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GI-SAXS with NANOSTAR – a Synchrotron Method in the Lab

Introduction

Grazing-Incidence Small Angle X-Ray scattering (GI-SAXS) was first introduced in 1989 [1] as a novel technique for investigating structures on or close to the surface. At grazing incidence conditions, the incident beam undergoes total external reflection if the angle is below the critical angle. Scanning the angle of incidence from below to above the critical angle is therefore a kind of non-destructive depth profiling. This is used for conventional X-ray reflectivity (XRR) measurements, which are sensitive for electron density differences along the surface normal. XRR is widely used for determining thickness, roughness, and densities of thin amorphous, poly-crystalline, or crystalline films. GI-SAXS instead is sensitive to in-plane correlations in surface and the interfaces. Therefore, periodic distributed electron density variations (height-height correlations e.g.) on or slightly below the surface can be investigated. Additionally the GI-SAXS signal is very sensitive to surface roughness. The principle of GI-SAXS is shown in figure 1.

Today, GI-SAXS is a commonly used technique for investigations of quantum dots, thin organic films, or nano-materials arranged on surfaces.

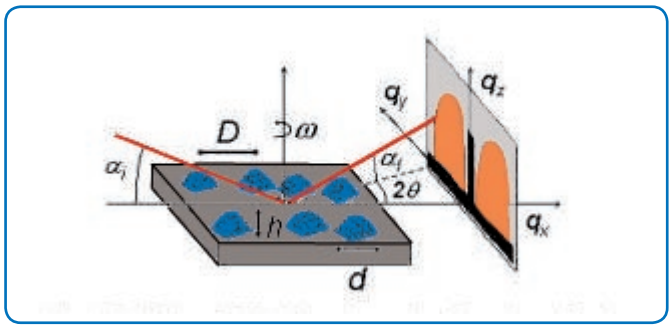

Figure 1: Principle set-up of a GI-SAXS experiment [2]: The x-ray beam impinges on the sample surface at grazing incidence and is undergoes total external reflection. The diffraction signal is collected at small exit angles in the detector plane.

Grazing incidence SAXS experiments require both high primary beam intensity and low divergence. Therefore, nearly all experiments published hitherto have been performed using dedicated synchrotron beam lines. We demonstrate the usability of the laboratory instrument NANOSTAR-U equipped with a simple sealed tube generator and cross-couple Goebel Mirrors for GI-SAXS experiments.

Experimental

A GI-SAXS setup has been implemented into the NANOSTAR-U by using an additional rotation stage and a modified rectangular beam stop. To assure reproducible sample mounting, a dedicated sample holder was designed.

The NANOSTAR provided highly parallel Cu-Kα (0.154 nm) radiation conditioned by a spot focus X-ray tube and cross-coupled Goebel Mirrors. The measurement time selected was between 500 and 1000 seconds. The original data were taken at Austrian SAXS Beamline at ELETTRA (Trieste, Italy), using a wavelength of 0.15 nm and a 2-dimensional CCD Detector. The measurement time was 4 seconds. For details see reference [3].

Fe-oxide doped silica films on Si-wafers were prepared by evaporation-induced self-assembly using an iron alkoxide-coordinated surfactant. Rectangular, orthorhombic and lamellar mesostructures were obtained by variation of the metal-surfactant complexes [3]. For data evaluation the obtained 2D-patterns were converted in arc versus q scale to obtain the 1D-scattering curves. The exact peak positions were fitted applying a Gaussian peak shape. Finally, the d-spacing was calculated using Bragg's law.

Results

The Fe-oxide doped silica films on Si-wafers, which were previously investigated at the Austrian SAXS Beamline at ELETTRA (Trieste, Italy) [3] were re-measured with the NANOSTAR. Figure 2 shows a measurement result obtained with the NANOSTAR.

The recorded 2D-pattern revealed that the material has formed a regular structure on the surface. This first qualitative result is in good agreement with the ELETTRA investigations. They showed that this type of material forms long cylinders on the substrate surface.

