	Experiment title: Phase identification in pure and rare earths (La, Er) doped ZrO_2 and HfO_2 thin films by high resolution grazing incidence X-ray diffraction	**Experiment number**: MA-1052
Beamline: BM 02	**Date of experiment**: from: 23 April 2010 to: 27 April 2010	**Date of report**: 20 Aug 2010
Shifts: 12	**Local contact(s)**: Dr. Nathalie Boudet	*Received at ESRF:*

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Report:

The general goal of the experiment was to identify the crystallographic polymorphs present in La-doped ZrO_2 and Er-doped HfO_2 polycrystalline thin films (5-30 nm thick) grown on Si(001) and Ge (001) substrates and annealed at different temperatures up to 900°C. The goal was reached. However a systematic and comprehensive study of a full set of samples could not be satisfied for all materials, due to lack of time; in particular few Er-doped HfO_2 films were only quickly measured, as a feasibility test measurements. We ran out-of-time, mainly for two reasons: (i) finding of proper measurement strategy; (ii) longer time (than expected) for scan acquisitions.

In a first attempt, the grazing incidence geometry was adopted, keeping beam energy at 8 keV, to maintain consistency with laboratory data and exploring the angular region where overlapped peaks from different phases in laboratory data existed, with the aim to separate each contribution. This approach failed because of the reduced dimensions of the diffracted domains, which is reflected in a peak-line intrinsically too broad for the discrimination of the separate contributions from the tetragonal and the cubic phases.

A new strategy was then pursued. Taking advantage of the high signal to noice ratio that was attaineable by working at E=13 keV, we concentrated our efforts on the identification of a single, intrinsically of low intensity, but well isolated, diffraction peak belonging to the tetragonal component, the t(102) peak, as indicated in **Fig.1** for HfO_2.

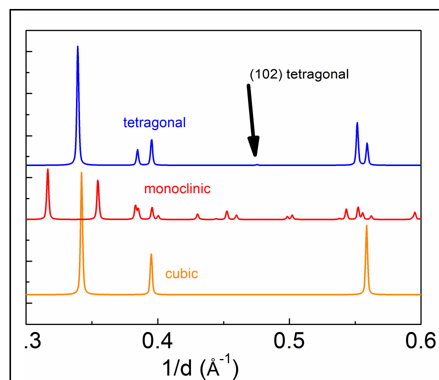

***Fig. 1**: Powder diffration patterns as reported in ICSD database for cubic (orange), monoclinic (red) and tetragonal (blue) HfO_2 phases. The arrow indicates the position of the t(102) reflection.*

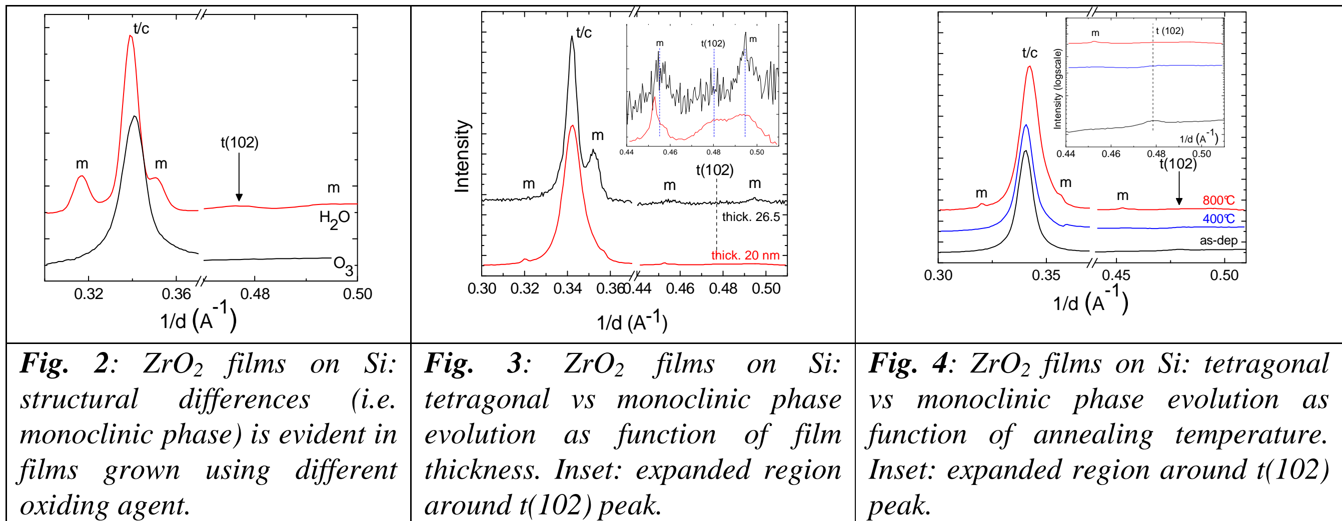

Fig. 2: ZrO₂ films on Si: structural differences (i.e. monoclinic phase) is evident in films grown using different oxiding agent.	*Fig. 3: ZrO₂ films on Si: tetragonal vs monoclinic phase evolution as function of film thickness. Inset: expanded region around t(102) peak.*	*Fig. 4: ZrO₂ films on Si: tetragonal vs monoclinic phase evolution as function of annealing temperature. Inset: expanded region around t(102) peak.*

This approach was very successful on ZrO_2 and La-ZrO_2 samples grown on Si, which could be systematically measured and critically analyzed.

