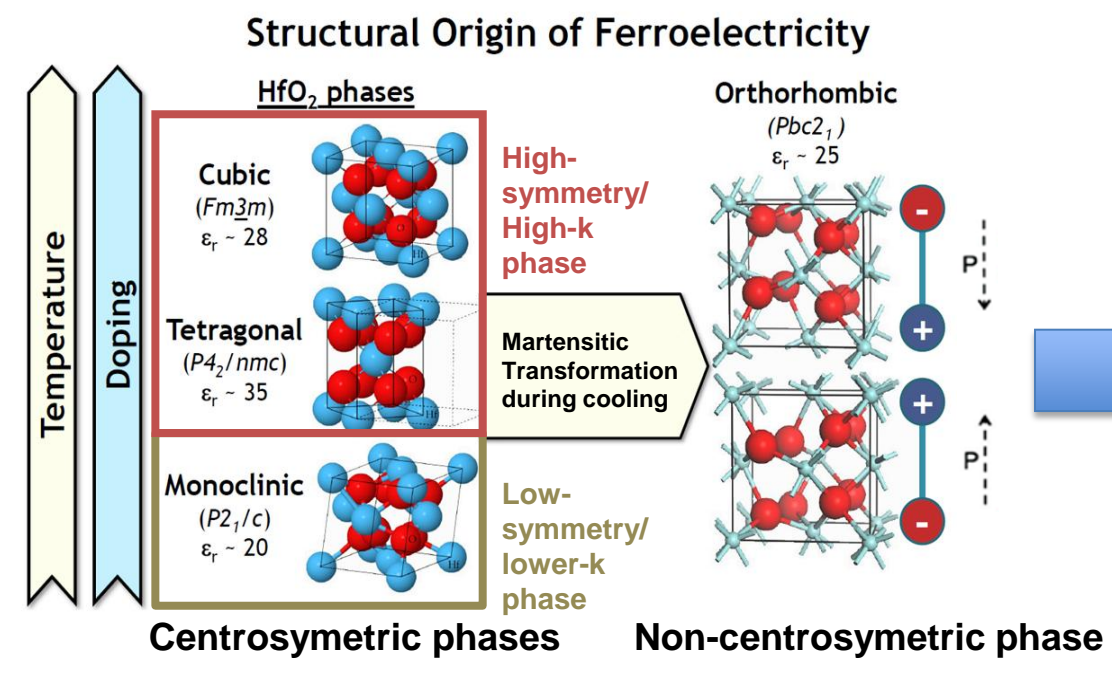
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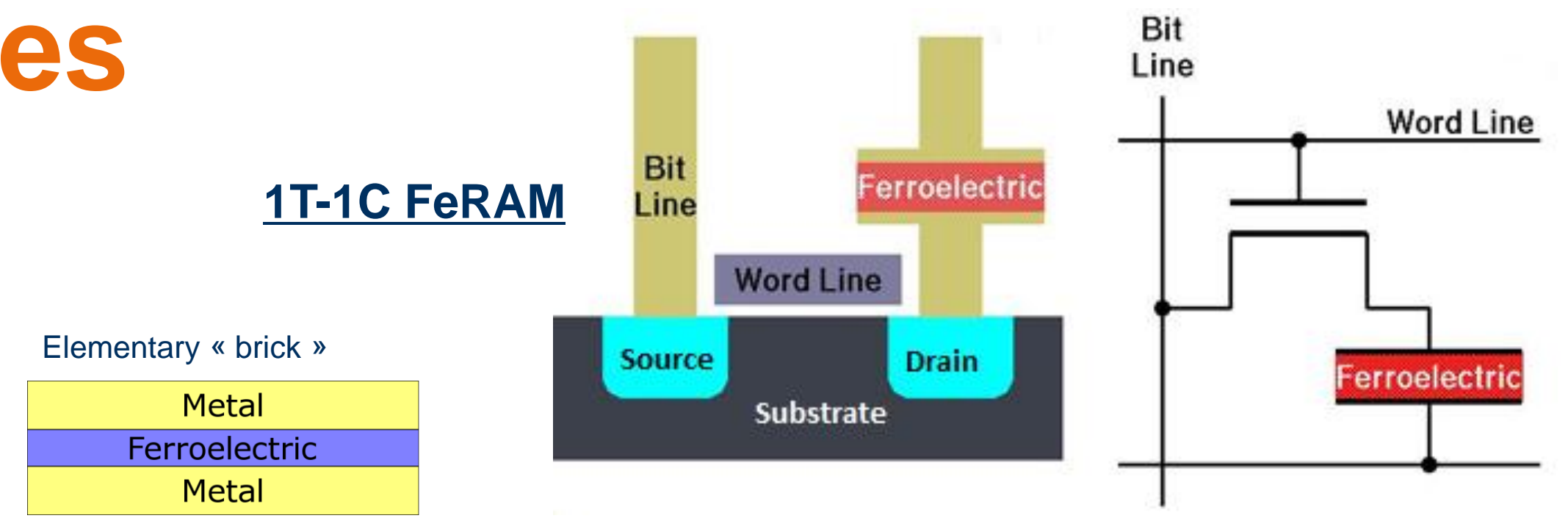
IoT sensor node requires edge computing, which means processing data at the source. These systems need highly energy efficient microprocessor units (MCU) using embedded non-volatile memories (eNVM). However eFLASH technology is limited by low write speed, high power and low endurance. Alternative fast, 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 HfO₂ [1] is a promising candidate to solve these problems. HfO₂ 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].



