

## Finding and tracking Bragg spots in GISAXS maps of Block Co-Polymer Thin Films

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# GISAXS 2019

20 - 22 November 2019  
DESY, Hamburg (Germany)

- Keynote and invited lectures
- Contributed poster session
- Visit to PETRA III and hands-on training
- From the effective interface approximation to theory and simulation

#### Keynote speakers

Harald Ade, Northwestern University (US)  
Alexander Hexemer, ALS, Berkeley (US)  
Moonhor Ree, POSTTECH (KOR)  
Frank Schreiber, University Tübingen (GER)

#### Invited Speakers:

Philippe Fontaine, SOLEIL, Gif-Sur-Yvette (FRA)  
Philipp Gutfreund, ILL, Grenoble (FRA)  
Emanuel Kentzinger, FZ Jülich (GER)  
Peter Müller-Buschbaum, TU München (GER)  
Gennady Pospelov, JCMS (GER)  
Adrian Rennie, University Uppsala (SWE)  
Stephan Roth, DESY Hamburg & KTH Stockholm (GER & SWE)  
Mark Rutland, KTH Stockholm (SWE)  
Matthias Schwartzkopf, DESY, Hamburg (GER)  
Peter Siffalovic, Slovak Academy of Sciences, Bratislava (SK)

#### Organising committee:

Stephan Roth (DESY, KTH), Peter Müller-Buschbaum (TU München)

Organising committee: Matthias Kreuzeder

The Registration is now open! Abstract submission deadline: 1 October 2019

<http://gisaxs2019.desy.de>



## GISAXS2019 Programme

### Nov 20th, 2019

09:00-10:15 Arrival and registration

10:15-10:25 Opening – Welcome (Christian Schroer, DESY)

10:25-10:35 Welcome organizers (Stephan Roth, DESY & KTH and Peter Müller-Buschbaum, TUM)

*Session 1 – Basic Introduction (Chair: Stephan V. Roth)*

10:35-11:20 Moonhor Ree, Pohang University of Science & Technology (POSTECH) (Korea): **"Self-Assemblies of Functional Polymers and Their Impact on Property Performances"**

11:20-11:55 Peter Müller-Buschbaum: **"Basic Introduction to GISAS"**

11:55-12:30 Gennady Pospelov **"Experiment planning, simulation and fitting for GISAS and reflectometry using BornAgain framework"**

12:30-14:00 Lunch @ DESY / Business lunch

*Session 2 – Grazing Incidence Diffraction (Chair: Peter Müller-Buschbaum)*

14:00-14:45 Frank Schreiber, Univ. Tübingen (GER): **"Grazing incidence diffraction on organic thin film donor-acceptor heterostructures: Watching complex structure formation in real time"**

14:45-15:20 Peter Siffalovic, Slovak Academy of Sciences, Bratislava (SK): **"Real-time tracking of growth of small organic molecules on 2D-substrates by means of GI-SAXS/WAXS"**

15:20-15:30 Group photo

15:30-16:15 Coffee break & Discussion

*Session 3 – Future Challenges (Chair: Matthias Schwartzkopf)*

16:15-17:00 Alexander Hexemer, ALS, Berkeley (US): **"Data Driven Approaches for Characterization Techniques with Applications in Materials Science"**

17:00-17:35 Stephan V. Roth, KTH & DESY (SWE & GER): **"In-situ grazing incidence x-ray scattering for thin film technology"**

*Session 4 – GISAS at the air-water interface (Chair: Peter Müller-Buschbaum)*

17:35-18:10 Philippe Fontaine, SOLEIL, Gif-Sur-Yvette (FRA): **"Contribution of in-situ GISAXS measurements to the study of semi-fluorinated alkane layers at the air/water interface"**

18:10-18:45 Mark Rutland, KTH Stockholm (SWE): **"Self-assembly induced 3D patterning at the water-air interface studied with neutron reflectivity and AFM"**

## GISAXS 2019 – Programme

19:00-21:00 Poster session with snacks

### **Nov 21st, 2019**

*Session 5 – GISAS exploiting tender X-rays and neutrons (Chair: Matthias Schwartzkopf)*

09:00-09:45 Harald Ade, North Carolina State University (US): "**in-plane and out-of-plane mesoscopic structure of polymer thin films determined by resonant soft x-ray scattering**"

09:45-10:20 Adrien Rennie, Univ. Uppsala (SWE): "**GISANS to Study Wet, Soft Matter Interfaces**"

10:20-11:00 Coffee break

*Session 6 – Advances in GISAS techniques (Chair: Peter Müller-Buschbaum)*

11:00-11:35 Emanuel Kentzinger, FZ Jülich (GER): "**3D vector magnetometry by polarised GISANS**"

11:35-12:10 Matthias Schwartzkopf, DESY (GER): "**Tackling High Data Rates in GISAXS: Current Status and Future Challenges**"

12:10-12:45 Philipp Gutfreund, ILL, Grenoble (FRA): "**The GISANS options at ILL for liquid and polymer interfaces: Recent examples and perspectives**"

12:45-14:00 Lunch @ DESY / Voucher

*Session 7 – Towards hands-on training (Chair: Peter Müller-Buschbaum)*

14:00-14:20 Introduction to MiNaXS (Matthias Schwartzkopf)

14:20-14:30 General safety training (Stephan V. Roth)

14:30-14:45 Division into training groups A/B/C/D

14:45-15:00 Break

15:00- Training sessions TR1-4 (until Nov 24th, 2019); soft drink available at training stations

15:00-17:00 Training session TR1

DPDAK - A

Bornagain - B

Visit of P03 - C

Break -D

## GISAXS 2019 – Programme

17:00-19:00 Training session TR2

DPDAK - D

Bornagain - A

Visit of P03 - B

Break - C

**20:00-22:00 Conference Dinner @ DESY**

## **Nov 22nd, 2019**

09:00—11:00 Training session TR3

DPDAK - C

Bornagain - D

Visit of P03 - A

Break – B

11:00-13:00 Training session TR4

DPDAK - B

Bornagain - C

Visit of P03 - D

Break – A

13:00-14:00 Lunch @ DESY

14:00-15:00 Closing remarks (organizers)

15:00 End of Workshop

Dear participants,

From November 20 to November 22, 2019, the international workshop GISAXS2019 will be held in Hamburg, Germany (<http://gisaxs2019.desy.de>). It is a continuation of the very successful series of several international GISAXS workshops at DESY (in 2005, 2007, 2011, 2013, 2016) and the satellite conferences to the SAS conference series in Hamburg (in 2009), in Kyoto (in 2012), in Nice (in 2015) and in Gyeongju (in 2018). This workshop brings together different communities working in the field of thin films, nanostructures, surfaces and interfaces, to gain insights to the very powerful method of grazing incidence small angle x-ray scattering and related techniques. In keynote and invited lectures the possibilities and new trends in GISAXS and GISANS will be highlighted with a special emphasis on real-time investigations and data analysis. As in all the years, we expect about 100 participants from all over the world. Keynote and invited lectures will highlight the possibilities and new trends in GISAXS and GISANS. Poster sessions will allow for a profound discussion among the participants. For poster contributions, you are kindly asked to submit your abstract using the template on under Abstract submission. Only poster contributions with a submitted abstract can be accepted This workshop addresses students, experienced researchers, senior scientists working in the field of and exploiting the potentials of GISAXS and GISANS in the area of thin film technology The program is divided in two parts: In the first part, introductory lectures will be combined with expert lectures by leading expert scientists of grazing incidence technology and application. In the second part of the workshop we will have hands-on GISAXS, focusing on on-line data treatment and simulation of GISAXS data. In addition, we will offer a visit to the new micro-and nano-focus beamline dedicated to GISAXS at the 3rd generation synchrotron radiation source PETRA III.

We wish you a very successful workshop GISAXS2019!

Peter Müller-Buschbaum (TUM) and Stephan V. Roth (DESY & KTH)

# **Abstracts of Keynote Speakers**



# Self-Assemblies of Functional Polymers and Their Impact on Property Performances

Moonhor Ree

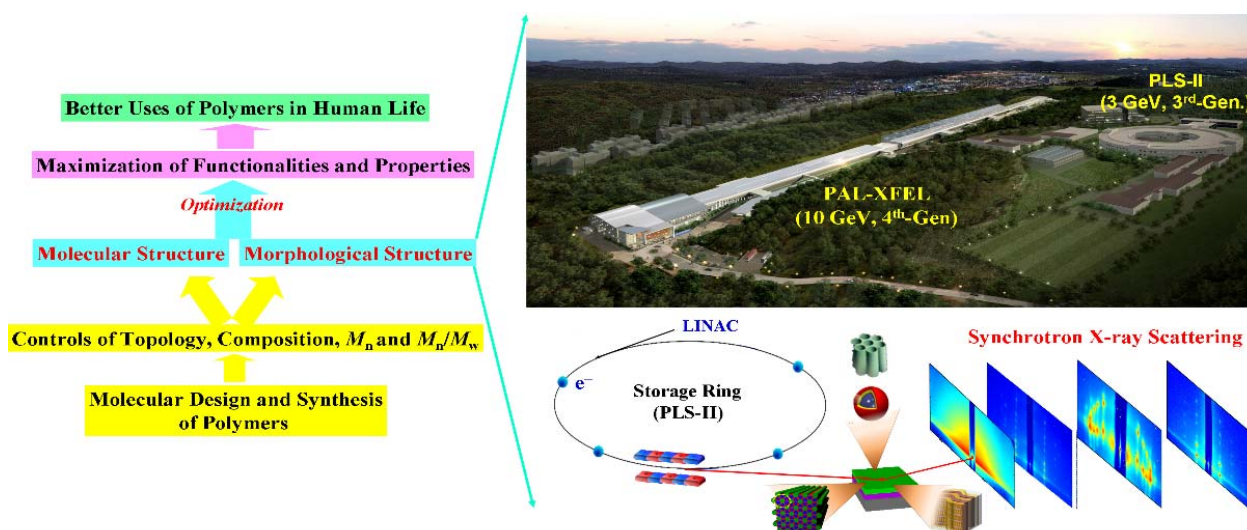
Pohang University of Science & Technology and Pohang Accelerator Laboratory (PLS-II/PAL-XFEL),  
Pohang 37673, Republic of Korea

Polymer can generally reveal very unique and specific properties depending on their molecular topology, chemical composition, molecular weight, polydispersity index, monomer sequence, chain structure, morphological structure, and so on. When a functional polymer is synthesized in the base of molecular topology, composition, molecular weight, polydispersity, and monomer sequence, its functional and property performances can be further maximized via controlling or optimizing molecular assembly (self-assembly), namely morphological structure, consequently providing good opportunities for better uses of the polymer product in human life (Figure 1).

The morphological structure of a functional polymer can be characterized and further optimized by scattering and microscopic analyses combined with processing. So far, several scattering and microscopic analysis techniques have been developed: light, neutron, and X-ray scatterings; optical, electron, and atomic force microscopies. All scattering techniques are nondestructive methods and indeed so convenient and applicable for all polymers. In contrast, microscopic techniques have some requirements in sample preparations because of their resolution limits; for example, electron microscopy is a destructive method because of requiring microtoming in sample preparation for getting a certain level of image resolution.

Grazing incidence scattering technique has emerged as a powerful and versatile tool for determining the morphological characteristics of nanostructures and atomic structural information. In particular, grazing incidence X-ray scattering (GIXS) is widely adopted in various advanced science fields including polymer science and nanoscience because of the availability of high quality X-ray sources which are produced by the 3<sup>rd</sup>- and 4<sup>th</sup>-generation synchrotron radiation facilities.

This presentation is covering most recent GIXS works of Ree research group on self-assemblies in a series of topological polymers, including miktoarm star polymers, macromolecular rotaxane block copolymers, and brush polymers, and their impact on properties, specially electronic device performances. This presentation further covers structural details of various nanoparticles for nanoscience and applications.



**Figure 1.** A schematic diagram of functional polymer developments with the aids of synchrotron photon source facilities.

# Grazing incidence diffraction on organic thin film donor-acceptor heterostructures:

## Watching complex structure formation in real time

Frank Schreiber

*Institute of Applied Physics, University of Tuebingen, Auf der Morgenstelle 10, 72076 Tuebingen, Germany*

Functional organic materials and devices are becoming increasingly complex. Their preparation and growth is, not surprisingly, similarly complex, and the resulting structure will be determined by a competition between kinetics and thermodynamics, which is not trivial to predict in particular for multi-component systems. We discuss general concepts [1] and recent examples of the thin film growth of organic semiconductors and their blends in the context of kinetic effects compared to thermodynamic (equilibrium) structure. These include unconventional structural motifs, such as a frozen-smectic structure formed in a blend of organic semiconductors, which form conventional crystals as pure compounds [2]. Particular attention is paid to the case of kinetically limited phase separation of a donor-acceptor pair (DIP:C60) used in organic photovoltaics [3,4]. This leads to asymmetric domain sizes near bottom vs top electrode due to the time (thickness) dependent phase separation with important consequences for device modeling. A further class of applications is the controlled “dilution” of pentacene by DIP or picene (PIC) to tune the charge transfer [5]. Finally, we discuss the implications for the optical and electronic properties as well as possible device applications with focus on the (generally anisotropic) coupling between donor and acceptor components in organic photovoltaics [6].

Financial support by the DFG and contributions by numerous students and external collaborators are gratefully acknowledged, as is support by large scale facilities.