It was found that the crystallographic phase of pure ZrO_2 films is highly influenced by the oxidizing agent used during the deposition process. While the use of H_2O gives films consisting of monoclinic, tetragonal and cubic polymorphs, the monoclinic phase is not detected in the as-deposited O_3-based films (**Fig.2**). The clear detection of the tetragonal t(102) reflection, allowed the identification of the ZrO_2 tetragonal phase and to follow its evolution as a function of film thickness and post deposition annealing. **Fig.3** and **Fig. 4** show that the tetragonal phase reduces, becoming hardly detectable, at increasing film thickness and with the annealing, at the expense of the concomitant development of the monoclinic phase. The measured dielectric constant values, $\kappa \sim 24$ or $\kappa \sim 30$ for the films deposited using H_2O or O_3, could be correlated with the differences in the ZrO_2 observed phases, in particular the increase of the monoclinic phase reducing the κ value. These results are accepted for presentation at the XTOP 2010 conference.

Considering films grown on Ge, at 13keV, the contributions from both the Ge (311) asymmetric reflection and the fluorescence from the excitation of the K_α transition sensibly increased the background, reducing the signal to noise ratio. La-ZrO_2 films on Ge were then evaluated at E=9 keV. At this beam energy, within the same scan, we could detect the presence of ZrO_2 tetragonal phase and evaluate the development of ZrO_2 monoclinic phase considering the m(-121) and m(112) reflections, which are located and well resolved around the t(102) peak. This study is particularly relevant, as the development of the tetragonal phase, without any monoclinic contribution, was believed to be the origin of the high-κ value measured on La-ZrO_2 films grown on Ge and annealed at 400 °C [1]. These measurements (**Fig.5**) are the first direct experimental evidence that very thin La-ZrO_2 films, grown on Ge, develop the tetragonal phase after annealing.

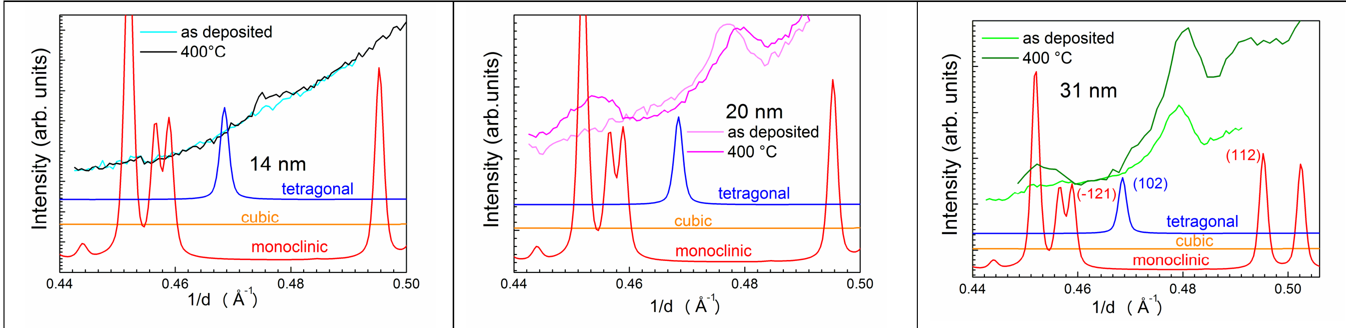

Fig. 5: GIXRD patterns, taken at 9 keV, of thin La-ZrO₂ films with different thickness, as grown and after annealing at 400°C. Left: 14 nm, center 20 nm, right 31 nm.

Finally, preliminary data (at E=9keV) on Er-doped HfO_2 (Er<10% at) films grown on Si showed the presence of the tetragonal phase and an unwanted monoclinic phase development after annealing at 900°C. We aim to systematically investigate the crystalline phase changes in Er-HfO_2 films grown on both Si(001) and Ge (001) substrates, as a function of Er content, in the submitted continuation proposal (Ref. N. 25590).

[1] L. Lamagna, C. Wiemer, S. Baldovino, A. Molle et al., Appl. Phys. Lett. **95** 122902 (2009).