Motivations and objectives

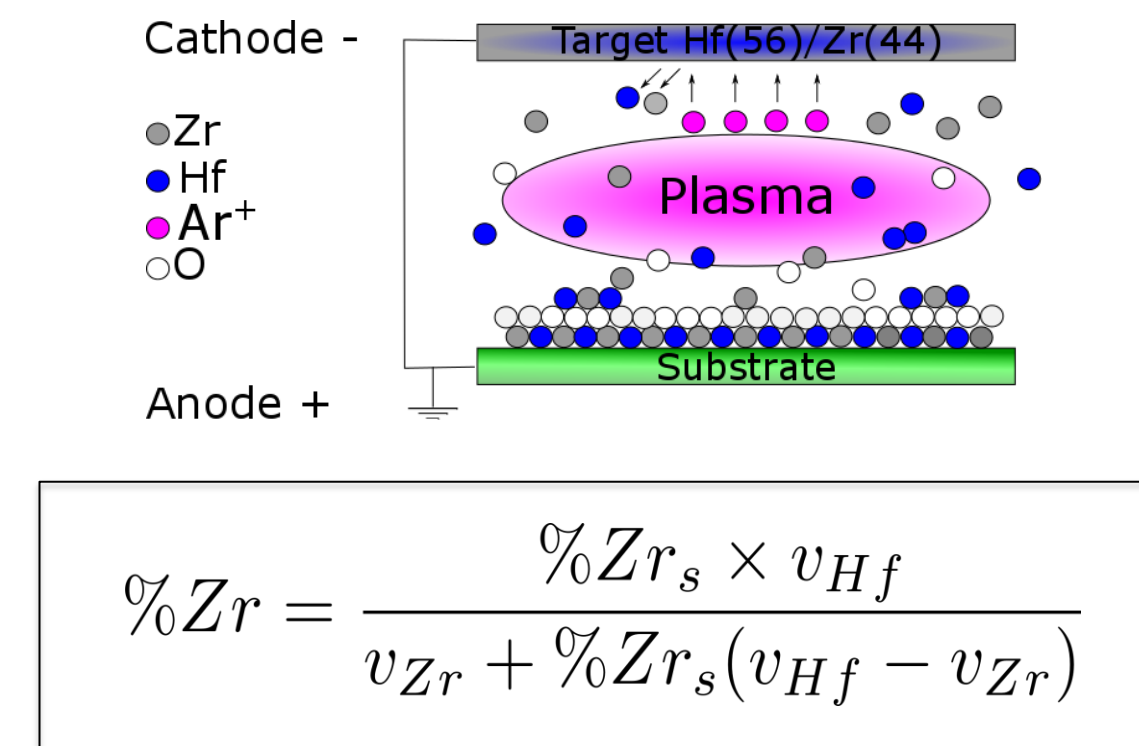
- Ferroelectric phase discovered in 2011 [1]
- Many advantages compared to « traditional » perovskite ferroelectrics
- Need Engineering :**
 - Strain from bottom **AND** top electrodes
 - Doping
 - Annealing



