ESRF	**Experiment title: Anomalous Grazing Incidence Small Angle X-ray Scattering of Solution-processed pyroelectric thin films for infrared detectors**	**Experiment number**: 02-02 863
Beamline: BM 02	**Date of experiment**: from: 7th November to: 12th November 2018	**Date of report**: 5th March 2019
Shifts: 15	**Local contact(s)**: G. Chahine	*Received at ESRF:*

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Report:

Objective & expected results:

The objective was to study the morphology of pyroelectric thin films elaborated by sol-gel and to link the morphological results with the film properties. Such films can be used for energy harvesting or infra-red detectors, provided the films have high pyroelectric coefficient and low permittivity. So far, many pyroelectric devices are made with polymers like polyvinylidene difluoride (PVDF). However, these materials have serious limitations like low pyroelectric coefficient, low electrical stability in time and integration difficulty. On the contrary, inorganic pyroelectric materials have high pyroelectric coefficient p, high electrical stability in time, and no integration problem. As the pyroelectric figure of merit is $F=p/\varepsilon$, low permittivity is desired. Anyhow, the permittivity ε of the inorganic bulk material is usually much higher than that of the PVDF. In order to decrease the permittivity, this material is elaborated by the sol-gel technique by creating porosity ($\varepsilon r = 1$). In addition, the sol–gel technique has several advantages over vacuum-assisted techniques, such as high throughput, cost-effectiveness, low prime material waste and above all, simplicity. It is also well-adapted for manufacturing materials or devices on large surfaces. The aim of the experiment is to study the morphology of the nanoparticles and that of the pores as a function of the substrate type, the thermal annealing and the number of deposited layers. The motivation for the present proposal is to modelize the permittivity decrease as a function of the porosity.

Results and conclusions of the study:

We used the D2AM beamline in GISAXS configuration to perform the experiment. The incoming energy was in the range from 16 to 19 keV, with incident angle 0.16 and 0.3 deg onto the sample surface to obtain 2D GISAXS images with different penetration depths. The XPAD3 detector was positionned at 330 cm from the centre of the sample. The samples were spin-coated on silicon wafers in advance at LITEN.

First, in situ GISAXS images were recorded on a BaSrTiO3 (BST) film during annealing at low annealing temperatures. The scattering (Fig. 1) allows to study successively the particle formation, the particle clustering and the particle growth during the dynamic sol-gel process.

Impact of substrate and of annealing temperature on morphology:

Ex situ GISAXS (Fig. 2) was performed on thin BST films (1 ML) at 600°C in order to study the pore morphology as a function of the substrate type and as a function of the annealing time. For smooth substrates,

the pores are well organized. For example, for Si hydrophobic substrate and 60 min annealing, the distance between the pores is approximately 90 nm.
GISAXS was also performed on thicker BST films (5 ML) as a function of the substrate type and of the annealing temperature (Fig. 3).

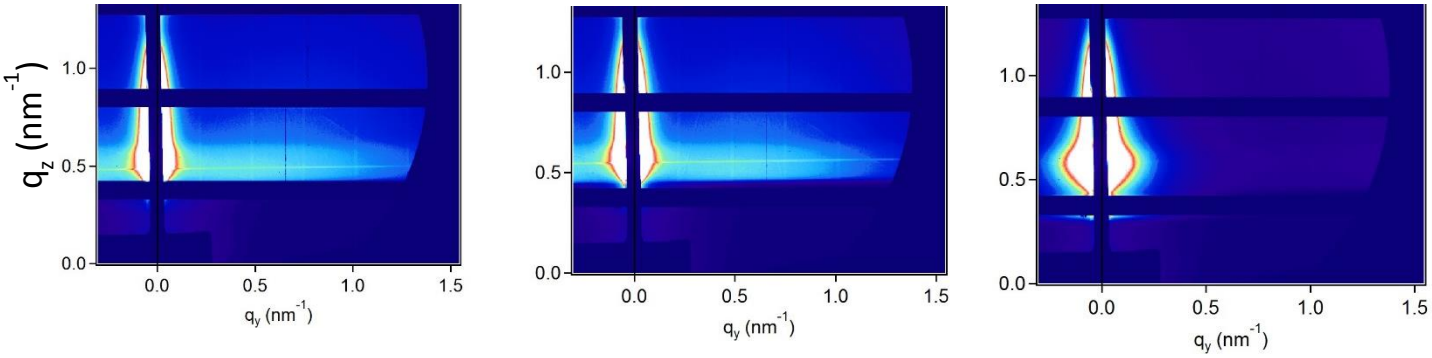

Figure 1. In situ GISAXS images of a BST film deposited by sol-gel and annealed at 140°C, 190°C and 200°C (from left to right).

