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X-RAY SCATTERING METHODS AND NEW X-RAY LABORATORY FOR COPLANAR AND NON-COPLANAR RECIPROCAL SPACE MAPPING OF SOLID AND LIQUID SURFACES AT THE INSTITUTE OF PHYSICS SAS

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Keywords: (GI)SAXS, GID, X-ray reflectometry, thin films, nanoparticles

Abstract

The contribution gives an overview of applications of X-ray scattering at the Institute of Physics of the Slovak Academy of Sciences over the last 40 years with emphasis on recent progress and developments of X-ray instrumentation. The period before 2005 is treated briefly while present research lines are described in more detail. The main part is devoted to a new laboratory where an original multipurpose set-up with a microfocus X-ray source has been installed recently, allowing combination of different techniques on the same sample. A brief outlook completes the presentation.

Historical background

Utilization of X-ray scattering at the Institute of Physics of the Slovak Academy of Sciences (IP SAS) has long tradition. The first strong impulse came in the 70-ies of the previous century when the research of metallic glasses prepared by rapid quenching started at the Department of Metal Physics of IP SAS. The Department was one of the world leaders in the development of these new materials with unique magnetic and mechanical properties. The X-ray diffraction provided basic characterization of the short-range order in the amorphous structure and radial distribution analysis gave insight into its irreversible structural transformations at elevated temperatures which limit practical applications (e.g. [1]). The measurements were performed on a Bragg-Brentano HZG-3 powder diffractometer which was later replaced by a HZG-4/A version (Freiberger Präzisionsmechanik). The diffractometer was additionally equipped with a focusing graphite monochromator in the diffracted beam path and after a general mechanical revision and upgrade of the control system it works reliably even nowadays.

Another impetus for development of X-ray scattering methods at IP SAS dates back to the early 90-ties when

novel multilayer-based structures for X-UV optics and spintronics with the individual layer thickness down to several nm started to be prepared at a newly established Department of Multilayers. The research was focused on interface phenomena which are crucial for multilayer structures. Here, specular X-ray reflectometry and diffuse (non-specular) scattering at grazing incidence coming from randomly rough interfaces provided a basic interface characterization in terms of the interface width, interface roughness and its correlation properties. To perform these studies, the X-ray instrumentation was extended by a high-resolution diffractometer (Stoe) equipped with a non-dispersive double-crystal GaAs(400) monochromator utilizing Fankuchen effect in the primary beam. Such a monochromator provided a good compromise between the beam intensity and spectral purity. Evaluation of the interface diffuse scattering was a challenging task as the underlying theory was formulated in the same period. Effects of deposition conditions and ion-beam treatment on the interface quality or multilayer stability under thermal load induced by excimer laser irradiation or rapid thermal annealing are typical examples of the multilayer studies of that period (e.g. [2, 3]). They continued later with pioneering studies of coplanar and non-coplanar X-ray scattering effects on patterned multilayers (multilayer gratings), utilizing also instrumentation at the collaborating Crystallographic Laboratory CNRS in Grenoble [4].

Present X-ray research and instrumentation

In 2005, a Consortium for multidisciplinary research of materials MULTIDISC was established from four institutes of SAS including the Institute of Physics. The Consortium obtained the first X-ray diffractometer with rotating anode in Slovakia D8 Discover SSS (Bruker) which was put in operation in February 2006. The diffractometer is designated primarily for thin film analyses. It is equipped with a Göbel mirror delivering a quasi-parallel primary beam (0.03 divergence) with 10⁹ photon/s flux and an Eulerian cradle with a motorized



sample stage. An own CCD camera with a LabView software was installed additionally to facilitate sample adjustment. The diffractometer design is modular. A 4-bounce Bartels monochromator for the primary beam with two Ge(022) channel-cut crystals, a pathfinder for the diffracted beam switching automatically between a slit and a 3-bounce Ge(022) channel-cut crystal analyzer, two Soller slits (0.12 and 0.35 divergence) for coplanar grazing incidence diffraction and a LiF monochromator for suppression of sample fluorescence are at disposal. Polycrystalline diffraction in symmetrical and grazing incidence geometries, high-resolution diffraction, stress, texture and (non-)specular reflectivity measurements are available as well as the corresponding evaluation software packages from Bruker. Excellent diffractometer possibilities for X-ray reflectometry were documented in 2 world-wide Round Robin tests with participation of 20 laboratories [5, 6].