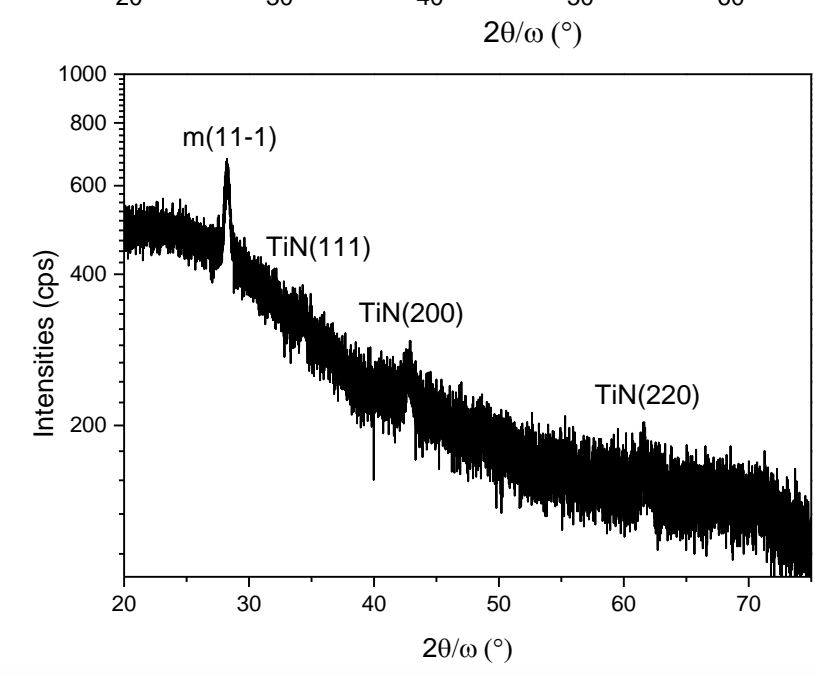
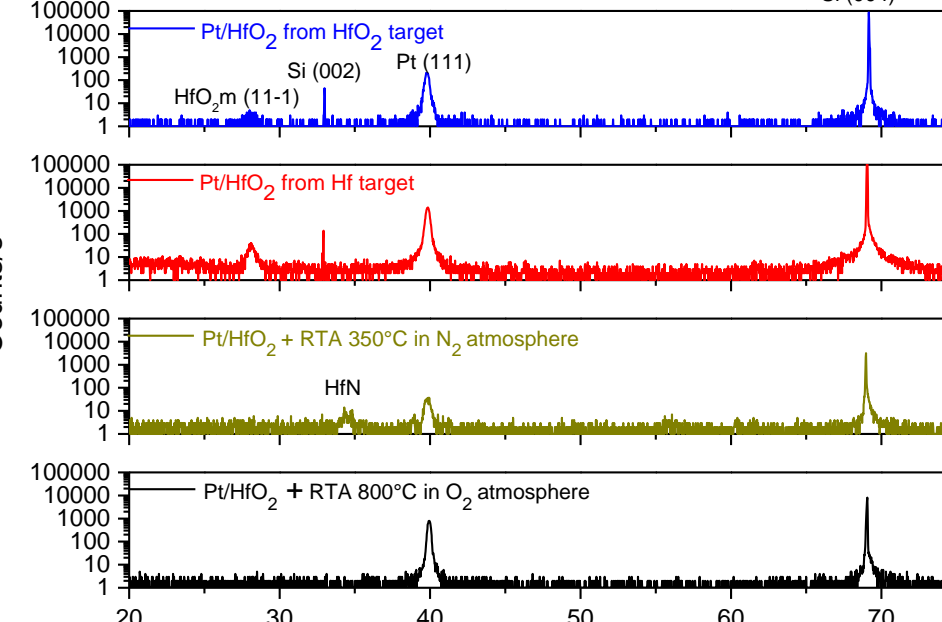
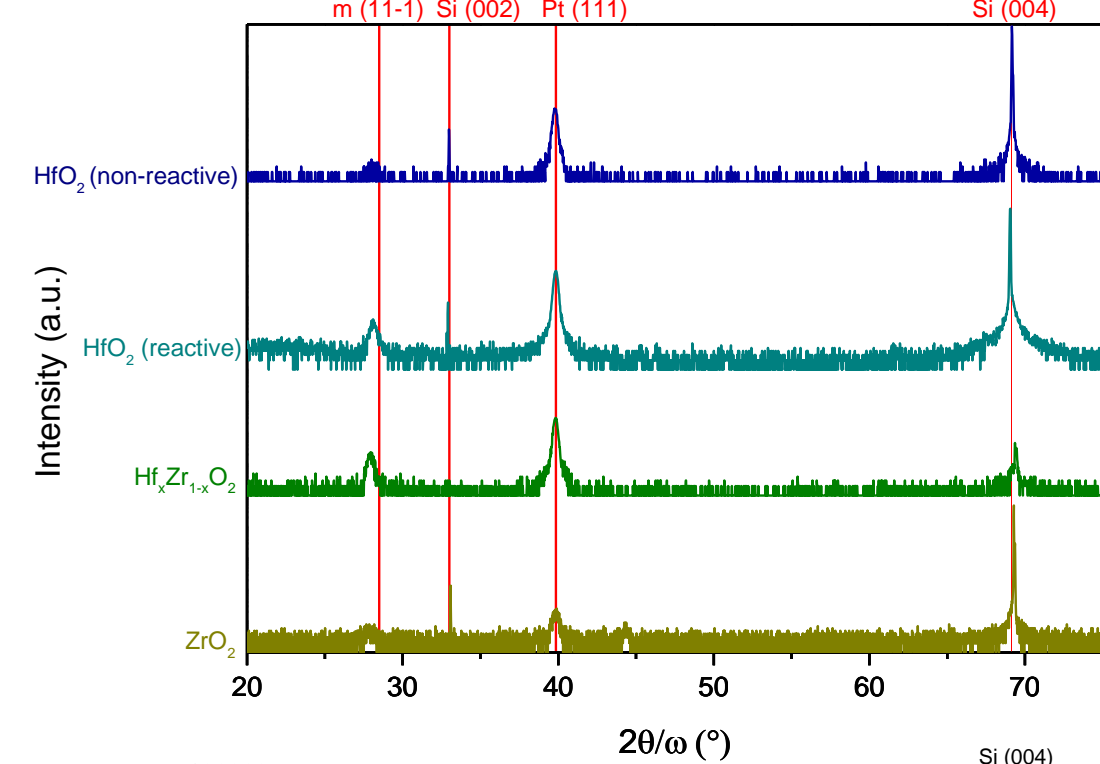
Materials Development

(Hf,Zr)O₂ solid solution from a Hf/Zr target on Pt and comparison with ZrO₂ and HfO₂

