ESRF	**Experiment title:** Sub-micronic quantitative chemical and structural in-depth gradient measurements into functional piezoelectric (PZT) thin film : a nano-pencil beam diffraction approach	**Experiment number**: Ma1738
Beamline: ID11	**Date of experiment**: from: 04/19/2013 to: 04/21/2013	**Date of report**: 29/08/2013
Shifts: 12	**Local contact(s)**: Gavin Vaughan	*Received at ESRF:*

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Report:

Summary

The aim of this proposal was to measure the **effect of composition gradient on micro-structural and mechanical properties in PZT thin films in the vicinity of the morphotropic phase boundary (MPB).** That analysis has been obtained through z-scan measurements along the film thickness, using a **high energy nano-line beam** in cross section (see report MI1046).

Experimental method

The experiment was carried out on second experiment hutch on ID11. The beam was monochromatized at E = 52 KeV and silicon nano-lenses were used. But only vertical nano-lenses were used to obtain the nano-line beam [1]. The sample was installed on piezo nano-stages. Experimental method and data analysis are described in [2]. The samples were previously prepared using equipments available in Leti. 1µm of PZT was deposited on 200 mm SOI wafer by sol-gel method on 100nm of Pt and recovered by 100nm of Ru. Specific sample shape preparation (parallelepiped 0.2 x 0.7 x 5 mm) was perform using a specific procedure including micro-cleaving and polishing steps. Samples was then fixed on a Si wafer and installed on the stages.

Results

Single PZT films with several levels of gradient Zr/Ti in the thickness of the film have been **prepared for this purpose**. Results of micro-structural and mechanical analysis obtained on sample n° µS9570P P14 (gradient standard: Zr/Ti gradient repeated every 300nm) will be presented.

Alignment procedure

200µm thick sample µS9570P P14 was fixed on a Si wafer and aligned using XRF scan on Ru and Pt layers of our sample. The z–scan resolution was determined by peak deconvolution as films' thicknesses are well known. The position could be set with high precision thanks to piezo nano-stages.

Phase analysis

After alignement, fluorescence z-scan (Fig.1 (a)) for chemical composition gradient of Pt, Pb, Zr, Ru and a set of diffraction patterns (Fig.1 (b) before and after integration) were obtained.

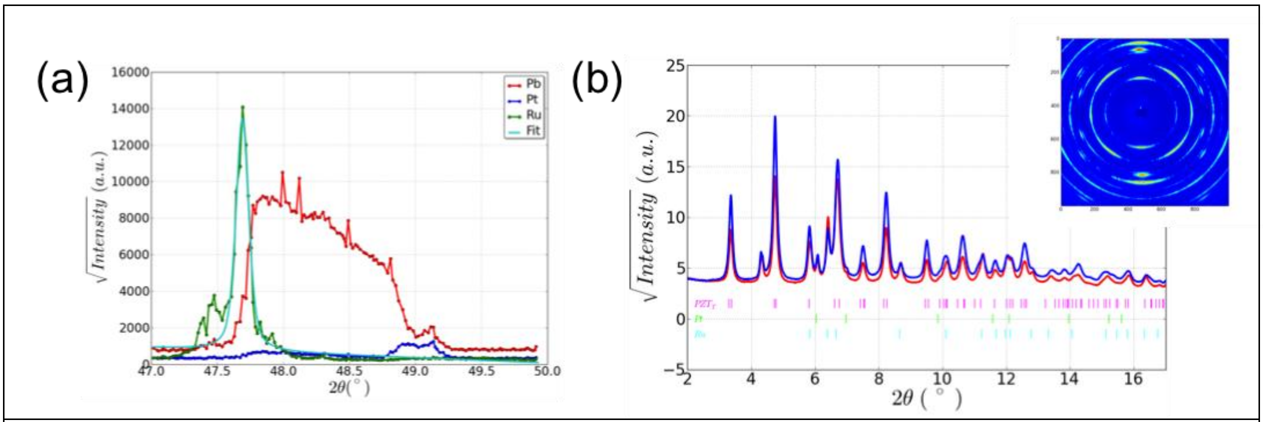

Fig. 1: (a) Fluorescence z-scan after alignement. Ru (top electrode) fluorescence peak is found 190 nm thick (FWHM). (b) Azimuthally integrated diffraction pattern for two Z position.

Even if the fluorescence analysis resolution doesn't allow seeing any gradient periodicity, it gives us roughly chemical profile of film cross section.