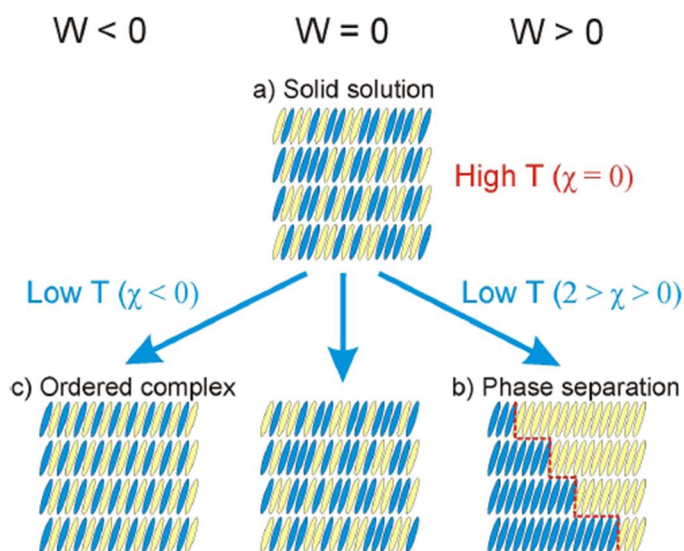


Figure 1: Simplified mean-field-theory-based schematic of possible phase behaviour in equilibrium, which is modified upon kinetically limited growth (after [1]).

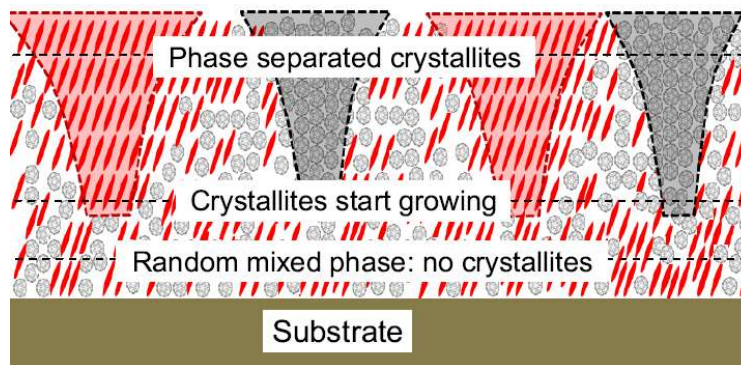


Figure 2: Schematic of non-equilibrium structure formation for a phase separating binary system (DIP:C60) (after [3]).

## References

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# Data Driven Approaches for Characterization Techniques with Applications in Materials Science

A. Hexemer<sup>1</sup>, S. Liu<sup>1</sup>, C. N. Melton<sup>1</sup>, R. Pandolfi<sup>1</sup>, D. McReynolds<sup>1</sup>, D. Kumar<sup>1</sup>,

M. Noack<sup>1</sup>, D. Ushizima<sup>1</sup> and J. Sethian<sup>1</sup>

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The materials discovery cycle contains many different components, including synthesis, characterization and data analysis and interpretation. In the past few decades, automatic synthesis pipelines have been established for many chemistry and materials systems. For characterization, many advanced techniques, such as X-ray scattering and NMR crystallography, have enabled the structure identification of various chemical, biological and materials systems, including polymers, inorganic materials and proteins. These techniques have been developed and improved substantially over the past few decades, which brings high-throughput experimental discovery into reach. Meanwhile, these breakthroughs produce very large data amounts. However, the process of understanding structural feature from data is still very labor-intensive. It requires many man hours of work by highly specialized and trained scientific staff to interpret the data and identify the structure correctly. Therefore, from the experimental side, the next generation of materials research requires a novel approach to address these challenges. From the computational side, high performance simulation methods have been developed to understand the structures of underlying materials systems. Even in the case that the simulation process is not the bottleneck, it is still not trivial to map the characterization result to the underlying structures. To accelerate materials research, a different and more flexible approach is needed to address these challenges from both experimental and computational sides and enable high-throughput materials discovery. Recently, machine learning, a branch of artificial intelligence, has demonstrated the capability to tackle many challenging chemistry and materials problems, including machine-learning-assisted materials discovery, drug design and crystal structure representations [1]. Previously, histogram of gradient (HOG) and Support Vector Machines (SVM) methods have been applied to predict X-ray scattering experiment configurations with more than 80 classes [2,3]. We propose a novel approach: integrate machine learning methods into characterization techniques to categorize and manage experimental data, identify the structures, understand the chemistry-nanostructure relationship, approximate state-of-art computational prediction results, and optimize characterization facility parameters.

X-ray scattering has been applied to characterize different materials chemistry systems. Nowadays, X-ray scattering experiments can be conducted in a high-throughput manner driven by high speed detectors and high brightness sources. It is important to develop scientific procedures to manage and analyse large-scale datasets. Herein, we propose a machine learning based hierarchical categorization approach to manage and classify the data, so that appropriate analysis pipelines can be applied autonomously. More importantly, this framework can be potentially integrated into an automatic materials chemistry discovery process, together with high-throughput synthesis and robotic X-ray scattering experiments. Scattering data can be categorized based on different criteria. For example, depending on the geometry of the experiment, the data can be categorized as transmission or grazing incidence small angle X-ray scattering data. In addition, the data can be categorized by characteristic features. Different features, such as rings, arcs, rods and Bragg peaks, usually require different analysis approaches and data reduction methods. For example, ring patterns in transmission X-ray scattering data, usually require radial integration. To expand on this approach, we propose a framework for materials discovery using X-ray scattering by leveraging a large-scale experiment database and different machine learning methods. To apply machine

learning algorithm to experimental data we start by organizing the scattering data using a flexible database containing experiment information, labels from domain experts and predicted labels from trained machine learning models. We built a database containing more than 500,000 images in collaboration with users of the SAXS/WAXS beamline at the Advanced Light Source. A convenient web application for data labelling was developed, and about 11,000 experimental images were labelled. The labelled data is used to train machine learning models using our hierarchical approach shown in figure 1, which allows us to categorize each X-ray scattering data's features individually, starting from the coarse-grain information (such as geometry of X-ray scattering experiment), to the fine-grain information (such as ring or crystalline features). The trained network was then applied to in-situ experiment data to demonstrate its ability to recognize and automatically adjust to phase transitions of real-time data.

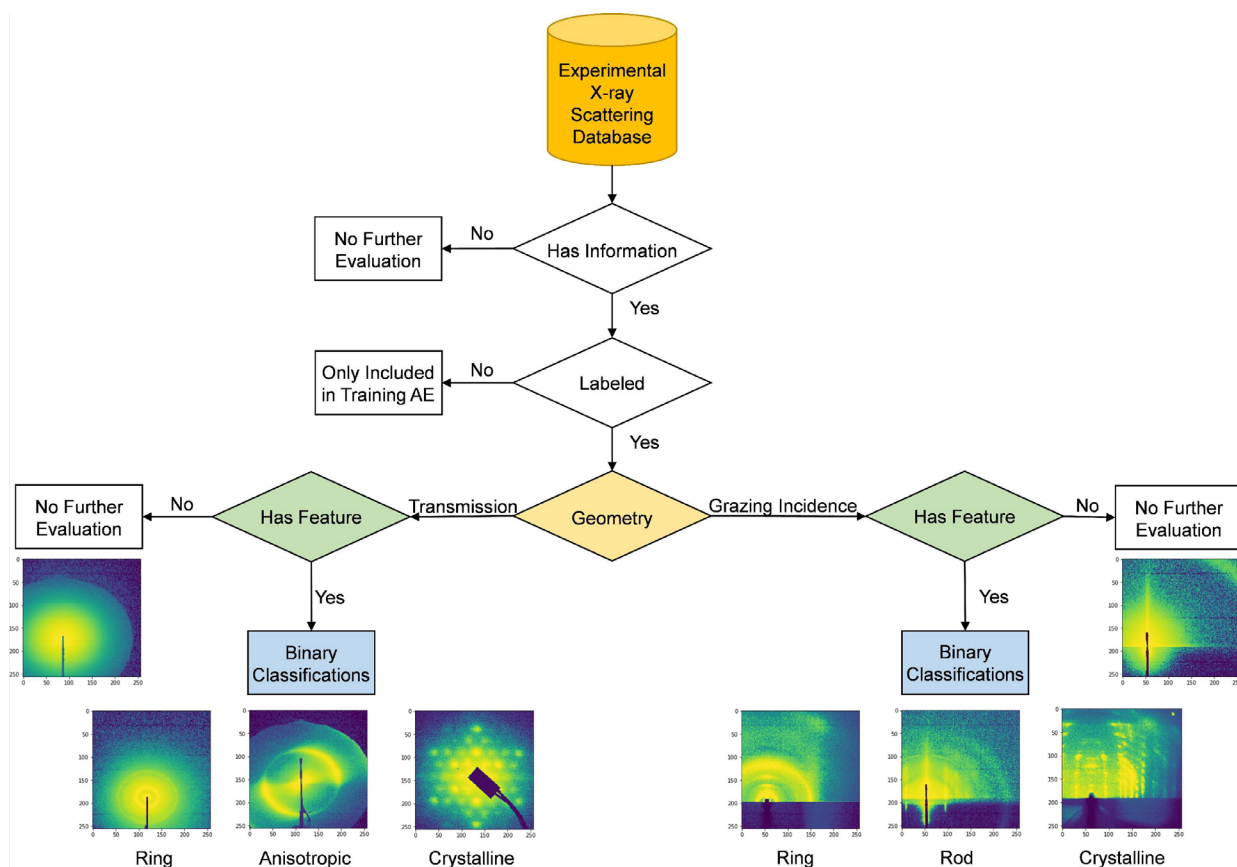


Figure 1: The hierarchical categorization method for X-ray scattering data.

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# Resonant Soft X-ray Scattering

H. Ade

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Since their inception approximately 15 years ago, resonant soft X-ray scattering (R-SoXS) methods [1-3] have become powerful techniques to investigate low Z materials, in particular thin films of organic molecules and polymers [4, 5]. This is in large part due to their ability to achieve high compositional contrast without labelling (e.g., staining, deuteration) and the ability to exploit rich materials specific spectral signatures at the Carbon K-edge [6, 7]. This intrinsic high scattering contrast allows the in-plane structure in 30-500 nm thin films to be investigated directly in a transmission geometry without resorting to a grazing incidence geometry. Additionally, the long wavelengths (~2-5 nm) used in R-SoXS yields much larger scattering angles than in traditional small angle x-ray scattering (SAXS, ~0.1 nm). Yet, the long wavelength-limit and the small angle limit yield the same mathematical approximation. The long and short wave-length methods thus result in equivalent data and measure the same structure in the samples, except that R-SoXS has a better signal/background ratio due to the lack of strong scattering from interfaces with the vacuum or the substrate and it is also easier to probe small q-regime (i.e. larger length scales) due to the larger wavelength utilized. Unique to R-SoXS, is its ability to be sensitive to bond orientation [8, 9]. The challenge of this sensitivity is the increased need for sophisticated analysis methods [10]. Despite these advantages, dedicated facilities for R-SoXS operation have been slow in being constructed. This might be due in part to the flipside of soft x-rays having high contrast and high cross-sections: (1) Significantly complexity is added of having to operate the sample and detector in a vacuum environment, (2) control of the sample environment (solvent, T, etc.) is very challenging, and (3) the optics of the beamline has to be kept clean from Carbon contamination [11]. A new facility in addition to the one at the ALS has recently come online at the NSLS-II. Additionally, both dedicated facilities aim to control the sample environment between two thin Si<sub>3</sub>N<sub>4</sub> windows.

This presentation will delineate some of the historic developments and similarities and differences between the short and long-wavelength X-ray scattering methods and exemplify the capabilities of R-SoXS through a number of examples, including recent method advances and use of R-SoXS in grazing incidence geometry. One example is presented below, focusing on the use of scattering anisotropy that results from molecular orientation contrast to understand the complex impact of molecular orientation relative to the donor/acceptor interface in an organic solar cell. 2D anisotropic R-SoXS patterns such as that exemplified in Figure 1 were utilized. The scattering anisotropy was quantified by using integration over sectors and calculating differences over sum ratios. At the same time, the total scattering intensity allowed to assess the relative composition fluctuations (related to the purity of the domains, and the intensity distribution to assess the relative lengths scales of the morphology created. No other parameter, including those describing molecular packing extracted from wide-angle x-ray scattering, but the molecular anisotropy parameter correlated to the short circuit current density and the fill factor, both of which are directly proportional to the device efficiency.

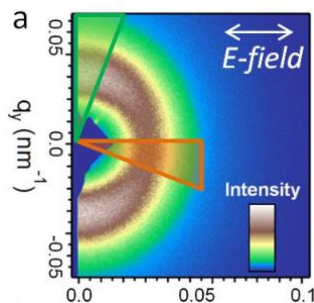


Figure 1: Anisotropic scattering patterns arising from orientation-composition correlations in an PNDT-DTBT:PCBM organic photovoltaic blend.

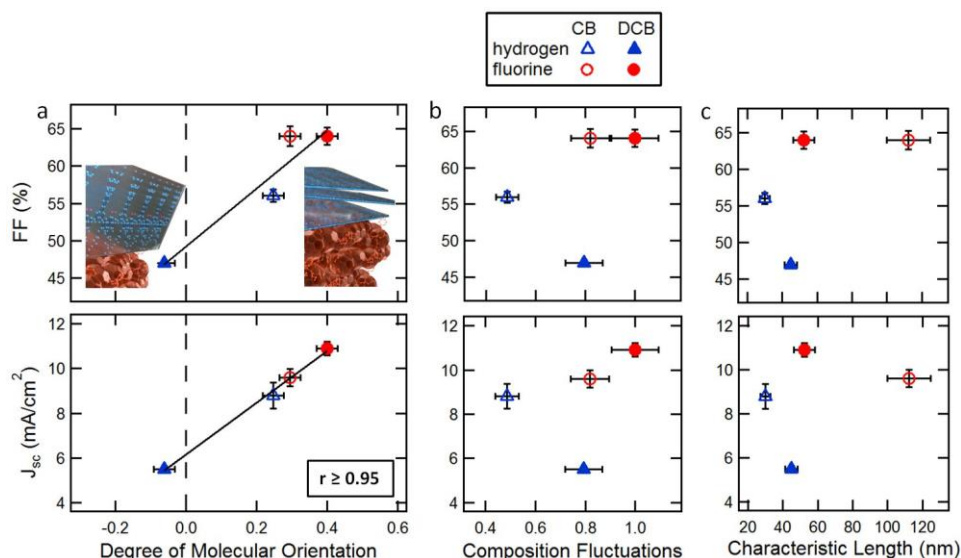


Figure 2: Device performance strongly correlates with the degree of molecular orientation for fluorinated and un-fluorinated PNDT-DTBT:PCBM blends cast from chlorobenzene and dichlorobenzene. – Inset in Fig. 2a visualizes an edge-on versus face-on location orientation of the polymer backbone with respect to a donor-acceptor interface.