Sputtering



Resistivity Pt :
 • Effet Hall : ~11,7μΩ.cm (bulk : 11,1.10⁻⁸ Ω.m)
 • Four-probe : ~ 15-31μΩ.cm



- Amorphous deposition at RT
- See below deposition at 350° C

Issues :

In littérature, Rapid Thermal Annealing (RTA) > 400° C lead to the deposition of polycrystalline HfO₂. For time being, we didn't observe any polycrystalline HfO₂ or (Hf,Zr)O₂

(Hf,Zr)O₂ on other substrates at 350° C

⇒ Apparence of the same monoclinic phase

TiN electrodes by reactive sputtering

Cathode -

• Ti
 • N
 • Ar+
 • O

Anode +

• Ti
 • N
 • Ar+
 • O

• Ti
 • N
 • Ar+
 • O

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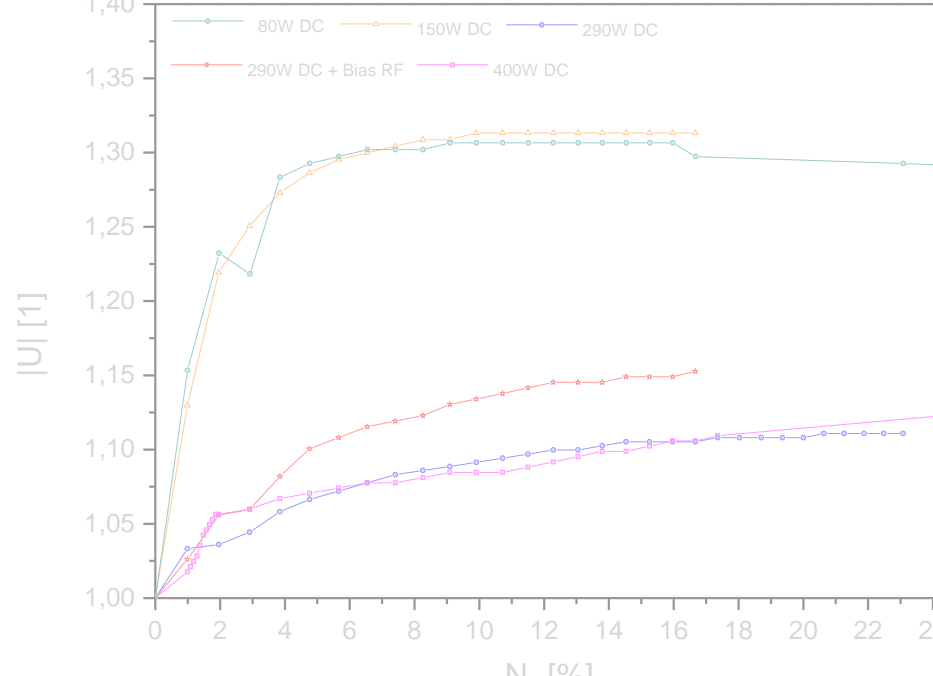
• Ti
 • N
 • Ar+
 • O

How to choose a recipe ?

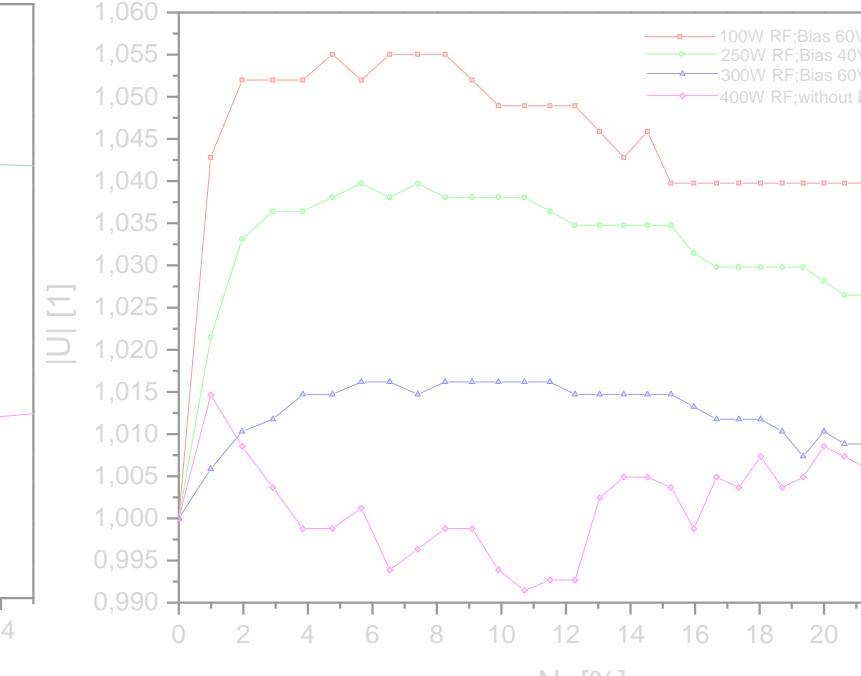
- Autopolarisation curves
- Color of the sample
- Resistivity
- Structural study of the growth