For a more detailed investigation on the arrangement of the tubes along the surface, the sample was rotated around the w-axis (figure 1). GI-SAXS patters were recorded at w-angles of 0°, 20° and 90°. Figure 3 shows the patterns and the corresponding intensity versus q scattering curves along the (11) direction.

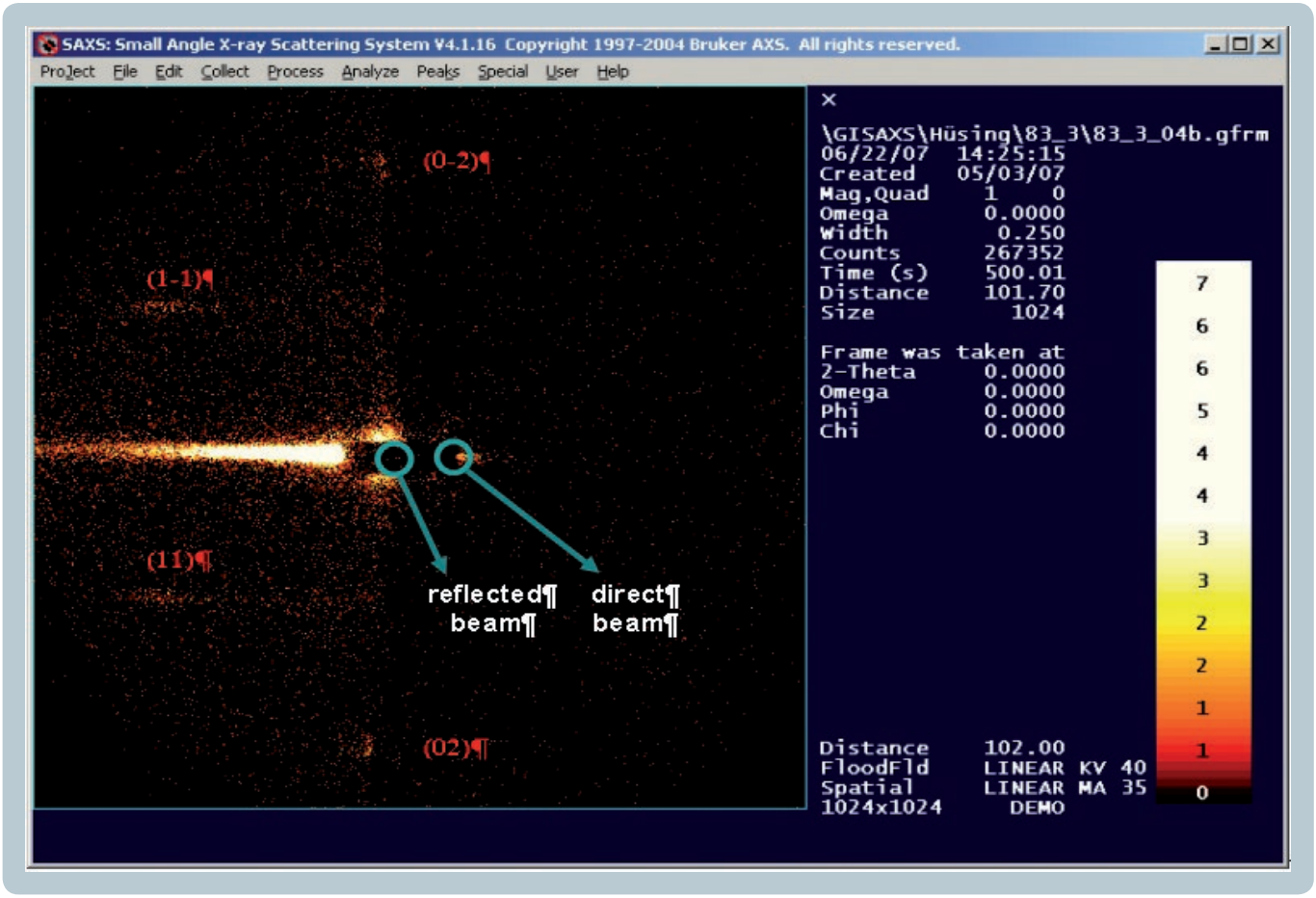

Figure 2: GI-SAXS pattern from the sample recorded with the NANOSTAR. The sample was oriented vertically. The measuring time was 500 s. The numbers in brakets indicate the indices (h,k).