R-SoXS has been particularly popular for assessing the morphology of organic photovoltaic devices, but other examples of its utilization include applications to block copolymers, nanofibers, micelles in milk, aerogels.

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# **Abstracts of Invited Speakers**



# Basic Introduction to GISAS

P. Müller-Buschbaum<sup>1,2</sup>

<sup>1</sup> Technische Universität München, Physik-Department, LS für Funktionelle Materialien, James-Franck-Strasse 1, 85748 Garching, Germany

<sup>2</sup> Technische Universität München, Heinz Maier-Leibnitz Zentrum (MLZ), Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Lichtenbergstraße 1, 85748 Garching, Germany

The investigation of nanostructures at surfaces, interfaces and in thin films requires dedicated analytical techniques, which provide information from a molecular to a mesoscopic scale. [1] Grazing incidence small angle x-ray and neutron scattering (GISAXS and GISANS) overcomes the limitations of conventional small-angle x-ray and neutron scattering with respect to extremely small sample volumes in the thin film geometry by the use of the reflection geometry [2-4]. GISAXS/GISANS involves a combination of two techniques, GID (grazing incidence diffraction), which uses a reflection geometry to obtain surface and near surface sensitive scattering, and SAS (small angle scattering), which measures structures of 1 - 100 nm length in normal transmission mode. It is a non-destructive structural probe and does not require a special sample preparation. GISAXS/GISANS yields excellent sampling statistics (averages over macroscopic regions to provide information on nanometer scale) and provides information on particle geometry, size distributions and spatial correlations. However, in GISAXS/GISANS experiments the high demand on collimation requests the use of high flux x-ray and neutron sources.

After a basic introduction to the GISAXS/GISANS technique, several different examples of thin nanostructured polymer films are presented to illustrate the possibilities and challenges of GISAXS/GISANS. In addition, the challenges and potentials of in-situ studies during printing and in-operando studies of organic solar cells are presented and discussed in detail. [5,6]

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# Experiment planning, simulation and fitting of GISAS data using the BornAgain framework - recent developments and advanced applications.

M. Ganeva, J. Fisher<sup>1</sup>, J.C. Loaiza, G. Pospelov, W. Van Herck, J. Wuttke and D. Yurov

Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ),  
Forschungszentrum Jülich GmbH, Garching, Germany

<sup>1</sup>Cape Analytics GmbH, München, Germany

One of the main challenges for the successful interpretation of feature rich data in the field of surface neutron and X-ray scattering rests with the accurate parametric data modelling and fitting. A community recognized software which gives access to the corresponding functionality in a reliable and user friendly manner, is of key importance for scientists running their experiments at various neutron and synchrotron facilities.

BornAgain [1] is a generic framework that provides scientists with the means for modelling multilayer samples with smooth or rough interfaces, various types of embedded nanoparticles and various models to treat finite size effects and the coupling between the type and position of a particle. Its name, BornAgain, alludes to the central role of the distorted-wave Born approximation in the physical description of the scattering process.

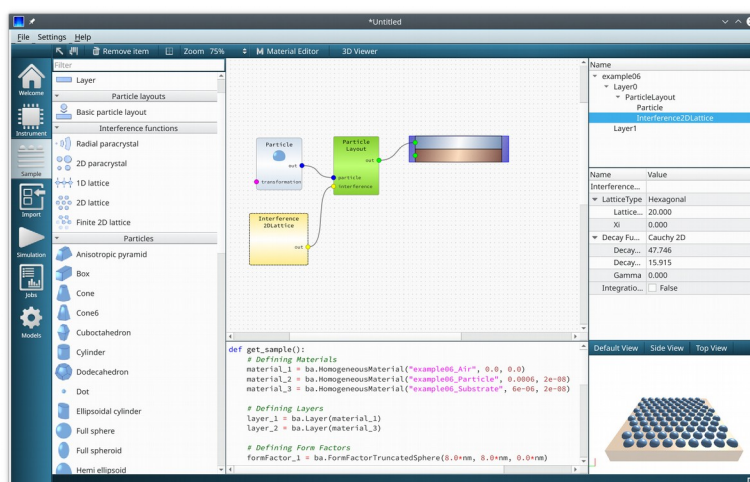


Figure 1: BornAgain graphical user interface

Carefully designed for a broad community of users, BornAgain offers a modern graphical user interface with the possibility to perform real-time simulations and to fit experimental data. The recent developments, such as a 3D real-space sample view and advanced instrument geometries facilitates virtual sample preparation and experiment planning.

BornAgain development has started in 2012 and initially the project was oriented to the needs of the users from the grazing incidence community with the aim to supersede the highly successful but no longer actively developed software IsGisaxs [2]. Since that time the project was continuously evolving following the requests of the growing user community to support multilayer samples of various complexity: from well ordered nanoparticle arrays [3] to disordered soft matter systems [4]. Currently the software supports both nuclear and magnetic neutron scattering, offering the user a way to analyze polarized SANS and GISAS [5].

Lately we have started to extend BornAgain from GISAS to specular reflectometry and off-specular scattering with the idea to provide scientists with a universal tool to plan and analyse their specular, off-specular and GISAS experiments within a single framework.

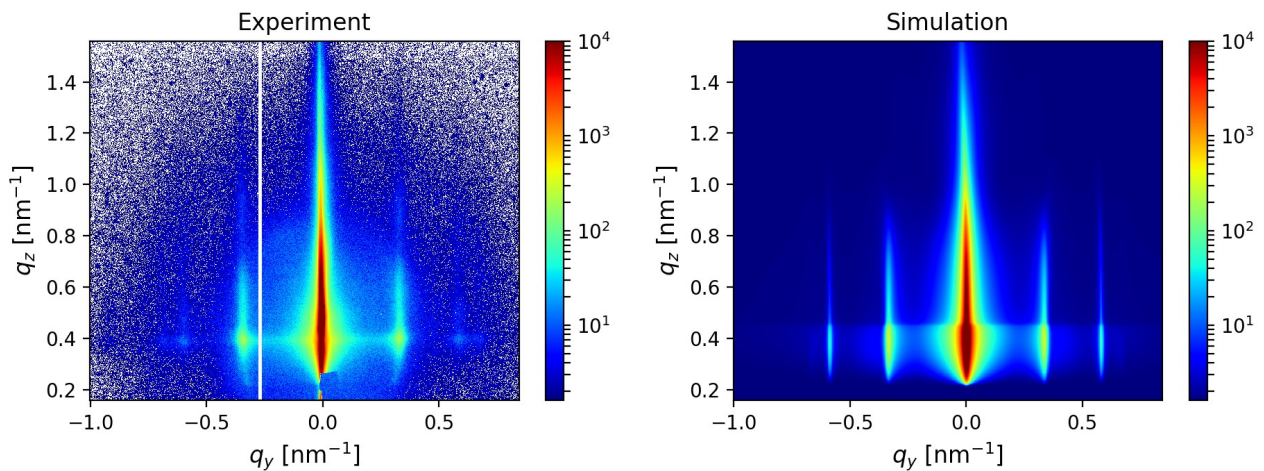


Figure 1: Close packed hexagonal monolayer, BornAgain/experiment comparison [3].

The BornAgain framework is fully exposed to Python to allow users to create complex sample models, define experimental geometries and fully control the analysis workflow. Particularly, it makes possible to go beyond conventional data fitting and to meet the challenge of automatic data analysis by using deep neural networks. Here, the role of BornAgain as an efficient platform for generating training data is self-evident.

The framework is actively maintained, free, open-source and released under the GPL3 license. It is multi platform, adherent to object-oriented design, fosters a professional approach to software development and lays a solid foundation for future extensions in response to specific user needs.

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# Real-time tracking of the growth of small organic molecules on 2D-substrates by means of GI-SAXS/WAXS

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The shape anisotropy of small organic semiconducting molecules is responsible for the observation of a large number of different thin film polymorphs. Depending on the given application, either the standing-up or the lying-down molecular configuration is preferable. In this contribution, we will review the potential of 2D layers to control the molecular orientation in vacuum-deposited thin molecular films. In order to track the molecular orientation and thin film morphology we employed real-time GI-WAXS/SAXS techniques. As a basic example, we will introduce the growth of pentacene on monocrystal graphene [1]. Based on the GI-WAXS data we determined the unit cell of the lying-down pentacene phase and its orientation with respect to the graphene's unit cell. Moreover, using GI-SAXS we followed the Volmer-Weber growth of highly anisotropic pentacene islands. As another example, we will present the growth of diindenoperylene (DIP) on the few-layer MoS<sub>2</sub> films. The recent advances in CVD growth enabled fabrication of the few-layer MoS<sub>2</sub> films with their *c* crystallographic axis oriented parallel or perpendicular to the sample's surface normal (*n*). As a result, we observed the growth of the lying-down or standing-up DIP phases depending on the orientation of MoS<sub>2</sub> *c*-axis (Fig. 1). Technologically, this enables a controlled growth of various molecular phases on the same substrate being solely controlled by the local crystallographic orientation of the underlying 2D substrate.

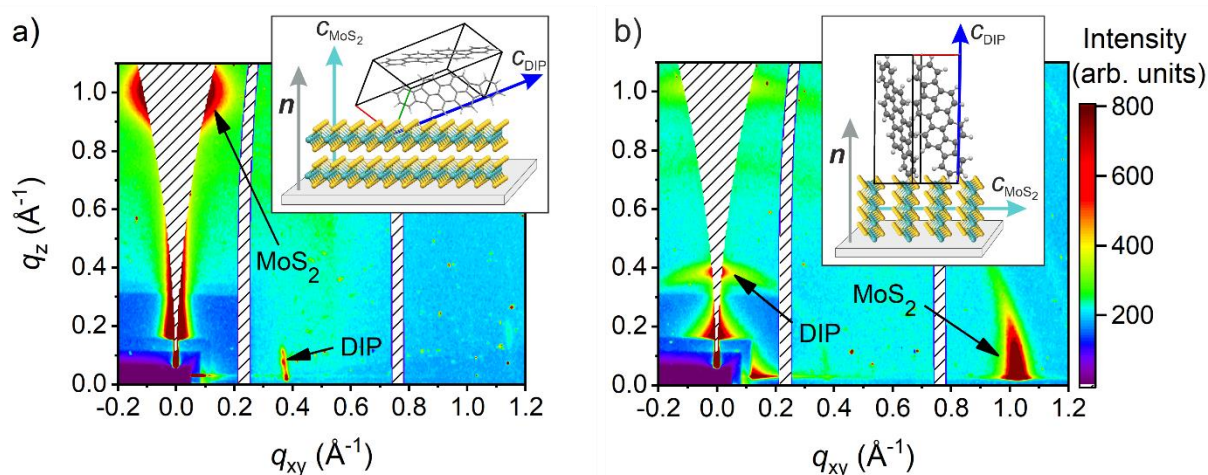


Figure 1: Reciprocal space map measured in the GIWAXS geometry for 12 nm thick DIP layer grown on a) 3 nm and b) 9 nm MoS<sub>2</sub> layer. Both patterns show 001 diffraction of DIP ( $q \approx 0.39 \text{ \AA}^{-1}$ ) and 002 diffraction of MoS<sub>2</sub> ( $q \approx 1 \text{ \AA}^{-1}$ ). The mutual orientation of the *c*-axes of DIP and MoS<sub>2</sub> is schematically shown in the insets.

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# *In-situ* grazing incidence X-ray scattering for thin film technology

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Thin film technology is a vast field. Fabricating nanoscale devices necessitates many process steps. They comprise many different deposition methods, ranging from fluid-based to physical vapor deposition (PVD), and are employed using layer-by-layer coating methods. The final device properties strongly depend on the precision – in terms of thickness, roughness, and nanostructural morphology – when depositing the different layers as well as their interaction at the interface of the multiple layers. Often, underlying layers are modified by and during subsequent deposition. Thus, it is crucial to observe the nanostructural growth of the coatings during the deposition. The kinetic processes involved are strongly in non-equilibrium. Here, grazing incidence X-ray scattering (GIXS) offers tremendous possibilities for observing in situ the development of coating using various thin film technologies [1,2].

I will give an overview of important applications of (GIXS) for elucidating growth mechanism on the nanoscale during the coating. PVD is widely used method for depositing tailored, dense metal layers, from nanogranular to thick coatings [3], depending on the device applications. Using GIXS, the full range of condensation, nucleation and growth of the metal layers is observed. GIXS reveals the different growth stages, their influence on the cluster shape and morphology [4]. In combination with optical spectroscopy, the nanostructure of the layers is related to their electronic properties [5]. Recently, industrial relevant sputter rates were employed, and the influence of them elucidated [6]. Besides the high temporal resolution and with ongoing device miniaturization, curved and line-type structures such as coated fibres come into focus. GIXS combined with nanobeams offers unique opportunities for investigating the coating morphology on these microscopic structures [7].

The second route is dedicated to the observation of spray coating. Spray coating presents a rapid, scalable, and layer-by-layer (LbL) capable coating method, vastly employed in coating science. With the quest for sustainability, the use of cellulose-based materials is crucial. These biomaterials offer highest strength by translating their nanoscale properties to macroscopic fibres [8]. Hence, they may serve in future for templates in flexible electronics. In a first step, we therefore investigated the LbL deposition of cellulose nanofibrils (CNF) by spray coating and combining with grazing incidence wide-angle and small-angle X-ray scattering (GIWAXS/GISAXS) [9]. Using modified CNF, layers with ultralow roughness and tailored wettability are fabricated. Here, the use of complementary neutron methods is highly useful [10]. To finalize, I will give an outlook on applications of GIXS for investigating 3D printing in flexible electronics [11].

