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Jordan Bouaziz, Bertrand Vilquin, Pedro Rojo Romeo, Nicolas Baboux, Bruno Masenelli. Comparison between Sputtering and Atomic Layer Deposition of ferroelectric doped and undoped HfO₂. EMRS Spring Meeting 2017, May 2017, Strasbourg, France. hal-02506676

HAL Id: hal-02506676

<https://hal.science/hal-02506676>

Submitted on 13 Mar 2020

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Comparison between Sputtering and Atomic Layer Deposition (ALD) of ferroelectric doped and undoped HfO₂

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We study the conditions to stabilize the ferroelectric phase (f-phase) in the doped and undoped HfO₂. It corresponds to the Pca2₁ space group and the orthorhombic III phase (o-III-phase). According to Böscke et al. [1], there is a transition from theoretical tetragonal phase (t-phase) at high temperature to the monoclinic phase (m-phase) or to the o-III-phase during cooling, respectively without a capping electrode or with a capping electrode. We compare the phases of our samples by X-rays Diffraction (XRD). We observe only amorphous phases in the case of samples deposited by ALD at 200° C (holder temperature) on Si, SiO₂, Pt and TiN, whereas we observe a monoclinic phase for HfO₂ and Hf_xZr_{1-x}O₂ samples deposited on Si/SiO₂/Pt at 350° C (sample temperature) by sputtering. The phase doesn't seem to be related on the thickness as the HfO₂ is ~15nm thick and the Hf_xZr_{1-x}O₂ is ~150nm thick. It leads us to believe we could stabilize the f-phase in-situ by sputtering in the future, which has never been done, to our knowledge, and compare its properties with Al:HfO₂ samples annealed ex-situ after ALD deposition. Moreover, using a Hf/Zr target has, as far as we are aware, also never been done.