Very nice results were found in diffraction. After camera corrections and psi integration of each pattern, diffraction profiles reveal a micro-structural periodicity. An alternation of rhombohedral and tetragonal phase was observed for each cca 300nm (Fig.2). This periodicity was evidenced by following the peak intensities of the rhombohedral (048) peak at $2\theta = 13.54°$ and the tetragonal (400) peak at $2\theta = 13.84°$. This result is related to the concentration gradient of Zr/Ti within the PZT layer, introduced by the Zr4+ and Ti4+ ions diffusion during crystallization by annealing, which is specific for sol-gel deposition technique. Crystallization of each 300 nm PZT layer begins from the substrate and continues through the layer reaching the surface of the sample. However, $PbTiO_3$ crystallization thermodynamic potential is a little bit lower than the $PbZrO_3$'s one. Therefore, Ti-rich PZT area is the first to be created. This offset from morphotropic PZT concentration introduces an offset in PZT phase diagram. Ti rich PZT crystallizes in tetragonal phase [3]. As the crystallization continues Ti is consumed more than Zr. For this reason, Zr rich PZT crystals are formed close to the sample surface. According to the phase diagram, Zr rich PZT crystallizes in rhombohedral phase. This explains the micro-structural periodicity.

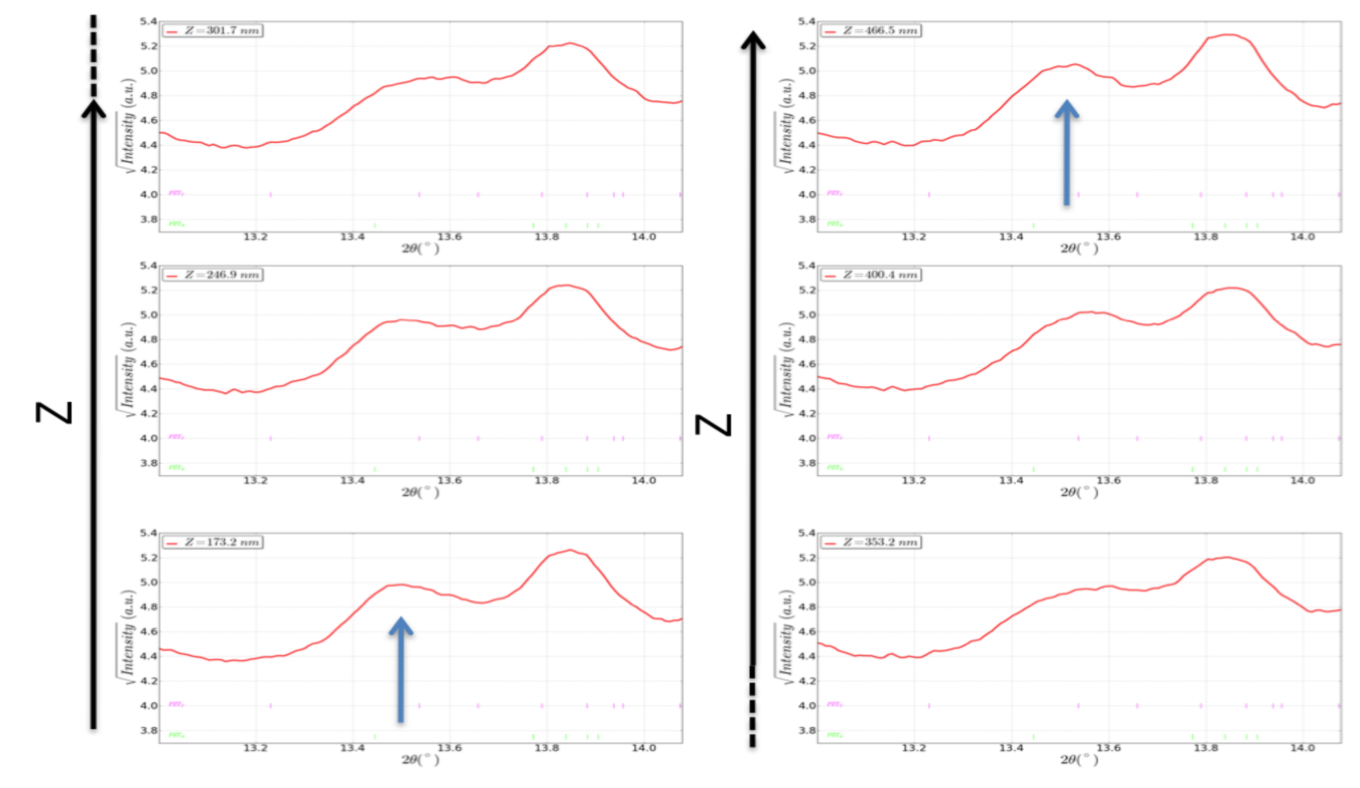

Fig. 2: Phase periodicity between rhombohedral and tetragonal is visible (a spectra is plotted each 50 nm step).