1. Autopolarisation curves

DC Deposition



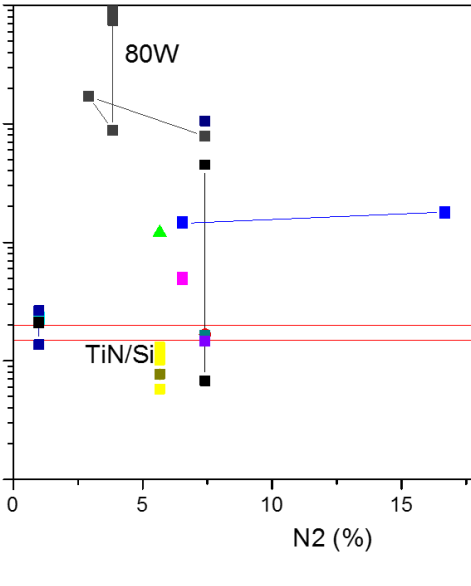
RF Deposition



3. Resistivity

- Four-probes

Qualitative Graph



Other TiN measured fabricated in the lab IMN : 83-357μΩ.cm

• Hall effect

Table

Recipe	Thickness (nm)	Resistivity (μΩ.cm)	Bulk resistivity(μΩ.cm)
IMN	1000	73,284	20-25
300W RF - 60V DC	350+/10	31,119	20-25
200W RF - 40V DC	~115	72,543	20-25
300W RF - 60V DC	50	61,978	20-25

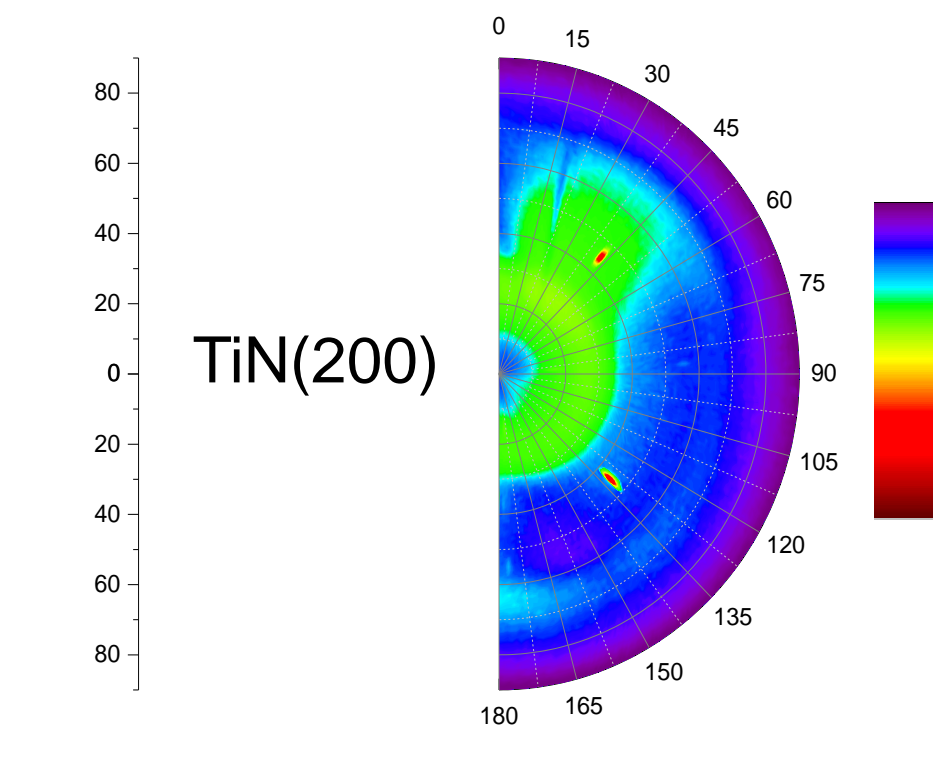
2. Color of the sample : no golden sample in DC deposition were fabricated.