Motivations

Applications

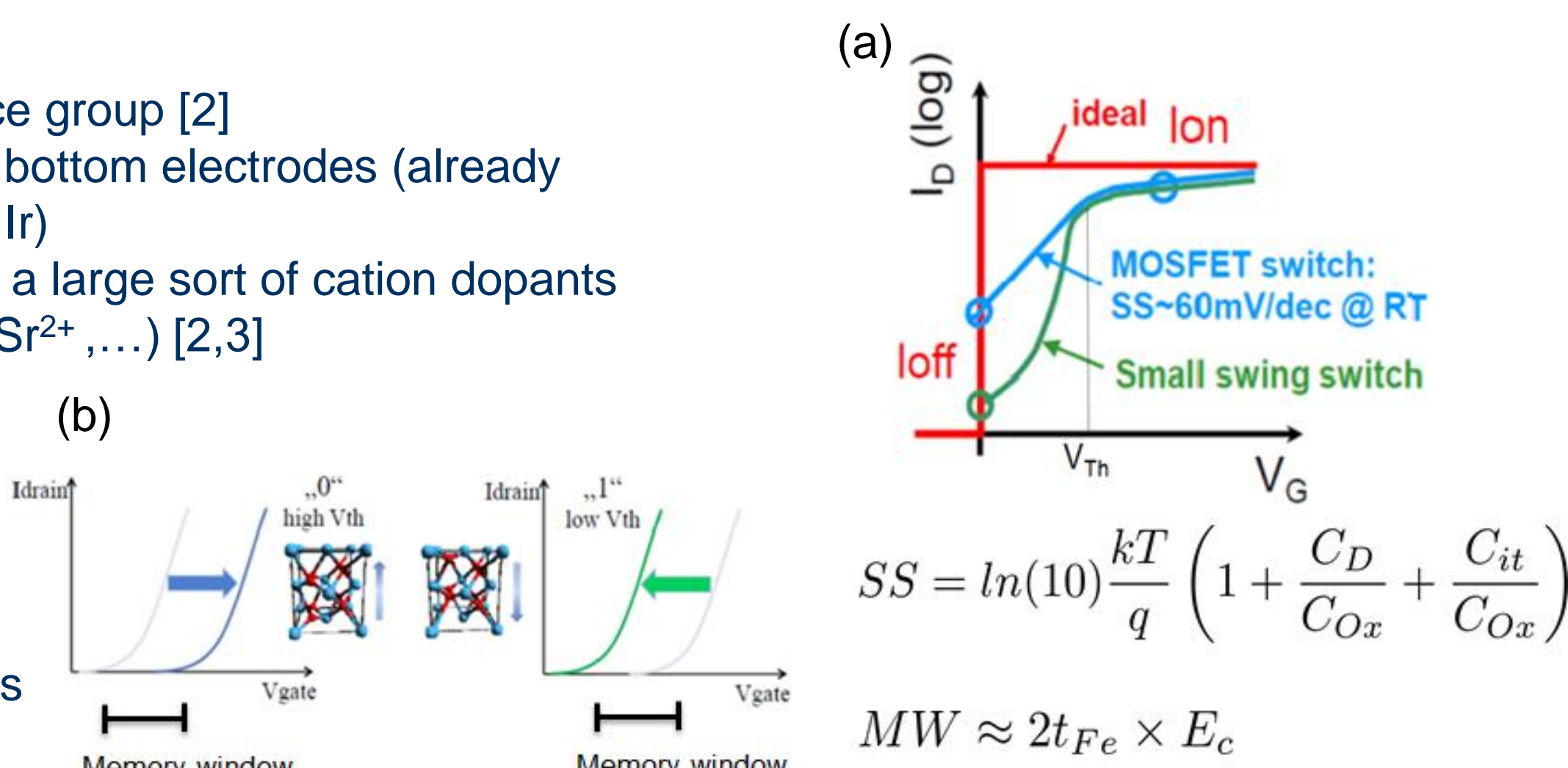
- Ferroelectric Field Effect Transistor (FeFET)
- Ferroelectric Random Access Memory (FeRAM) → embedded Non-Volatile Memory (eNVM) in MicroController Unit (MCU) (the "heart" of Internet of Things (IoT) devices)

Ferroelectric HfO₂

- Discovered in 2011 [1]
- o-III-phase and Pca2₁ space group [2]
- Stabilized between up and bottom electrodes (already tested : TiN, TaN, Pt, RuO, Ir)
- Ferroelectricity appears for a large sort of cation dopants (Zr⁴⁺, Y³⁺, Al³⁺, La³⁺, Gd³⁺, Sr²⁺, ...) [2,3]

