<table>
<tr><td>ESRF</td><td>Experiment title:
In situ measurement of the thickness of barrier layer in anodic aluminium oxide films</td><td>Experiment number:
MA-3829</td></tr>
<tr><td>Beamline:
ID10</td><td>Date of experiment:
from: 16-11-2017 to: 20-11-2017</td><td rowspan="2">Date of report:

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<tr><td>Shifts:
12</td><td>Local contact(s):
Andrei Chumakov</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
Kirill Napolskiy*, Aleksei Leontev*, Ilya Roslyakov*, Andrei Eliseev* (Lomonosov MSU)</td></tr>
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In situ X-ray scattering experiments were carried out during the growth of Anodic Aluminium Oxide (AAO) films on Al single-crystal substrates in 0.3 M H_2SO_4 at 25 V and electrolyte temperature of *ca.* 10 °C. Prior to anodization substrates were mechanically polished using 3 μm diamond suspension and finally electropolished in a mixture of CrO_3 and H_3PO_4 at 80 °C. According to Atomic Force Microscopy measurements the average surface roughness of the mirror-like aluminum single crystals was equal to 2 nm. We should stress, that global surface curvature of polyshed Al single crystals restricts the implementation of the X-Ray Reflectometry (XRR) technique to in situ measurements of AAO barrier layer thickness.

As an alternative technique to analyse dynamic of porous film growth a Grazing-incidence Transmission Small-Angle X-ray Scattering (GTSAXS) was used [1]. Figure 1 demonstrates a typical GTSAXS pattern recorded during Al single crystal anodization. To evaluate AAO structure dynamic in the radial (q_r) and longitudinal (q_z) directions, time dependences of intensity distribution in blue and red boxes, have been analysed, respectively.

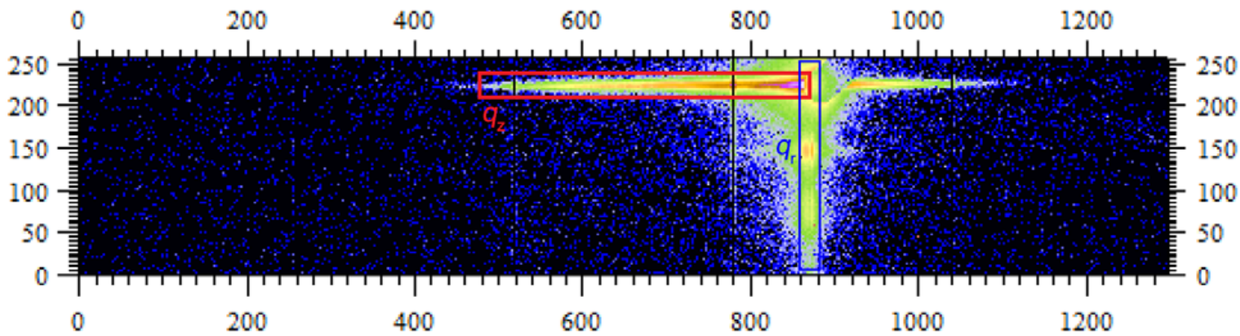

Fig. 1. Grazing-incidence transmission small-angle x-ray scattering pattern recorded during Al single crystal anodization in 0.3 M H_2SO_4 at 25 V and electrolyte temperature of *ca.* 10 °C. In experimental setup the 2D detector was mounted vertically orthogonal to the beam. Projection areas used for evaluation of the intensity distributions in radial (q_r) and longitudinal (q_z) directions are shown by blue and red boxes, respectively.

A set of time resolved q_r projections of GTSAXS patterns is given on the left panel of figure 2. A strong peak at 0.11 nm^{-1} and two overlapping peaks at *ca.* 0.20 and 0.22 nm^{-1} correspond to 2D hexagonal arrangement of the AAO porous structure and can be indexed as (10), (11), and (20), respectively. Peaks positions were used to calculate time dependence of interpore distance (D_{int}) during initial stages of anodization (see right panel of fig. 2). At the initial stage of anodization up to 200 second interpore distance sharply rises along with significant increase in anodization current (I) and finally asymptotically reaches the value of 63.5 nm, which is in a good agreement with the literature data [2]. Such behaviour corresponds to the reduction in pore density recently proved by analysis of Scanning Electron Microscopy images [3].