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# Contribution of in-situ GISAXS measurements to the study of semi-fluorinated alkane layers at the air/water interface

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Despite the lack of polar head group semifluorinated alkanes ( $C_nF_{2n+1}C_mH_{2m+1}$ , FnHm for short) form Langmuir monolayers *ie.* mono-molecular thick layer at the air-water interface. The molecular and sub-nanometric structure of such layers remains controversial in the literature until Grazing Incidence Small Angle X-ray Scattering (GISAXS) was applied in-situ on the surface of water.

Using this technique, we demonstrated that these molecules on liquid surface self-assemble in a hexagonal array of nano-domains with a very large parameter (typ. 30 nm) [1] (Fig 1-A). Such structure was not expected since only disordered domains were evidenced by AFM on solid substrates [2]. This network is observed on water for different hydrocarbon chain length [3]. We succeed to reproduce this structure on solid (silicon) substrate using a spin-coating technique and found the same structure with the same lattice spacing by Atomic Force Microscopy (AFM) immediately after deposition [4].

However, the stability even after collapse [5] of such domains remains puzzling. On high-resolution AFM images, the domains shape appears as separated by a hump (Fig. 1-B). Macroscopic measurement combined with GISAXS and wide-angle x-ray scattering (GIXD) suggest that some molecules do not belong to the domains made of upright molecules. Indeed, we make simulations of the  $Q_{xy}$ - $Q_z$  GISAXS spectrum using the BornAgain software of truncated cone domains surrounding a corona representing lying molecules (Fig. 1-C) that qualitatively reproduce the out-of-plane behaviour of the experimental GISAXS spectra with only one fit parameter, the angle of the truncated cone.

The presence of such lying molecules could explain the stability of the structure against coalescence of the domains upon compression of the monolayer in relationship with the polar nature of the substrate and the dipole of the SFA molecules [6].

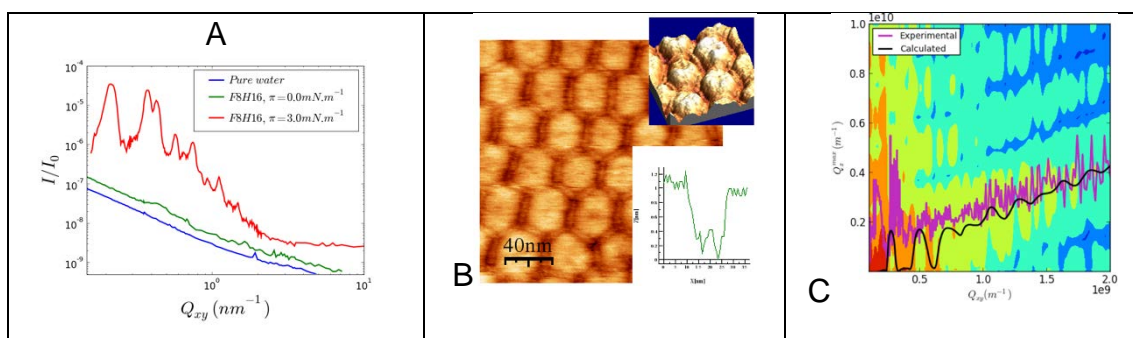


Figure 1: – A:  $Q_z$ -integrated GISAXS spectrum of a F8H16 monolayer. All diffraction peaks can be indexed on a hexagonal lattice of parameter 33.6nm. B: AFM image of a spin-coated F8H18 layer on silicon substrate. C: Simulated GISAXS spectra of FnHm domains surrounded by a corona of lying molecules, lines are the position of the maximum of intensity along  $Q_z$  for simulation and experiment.

Finally, we will show that recent in-situ and time resolved GISAXS experiments performed just after the deposition of the molecule through the classical Langmuir monolayer deposition scheme during the solvent evaporation give interesting information about the formation of the final nanostructured lattice at the air-water interface.

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# Self-assembly induced 3D patterning at the water-air interface studied with neutron reflectivity and AFM

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Among the several compounds protecting the outermost surface of mammalian hair, the branched fatty acid 18-methyl eicosanoic acid (18-MEA) is the most abundant and the most intriguing as the precise function and role of positioning of its isoprenultimate methyl branch is still debated. One suggested reason for its structure is the decrease in melting temperature that would result - without the introduction of a double bond which is otherwise inherently prone to oxidation. In addition, a decreased packing density compared to the straight chain analogue has been proposed to better correspond to the limited number of binding sites on the underlying protein matrix

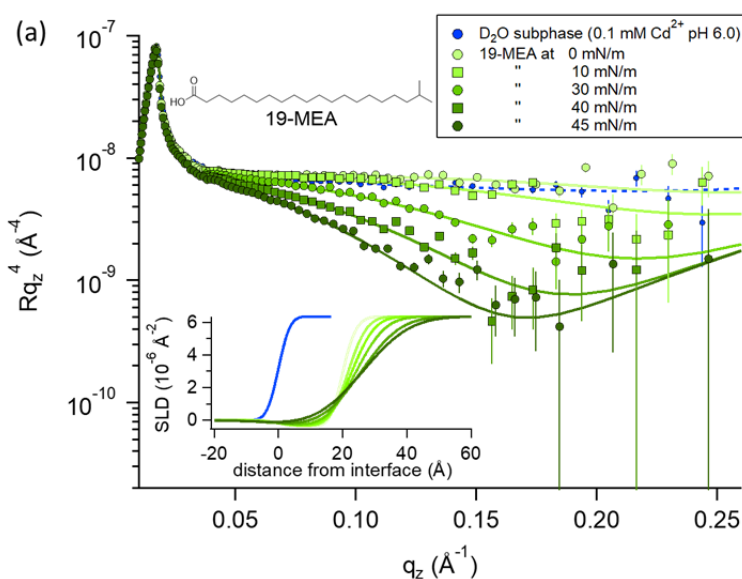


Figure 1: Neutron reflectance as function of surface pressure for 19-MEA.

These hypotheses remain just that; hypotheses. Irrespective of the true role(s) of the methyl branch the orientation of these molecules in films should be important for their biological function. We have earlier performed Vibrational Sum Frequency Spectroscopy (VSFS) experiments to attempt to determine the orientation of the two methyl groups present in the chain, and compared to the straight chain eicosanoic acid (EA), and 19-methyl eicosanoic acid (19-MEA). [1] Langmuir monolayers at the aqueous-air interface and deposited monolayers were studied.

No difference between the chiral (S) form and the racemic mixture of the 18-MEA was observed with any of the utilized techniques. The aliphatic chains of the straight chain fatty acids appeared to

be oriented perpendicular to the sample surface, based on an orientational analysis of VSFS data and the odd / even effect. Interestingly it was noted that while the straight chain fatty acid formed smooth, featureless, monolayers, all the branched chain fatty acids display 10 – 50 nm size domains (larger for 19-MEA than the 18-MEA) with a homogeneous size distribution.

A model was proposed to explain the domain formation and size in terms of the branched fatty acid packing properties and the formation of hemispherical caps at the liquid-air interface.

There was however no **direct** experimental evidence for the presence of such spherical caps, and the notion of self-assembly forces deforming the water interface is rather novel. Here we present direct experimental evidence for the 3 D patterning of the **water** surface by an adsorbed overlayer.

Neutron reflectance of monolayers at the liquid air interface was performed on branched fatty acids as a function of surface pressure. The results clearly show that the “roughness” of the water surface changes systematically with the pressure and correlates well with the dimensions extracted from AFM images on deposited monolayers.

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# GISANS to Study Wet, Soft Matter Interfaces

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Varying either the wavelength or the angle of incidence allows the grazing incidence scattering from different typical depths below an interface to be investigated. Neutron scattering is of particular interest because the incident beam can pass through long paths in several solid materials and the contrast of light elements, particularly when exploiting isotopic contrast with hydrogen and deuterium allows identification of structures in complex multicomponent systems. These studies of ‘buried’ interfaces are important for studies of processes that occur between two bulk phases of materials. In practice, many studies of these interfaces with neutrons are more correctly described as near-surface small-angle scattering rather than grazing incidence small-angle scattering as the incident angle is typically well-beyond the critical angle and penetration of the beam extends to some micrometres. In many colloidal systems this range of depth sensitivity is very interesting as it matches other length scales within samples. This talk will present two studies that highlight these features and identify crucial distinctions to corresponding X-ray experiments.

The arrangement of colloidal particles in a dispersion near charged interfaces is of considerable practical and fundamental importance. The density of particles can modify rheology and might give rise to apparent slip layers. The extent of lateral order important when using particles to template interfacial structures. A number of experiments have been made with polystyrene particles near sapphire and silica surfaces [1]. Strong Bragg diffraction can be seen in grazing incidence scattering. The intensity of the observed Bragg peaks can be compared with models calculated for structures with particles at different distances,  $z_0$  from the surface, see Figure 1. Although the system investigated did not allow resolution of separations of 10’s of nanometres. The comparison with scattering from the bulk phase indicated clearly that oriented layers exist to a distance of some  $\mu\text{m}$  but not 0.5 mm. The results can be compared with data from quartz crystal microbalance with dissipation [2].

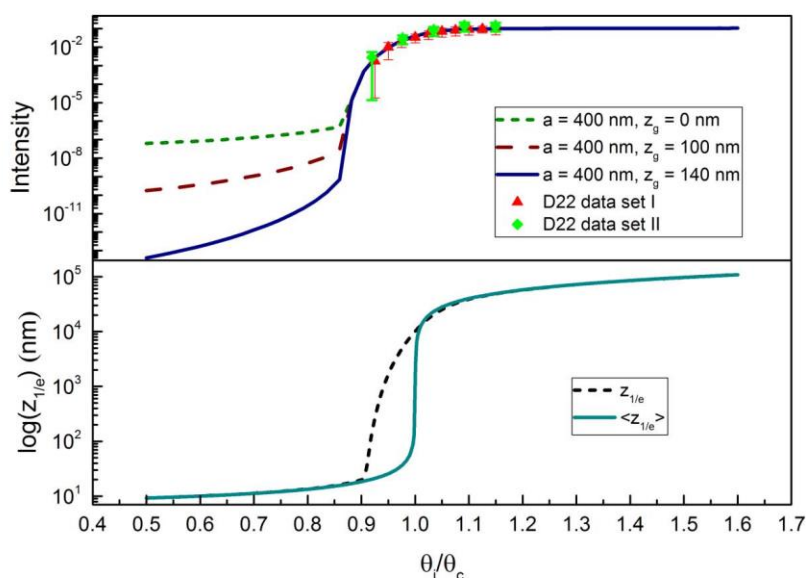


Figure 1: Lower: mean penetration depth of neutrons in a GISANS experiment as a function of angle with the effects of angular divergence and wavelength spread shown as a dashed line in comparison to that for an instrument with perfect resolution. Upper: comparison of measured GISANS peak intensities with models using the estimated penetration depth and instrument resolution. Data measured on D22 at ILL, Grenoble.

In another experiment, reflectivity and scattering has been used to determine the extent of lamellar order for a surfactant near interfaces with different roughness. Example data is shown in Figure 2.

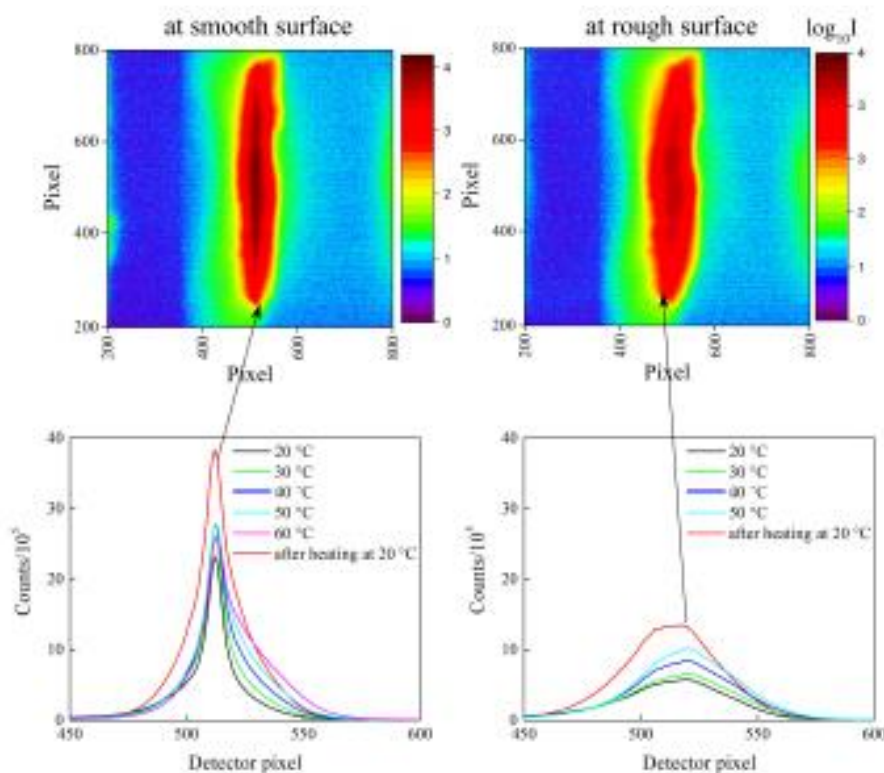


Figure 2: First order Bragg peak from 55% Brij L4 in D<sub>2</sub>O at the specular reflection after heating the sample (top) and the vertical sum over the pixels on the detector at different temperatures (bottom). Data measured at Maria, MLZ [3].