The new diffractometer and software stimulated new X-ray related research at IP SAS. Rietveld refinement (with TOPAS code), stress profiling and texture analyses of nanocrystalline alloys started at the Department of Metal Physics. Reflectivity studies (with LEPTOS evaluation code) and coplanar reciprocal space mapping in an extremely large dynamical range of 9 orders of magnitude became possible at the (renamed) Department of Multilayers and Nanostructures which allowed measurements of ultrashort-period multilayers with the period below 1 nm. The Department started collaboration with industrial and academic partners in advanced interface characterization of extreme multilayer optics giving a feedback for technology development. A combination of reflectometry with grazing-incidence small-angle X-ray scattering (GISAXS) measurements (BW4 beamline at DESY Hamburg) proved to be necessary to achieve the lateral resolution at nanometer level and to address special questions such as multilayer growth mechanism, clustering effects at ultrashort periods or interface scaling behaviour and morphology in terms of the power spectral density and its replication across the stack (e.g. [7]). X-ray studies of Néel coupling in spin valves exemplify application of the X-ray reflectometry to spintronic multilayers [8].

Since 2000 the research scope of the Department of Multilayers and Nanostructures was extended by colloidal metallic nanoparticles (mostly Ag and superparamagnetic Fe_2O_3) prepared in collaboration with the Polymer Institute SAS. The nanoparticles are monocrystalline, covered with a ~ 1 nm thick organic shell (surfactant) to prevent agglomeration. The typical size is 6-7 nm with a maximum dispersion of 10%. The interest in the nanoparticles is driven by development of supported and self-standing nanoparticle membranes for sensors and actuators or by novel spintronic elements with nanoparticle arrays. Therefore the effort was focused on studies of self-assembling phenomena where GISAXS with synchrotron radiation proved to be a very convenient tool (ID10A at ESRF Grenoble and BW4 at DESY Hamburg). An original strategy for time- and spatially-resolved GISAXS was developed for *in-situ* studies to address the origin of self-assembling [9, 10]. Re-ordering effects of nanoparticle assemblies on silicon induced by UV photolysis or ozonolysis of the surfactant were studied

as well [11]. A modified Langmuir-Blodgett (LB) technique was developed for preparation of ordered nanoparticle monolayers on solid substrates over large areas (larger than 10 cm^2). Both the nanoparticle preparation and the modified LB technique are patented at present.

From synchrotron to laboratory

GISAXS measurements of nanostructures such as multilayers or nanoparticle assemblies have been confined to intense X-ray sources so far as the scattering effects are weak. Because of well-known reasons, synchrotron facilities cannot provide immediate or sufficiently flexible access which aggravates systematic investigations. Therefore it was decided to build a laboratory X-ray set-up with a microfocus source at the Department of Multilayers and Nanostructures which will allow not only GISAXS (and SAXS) but also non-coplanar grazing incidence diffraction (GID), reflectivity and coplanar diffraction measurements on solid and liquid surfaces. This combination of different techniques on the same sample with the same device will provide unique possibilities for structure characterization. The assembling of basic configuration has finished in April 2010. Various types of measurements are tested at present while some final solutions are still under development (Fig. 1).

