	Experiment title: 3D Bragg Ptychography of ferroelectric "superdomains" in perovskite thin films	Experiment number: HC-3211
Beamline: ID01	**Date of experiment**: from: 26 Oct 2017 to: 31 Oct 2017	**Date of report**: 15.03.2018
Shifts: 18	**Local contact(s)**: Dr. Steven Leake	*Received at ESRF:*

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Report:

Ferroelectric thin films display domain structures which depend on the electrostatic and elastic boundary conditions they are subjected to. The latter can be tailored by depositing the film epitaxially onto a substrate of appropriate lattice constants and symmetry, as well as by varying the film chemistry and thickness. Tuning these parameters changes the strain state of the film, promoting the formation of a particular domain structure. When $PbTiO_3$ (PTO) is tensile strained to approx. 0.85% by epitaxial deposition on $KTaO_3$ (KTO), its calculated phase diagram predicts a mixed in-plane and out-of-plane polarised domain population.

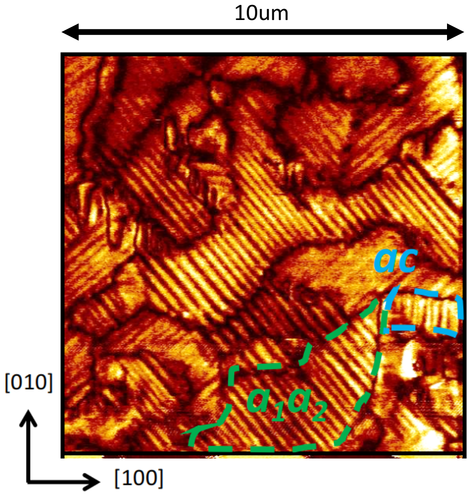

Figure 1. A 10um PFM lateral amplitude image of a 62nm PTO//KTO thin film. An in-plane a1a2 superdomain is marked in green, while an ac out-of-plane superdomain in blue.

We prepared PTO//KTO samples by RF magnetron sputtering and performed laboratory X-ray diffraction as well as Piezoresponse Force Microscopy (PFM) to investigate their domain structure. We found that a hierarchal arrangement is formed, whereby individual domains organise in two kinds of distinct bundles, or "superdomains".

Within in-plane $\boldsymbol{a_1a_2}$ superdomains the domains are stripe-like and periodic in a specific direction (marked in green in Fig. 1), which results in a well-defined signal in reciprocal space around *h0l* Bragg peaks. Because of the combination of a tetragonal unit cell and domain boundaries being coherent, out-of-plane ***ac*** superdomains contain domains which are slightly tilted with respect to the substrate interface (marked in blue in Fig. 1). This tilt is visible in reciprocal space around the *00l* Bragg peaks.

The presence of distinguishable diffraction signal from ***ac*** and $\boldsymbol{a_1a_2}$ domains allows to investigate their arrangement and morphology via scanning X-ray nanodiffraction (SXRND) and ptychography. In this experiment we attempt to determine such domain arrangement via both techniques while applying *in situ* electric field and temperature. The motivation behind this kind of work is the determination of the response of engineered domain structures to device-like conditions.

Field. A 62nm thick PTO//KTO thin film sample was patterned with 8nm thick Au interdigitated electrodes to probe the domain structure's response to in-plane electric field. The electrodes were connected to a Keithley 6487 to apply a voltage in the range ±70V with 10V steps. KB mirrors were used on ID01 to focus the fully coherent beam to a

FWHM of 180x350nm to perform ptychography. A slightly smaller beam (unmeasured) could be produced by sacrificing the coherence condition and was used to perform SXRND. Both SXRND and 3D & 2D ptychography datasets were collected at each voltage step around the 103 and 001 PTO Bragg reflections. SXRND maps are useful to measure potential drifts since the superdomains are trackable features on the film's surface. Figure 2 displays some preliminary results from the SXRND only; ptychography data is still under analysis, which is particularly laborious.