The reduced intensity and increased width of samples near the rough surface is apparent. In these measurements, the width of the diffraction peak from the lamellar structure provides information about the extent of the order away from the solid interface. Further results of measurements made as the sample is rotated, rocking curves, allow the orientational alignment to be determined and information about the extent of order in different directions.

These results illustrate the potential of grazing incidence scattering of neutrons to provide important information about the structures in proximity to buried interfaces that are not accessible to other measurement techniques.

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# 3D vector magnetometry by polarized GISANS

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Neutron reflectivity with polarization analysis gives access to the amplitudes and directions of the magnetizations along the depth of thin film heterostructures. The information is averaged over the in-plane coordinates. With GISANS, correlations between in-plane magnetic fluctuations can be accessed at nanometre and mesoscopic length scales. Using polarization analysis, it allows full 3D vector magnetometry.

In this talk, we will present the calculation of GISANS with polarization analysis within the distorted wave Born approximation (DWBA) [1] and its application in the simulation of data obtained from a polarizing supermirror [2] and from a magnetic layer with perpendicular magnetic anisotropy [3]. Those data were collected respectively on the MARIA and KWS-3 instruments at the MLZ.

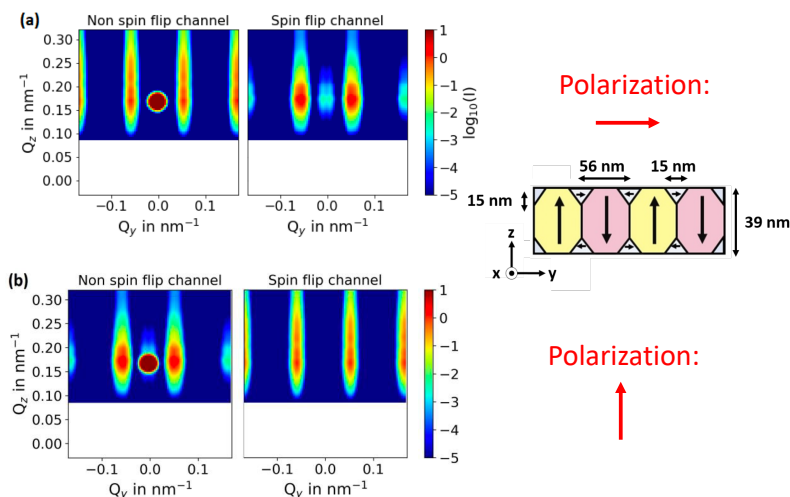


Figure 1: DWBA simulations of GISANS with polarization analysis from a magnetic layer with perpendicular anisotropy exhibiting a stripe domain structure with closure domains. The sketch on the righthand side represents a cross section of the layer perpendicular to the stripes. In (a) the polarization of the neutrons (red horizontal arrow above the sketch) is parallel to the magnetizations in the closure domains; in that case, the GISANS signal from the closure domains appears in the non-spin flip channel and the signal from the bulk of the domains appears in the spin-flip channel. Both types of signals are exchanged when the polarization (red vertical arrow below the sketch) is set parallel to the magnetizations in the bulk of the domains (b).

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# Tackling High Data Rates in GISAXS: Current Status and Future Challenges

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With the emergence of 3<sup>rd</sup> generation synchrotron sources and 2D single photon count detectors with fast readout, *in situ* and *operando* real-time GISAXS investigation of nanoscale process kinetics with high acquisition throughput becoming more and more relevant [1]. The high time resolution in the millisecond regime allows for instance the determination of kinetics of initial nucleation and subsequent cluster growth during sputter deposition and enables a precise investigation of gold cluster growth kinetics under conditions advancing towards industrial manufacturing [2,3,4]. All of those studies yield results to identify four different stages of growth including their thresholds with sub-monolayer resolution during the first 8 nm of deposited gold. Each stage can be characterized by a predominant surface process and its intrinsic kinetics: nucleation, diffusion, adsorption and grain growth. The quantitative analysis is based on an analytical geometrical model [2]. This novel approach allowed simulating, visualizing and unambiguously interpreting gold nanocluster growth kinetics in terms of nanoscopic processes (Figure 1). Morphological real space parameters such as cluster size and shape, centre-to-centre distance, and the onset of long-range connectivity (percolation) are extracted, being of key importance for a high efficiency of plasmonics, sensors, and catalysts.

However, these fascinating experimental opportunities raise further challenges regarding data analysis of extensive data sets. In this context, the software package DPDAK developed at DESY (Hamburg) in collaboration with MPIKG (Golm) operates in a user defined plugin framework for specified reduction of huge amount of scattering data [5]. The software allows visualizing and quantifying the evolution of key scattering features in convenient clear presentations as contour plots even during the experiment. In near future, the rise of even more advanced light sources and much faster detectors with higher pixel density will enable submillisecond time-resolved GISAXS experiments and in turn potentiate the necessity for a fast data reduction and analytical modelling.

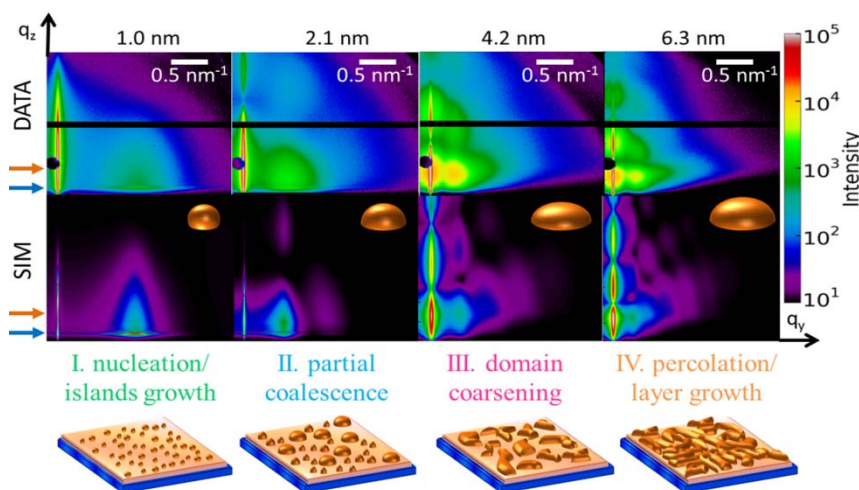


Figure 1: Sputter deposition of Au on PS. **Upper row:** Selected 2D GISAXS patterns with increasing effective Au film thicknesses  $\delta_{Au}$ . The critical angles of PS (blue) and Au (orange) are indicated by arrows. **Middle row:** model-based simulation of the GISAXS pattern, based on the object shape sketched in the upper right corners. **Lower row:** Sketch of the cluster growth morphology with ongoing sputter deposition in the four stages of growth. See [4].

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# **The GISANS options at ILL for liquid and polymer interfaces: Recent examples and perspectives**

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I will present the possibilities and some examples of grazing incidence small angle neutron scattering (GISANS) experiments at the Institut Laue-Langevin (ILL) in Grenoble, France, mainly performed on two instruments: The SANS machine D22 and the neutron reflectometer FIGARO. I will put a particular emphasis on the different options of sample environment available for GISANS. I will focus on interfaces confined at liquid/gas, liquid/solid, solid/solid and polymer/polymer interfaces.

To illustrate the possibilities, I will show recent scientific results obtained by GISANS at ILL. These will include two studies at the solid/liquid interface under *in situ* shear using a cone/plate rheometer mounted on the FIGARO sample stage [1]. In one study, we followed the destruction of lamellae multilayers of an anionic surfactant on sapphire surfaces under shear stress. By a combination of specular neutron reflectometry (NR) and GISANS we observed an alignment of the lamellae parallel to the interface which is either completely lost for steady shear above a threshold shear stress (see Fig. 1) or partially lost for oscillatory shear. In both cases the monolayer in direct contact with the solid surface stays intact [2]. In the second example, using the same sample environment, we observed the inverse effect, namely alignment of peptide nanotubes in water close to a silicon surface above a certain shear rate [3]. In both examples the structural data is complemented with the mechanical response measured with the rheometer *in situ*.

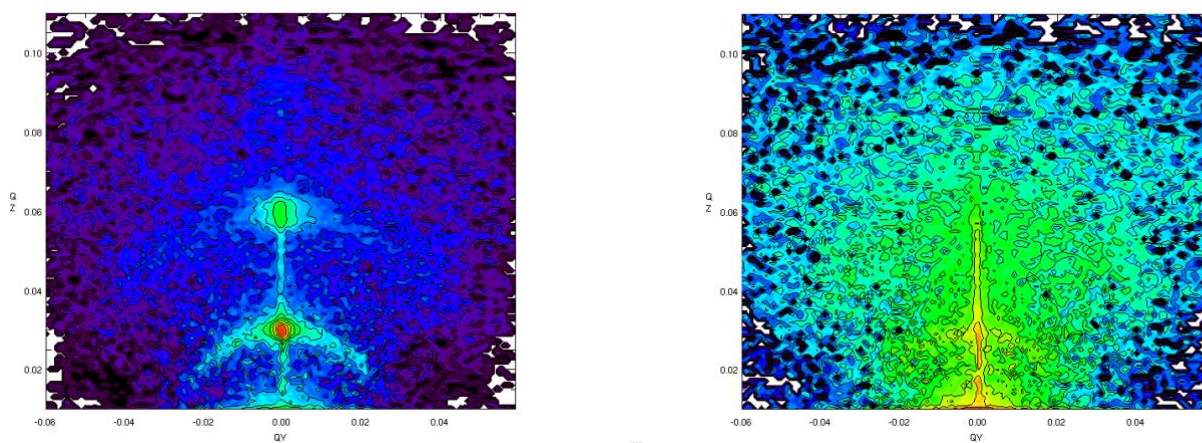


Figure 1: GISANS patterns recorded on FIGARO at  $\theta_i = 1.4^\circ$   $\lambda = 2-20 \text{ \AA} < \lambda_c$ .

Left: Static sample. Right:  $2 \text{ s}^{-1}$  shear rate.

I will show also recent examples of thin polymer film investigations on polymer multilayers supported by silicon substrates investigated by a combination of NR, off-specular neutron reflectometry, GISANS and transmission SANS. One example will include the determination of the single chain conformation of polyelectrolytes arrested in a polyelectrolyte multilayer assembly prepared by the layer-by-layer technique. The out-of-plane conformation was inferred from NR, whereas the in-plane conformation was measured using (GI)SANS showcasing the necessity of the combination of several techniques to get a full (3D) picture of the system. We confirm the expected flattened coil conformation for poly(styrenesulfonate) (PSS) / poly(allyl amine hydrochloride) (PAH)

multilayers and determine quantitatively the extend of single PSS coils as a function of different preparation techniques, namely dipping, spraying and spin-coating as well as the influence of salt concentration during preparation [4].

In the last part of my talk I will show the current status of GISANS capabilities at the air/liquid interface on FIGARO using Langmuir troughs and an outlook including the development of a confinement cell for GISANS on D22 allowing the nanometric confinement of a liquid sample between two solid surfaces, eventually allowing the application of shear stress as well [5]. The suitability of these sample environments for GISANS will be assessed by using a monolayer of silica nanoparticles as model system.

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# Poster Abstracts

# Photoactive nanomaterials studied by (GI)SAXS

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Nanostructured catalysts from naturally resource-abundant materials are of great interest for clean energy-harvesting due to their large accessible surface area. In the joint BMBF project LUCENT of LMU Munich and the University of Hamburg we want to understand structural aspects of such nanomaterials, namely nanoparticles and thin films, in in-situ and in-operando conditions. We develop optimized sample environments for X-ray diffraction experiments at the high-energy beamlines P07 and P21.1 for temperature control and continuous or pulsed light illumination. These sample environments are equally suited for microbeam scanning and GISAXS.

In-situ and in-operando X-ray diffraction experiments are challenging for various reasons: The reaction conditions such as temperature, pressure, and light illumination have to be ensured and beam-induced degradation must be minimized. Minimal background and sufficient real-space resolution in the case of microstructured materials also have to be achieved. We present results from high-energy microbeam diffraction experiments on perovskites grown in porous films [1], solution SAXS results of the growth of cobalt oxide nanoparticles and (GI)SAXS data of perovskite nanocrystals embedded in protective polymer micelles [2] on silicon substrates. We compare the advantages of the three diffraction geometries in view of their applicability to photoactive nanomaterials. The results presented here will facilitate planning of in-situ and in-operando studies with novel catalytic nanomaterials, and benefit the quest for more reliable nanoparticle synthesis routes.

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# Status and outlook of SAXS-CT processing at the Beamline P62

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Since the arrangement and orientation of structures in hierarchical materials play an essential role, experimental non-destructive methods for probing the spatially varying of them are in increasing demand. Usually, texture analysis has been used for this purpose[1]; nevertheless, when the preferred orientation varies with spatial position, texture analysis will be only able to give the spatially averaged orientation distribution[2]. Small-angle X-ray Scattering Computed Tomography (SAXS-CT) is currently attracting enormous interest since it provides access to the volume-resolved spatially varying structural organization of embedded structures. Thereby, allows overcoming the limitation of the texture analysis.

Therefore, to address this urgent need of the scientific community, the beamline P62 at PETRA III storage ring at DESY in Hamburg-Germany is planned to carry out as standard as advanced X-ray elastic scattering methods, among them SAXS-CT. A dedicated versatile sample environment has been designed to fit different sample shapes on a six degree of freedom holder and able to run the experiment either in air or in vacuum. Furthermore, to match the broadness of the current SAXS-CT approaches[2–5] and those that certainly will emerge, a robust and reliable processing pipeline is under development. This pipeline includes the four steps after data collection: (i) pre-processing, (ii) reconstruction, (iii) post-processing and (iv) data analysis. Each one of those steps will have different options depending on the type of sample (isotropic or anisotropic scattering), type of SAXS-CT approach used to collect the data, allowing retrieve information from four to six dimensions (real + reciprocal space).

