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Application for beam time at ESRF – Experimental Method

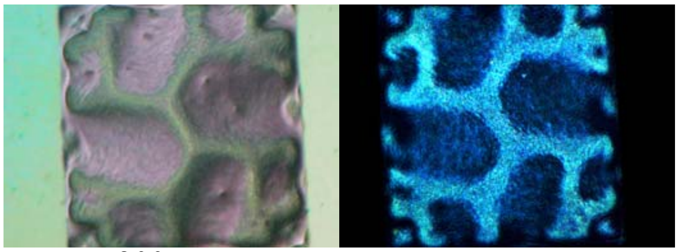
Orientation distribution of crystallites in buckling ferroelectric membranes.

Aims of the experiment and scientific background

The aim of the experiment is to study the correlation between curvature and crystallite arrangement in buckling substrate-free ferroelectric films (membranes). To this end, we propose to map the orientation distribution of tetragonal $BaTiO_3$ crystallites in polycrystalline membranes (Fig. 1) [1].

Thin ferroelectric films are very promising for a number of applications ranging from actuators to ferroelectric memories. In most of these applications the films are clamped. However, a number of applications, such as surface acoustic wave filters, piezoelectric actuators, pyroelectric sensors etc., employ films that have some freedom to bend.

$BaTiO_3$ membranes [2] (200-600 nm thick, 200-300 μm lateral dimensions) were prepared from amorphous films [3] deposited on Si substrate by etching of the respective windows in the Si wafer. The as-deposited substrate-free amorphous films are flat but corrugate after heat treatment. The shape of some membrane after crystallization at a temperature above 550° C is shown in Figure 1a. Coexistence of the areas with different radii of curvature is clearly seen in the picture. Comparing the optical image (Fig. 1a) and the transmitted cross-polarized light picture (Fig. 1b) one can conclude that the areas with curvature of opposite sign give different polarization contrast. It was observed that regions with large curvature rotate the polarization vector of the transmitted light while the regions with small curvature are not optically active in the corresponding direction. Therefore, the bright and dark regions (Fig. 1b) must have different alignment of spontaneous polarization of individual grains. To determine the interplay between film curvature and the orientational arrangement of small crystallites requires a high resolution (few microns) mapping of the spatial orientation of $BaTiO_3$ lattice parameters $\boldsymbol{a}$ and $\boldsymbol{c}$. Preliminary information about the size and shape of crystallites in buckling films was obtained by the transmission electron microscope (TEM, Fig. 2). According to electron diffraction, most crystallites belong to $BaTiO_3$ (PDF # 05-0626) phase but some of them fit $Ba_6Ti_{17}O_{40}$ (PDF # 35-0817). The $BaTiO_3$ phase was also identified in the films by wide angle X-ray scattering (Laue case).



200 μm

Fig. 1 a) b)

a) Optical microscopy image of a 500 nm thick polycrystalline $BaTiO_3$ membrane
b) The same membrane viewed in transmitted cross-polarized light demonstrating different regions of domain organization.

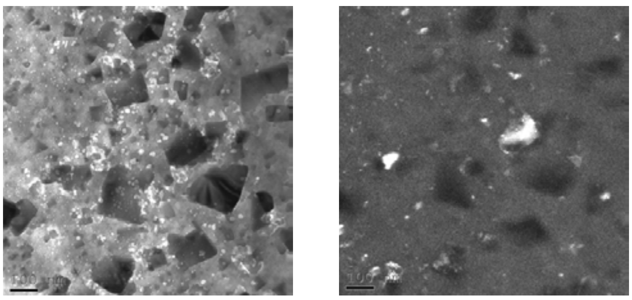


Fig. 2 a) Bright Field b) Dark Field
Transmission electron microscope (TEM) images of the same area of buckling freestanding $BaTiO_3$ film.

Experimental method

In order to map an orientation distribution of $BaTiO_3$ crystallites in buckling membranes (Fig. 1) with the necessary resolution, two main requirements must be realized:

1) X-ray beam size must be less than 5 microns;
2) θ-angle resolution must be better than $0.001Å^{-1}$(sinθ/λ) in order to distinguish between the $BaTiO_3$ lattice parameters ***a*** and ***c***.

Transmission X-ray diffraction (Laue geometry) is preferred for substrate-free thin film (~ 0.5 µm thickness) characterization. A mapping can be done using an X-ray diffractometer for high resolution texture analysis equipped with a stepping motor for 2D-motion of the sample. The step size must be around 10-15 microns in order to accurately follow the curvature variations in the buckling films (Fig. 1).

Choosing the optimal X-ray wavelength we need to take into account the following: the $BaTiO_3$ membrane is located above the window in the Si wafer, which has a thickness of 275 µm. Therefore, if the window dimension is about 200 µm, a sample can be turned a maximum 20º without the X-ray beam passing through the Si wafer. Thus, the X-ray wavelength must be small enough in order to measure till 20º the required number of reflections for phase analysis. At the same time, θ–resolution and, therefore, X-ray wavelength must be high enough in order to resolve the $BaTiO_3$ lattice parameters ***a*** (3.994 Å) and ***c*** (4.038 Å).

It is planed to measure up to 20 films with different patterns of buckling including several samples of flat membranes. It would be also interested to analyse the removed pieces of the buckling membranes.

The first stage of a run is proposed to be a phase analysis in order to reveal possible phase contamination (see scientific background section).

Then, we suggest to perform the pole figures of (200) and (002) reflections of tetragonal $BaTiO_3$ phase taking into account that the peaks positions differ by Δ(sinθ/λ)=0.0023 $Å^{-1}$.

It is also desirable to follow the dependence of the orientation distribution of $BaTiO_3$ crystallites as function of temperature (from 10º to 50º C). Our preliminary results show a clear change in the polarization contrast with temperature while no visible changes of the optical picture were registered at the same time.

Results expected

Using the synchrotron X-ray microbeam it is proposed to map the dominant orientation of the $BaTiO_3$ lattice parameter ***c*** in buckling membranes with lateral resolution of 5 microns. We expect that the $BaTiO_3$ lattice parameter ***c*** coincides with the direction of the tangent to the curve of minimal radius in the regions with high buckling. In the regions with small curvature we anticipate a random distribution of lattice parameters.

References.

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2. J. P. Nair, N. Stavitski, V. Lyahovitskaya, I. Zon, I. Lubomirsky, *Materials Science in Semiconductor Processing*, 5, 195, 2002
3. V. Lyahovitskaya, I. Zon, Y. Feldman, S. Cohen, A. Tagantsev, I. Lubomirsky, *Adv. Mater.*, 15, 1826, 2003