4. Structural study

Chosen Recipe : 300W RF + 60V Bias – 700° C

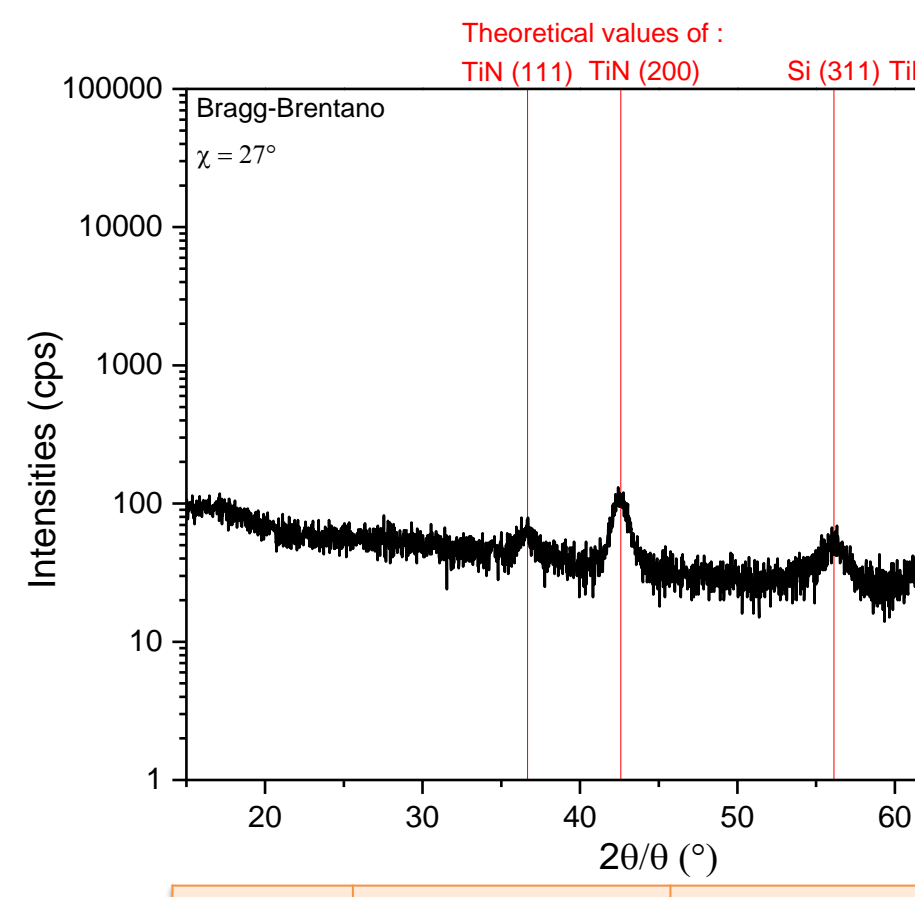
Growth :

- Epitaxy ?
- Fiber ?
- Powder ?



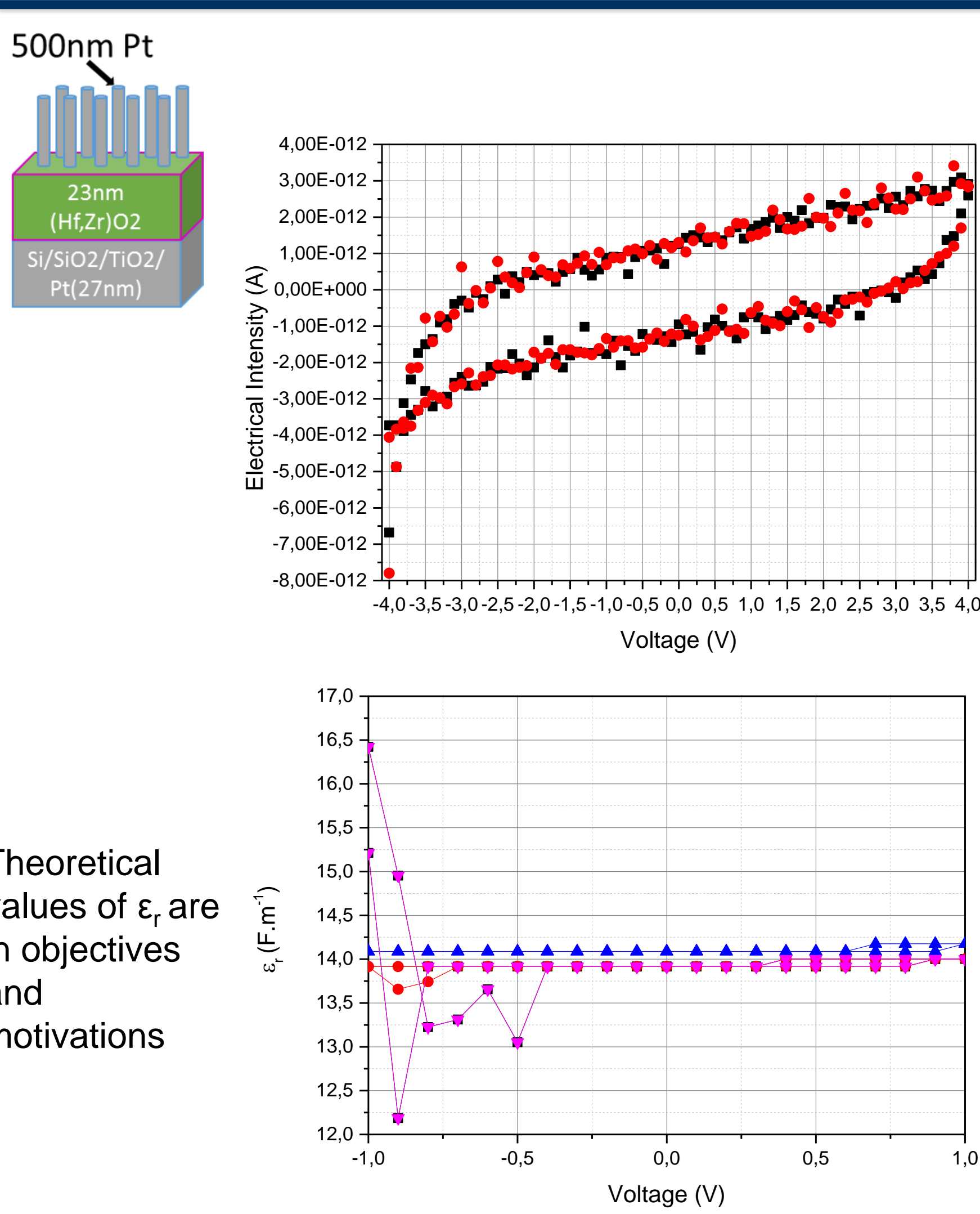
• The material seems to be a fiber (or maybe a powder).