At GISAXS 2019, the results of the initially processed data from a rod-shaped SAXS-CT phantom with two cylindrical insertions containing an isotropic (quasi-monodisperse Si 80 nm nanospheres) and an anisotropic (high-aligned dried collagen fibres) sample will be presented. As well, the developed approach, named by reverse analysis, to retrieve the SAXS profiles from a region of interest and the further structural modelling of the imaged structures.

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# GTSAXS measurements on resistively switching $\text{SrTiO}_3$

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In the last several years there has been a growing interest in Resistive Random Access Memory (ReRAM) as it is a promising candidate for novel data storage techniques [1]. Such ReRAM cells basically consist of metal-insulator-metal structures. The active layer, sandwiched between the two electrodes, can be locally switched between different resistive states by applying a voltage pulse. One of the model materials for bipolar resistive switching is strontium titanate ( $\text{SrTiO}_3$ ), which shows the valence change mechanism by creating filaments due to localized redox reactions [1].

Here we present an application of a novel variant of the small angle x-ray scattering under grazing incidence (Gracing incidence transmission small angle x-ray scattering (GTSAXS) [2]) to analyse structural changes between the different resistive states. Different to GISAXS we record the transmitted signal through the side edge of the sample underneath the sample horizon. We observed a very strong signal along  $q_z$  between the direct beam and the sample horizon (Figure 1). This surprisingly intense oscillations are probably related to anomalous absorption. This signal is influenced by the active layer and especially by the creation of filaments as we were able to detect significant changes between the initial state and the low resistive state after switching the first time. Recent approaches to modulate this signal show a strong dependence between the form factor of the inhomogeneities and the shape of the oscillations. However, the signal depends on the substrate. A different kind of substrate of same material does not allow this oscillations. Nevertheless even in that case we observed significant changes of the intensity due to the switching between the initial state and the low resistive state.

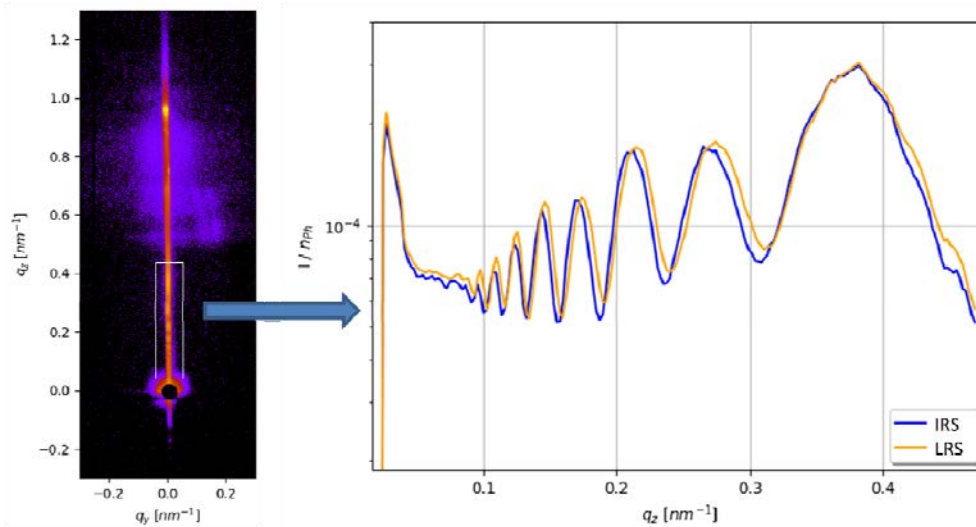


Figure 1: left) Representative GTSAXS pattern at  $0.6^\circ$  incident angle. Strong oscillations appear between the direct beam and the sample horizon, right) Line profiles at  $q_y = 0$  of the initial resistive state and the low resistive state.

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# Nanoisland formation on Pt(111) and Pt(100) by repeated electro-oxidation and -reduction

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Pt-based electro-catalysts are still the most common anode material in proton exchange membrane fuel cells given their high oxygen reduction reaction activity and stability. However, practical applications are limited by catalyst performance loss and degeneration. A main cause for this is nanoscale Pt surface restructuring, which mainly occurs if the electrode potential reaches the oxidation region during fuel cell operation. Under these conditions, Pt surface atoms are extracted from the electrode and form an oxide layer on the surface. Upon subsequent oxide reduction these atoms can agglomerate. Detailed studies of this process have been performed on Pt(111) electrodes, revealing the formation of adislands with a well-defined lateral size after multiple oxidation and reduction cycles [1-4]. However, the influence of surface structure and orientation is largely unclear. We present a first comparative in situ GISAXS study of the nanoisland formation on Pt(111) and Pt(100) in acidic electrolyte, showing faster island growth on Pt(111) than on Pt(100) (fig. 1). The measurements were performed at a high photon energy of 70 keV, which lowered background scattering from the electrolyte, enabling us to resolve the adislands after the very first oxidation cycle.

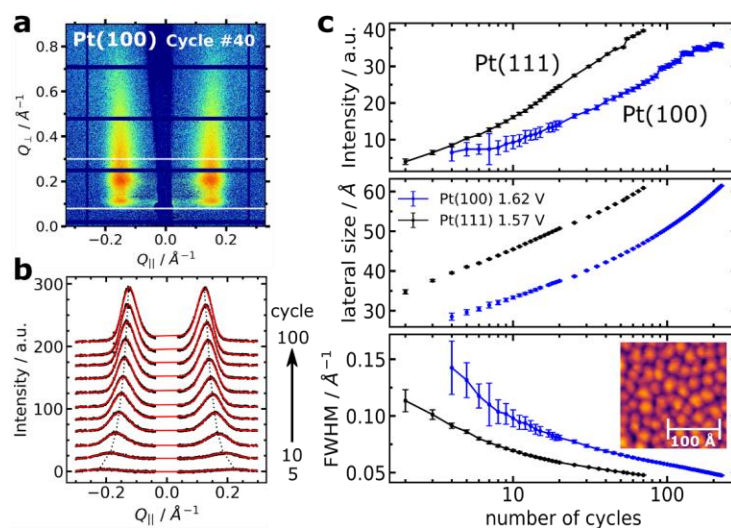


Figure 1: **a.** Background corrected in situ High-Energy GISAXS data of the nanoislands formed on Pt(100) after 40 oxidation and reduction cycles to 1.62 V. **b.** Evolution of the in-plane GISAXS intensity during island formation on Pt(100). **c.** Integrated GISAXS intensity, characteristic lateral island size and FWHM of the GISAXS intensity peak of Pt(111) and Pt(100). inset: STM image of the islands on Pt(100) after 50 cycles to 1.62 V.

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# Flow of Microemulsions Adjacent to Planar Surfaces

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Microemulsions consist of water, oil and surfactant. Although thermodynamically stable, domains of pure water and oil are formed on nanometer length scales and a surfactant film in between that are ideally observable by small angle scattering experiments. The bicontinuous microemulsion displays a sponge structure that forms when equal volumes of water and oil are mixed. Being exposed to hydrophilic planar surfaces, a lamellar order is found in the vicinity to the solid-liquid interface. The typical depth of the lamellae is 40 to 60nm, i.e. 4 to 6 perfect domains [1,2], before the perforations describe the decay to the bicontinuous phase. The membrane modes observed by neutron spin echo spectroscopy under grazing incidence are faster at the interface than in bulk [3]. This is an evidence for the *lubrication effect*, a facilitated flow of the lamellae along the interface. Employing clay platelets, the same effect could be observed in a bulk sample [4]. Furthermore, at smaller platelet diameters, the favorable modes of the lamellae were cut, and the overall dynamics slowed down similar to the bulk. Thus, the perfection of modes at the interface is connected to the platelet diameter. At rather high flow rates, the perforated transition region was reduced in size, while the perfect lamellae were persistent [2]. In macroscopic rheology experiments (Fig.1 left), the microemulsion with rather large clay platelets showed evidence for the *lubrication effect* on macroscopic scales, while at lower clay dimensions the viscosity was extraordinarily high [5] (Fig.1 right). Motivated by this effect, the rheology of crude oils with large clay platelets showed decreased viscosities at low temperatures (below 0°C). The dynamic asymmetry of the aromatic and aliphatic portions and the lamellar alignment of the domains may explain these findings.

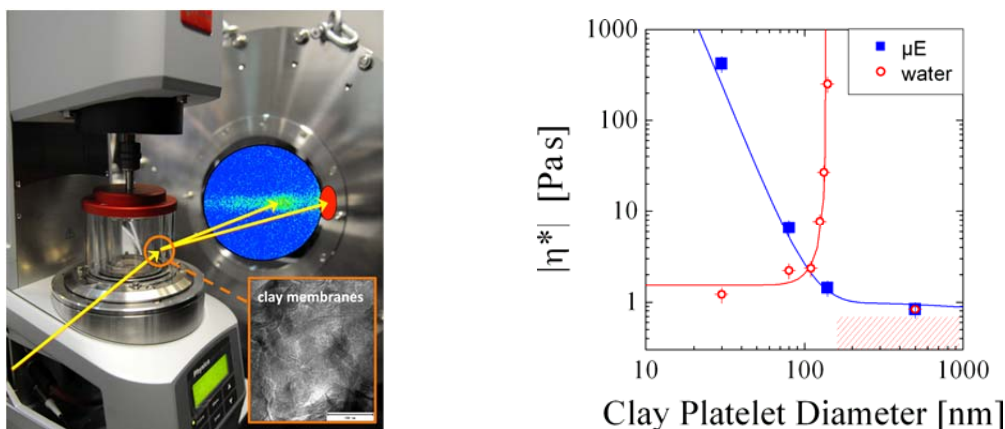


Figure 1 (left): A rheometer in tangential geometry in a SANS instrument. (right): Complex viscosities of clay dispersions in water and microemulsion with varying platelet diameter.

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# Time resolved GISAXS/GIWAXS upon Atmospheric Plasma Treatment of Conductive Silver-Nanowire- Networks

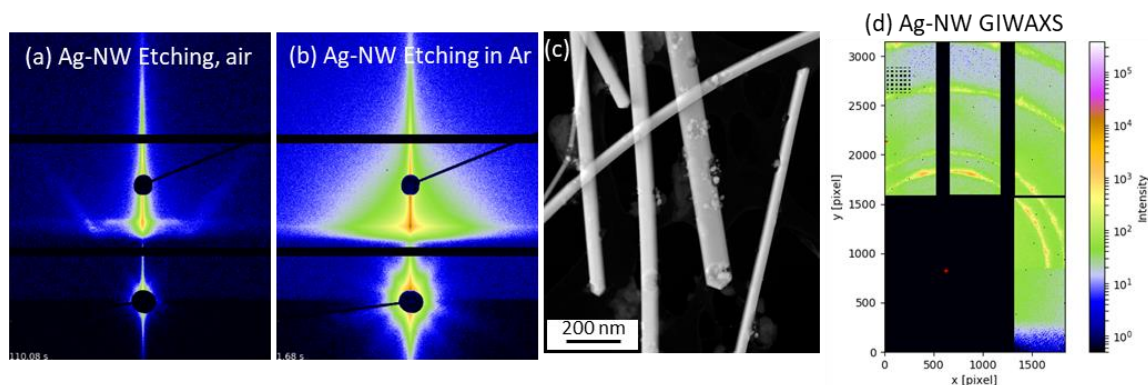
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Recently, nanoparticles as well as nanowires in (metal-polymer) composite thin films are becoming strong alternative candidates in many functional applications such as optoelectronics, organic light emitting diodes (OLED), sensors, and magnetic data storage [1]. Silver-nanowire-networks (Ag-NWs) are best candidates for such applications as being simple and cheap to fabricate, exhibit good aspect ratio, and are highly scalable [2]. Here, we synthesized Ag-NWs via the polyol route with resulting average diameter of 80 – 120 nm and a length of up to 100  $\mu\text{m}$  as confirmed with the SEM. Also, an atmospheric plasma pen as being compatible with potential 3D printing applications was exploited and tested with different gases (ambient air and Argon) for a fast removal of the insulating PVP layer shielding the Ag-NWs and *in situ* GISAXS and GIWAXS were performed simultaneously (see Fig. 1a and b). From the time resolved GISAXS, a transition from PVP polymer coated Ag-NW to a bare Ag-NW as well as a deformation of the Ag-NW (100)-facets due to longer etching time of the plasma etcher were tracked. Furthermore, the time-resolved GIWAXS (see Fig. 1d) allows the study of the effect of the plasma etcher on the Ag-NW crystallinity and their periodicity.