The X-rays ($\text{CuK}\alpha$) are delivered by an air-cooled 30 W Incoatec Microfocus Source (I α S) equipped with a 2D focusing Montel optics (5 mrad divergence). The X-ray beam is reflected twice in L-shaped monolith with optical surfaces coated with laterally graded multilayers (two Göbel Mirrors). Suppression of the $\text{K}\beta$ component is more effective here than with a single-reflection 2D focusing while the flux is still high (10^8 photon/s). The optics housing is evacuated by a membrane pump. The nominal focal distance (source to image) is 560 mm and the measured focal spot size is 270 μm (FWHM). The optics monolith is adjustable to maximize the useful intensity as well as the exit aperture of the optics housing to block the direct and singly reflected beams. Another aperture of optional size in front of the sample defines the primary beam size. The sample is located in the focus and the sample-detector distance controls the magnification of the scattering pattern at PILATUS 100K 2D detector (Dectris). This is CMOS hybrid pixel array detector (pixel size $172 \times 172 \mu\text{m}^2$) which operates in single-photon counting mode. The main features include no read-out noise, no cross-talk effects, superior signal-to-noise ratio, read-out time of 2.7 ms, framing rate 200 Hz, counting rate per pixel $2 \times 10^6/\text{s}$, dynamic range of 6 orders of magnitude, high detective quantum efficiency (99% at 8 keV) and the possibility to suppress fluorescence by an energy threshold that is set individually for each pixel. These features render PILATUS detectors superior to CCD and imaging plate detectors, especially for fast time-resolved experiments or studies of weak scattering phenomena such as diffuse scattering if high spatial resolution is not required. Such experiments are envisaged on the new set-up. A tungsten beam-stop behind the sample protects the detector against the primary beam while the specularly reflected beam cannot cause any damage to the detector used.

