ESRF	**Experiment title:** DEPTH GRADIENT ANALYSIS BY GRAZING INCIDENCE SMALL ANGLE X-RAY SCATTERING OF THE PORE MORPHOLOGY IN POROUS SILICON OVERLAYERS	**Experiment number**: HS-452
Beamline: ID1	**Date of experiment**: from: 14-5-98 to: 18-5-98	**Date of report**: 3.3.99
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Report:

We performed combined GISAXS and reflectivity measurements on 8 different porous silicon (PS) overlayers the thickness of which was 300 nm. The current density used to anodize the silicon substrates ranged from 15 to 300 mA/cm^2 . Half of the samples were treated with glycerine which is believed to make the interface between PS and the substrate smoother and to reduce the porosity depth gradient. All samples were prepared at room temperature and at –35 ^{o}C. The measurements were performed under the following experimental conditions:

- pressure of 0.005 Torr in the diffractometer chamber
- photon energy 7.112 keV
- slit aperture downstream of the monochromator 0.05 mm
- sample-to-detector distance 1.5 m

The detector used for the GISAXS measurements was a 2D gas-filled detector, whereas a scintillator was employed for the reflectivity measurements.

We first performed reflectivity measurements in the α-2α scanning mode so as to get a crude estimate of the critical angle (α_c) and of the average porosity.
In the first instance we noticed that these measurements were not reproducible under identical experimental conditions. At that point we had to investigate whether this was due

to a partial evolution of the sample under irradiation or rather to some faults in the beam geometric configuration.
After several trials we stated a misalignment in the sample-analyser geometrical coupling. A proper realignment of it caused the reflectivity curves to be eventually reproducible.
After each reflectivity measurement we recorded several GISAXS patterns at different α-values around α_c in order to observe possible correlation length and pore size depth gradients.
Several frames were recorded for every sample under the same conditions in order to obtain a good statistical quality of data.
A rough estimation of the pore correlation lengths obtained by GISAXS could be done on-site. The preliminary results for one of the samples show that the correlation length decreases from 15 nm to 10 nm approximately with depth.
The analysis of the reflectivity curves is currently being performed with our computer code, which can take into account all the optical parameters of the beamline. By best-fitting the experimental curves one obtains estimations of the layer thickness, porosity gradient and interface roughness. An example of the agreement between calculated and experimental curve is shown in the enclosed figure for one of the samples. For this particular sample we observe a rather flat depth distribution of the porosity inside the porous silicon layer thickness of 268 nm. The porosity values agree well with the nominal one of 40%.
The whole evaluation campaign is just under way. We intend to publish the results of this experiment, as they look quite promising and of potential interest for the porous material scientific community.

Best fit (left) of the reflectivity curve of a sample covered by a porous silicon layer obtained by anodization at low temperature with a current density of 300 mA/cm^2 without glycerine. Depth profile of the porsity (right) resulting from the best fit.