**Fig. 1:** (a) GISAXS pattern of a PVP core-shell Ag-NW layer on top of a 100-silicon wafer. (b) GISAXS pattern of an Argon etched PVP-Shell-Ag-NW-film. (c) SEM image of Ag-NW ensemble depicting the pentagonal shape. (d) GIWAXS pattern of Ag-NW etching in air environment

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# In-situ time-resolved GISAXS studies of solvo-thermal vapor annealing of a homologous series of ABC miktoarm star terpolymer thin films

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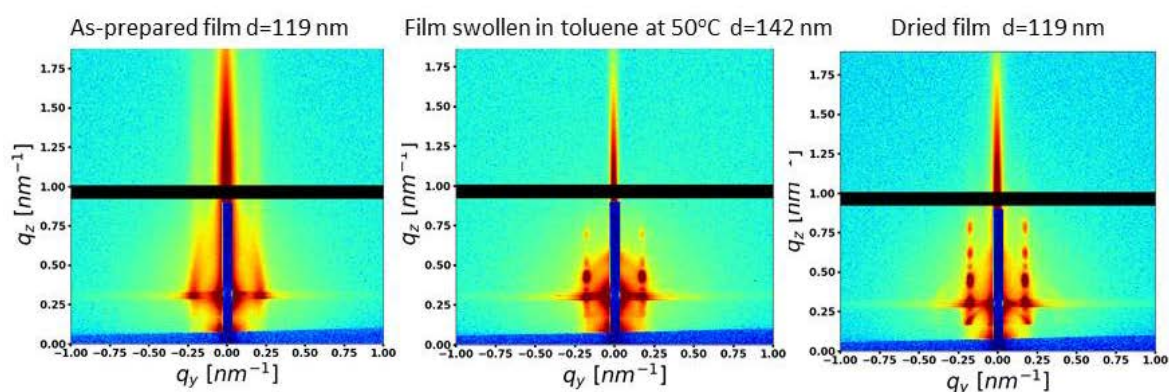
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Thin films of ABC miktoarm star terpolymers (ABC stars), where three chemically different polymer blocks are linked at a common core, have potentially a very rich phase diagram with occurrence of different types of nanostructures. Solvo-Thermal Vapor Annealing (STVA), i.e. interaction with solvent vapor at somewhat elevated temperature, is a versatile method for healing of structural defects and for controlling and manipulating the thin film nanostructure [1, 2]. In the present study, we follow restructuring processes during STVA of three nominally 100 nm thick ABC star films using in-situ time-resolved GISAXS with simultaneous Optical Film Thickness Measurement. The three ABC stars are composed of poly(isoprene) (I), poly(styrene) (S) and poly(methyl methacrylate) (M) with equal sized I and S blocks while the M block length is varied systematically: ISM2.2 has an arm length ratio 1:1:2.2; ISM3.7 has arm length ratio 1:1:3.7 and ISM5.4 correspondingly 1:1:5.4. The STVA protocol was using toluene at 50C and featured slow swelling followed by fast drying. The thin film samples were characterized using Atomic Force Microscopy and Scanning Electron Microscopy. These measurements indicate that the structure of the outermost surface layer is alternating lamellae for ISM2.2 and is consistent with hexagonally packed perpendicular core-shell rods for ISM3.7 and ISM5.4. The GISAXS maps below are from STVA of ISM3.7. The initial film thickness,  $d$ , is 119 nm and the film is swollen to a maximum swelling ratio 1.8. The middle GISAXS map is from the initial stages of drying and shows development of structure and the final dry film GISAXS map to the right show a high degree of order corresponding to core-shell rods being aligned with their axis perpendicular to the film normal.



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# **Asymmetric Ostwald ripening described via GISAXS from PtNi bimetallic alloy degradation under operational conditions of Proton Exchange Membrane Fuel Cell**

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Bimetallic alloys have been extensively studied in the last years because of their high interest in different research fields, such as energy storage or electro-catalysis. Moreover, PtNi alloy was found to be a promising substituent of pure Platinum catalysts in Proton Exchange Membrane Fuel Cells (PEMFCs) to strongly reduce production cost. The main drawback in using PtNi alloy is related to the acid-based environment in which the catalyst has to operate, which causes the dissolution of the less noble metal and the consequent degradation of the catalyst layer. In this framework, Electro-Chemical AFM and Inductively Coupled Plasma Mass Spectrometry, have been complemented with *in situ* Grazing Incidence Small Angle X-ray Scattering (GISAXS) to investigate the surface degradation of PtNi alloy during electrochemical cycling voltammetry using different alloy compositions. In order to simulate the realistic fuel cell operation conditions, different upper potentials have been used. Data revealed in depth the degradation of the aforementioned catalyst during fuel cell operation and the asymmetric Ostwald ripening process has been here described in electrochemistry the first time.

The authors acknowledge the financial support from project CEROP, which is a CERIC-ERIC internal research project.

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# Finding and Tracking Bragg Spots in GISAXS maps of Block Co-Polymer Thin Films

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Real time restructuring behaviour of ~100nm spin-coated nanostructured ABC miktoarm star terpolymer films during solvent vapor annealing was monitored using GISAXS. Throughout the investigation, a large quantity of 2D GISAXS maps was produced. Some of these maps exhibit Bragg rods or Bragg spots and other features, which changes position, shape and intensity in accord with structural changes in the film. For the purpose of identifying and tracking Bragg spots with changing position, two different feature extraction algorithms have been tested: 1) a cascade based algorithm based on the Viola-Jones algorithm [1] and 2) an approach based on the Circular Hough Transform [2]. The cascade based algorithm is able to identify the Bragg spots in the dataset tested, consisting of ~3000 maps, with very few false positives or false negatives (< 10) at a rate of ~18 frames per second. The Circular Hough Transform is generally a faster algorithm (~70 frames per second) but fails for part of the dataset, during the drying stage of vapor annealing, due to changes in the shape of the Bragg spots tracked.

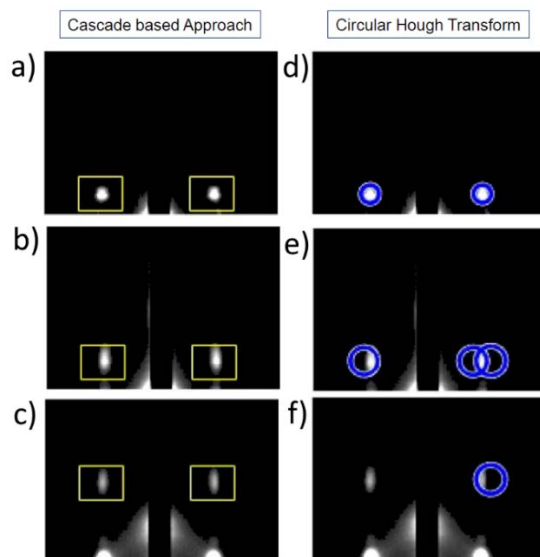


Figure 1: a), d) GISAXS maps and identified Bragg spots (marked with yellow frame and blue circle respectively) during a high degree of film swelling. b), e) As a. and d. during drying stage. c), f) As b. and e. where Bragg spots have changed positions.

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# CD-GISAXS: Reconstruction of Form-factor in Line Patterns

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Microprocessor features now ranging  $O(10)$  nanometers, new measuring techniques are required to ensure quality across the manufacturing process. X-ray scattering provides a fast and non-destructive method to investigate the nanostructures with potentially high resolution and accuracy. Fast algorithms and analyses are needed to complement the speed and accuracy of the X-ray scattering measurements. In this vain, Critical Dimension Small Angle X-ray Scattering (CD-SAXS), was developed at NIST. It recovers the morphology of gratings in transmission geometry. We at CAMERA, employing a similar framework, have developed a technique to use Grazing-Incidence geometry. GISAXS is a well-established technique for measuring surface morphologies. The characteristics of line patterns morphologies exhibit strong Bragg scattering, resulting in suppression of signal from the form-factor. We use a precise spinning stage to measure the sample. Continuously rotating lines result in Bragg rods, in-process amplifying the signal from the form-factor.

However, the commonly used, Born Approximation, is no longer valid in the GISAXS regime. One must use the Distorted Wave Born Approximation (DWBA), to calculate the form-factor. We use a stack of trapezoids to approximate the cross-section of lines.

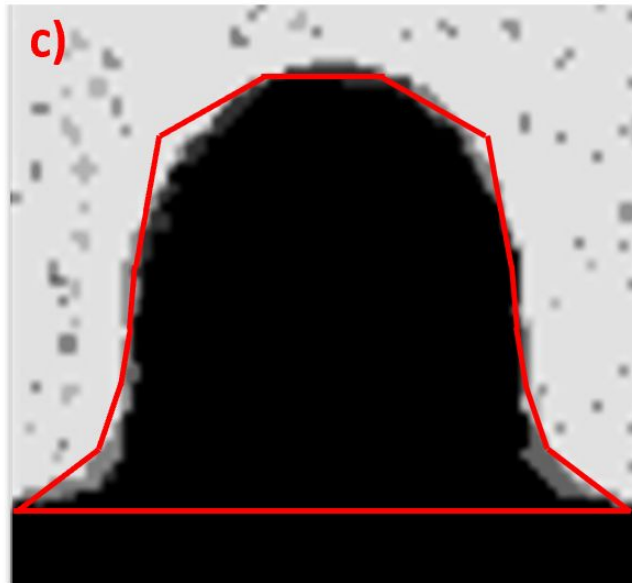


Figure 1: Comparison of CD-GISAXS reconstruction and transmission electron microscope.

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# Incidence Angle Resolved Scattering for Optical Characterization of Thin Films

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Grazing incidence x-ray scattering provides nanostructure morphology for thin film systems, but single images do not provide depth-resolved information, or the full complex index of refraction. X-ray reflectivity is a complementary technique that can provide this data, but it is most often done ex-situ and not an inherent capability for a GIXS-capable beamline. We cover our efforts to develop an in-situ method to extract these parameters using scattering images taken across a range of incident angles. The observed scattering intensity as a function of incidence angle is proportional to the local electric field intensity (EFI), which can be modeled and fit to the data using Parratt's recursion [1],[2]. The technique is validated with model single- and bi-layer films. The effects of angular divergence and energy resolution are also presented.

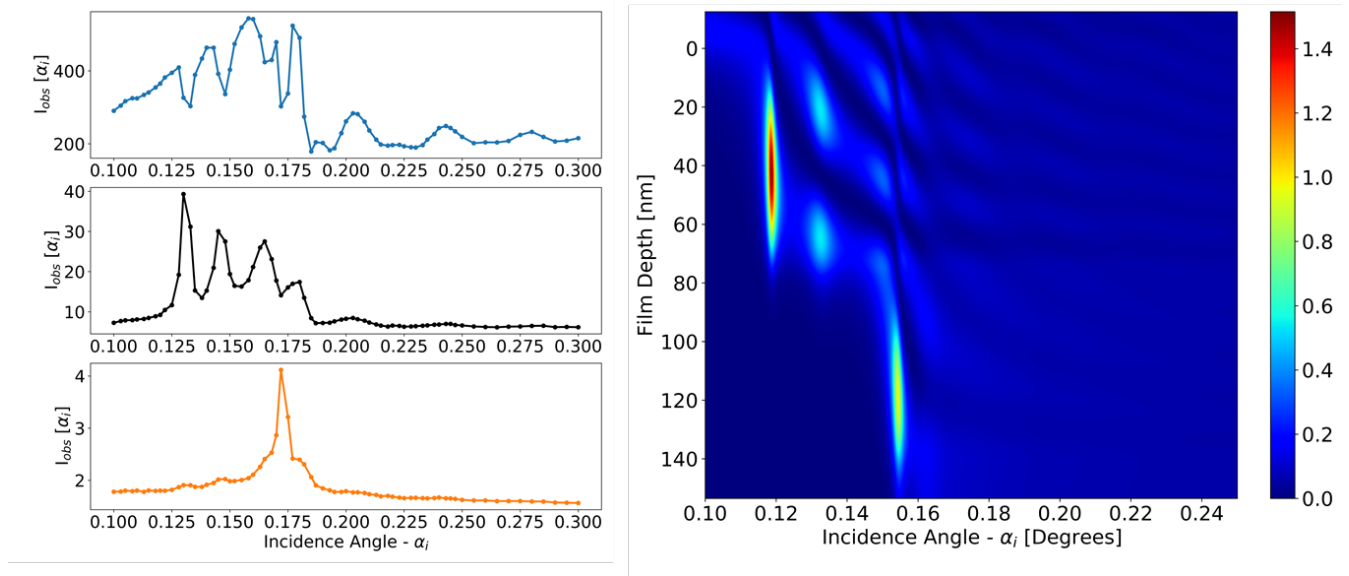


Figure 1: a) Incidence angle resolved data from a model bilayer film showing the modulation in observed scattering intensity for the specular rod, top layer, and bottom layer, respectively. b) Electric field intensity modelling for the bilayer film.

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# Sputter deposition of Al & Ag on nanostructured PMMA-b-P3HT and PS-b-PMMA copolymer thin films

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Nanostructured polymer-metal-composite films demonstrate great perspectives for optoelectronic applications [1], e.g. as sensors or photovoltaics. To enhance properties of such devices the self-assembly process needs to be understood. We studied the cluster morphology growth by grazing incidence small-angle X-ray scattering (GISAXS), as well as the crystallinity of the metal film formation with grazing incidence wide-angle X-ray scattering (GIWAXS) in situ during sputter deposition. The scattering experiments were combined with surface differential reflectance spectroscopy (SDRS) [2]. Our study reveals the selective wetting of aluminum and silver on the polymer blocks and the influence of the template on the percolation behavior of the metal layers [3]. The measured crystalline structure revealed sputtered aluminum and silver nanoparticles without oxidation.

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# In situ GISAXS Investigations of Multi-responsive Block Copolymer Thin Films during Solvent Vapor Annealing

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Responsive block copolymer thin films are of interest for many applications, e.g. as fast sensors or switchable membranes. They may be based on physical hydrogels formed by telechelic copolymers featuring a stimuli-responsive midblock and hydrophobic end blocks. For temperature-responsive end blocks, a weak gel is formed below their collapse temperature, while a frozen network is formed above [1]. In thin films, a pH-responsive midblock, e.g. a weak polyelectrolyte, may be used to tune the self-assembly process, while a temperature change may be used to immobilize the end blocks and to freeze the so created nanostructure. The latter feature is especially interesting for solvent vapor annealing (SVA), which is a versatile technique to improve long-range order in polymer thin films and alter its morphology, but with the drawback that non-equilibrium morphologies are often difficult to preserve during solvent removal [2,3].

In the present work, thin films from the telechelic pentablock quaterpolymer  $P(n\text{BuMA}_8\text{-}co\text{-TEGMA}_8)\text{-}b\text{-PDMAEMA}_{50}\text{-}b\text{-PEG}_{46}\text{-}b\text{-PDMAEMA}_{50}\text{-}b\text{-P}(n\text{BuMA}_8\text{-}co\text{-TEGMA}_8)$  were investigated in-situ during SVA with water and toluene using grazing-incidence small-angle X-ray scattering (GISAXS). The endblocks are statistical copolymers of the thermoresponsive TEGMA (triethylene glycol methyl ether methacrylate) and the hydrophobic  $n\text{BuMA}$  ( $n$ -butyl methacrylate). The intermediate PDMAEMA (2-(dimethylamino)ethyl methacrylate) block is a weak cationic polyelectrolyte, which becomes ionized at low pH values and assumes a stretched conformation. The permanently hydrophilic poly(ethylene glycol) (PEG) block enhances water solubility. The role of the solvents used for film preparation and for SVA on the structural evolution will be presented, and details about the GISAXS data analysis, which was carried out using BornAgain, will be given.