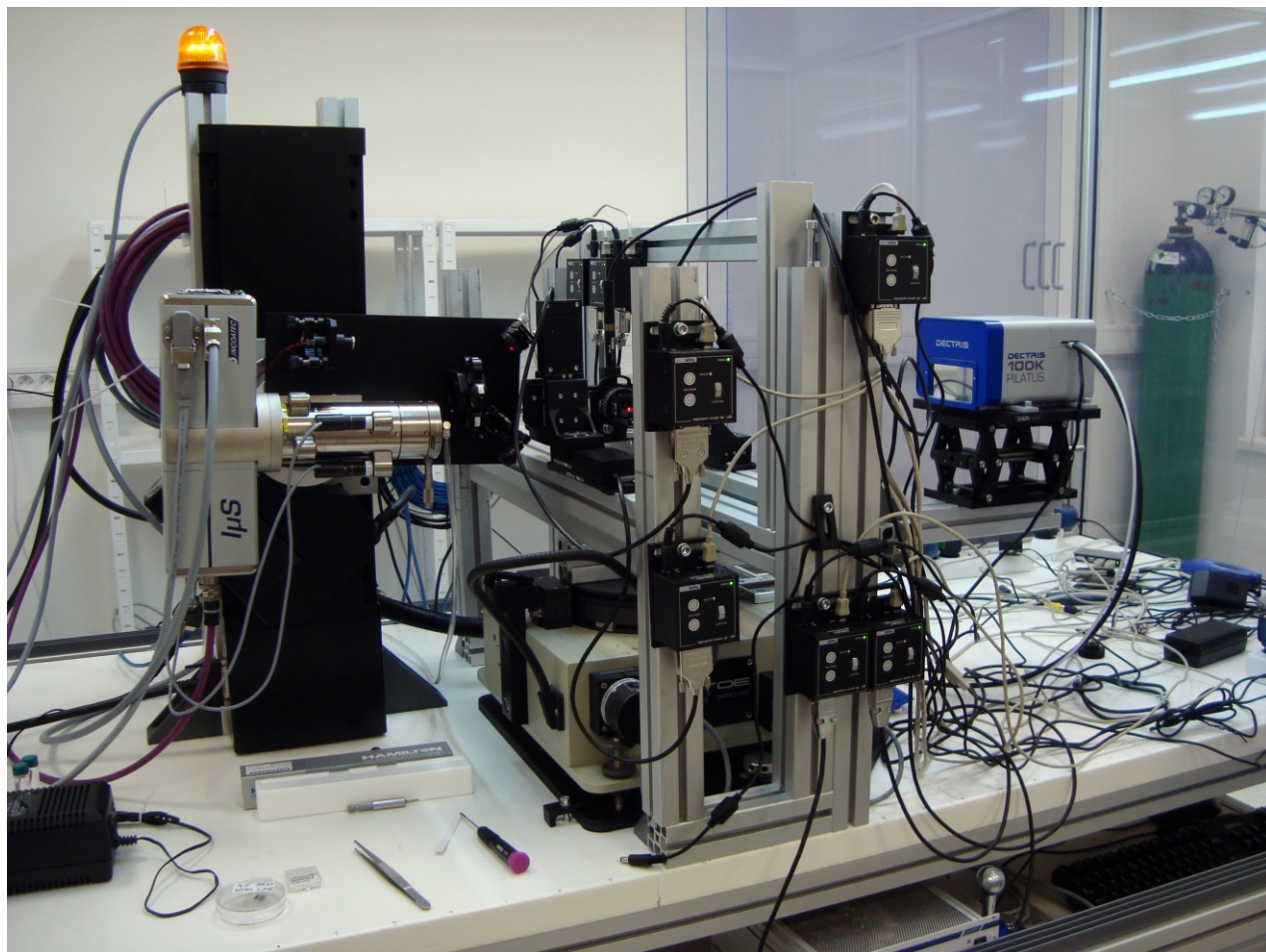


Figure 1. A total view of the set-up with microfocus source.

As the set-up is designed also for liquid surfaces, the non-coplanar measurements are performed in the horizontal plane while the coplanar ones are designed vertically. For them, the X-ray tube housing with attached optics can be vertically translated and simultaneously rotated around a horizontal axis to change the angle of incidence of X-rays on the same spot. Independent translation and rotation are possible as well. The adjustments of apertures, sample or beam-stop are facilitated by a visible semiconductor laser beam which is set before to follow exactly the path of the primary X-ray beam exiting the optics housing. The dynamic range is enhanced by a set of rotating absorbers in the primary beam. For measurements of solid samples in transmission or reflection geometries, a sample stage is used which can be replaced by a container such as LB trough for liquid samples. To change the vertical position, the detector is fixed on a lab-jack which is attached to a horizontally rotating arm of a goniometer (Stoe) placed below a console supporting the sample stage. A Soller slit of 5 mrad horizontal divergence can be fixed on the detector arm to define the 2θ angle for GID measurements. A special attachment for keeping the liquid sample surface at a constant vertical position is under development. It uses a laser reflection from the liquid surface as a feedback to control a motorized lab-jack supporting the liquid container. Such a compensation is necessary e.g. for GISAXS experiments on organic Langmuir films which evaporate fast. All movements and adjustments (tube housing, aper-

tures, sample stage, beam-stop, lab-jack) are motorized (Newport, Thorlabs). An own software on LabView platform facilitates the motor control and instant data visualization. An antivibration optical table with pneumatic legs (Melles Griot) for the whole set-up is under delivery.

The first SAXS and GISAXS measurements were done on silver behenate which is used as a standard for SAXS and allows a detector calibration. The horizontal beam position was adjusted with a small MarCCD camera (delivered with the I S source) which has the pixel size smaller by one order of magnitude than Pilatus 100K. Subsequently, different types of test experiments were performed. A comparison of our set-up with a commercial device Nanostar (Bruker) was done by measuring GISAXS at 0.45° angle of incidence on the same monolayer of Fe_2O_3 nanoparticles (~ 6 nm diameter) LB deposited on silicon (Fig. 2). Nanostar is designated for SAXS measurements and utilizes microfocus source with parallel beam optics from Incoatec. In our case it was additionally equipped with a goniometer to allow also GISAXS. Side truncation rods in the GISAXS pattern prove existence of a short-range order in the monolayer (Fig. 2a). A q_y cut across the Yoneda peak (i.e. at the critical angle of silicon) integrated over $q_z = 0.05 \text{ nm}^{-1}$ shows some differences (Fig. 2b). A smaller background of Nanostar is due the evacuation of the beam path but in spite of this the intensity and statistics of our set-up is better for the same collection time of 1 hour. The parallel beam size at Nanostar was