Stress analysis in cross section

The residual stress σ_r analysis was performed as well. In order to determine σ_r variation within the PZT layer, we use the classical $\sin^2$psi method (Fig. 3) on (111) PZT peak, assuming an isotropic behaviour and a biaxial state of stress. Cell parameter free of stress is 2.343A. Taking values of 82.1GPa for Young modulus and 0.39 for Poisson ratio [4], the residual stress calculated for z = 880nm is $\sigma_{(Z=880\ nm)}$ = 128 MPa, which is in agreement with macroscopic stress measurement deduced from curvature analysis.

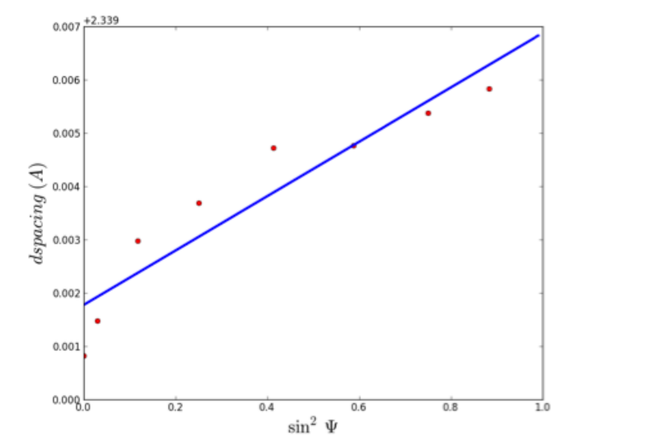

Fig. 3: Strain/stress analysis (Z = 880 nm)

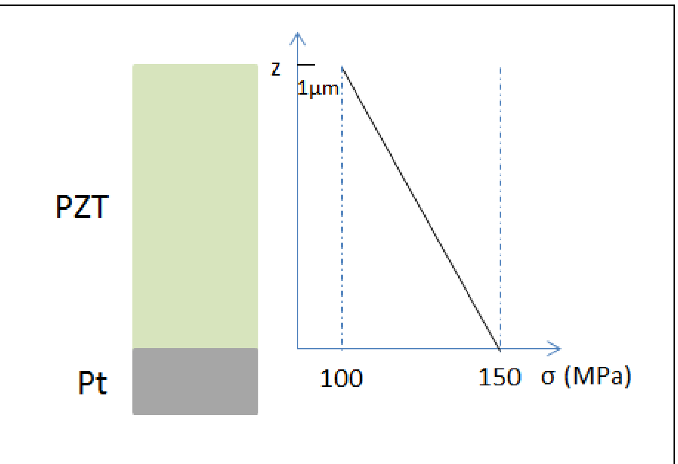

Fig. 4: Stress analysis in PZT cross section

The stress analysis in cross section (Fig. 4) shows a linear variation of σ_r, going from 150 MPa when close to the bottom Pt electrode, to the value of 100 MPa on the sample surface. The tensile stress within the PZT layer is explained by the difference in CTE between PZT and the silicon substrate when the sample is cooled down from 700°C to ambient after crystallization of PZT.

Full data treatment (Rietveld/combined analysis) is still under investigations for different samples measured during this experiment.

Conclusion

This experiment was a success. A gradient between rhombohedral and tetragonal phase due to sample preparation process has been evidenced. Moreover, a strain/stress profile in film cross section has been revealed. Our observations will give rise to a future publication. Next step is to perform similar experiment along an electric cycling in order to address the issue of phase, texture and strain evolution during polarization in PZT thin films in the vicinity of MPB.

References:

[1] G. Vaughan, et al *J. Synchrotron Rad.* 18, 125-133 (2011)
[2] N. Vaxelaire et al, *J. Appli. Cryst.* Submitted and report MI1046
[3] B. Noheda, J.A. Gonzalo et al, *Phys. Rev. B*, 61 (2000) 8687
[4] F. Casset, *ULTSYM* (2012) 0544