Problems with other ferroelectrics

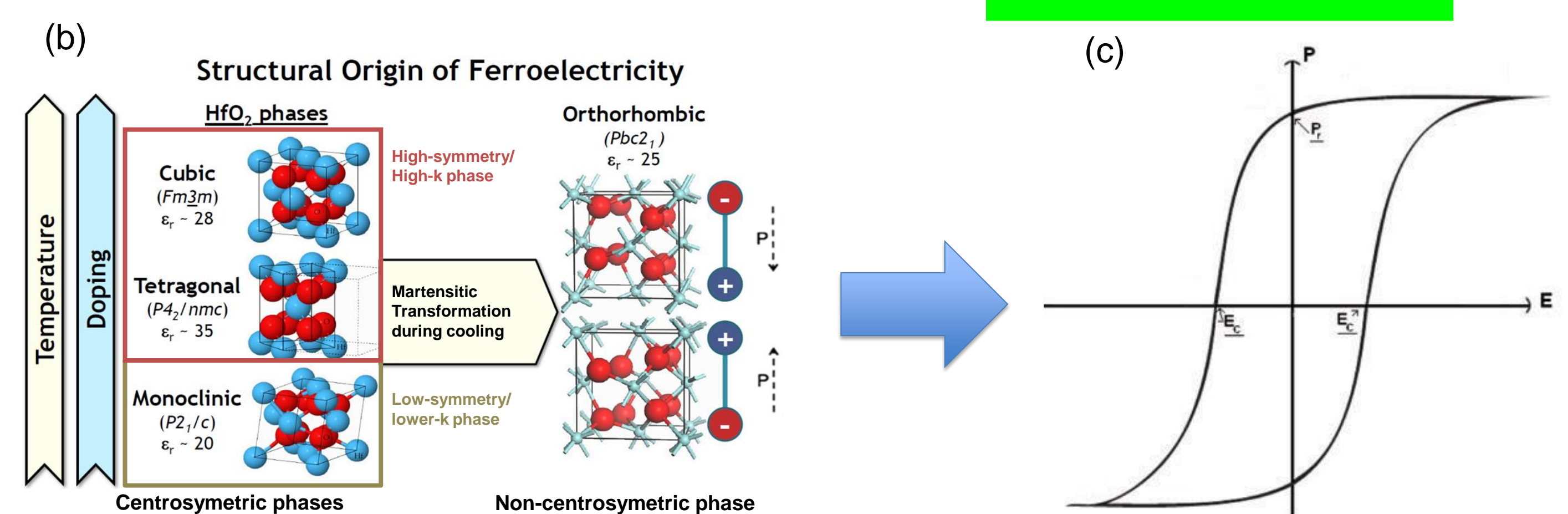
- Cost
- Compatibility with Si processing
- Memory Window limitations lead to scalability issues
- "dead layer" effects lead to scalability issues



(a) Drain current vs. gate voltage and formula to calculate the thermodynamic limit of the switch slope. It is theoretically possible to obtain a sub-threshold slope for transistors using a ferroelectric oxide [4] (b) Drain current vs. gate voltage where it is represented the difference between the two threshold voltages in function of the ferroelectric state → Memory Window. The Electric Field E_c is in the right range (see objectives) to induce ferroelectricity in the oxide with very small thickness (<10nm).