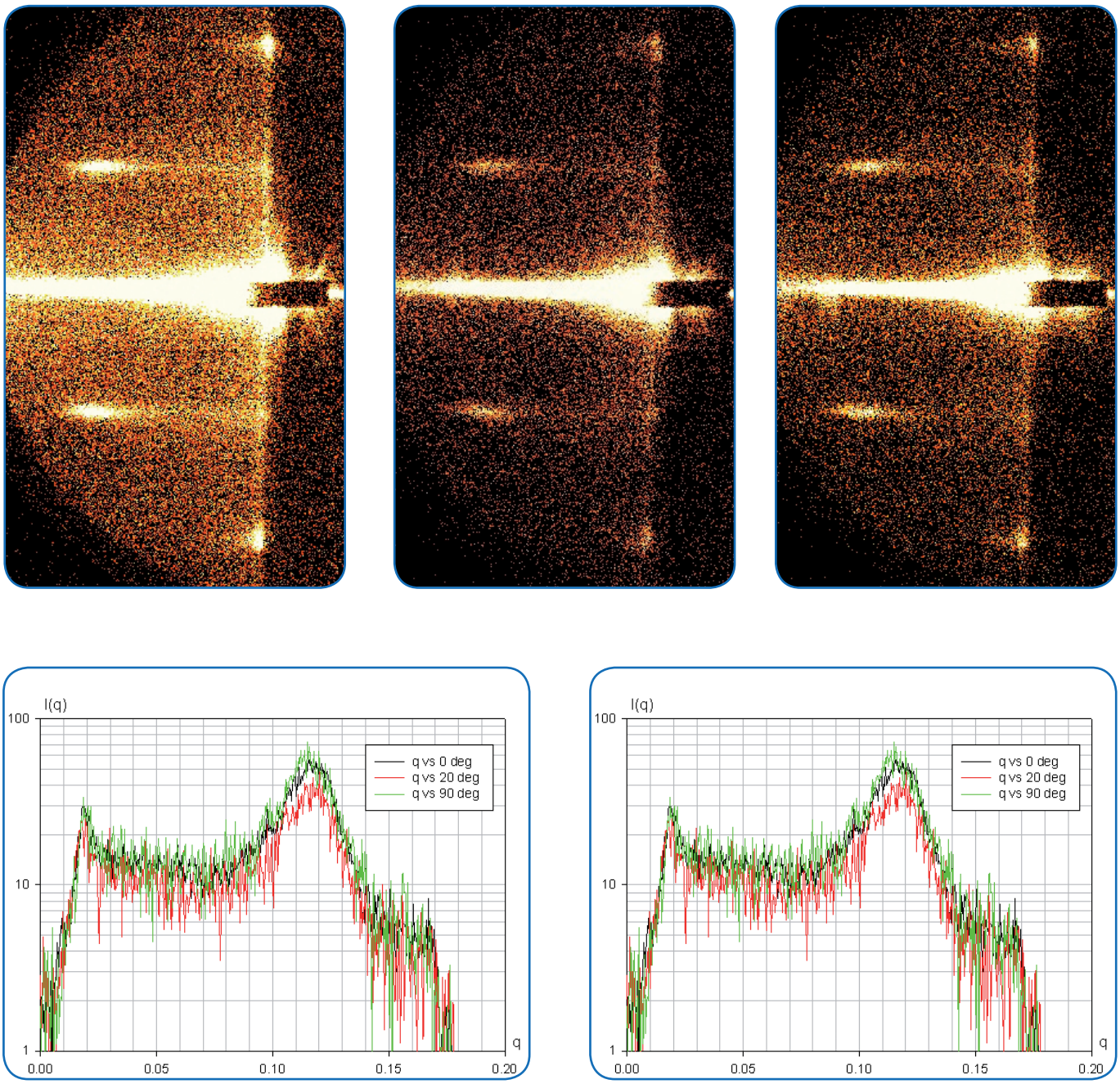

Figure 3: Top, left to right: GI-SAXS pattern recorded at rotation angles of ω = 0° (3h), 20° (1h) and 90° (1h). Below: scattering curves of the (11) reflection.

