

Quantifying Porosity in Thin Porous Films by GISAXS (Grazing Incidence Small-Angle X-Ray Scattering)

Introduction

The characterization of thin-film porosity and pore structure is in the reach of today's X-ray analytical tools. The analysis of porous bulk media by small-angle X-ray scattering (SAXS) is a well-established technique. It can measure the specific inner surface area, average pore size and size distributions. It is non-invasive, rapid and applicable to routine-laboratory practice. However, for thin porous films, it needs to be modified such that the measured scattering signal should come from the thin film only. For this, the X-ray beam incident on the sample essentially grazes the surface film, and does not reach into the supporting material structure: this can be achieved by the grazing-incidence (GISAXS) geometry. GISAXS provides information about the depth density profile and the in-plane density heterogeneities – pore or particle distribution - of thin films as schematically shown in Figure 1.

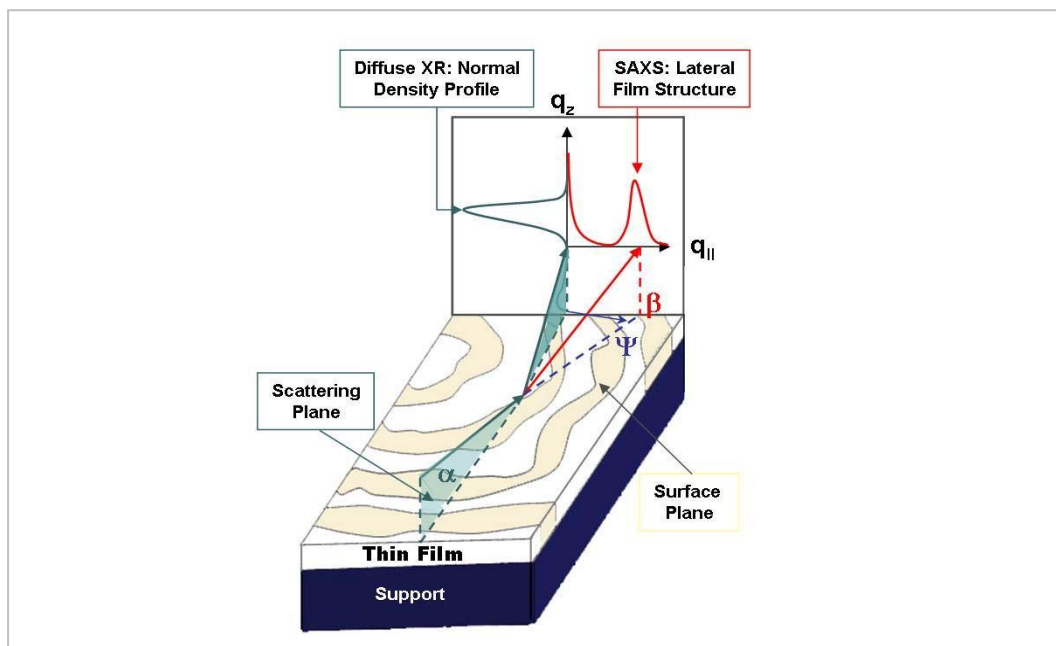


Figure 1 (<http://staff.chess.cornell.edu/~smilgies/gisaxs/GISAXS.php>)

Due to its high resolving power and versatility the GISAXS technique has become extremely valuable in nanotechnology and in the development of functionalized surfaces. So far, however it has been largely exclusive to synchrotron X-ray facilities since conventional laboratory X-ray instruments were unsuitable due to their generally lower brilliance. This situation has recently changed with the availability of high-performance microfocus X-ray sources and efficient multilayer optics, which exceed the brilliance of conventional line-focusing instruments by 2-3 orders of magnitude.

Hecus XRS have pioneered this new type of point-focussing SAXS cameras with the introduction of S3-MICRO (see www.hecus.at). The possibility of performing high-quality nano-structural characterization of thin films by GISAXS with this new laboratory system has been demonstrated. The technical realization of a laboratory GISAXS instrumentation dedicated for the characterization for porous films is novel. Hecus XRS offers to cooperate in R&D collaborations for specific applications.

Some Technical Facts

In the following, the most important performance specifications of the new S3-MICRO system are summarized:

<i>X-ray source and optics</i>	50-Watt microfocus source creating a point-focussed beam with a brilliance of $> 5 \times 10^9$ photons/(s.mm ² . mrad ² .% $\Delta\lambda/\lambda$); divergence < 1 mrad ² , $\Delta\lambda/\lambda < 1$ % of 1.54 Å (8keV photons)
<i>Variable grazing-incidence angle</i>	with angular precision of < 1 mdeg, enabling depth scanning of thin films
<i>Sample area</i>	typically 1 cm ² ; area of integration under the beam: typically 0.1 x 10 mm ²
<i>Detectors</i>	1-D linear PSD (pixel resolution 54µm), and 2-D area CCD (12,5x12,5µm ²)
<i>Ambient conditions</i>	variable temperature (-20 – 300 °C), controllable gas/humidity atmosphere
<i>Real-space resolution range</i>	0.5-150 nm

The camera system is designed as standard laboratory instrument requiring no special adaptations concerning radiation shielding, power and cooling (Figure 2).



