| ESRF | **Experiment title:** **Piezoelectric response of nano-scale ferroelectrics by nano X-ray beam diffraction** | **Experiment number**: MA-1552 |
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**Report:**

The goal of the experiment was to investigate the piezoelectric response of ferroelectric thin films and nanostructures in order to quantify the contribution of the flexoelectric effect in strained ferroelectrics, using nano X-ray beam diffraction during the application of an AC electric field (by an AFM tip) at ID01. This represents an unique tool to have direct access to the quantitative piezoelectric response of films and nanostructures with a lateral resolution ultimately given by the beam size.

The experiment has demonstrated technically extremely challenging, therefore we have started this challenging project by focusing on the study of thin films of various thicknesses before nanostructuration. Beside measuring the piezoresponse of the studied samples, this experiment has allowed us to determine the best experimental conditions to pursue our final goal of studying the piezo-response of strained nanostructures. We have measured and compared diffracted intensity from films of different thicknesses and we have learned to optimise the measurement conditions. In particular we have learned a strategy to find the best frequency of the oscillating electric field, obtained as a compromise between leakage currents and diffracted intensity at different Bragg peaks.

During the performed experiment, different values of oscillating electric fields have been applied on the thin films *in situ* and the synchronized diffraction signal has been collected. Shifts of Bragg peaks under electric field have been observed, giving access to the piezoelectric response of the ferroelectric thin films. Figure 1 shows a typical result obtained on a 200nm-thick $PbTiO_3$ thin film grown on $SrRuO_3$(10 nm)-$DyScO_3$ (110). This film presents ferroelectric domains with a well-defined periodicity visible on the AFM topography picture (Fig.1(a)). In these nano-sized domains, polar rotations are created by the presence of strain gradients [1], and are expected to enhance the piezoelectric properties at the nanoscale. Figures 1(b) and 1(c) show the variation of the film out-of-plane lattice parameter with the applied electric field. An elongation of the unit cell has been measured when applying a negative voltage to the film surface, in agreement with the preferential orientation of the electrical polarization in the films. From these data, a quantitative determination of the piezoelectric coefficient $d_{33}$ has been obtained. A coefficient of the order of 15 pm/V has been measured, which is consistent with usual piezoelectric response of $PbTiO_3$ thin films. We expect that the value of piezo-response will be larger in the case of nanostructures with lateral size comparable with film thickness [1]. Experimental demonstration of this effect would be a world first, with an extremely high impact on fabrication on ferroelectrics-based devices. The common technique to characterize the piezoelectric response in thin films is the Piezoresponse Force Microscopy (PFM). This technique isnot very suitable for quantitative determination of the $d_{33}$ coefficient because of the difficulty to differentiate between intrinsic and extrinsic contributions to the piezoresponse. The use of X-ray diffraction during the application of an electric field is thus really useful because it allows to quantify only the intrinsic piezoelectric response of the materials, without any extrinsic contributions coming mainly from domain walls motion.

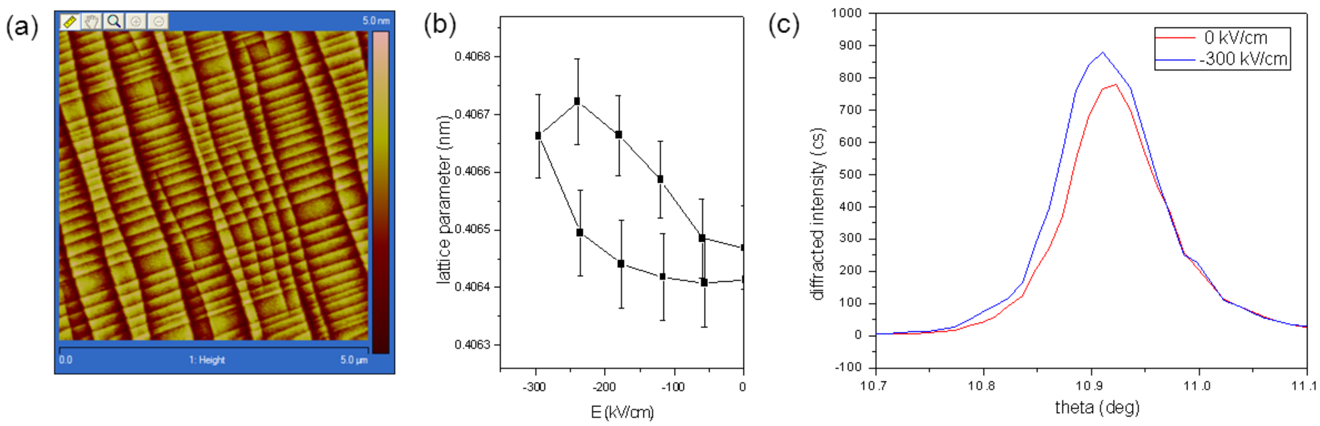


Fig.1: (a) AFM topography of a 200nm-thick $PbTiO_3$ thin film grown on $SrRuO_3$(10 nm)-$DyScO_3$ (110), showing the presence of periodic ferroelectric domains, giving rise to polar rotations by flexoelectricity. (b) Variation of the out-of-plane lattice parameter of the film by applying an *in situ* electric field and (c) corresponding shifts of the (001) Bragg peak.

The results obtained are very promising and set the basis for further exploration of piezo-response in nanostructures. Experimental conditions have now to be improved to be able to apply the electric field on a single nanodot. Firstly, the control of the AFM tip movement onto the surface needs be more precise in order to reduce at the minimum the contact force with the sample. Secondly, the use of top electrodes on each nanodots should be used to provide an homogeneous electric field through the structures. These two improvements will allow to study the piezoresponse of single nanodots and thus investigate the effect of the lateral size reduction on the piezoresponse (clamping reduction) as well as reveal the contribution of the flexoelectric effect at the nanoscale.

[1] G. Catalan, *et al* and B. Noheda, Flexoelectric rotation of polarization in ferroelectric thin films *Nature Materials* **10**, 963 (2011).