• However the peaks position matches very well with theory → Further studies need to be done.

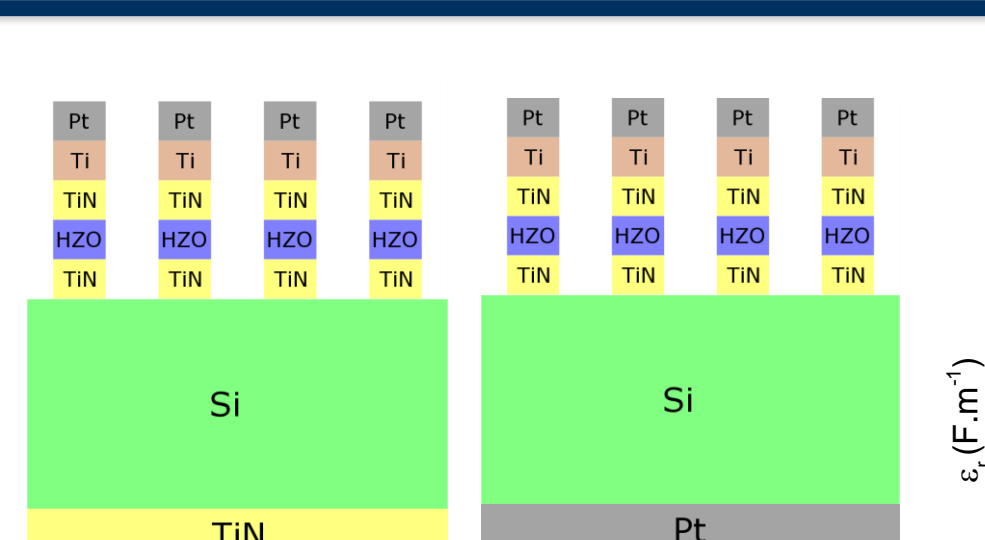


Cubic TiN peak	Theoretical Lattice parameter (Å)	Measured Lattice parameter (Å)	Error (Å)
(111)	a = 4,24173	4,2444	-0,0001
(200)		4,2413	0,0022
(220)		4,2537	0,0012