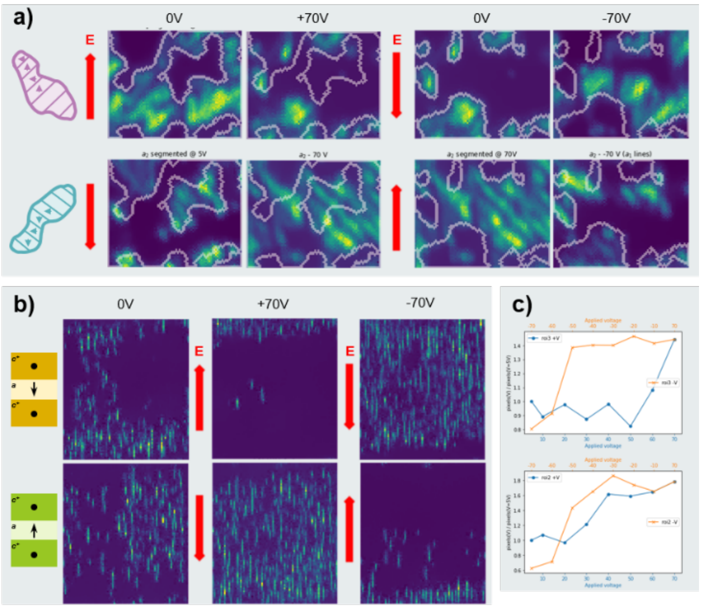

Figure 2. In-plane ferroelectric switching of a 62nm PTO//KTO film. See the main text for a detailed description of each part.

Part **a)** of Fig. 2 shows the redistribution of superdomain SXRND intensity due to their switching under applied fields. The top row of images corresponds to the signal stemming from the **a_1a_2** superdomain variety depicted in pink; the bottom row to the one depicted in blue. Images are 1.8x1.3um. Red arrows indicate the electric field lines direction for +70 and -70V applied voltage. Grey lines in the images are segmented areas used for further analysis as well as to ease the visualisation of the superdomains switching. It can be noticed that the SXRND intensity in the images is transferred from the top (bottom) to the bottom (top) for positive (negative) voltage application, i.e. the superdomain variant with in-plane polarisation components unfavourably oriented with respect to the applied field is switching in to the other one by changing the stripe periodicity direction. A similar effect can be seen in **b)** in the case of ***ac*** superdomains; images are 6x5um and are arranged as in **a)**. The same redistribution of intensity mentioned above can be noticed. Part **c)** shows the percentage of switched superdomains with increasing (blue curve) and decreasing (orange curve) voltage, for **a_1a_2** superdomains (top graph) and ***ac*** superdomains (bottom graph). An hysteretic behaviour can be clearly seen in the **a_1a_2** case only.

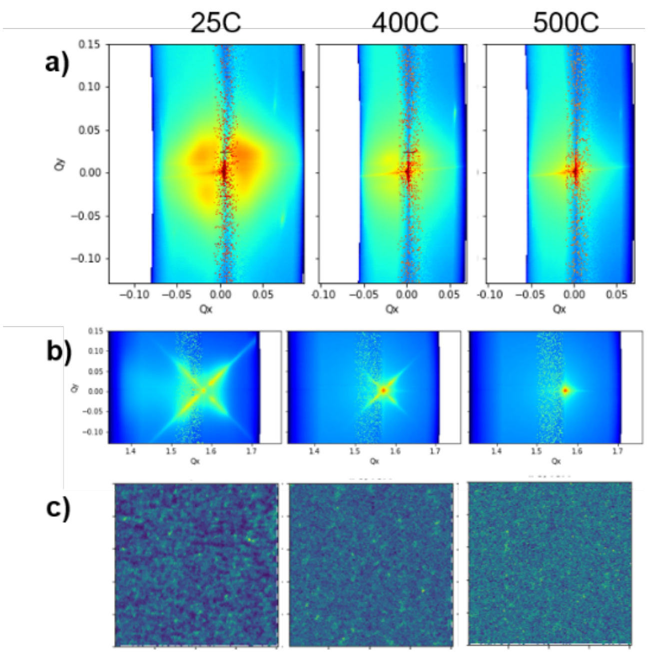

Figure 3. Effect of temperature on a 30nm PTO//KTO film; a detailed description is in the main text.

Temperature. A 30nm thick PTO//KTO thin film was mounted on the ID01 furnace and used for temperature-dependent measurements. The ceramic paste used for mounting the sample did not result in the required sample stability for performing ptychography measurements, so only SXRND maps were collected in this case. Since coherence was thus not required, a Fresnel Zone Plate (FZP) was mounted in place of the KB mirrors to employ a smaller (FWHM of 60x140nm) incoherent beam and improve the resolution of SXRND maps. 3D reciprocal space maps were collected in the temperature range 25-650°C in 100 and 50°C steps for heating and cooling respectively, around the 001 and 103 PTO Bragg peaks. A selection of results can be seen in Fig. 3.

Part **a)** and **b)** of Fig. 3 display the temperature evolution of the tilt and periodicity signal around the 001 and 103 reflections respectively. These correspond to the ***ac*** and **a_1a_2** superdomains, respectively. It can be seen that the signal disappears in both cases between 400-500°C, indicating that the ferroelectric to paraelectric transition must be happening in this temperature range. The transition must correspond to the disappearance of the superdomains, as further evidenced by the SXRND maps shown in part **c)** of Fig. 2. It has to be noted that no shape, size, or arrangement change is visible in the superdomain structure as the temperature is increased; merely a gradual disappearance of contrast is seen.