The pattern show distinct maxima indicating a regular arrangement of the tubes. Their positions are q_r = 0.1160 Å-1 along the surface and q_l = 0.0735 Å-1 normal to the surface, respectively. From the position of the maxima a orthorhombic unit cell could be determined. The unit parameters a, b of the cell were 54.4 Å and 85.5 Å respectively. The intensity of the peaks as well as the peak positions are independet of the rotation angle. That indicates, that the film consisted of coherent domains which had a texture free, isotropic arrangement. Figure 4 shows a sketch of the symmetry of the film.

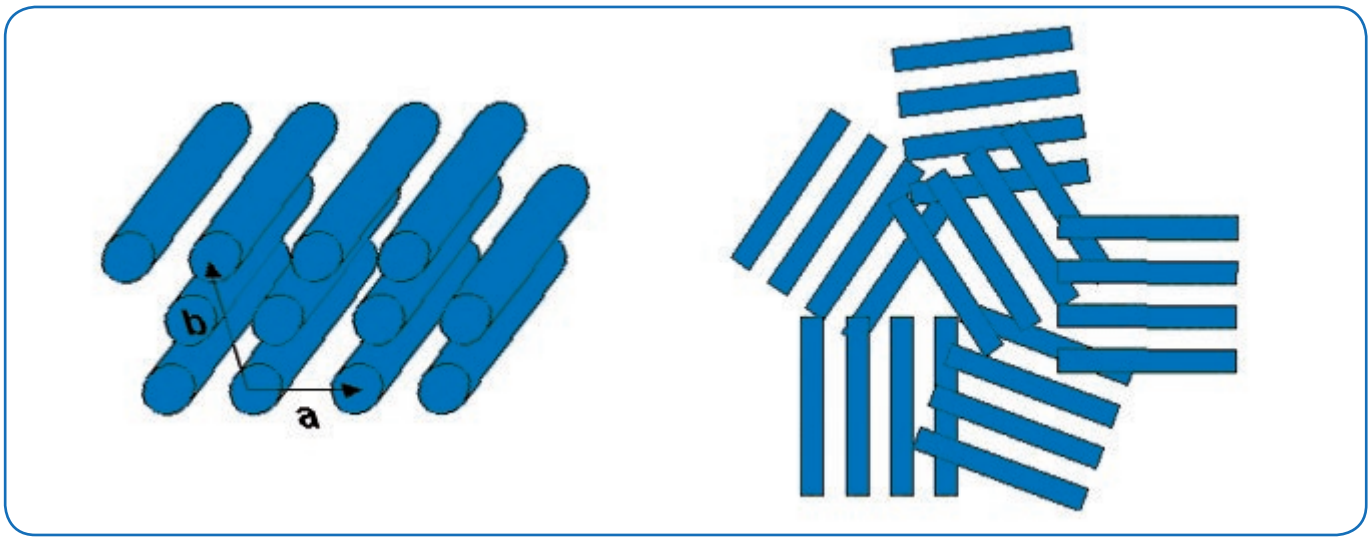

Figure 4: Sketch of the structure of iron oxide doped silica films according to [3]. On the left hand, the side view, on right hand the the top view on the film.

Summary and Discussion:

We showed a GI-SAXS experiment performed on Fe-oxide doped silica films deposited on Si-wafers using the laboratory SAXS system NANOSTAR-U. The evaluation of the obtained data indicate that the iron-oxide doped films formed long cylindrical structures which were arranged in an orthorhombical lattice. The film consisted of orthorhombic domains wich were randomly oriented on the suface. The results are in very good agreement with finding generated from synchtrontron experiments. This clearly shows the usibility of a sealed tube instrument for GI-SAXS investigations. Although requiring much longer measurement times the laboratory instrument may make a number of travels to a synchrotron source obsolete.

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