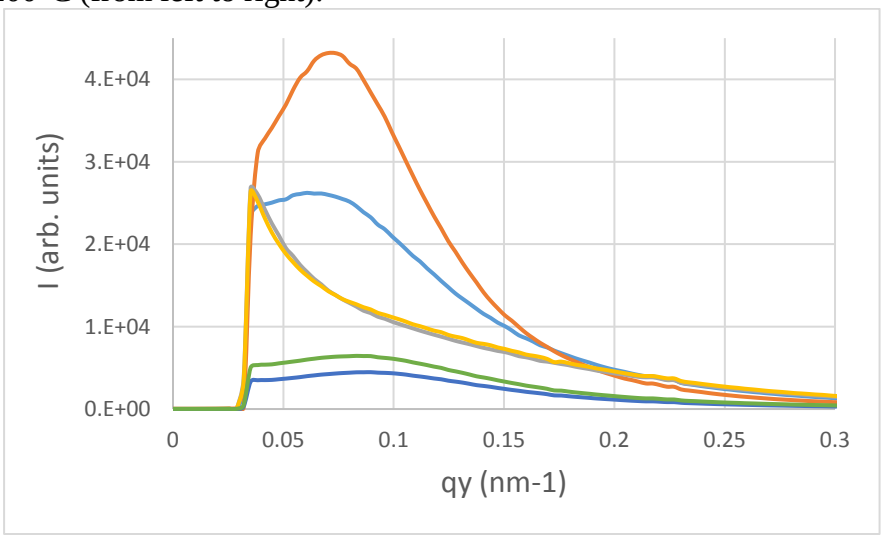

Figure 2. GISAXS as a function of qy. The substrate is hydrophilic Si (5 min: dark blue, 60 min: green) , hydrophobic Si (5 min: blue, 60 min: orange), and CrPt (5 min: grey, 60 min: yellow).

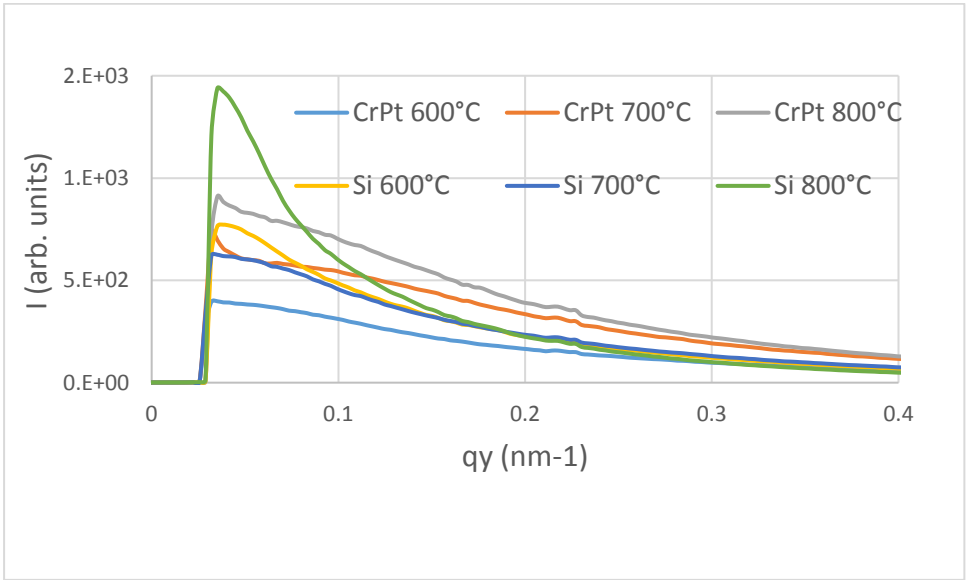

Figure 3. GISAXS as a function of qy. The substrate is CrPt or Si and the annealing temperatures varies from 600 to 800°C.

The anomalous data were recorded near the Sr K-edge (16105 eV) for the BST and the SrBaNbO3 and near the Nb K-edge (18986 eV) for the SrBaNbO3. The anomalous GISAXS analysis is under way. The goal is to study a possible separation of phase between the oxides.

Publication(s): in preparation