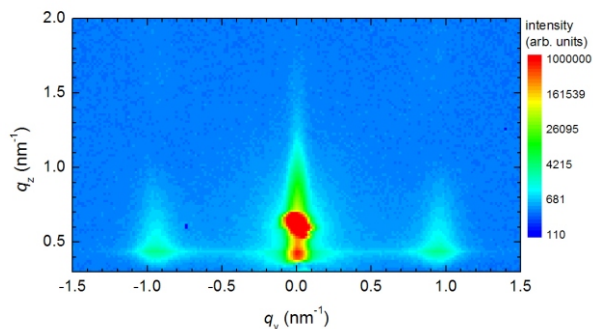


Figure 2a. GISAXS pattern of a Fe_2O_3 nanoparticle monolayer deposited on silicon measured on the set-up at IP SAS at an angle of incidence of 0.47° .

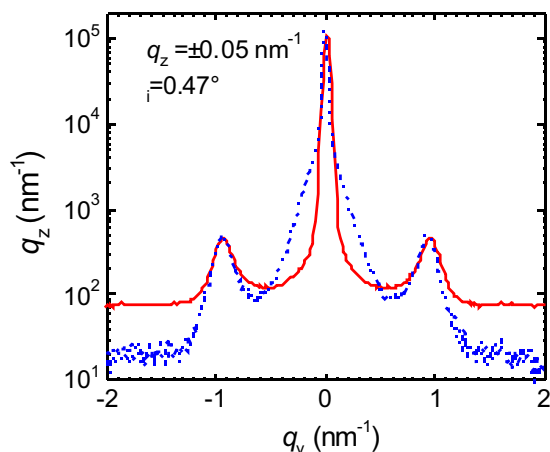


Figure 2b. The q_y cuts of the GISAXS patterns across the Yoneda peak calibrated on the same central peak intensity (full line - set-up at IP SAS, dashed line - Nanostar).

400 nm while the aperture of 350 μm was applied in the divergent primary beam at our set-up. The resolution at these conditions calculated from the FWHM of the central peak is comparable for the two devices and exceeds 60 nm. A spurious broadening of the central peak at Nanostar comes presumably from the cross-talk effects of the detector (Vánteč 2000).

SAXS measurement of a colloidal solution of ~ 6 nm silver nanoparticles with 350 μm aperture showed the form factor with even the second oscillation which proves a small dispersion of the nanoparticle size and high sensitivity of the set-up. Diffraction from a polycrystalline copper foil gave well resolved rings with grainy structure due to a small diffracting volume. The GID was tested on the 022 diffraction of a (100) cut silicon wafer at the angle of incidence of 0.5° . As the beam spot on the sample is elongated in the primary beam propagation direction, the non-coplanar diffracted beam is inherently broad and a Soler slit accepting the natural beam divergence of 5 mrad proved to be necessary to define the diffraction angle for GID. The 2D detector shows a broad truncation rod with a well resolved Yoneda stripe.

Time-resolved experiments were tested on a Langmuir film composed of silver nanoparticles used also for the SAXS test mentioned above. The film was created by spreading a colloidal solution onto the aqueous subphase and subsequently compressed with a constant velocity by

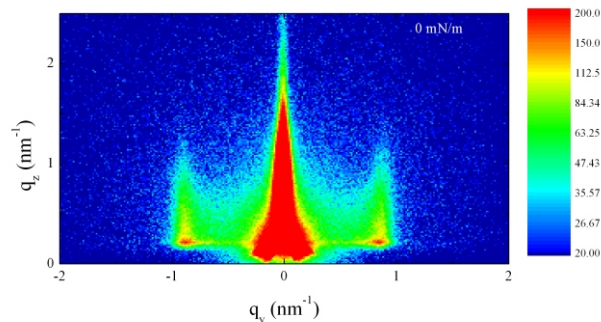


Figure 3a. GISAXS pattern of the Langmuir film of silver nanoparticles at zero surface pressure.