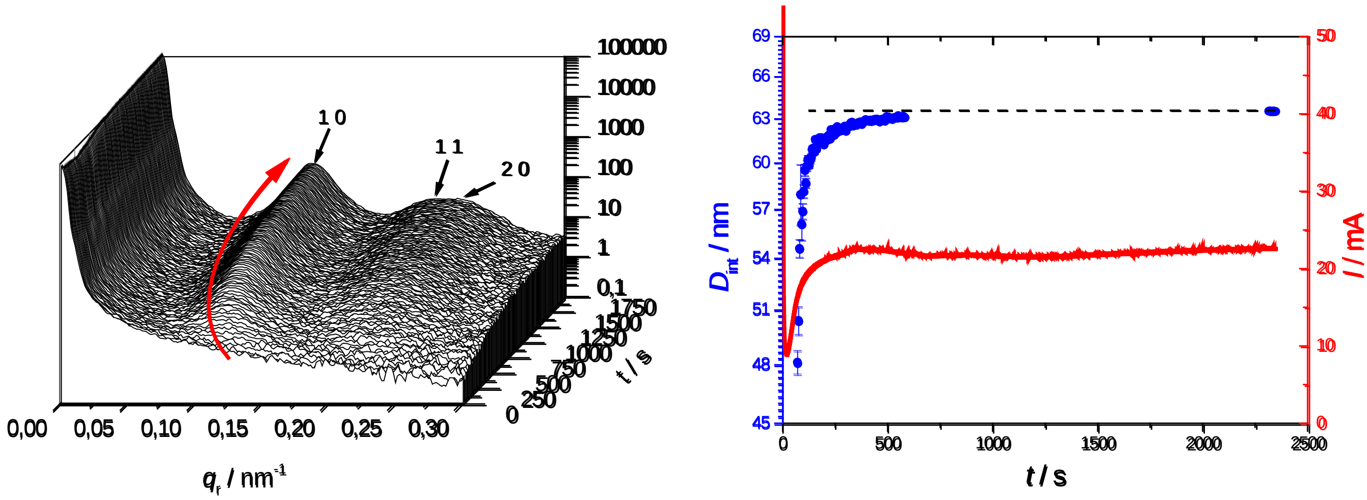

Fig. 2. A set of time resolved q_r projections of GTSAXS patterns collected during Al single crystal anodization in 0.3 M H_2SO_4 at 25 V and electrolyte temperature of *ca.* 10 °C (left panel). Time dependences of interpore distance (D_{int}, blue circles) and anodization current (I, red curve) (right panel).

Time resolved q_z projections of GTSAXS patterns (fig. 3) demonstrate a set of Fabry–Pérot oscillations, which shift in the small q-range during the porous film growth. This behavior is caused with the increase in AAO film thickness. The results of more detailed analysis of complex structure of q_z projections will be published soon.

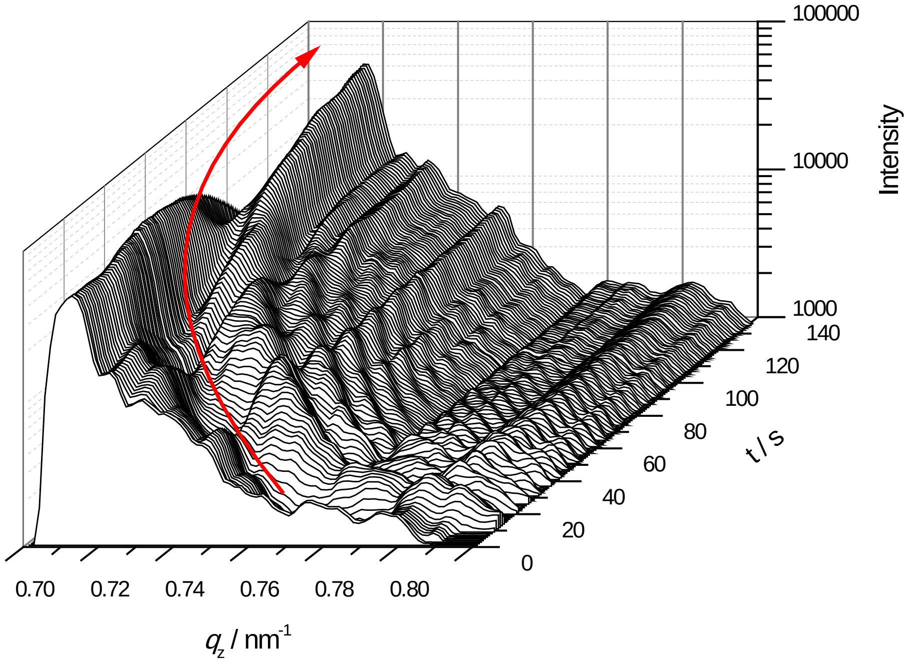

Fig. 3. A set of time resolved q_z projections of GTSAXS patterns collected during Al single crystal anodization in 0.3 M H_2SO_4 at 25 V and electrolyte temperature of *ca.* 10 °C.

To sum up, we demonstrate a great power of the surface scattering techniques, such as GTSAXS, in analysis of the structure parameters of AAO porous films at beginning stages of pores formation. This sort of structural information cannot be obtained using in situ experiments in conventional SAXS geometry [4].

Finally we would like to thank Oleg Konovalov and Andrei Chumakov for their excellent support during the experiment.

References:

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