Objectives

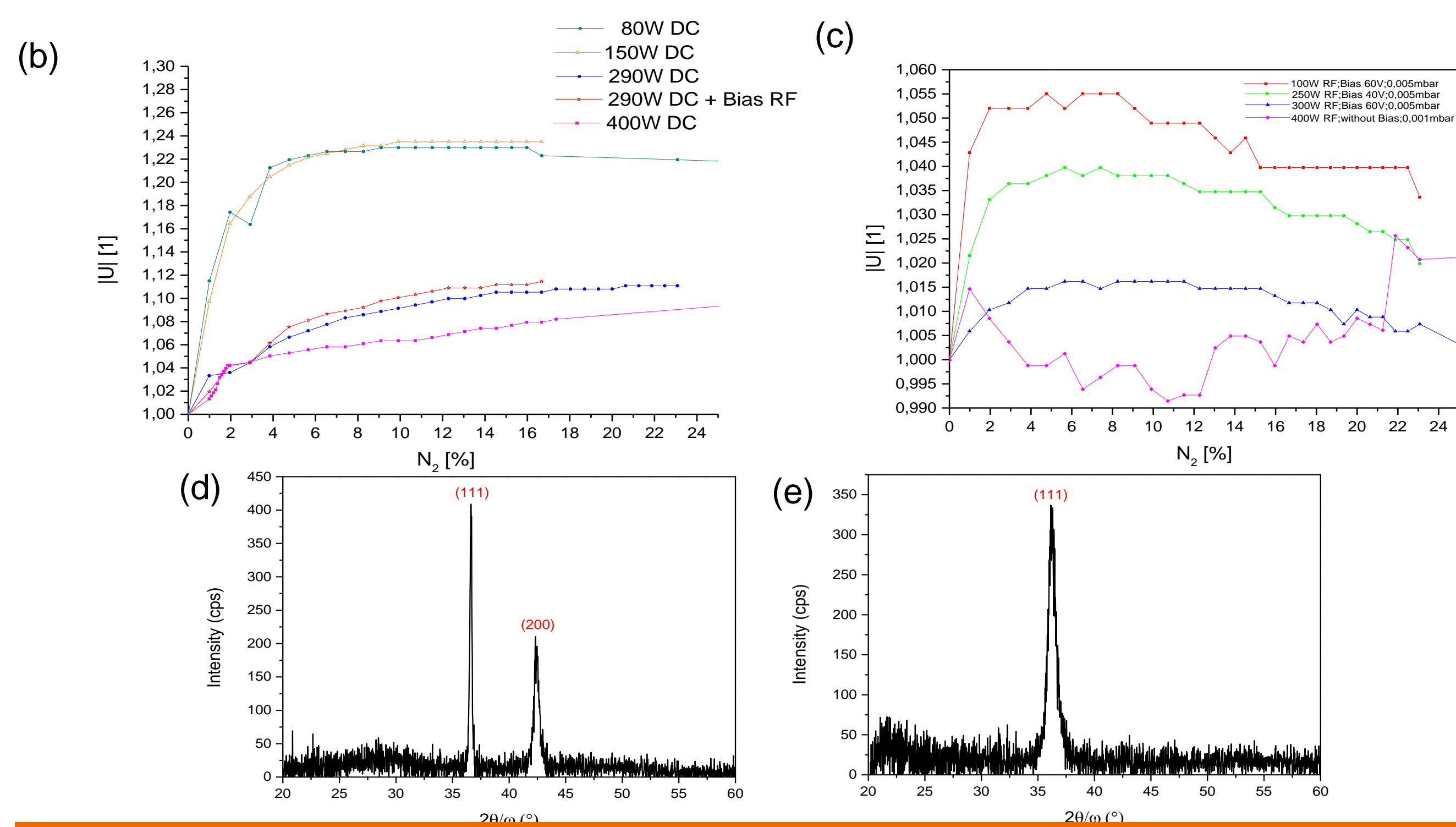
- Electronic component using the properties of ferroelectric doped HfO₂
- Studying the materials properties
- Comparing different deposition technics



(a) NC-FinFET [5] (b) Structural origin of ferroelectricity in doped (or undoped) HfO₂ with a phase change from the tetragonal phase to the o-III-phase. (c) The structural phase change leads to the classical hysteresis for ferroelectric with a coercive electric field E_c in the order of 1MV/cm for less than 10nm of HfO₂.