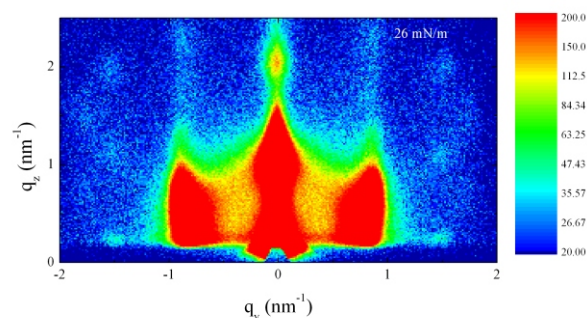


Figure 3b. GISAXS pattern of the Langmuir film of silver nanoparticles at the surface pressure of 26 mN/m.

movable barriers. The GISAXS was measured with 850 μm aperture at 0.2° angle of incidence (slightly above the critical angle of water) at the initial and final barrier positions in steady-state regime for 180 s as well as dynamically during the barrier movement (0.5 s exposition time). The surface pressure changed from 0 mN/m (discontinuous monolayer - gas phase) up to 26 mN/m (solid phase). From the very beginning, the film exhibited truncation rods at $q_y \sim 0.8 \text{ nm}^{-1}$ suggesting self-aggregation of the nanoparticles into locally ordered domains (Fig. 3a). The peaks became temporarily broader with increasing pressure above 5 mN/m which may be explained by boundary effects during the domain coalescence before a continuous monolayer was formed. This process was completed presumably at ~ 15 mN/m as at higher pressures, the truncation rods became modulated with the peaks located at different q_z for different truncation rod orders (contrary to Yoneda peaks) suggesting a phase transition (Fig. 3b). In particular, the monolayer collapsed and a 3D ordered multilayer stack with a local order not only in the lateral but also in normal direction was established.

Keeping the barriers at 26 mN/m surface pressure, the multilayer stack of silver nanoparticles was exposed to *in-situ* ozone treatment in a laboratory made UV reactor with a low pressure mercury lamp ($h\nu = 4.9 \text{ eV}$, 6.7 eV) which was temporarily installed on the set-up. Such a treatment is an efficient way to remove the surfactant shell which is necessary for some applications of nanoparticle assemblies. A 10 minute exposure resulted in a disappear-



ance of the truncation rods and loss of the ordered multilayer structure while after another 10 minute exposure, the GISAXS pattern was transformed into that of the aqueous subphase (the subphase was measured for reference still before the nanoparticles were applied). Obviously, the surfactant stripping resulted in a collapse of the Langmuir film and immersion of metallic nanoparticles which sank to the bottom of the trough. Comparing with our previous studies at synchrotron sources, these results document principal differences between the nanoparticle behaviour on liquid and solid surfaces under similar treatments. They also confirm excellent performance of the new set-up which enables us laboratory experiments confined before solely to synchrotron sources.

Outlook

Future X-ray related research at IP SAS will continue in developments of complex structural characterization based on efficient combination of different X-ray techniques. The interest in new approaches to X-ray structural analysis is triggered by development of advanced nanostructures such as those for X-UV optics, spintronics, solar cells or sensors. They include nanostructures built on bottom-up (nanoparticles) and top-down (thin films) principles or combination of both of them (hybrid nanostructures). In addition to *ex-situ* experiments providing information on (meta)stable structure, time-resolved studies will be done to give insight into dynamics of the processes of interest. It is important that the Department of Multilayers and Nanostructures has its own technology base. It will be under permanent technical development financed by several new projects funded from Structural Funds of EU.

Acknowledgement

The construction of the new multipurpose X-ray set-up was supported by Structural Funds of EU, project no. ITMS 26240120011 of the Ministry of Education of the Slovak Republic.

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