Figure 2: Natural View of S3-MICRO

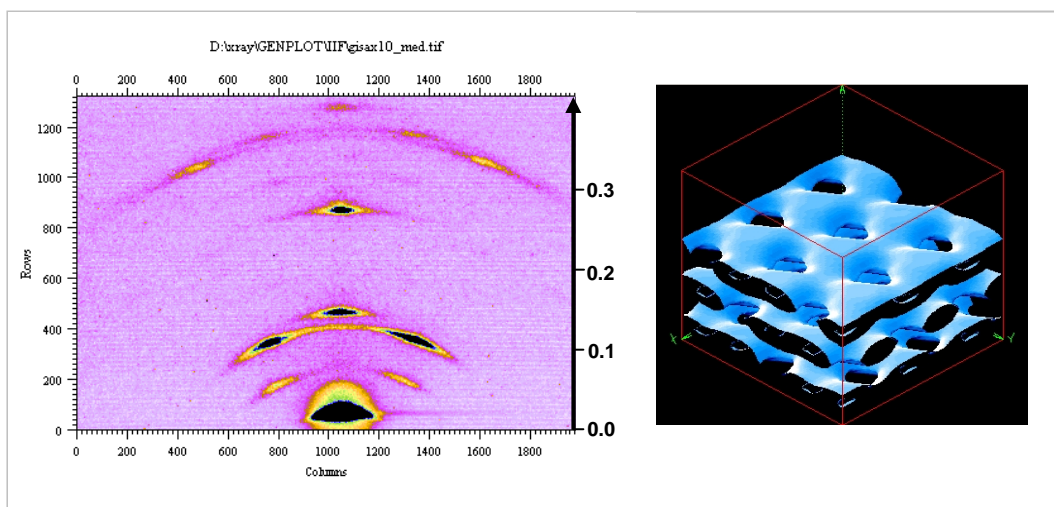


Figure 3: GISAXS pattern (left) taken with S3-MICRO from a thin DOPC lipid film on Si support; structure model (right)

Advantages

a) Analysis of both, classical (Euclidean) and fractal surfaces

The information obtained by GISAXS depends crucially on the type of film structure. If the film consists of a thin layer with well-defined pores, in the sense of classical Euclidean geometry, the information to be immediately obtained is the specific inner surface (hole area per volume). This connects to overall porosity and pore size distribution. However, if the film geometry is fractal, as is the case with many vapour or solution deposited systems, this simple geometrical model fails. It is a particular strength of X-ray scattering, that the fractal dimension can be obtained directly from the scattering pattern. In principle, the fractal dimension can be determined both for the vertical profile and for the in-plane structure or the film, by measuring the 2-D intensity profile vertically and horizontally to the plane of the film (see Fig.1).

b) Variability of ambient conditions

GISAXS is essentially non-invasive and can be performed under variable ambient conditions, e.g. controlled gas and/or relative humidity atmospheres. It is even possible to perform measurements under a liquid layer in a perfusion cell. This allows not only to study the influence of the ambient conditions on the film structure, but is also a strategy to discern between accessible and inaccessible pores, e.g. by using Ar or Xe, or capillary wetting liquids as contrast matching media which penetrate only into the accessible pores.

c) Speed of measurement

It can be estimated, that a high-quality GISAXS pattern of the thin porous films can be initially obtained within less than 30 min, given the brilliance of the S3-MICRO optics and the efficiency of the 2D-area detectors. At a later stage of development, where the essential steps in data acquisition and analysis have been optimized for specific conditions, this time can probably be reduced to a few minutes, thus providing the potential for production quality control.

d) Low costs per analysis

Contrary to conventional X-ray sources that operate at powers of several kilowatts of which most has to be cooled away at high budgetary and environmental costs, the S3-MICRO is powered by a 50-Watt generator without the need for cooling water. The costs per analysis (equipment, energy) can be estimated to be hundred times lower than with conventional X-ray systems.

Limitations

a) Length scale range

The accessible information is limited to the nanometric scale, it covers pore diameters smaller than 100 nm. In terms of specific inner surface, this corresponds to typical values of 5 - 1500 m²/g. Due to the reciprocity between scattering and real space, it is easier by GISAXS to measure large specific surface areas than small ones. This leaves μ m-sized pores (with inherently smaller specific surface) undetected. However, these are in any case more suitable objects for optical microscopic measurement.

b) Depth profiling

While the depth density profile of the film can be explored by changing the angle of grazing incidence, this has its technical limits in the optical divergence of the incident beam. Through the choice of parallel-beam optics this can be reduced to some extent, however it is presently envisaged, that for a 10 μ m film thickness, the profile resolution will not be better than 10 % (i.e. 1 μ m).

c) Radiation damage

With ionizing radiation, the danger of radiation damage always exists. It has to be explored by repetitive measurements with increasing total radiation dose, whether this is a problem for any given case. Strategies to minimize this effect can include the elimination of oxygen, as the most frequent cause for secondary radiation damage, and continuous change of the irradiated area at the film during exposure.