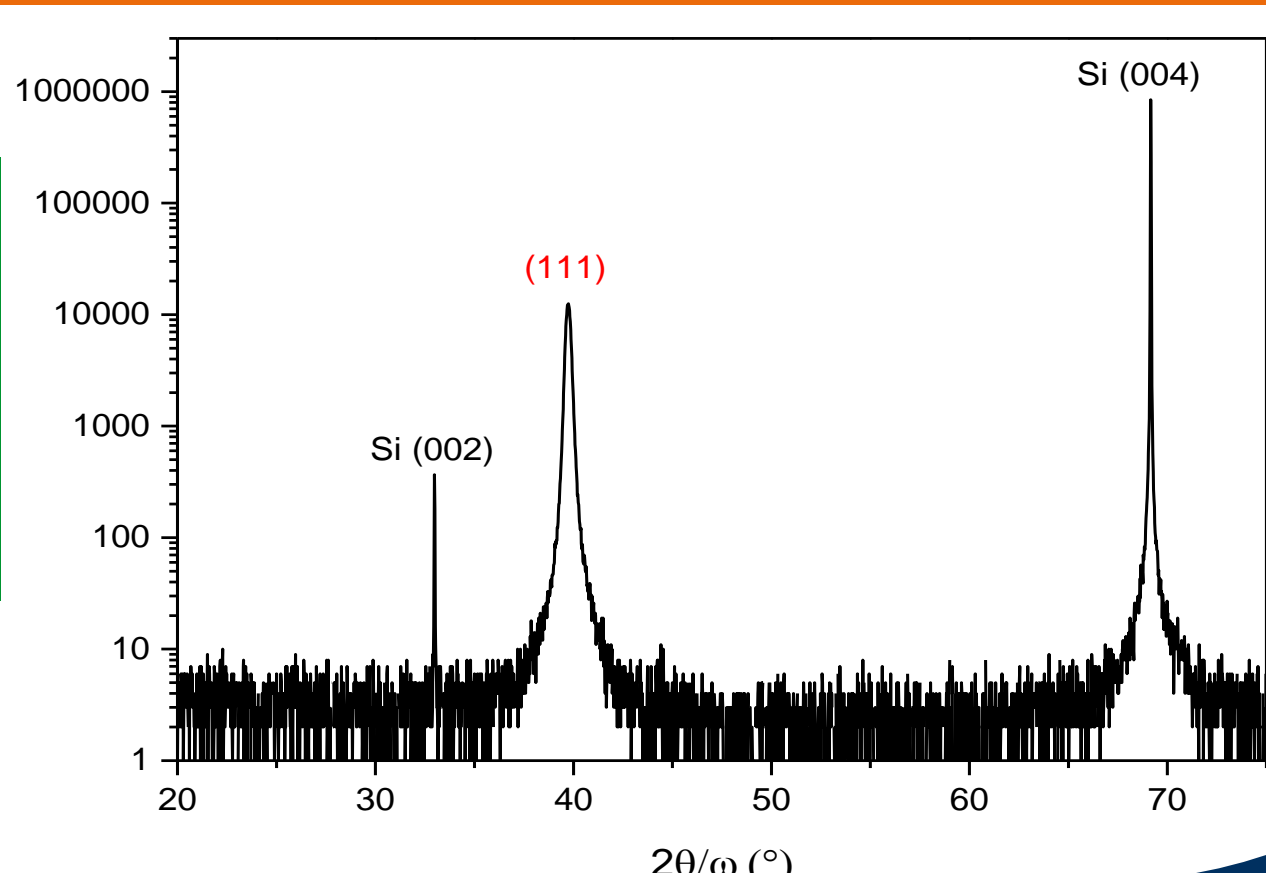
Electrodes

Titanium nitride (TiN) sputtering : (a) mechanisms; (b) and (c) Discharge vs. Nitrogen quantity give us the poisoned and metallic regims for (b) during current sputtering and (c) radiofrequency sputtering