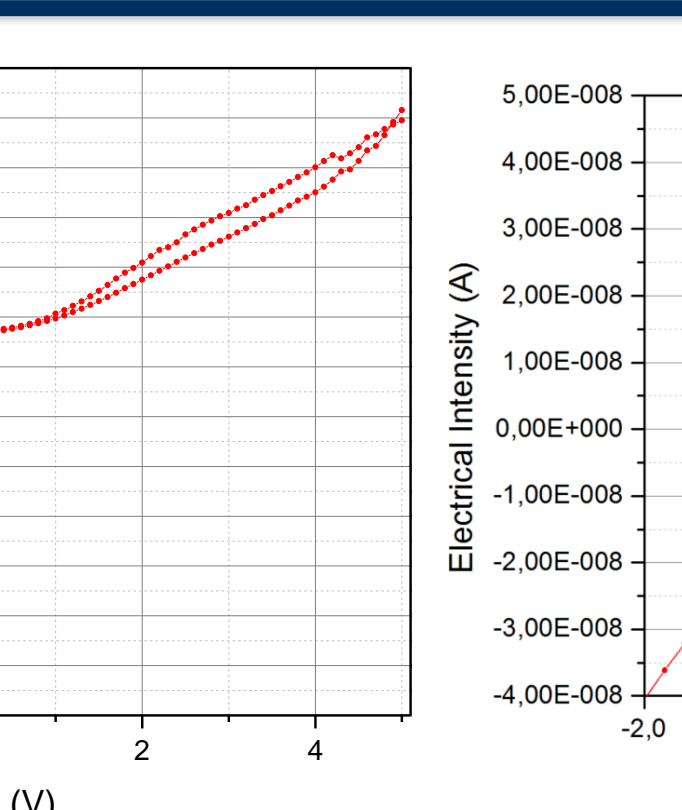
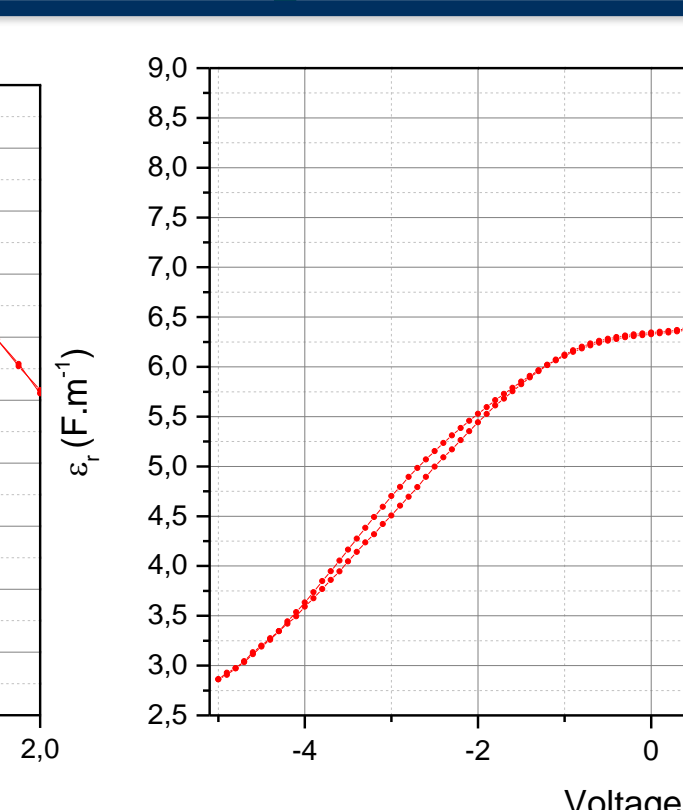
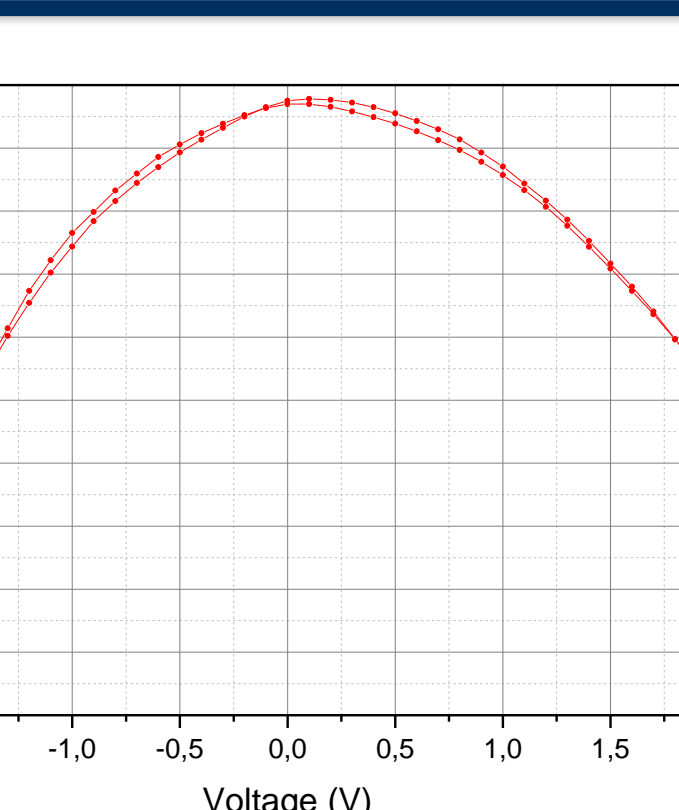
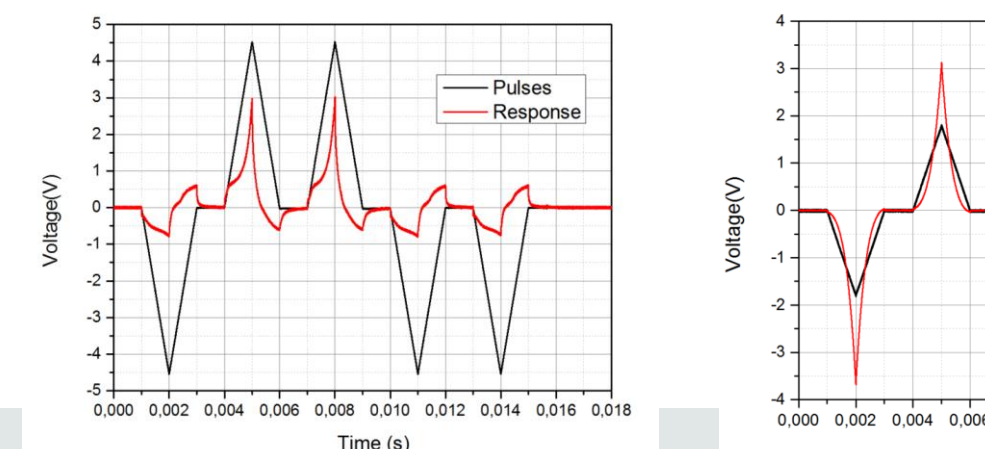
Electrical characterization of Metal/Insulator/Metal capacitors



Theoretical values of ε_r are in objectives and motivations



ε_r matches with monoclinic phase (see theoretical ε_r in objectives and motivations)



no apparent ferroelectricity but only one cycle

Conclusion and prospects

- XRD measurements ⇔ Hf_{1-x}Zr_xO₂, HfO₂ and ZrO₂.
- Hf_{1-x}Zr_xO₂ phase diagram : monoclinic phase (probably paraelectric) by in-situ annealing at 350° C => undesirable low-K phase
- Apparently no high-K or ferroelectric phase...
- New studies on technological steps process (etching,...) needed for capacitors and devices
- The growth of TiN by reactive sputtering seems to lead to undesirable fiber or powder textures => further investigations required
- The growth processes could be changed to non-reactive sputtering in the future processes
- Understand RTA issues and growth in-situ annealing processes