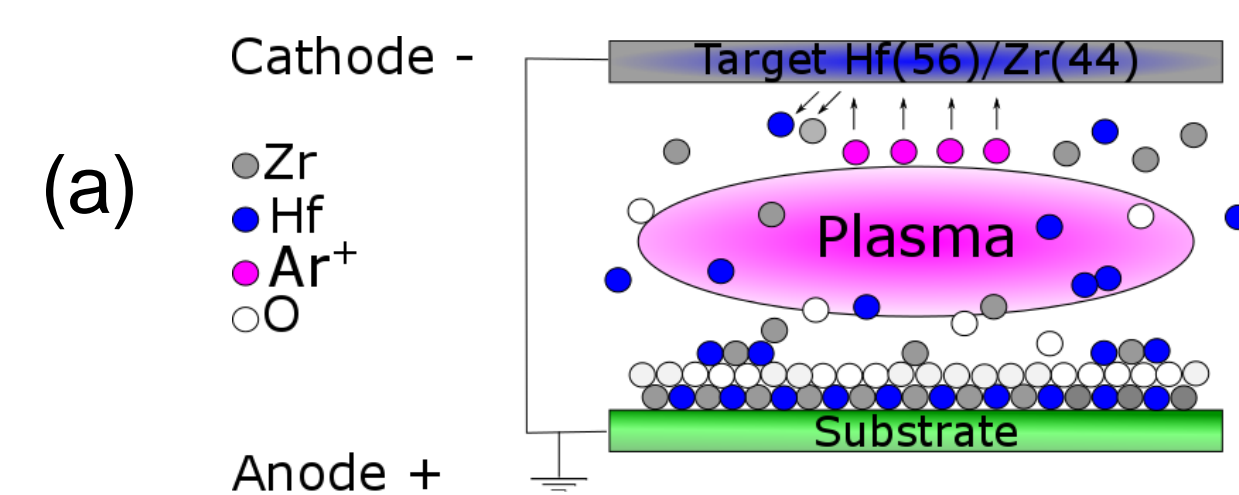


(d) XRD of a ~1μm sample realized at Institut des Matériaux Jean Rouxel (Nantes) compared with a (e) Textured TiN sample realized at INL by sputtering in both cases.

(f) Platinum electrodes : XRD of a ~100nm platinum sample realized at INL by sputtering



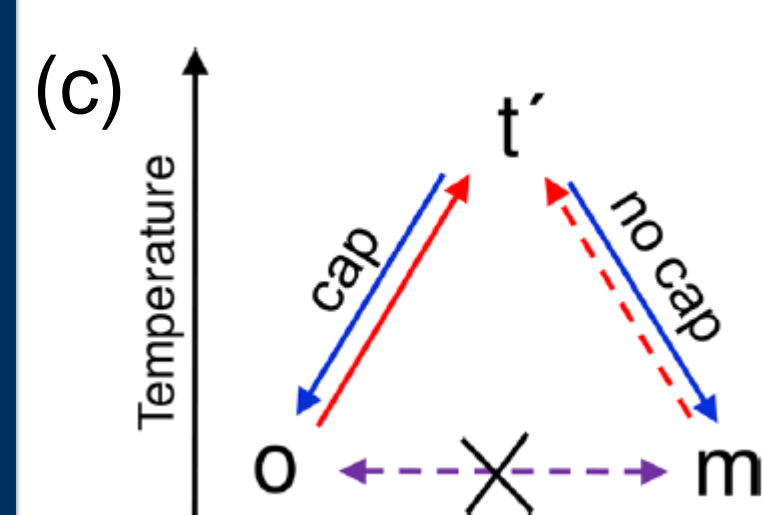
Oxides



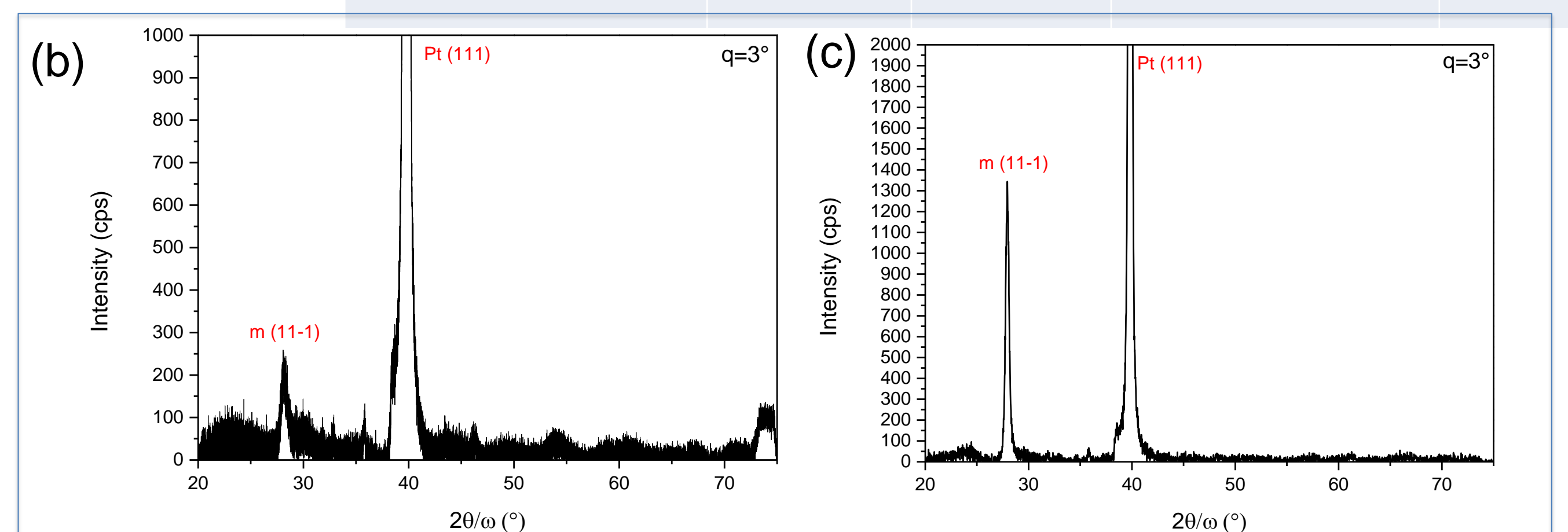
$$\%Zr = \frac{\%Zr_s \times v_{Hf}}{v_{Zr} + \%Zr_s(v_{Hf} - v_{Zr})}$$

(a) HfZrO₂ sputtering ideal mechanisms (b) Formula to deduce the quantity of necessary zirconium to theoretically realise stoichiometric HfZrO₂.

(c) Phase transition in doped-HfO₂ according to [1]



Materials	Templates	Technics	Temperatures during deposition	phases
• HfO ₂ • Al-doped HfO ₂	• Si • Si/SiO ₂ • Si/SiO ₂ /Pt • Si/SiO ₂ /TiN	ALD	200°C (holder temperature)	amorphous
• HfO ₂ • Zr-doped HfO ₂	• Si • Si/SiO ₂ • Si/SiO ₂ /Pt • Si/SiO ₂ /TiN	Sputtering	Room temperature	amorphous
• HfO ₂ • Zr-doped HfO ₂	• Si/SiO ₂	Sputtering	350°C (sample temperature)	amorphous
• HfO ₂ (b) (15nm) • Zr-doped HfO ₂ (c) (150nm)	• Si/SiO ₂ /Pt	Sputtering	350°C (sample temperature)	monoclinic



Next :

- Capping the samples that present a monoclinic phase without cap during process (at 350° C)
- Finding annealing conditions to obtain the orthorhombic ferroelectric phase
- Understanding the properties of grown doped-HfO₂ on textured/untextured TiN

References

- [1] T.S. Böscke et al., "Ferroelectricity in Hafnium Oxide Thin Films," Applied Physics Letters 102903, no. 2011 (2011): 0-3, doi:10.1063/1.3634052.
- [2] Min Hyuk Park et al., "Ferroelectricity and Antiferroelectricity of Doped Thin HfO₂-Based Films," Advanced Materials, 2015, 1811-31, doi:10.1002/adma.201404531
- [3] S Staszchich and U Boettger, "An Extensive Study of the Influence of Dopants on the Ferroelectric Properties of HfO₂," Journal of Materials Chemistry C, 2016, doi:10.1039/C6TC04807B.
- [4] Sayeef Salahuddin and Supriyo Datta, "Use of Negative Capacitance to Provide Voltage Amplification for Low Power Nanoscale Devices," Nano Letters 8, no. 2 (2008): 405-10, doi:10.1021/nl071804g.
- [5] Kai-shin Li et al., "Sub-60mV-Swing Negative-Capacitance FinFET without Hysteresis," 2015, 620-23.
- [6] Erich H. Kisi and Christopher J. Howard, "Crystal Structure of Orthorhombic Zirconia in Partially Stabilized Zirconia," Journal of the American Ceramic Society, 72 (1989): 1657, doi:10.1361/asmhba003801.