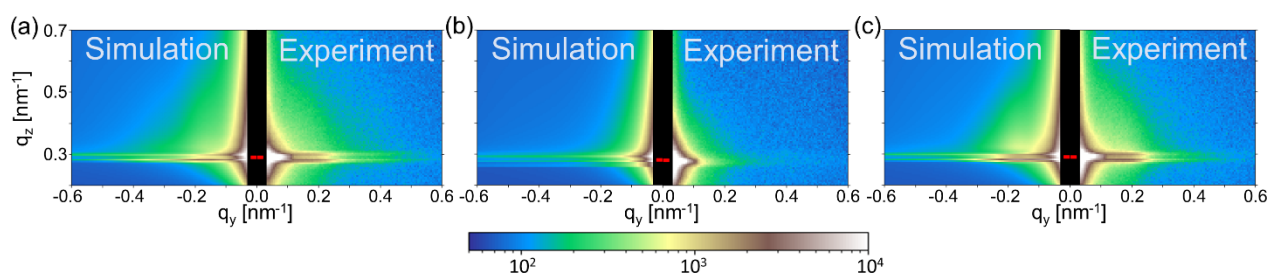


Figure 1: Experimental 2D GISAXS maps ( $q_y > 0$ ) and corresponding simulations ( $q_y < 0$ ) of (a) an as-prepared film, (b) the same film swollen in water vapor and (c) after water removal.

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# Morphologies and Solvent Distribution During Solvothermal Vapor Annealing of Block Copolymer Thin Films: In situ, Real-time GISAXS Investigations

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Block copolymer (BCP) thin films have been proposed for a number of nanotechnology applications. Solvent vapor annealing (SVA) is a powerful technique for manipulating and controlling the structure of BCP thin films. Combined GISAXS/SVA setups at synchrotron sources have enabled in-situ and real-time studies of the SVA process, giving important insight into the pathways and mechanisms of SVA induced restructuring [1]. A new method is solvothermal vapor annealing (STVA) at elevated temperature with two independently prepared vapors of different selectivities for the two blocks [2]. An example is shown where STVA with *n*-heptane and toluene is applied to a thin film from a cylinder-forming polystyrene-*b*-poly(dimethyl siloxane) (PS-*b*-PDMS) diblock copolymer. The film is first swollen in the vapor of *n*-heptane. This vapor is stepwise replaced by the vapor of toluene. The initial cylindrical morphology is transformed into, among others, the lamellar one. The morphologies determined from the 2D GISAXS maps are corroborated by the ones calculated from thin films generated by computer simulations. The trajectory is calculated using the intensity of a Bragg reflection along with the swelling ratio of the film. This way, the overall polymer volume fraction as well as the cylinder volume fraction can be determined throughout the STVA experiment, and the morphologies can be related to the distribution of the two solvents in the two types of nanodomains.

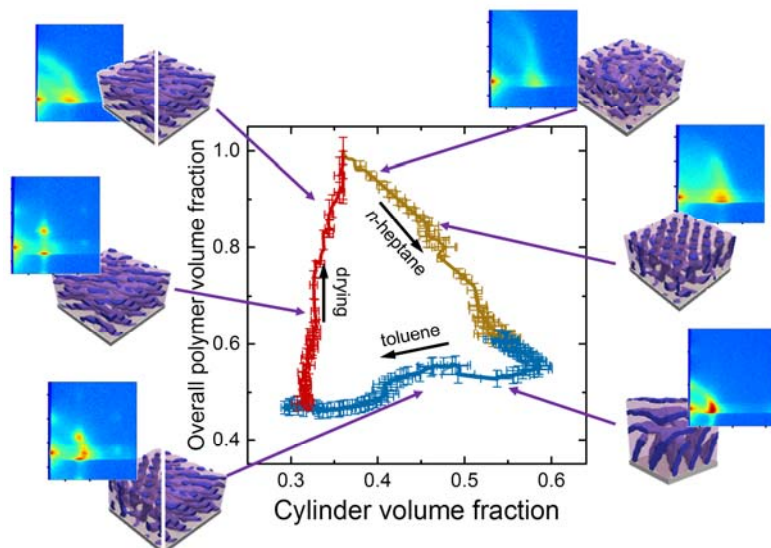


Figure 1: Navigating through phase space of a BCP thin film is possible using STVA with vapors of two solvents having different selectivities. A number of morphologies are encountered on the way [2].

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# Insights into the structure and self-assembly of inorganic nanocrystals with small organic semiconductors via *in situ* grazing incidence X-ray scattering.

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Solar energy conversion materials coupling small-molecule organic semiconductors (OSC) with inorganic semiconducting quantum dots (QDs), capable of photon up- or down-conversion *via* multiexcitonic processes, offer routes for increasing the efficiencies of for single-junction photovoltaics.<sup>1-7</sup> In such hybrid organic/inorganic materials, “active” OSC-ligands are often directly attached to the QD surface, post-synthesis *via* ligand exchange.<sup>8, 9</sup> This work demonstrates how controlling the proportion of active OSC-ligands bound to QDs affects the subsequent self-assembly of an OSC:QD blend during film formation via solution processing.

Combined small angle scattering [both X-ray(SAXS) and neutron (SANS)] studies are employed to provide quantitative structural insights into a series of OSC-ligated QD species, possessing different grafting densities of OSC ligands. To gain insight into the self-assembly behaviour of blends of OSC with the series of OSC-ligated QDs at relevant lengthscales, spanning; Å (OSC crystallinity)  $\rightarrow$  nm (QD distribution/ordering) *in situ* grazing incidence X-ray scattering is performed on drop-cast solutions of blends of OSC with OSC-ligated QDs.

Results show that the QDs dramatically alter the crystallization kinetics of the OSC and that the grafting density of OSC ligand bound the QD surface is crucial in determining how the QDs self-assemble within a crystalline OSC matrix (Fig.1). For low OSC ligand grafting densities QDs form face-centred-cubic paracrystal structures, whilst for high OSC ligand grafting densities promotes dispersion of the QDs within the OSC crystalline matrix, with >90% of dots well-dispersed with liquid-like order. This work demonstrates how controlling QD ligand chemistry controls the self-assembly of a hybrid OSC:QD blend during solution processing and builds an important road map for the use of multi-scale X-ray/neutron scattering and grazing incidence X-ray scattering techniques to understand the self-assembly of Solar energy conversion materials.

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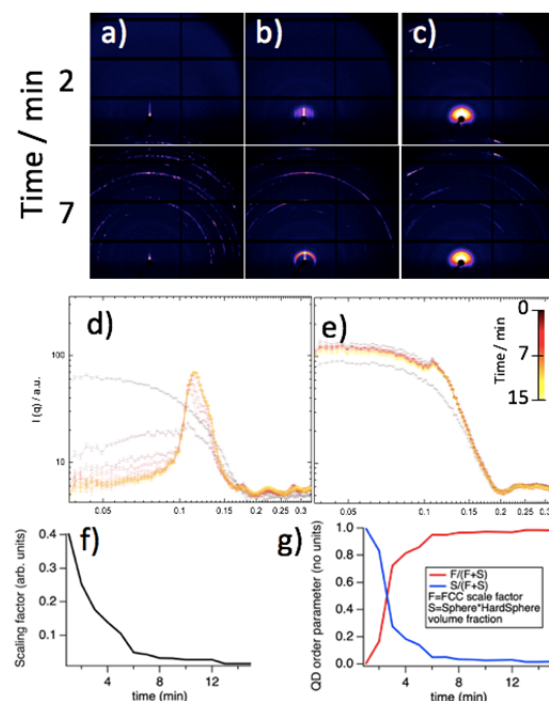


Figure 1: GIWAXS for drop-cast films at 2 and 7 mins for; a) OSC, b) OSC:native-QD, c) OSC:OSC-ligated QD showing the evolution of OSC crystalline structure and QD ordering with corresponding radially integrated scattering data highlighting QD ordering for; d) OSC:native-QD, and e) OSC:OSC-ligated QD. Fit results showing; f) arbitrary scaling factor of GIWAXS allowing straightforward tracking of drying progress and g) a simple order parameter to quantify the of fraction of QDs in either hardsphere or FCC conformations.



# Tailored functionalization of nanocellulose thin films using grazing incidence X-ray and neutron scattering

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Sustainable devices experience a massive increase of attention over the last years. Our whole economy and mindset should follow and minimize the use of fossil resources. Nevertheless, it is yet not fully understood how sustainable devices perform and degrade under environmental influences. Wood-based cellulose as one of the most earth abundant nature materials consists of so-called cellulose nanofibrils (CNF). These nanoscale building blocks have high potential in applications due to their low density, high material strength and sustainability [1]. CNFs as produced with the so-called TEMPO oxidization process yield tunable surface charge densities. These surface charges result from variable hydroxyl group densities on the fibril surface. Nowadays it is not only in focus to study fundamental particle morphologies rather than finding techniques to be able to manufacture materials with desired physical properties [2]. Spray deposition as industrial style deposition technique with roll-to-roll applicability is our choice to fabricate large-scale (20x100 mm) thin films (< 200 nm) with unprecedented low surface roughness down to 2 nm [3-4].

The sample preparation leads to thin films with nanometer sized pores which allow functionalization. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is nowadays widely used as high performance conductive polymer for example in bulk heterojunction solar cells or organic super capacitors. It is a water-soluble polymer and it fulfils therefore the sustainable approach of using less solvents. Hence, we elucidated the combination of PEDOT:PSS and CNF thin films to study the polymer intrusion inside the porous nature of the CNF thin film.

We studied the self-assembly kinetics during drying of the spray coated CNF thin films using grazing incidence small-angle neutron/X-ray scattering (GISANS & GISAXS) [3, 4]. The GISANS measurements were conducted in a humidity chamber, where the humidity was cycled between 0 – 95% RH. We investigated the morphological changes of water sorption as well as when PEDOT:PSS is applied as multilayer or when pre-mixed in the CNF dispersion prior spraying. In situ GISANS was performed when the humidity was changed to understand the morphological re-arrangement under water sorption or drying. This knowledge of the three-dimensional nanoscale structure and possibility of back-filling the porous CNF template opens completely new paths for organic electronics.

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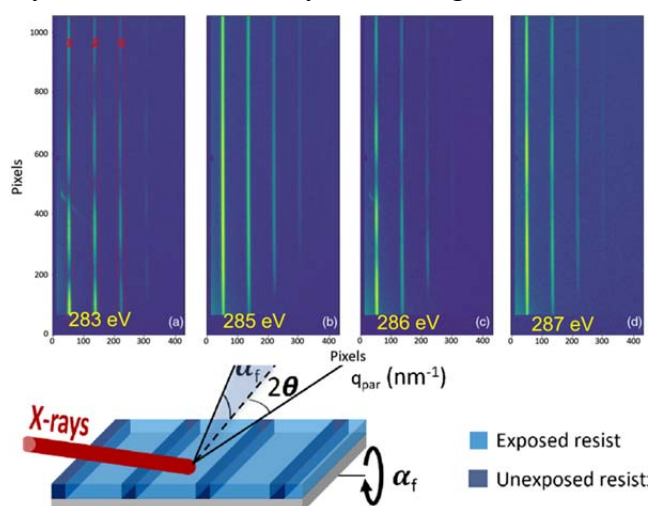
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# Latent Imaging of EUV Resists via Grazing-Incidence Resonant Soft X-ray Scattering

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Extreme ultraviolet (EUV) lithography is one of the most promising printing techniques for high-volume semiconductor manufacturing at the 14-nm half-pitch device node and beyond. However, key challenges around EUV photoresist materials, such as the exposure-dose sensitivity or the line-width roughness, continue to impede its full adoption into industrial nanofab facilities. Metrology tools are required to address these challenges by helping to assess the impact of the EUV materials' properties and processing conditions along different steps of the nanofabrication process. We apply the resonant soft x-ray scattering (RSoXS) technique to gain insights into the structure of patterned EUV resists before the development step takes place. By using energies around the carbon K-edge to take advantage of small differences in chemistry, the electronic density contrast between the exposed and unexposed regions of the resists could be enhanced in order to image the patterns with subnanometer precision. Critical-dimension grazing-incidence small-angle x-ray scattering is then performed at energies where the contrast is maximized, enabling the reconstruction of the three-dimensional shape of the latent image. We demonstrate the potential of RSoXS to provide a high-resolution height-sensitive profile of patterned EUV resists, which will help in quantifying the evolution of critical features, such as the line-edge roughness, at a key step of the nanofabrication process. Here, we will present the latest development and applications of the technique using the full energy range provided at the advanced light source and more specifically of the chemical sensitivity provided by soft and tender x-rays scattering.



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# Structural and magnetic properties of self-assembled iron oxide nanoparticle films

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Self-assembled iron oxide nanoparticles (NPs) with various sizes (5-20nm) have been studied using magnetometry, X-ray powder diffraction, Small Angle X-ray Scattering and Grazing Incidence Small Angle X-ray Scattering (GISAXS). 2D self-assembled NP films have been fabricated using various methods (e.g. drop-casting, liquid-air-interface) and characterized using scanning electron microscopy and GISAXS. The GISAXS patterns are compared with the simulation results from the software BornAgain. Magnetometry results show an exchange bias effect in hysteresis loops. By comparing hysteresis loops cooled at different magnetic fields, a hardening effect can be observed, i.e. the squareness and hardness of hysteresis loops is significantly enhanced with increasing magnetic cooling field. Due to the antiferromagnetic wustite component, the spins of the ferromagnetic magnetite/maghemite components are exchange biased and an anisotropy axis is induced. By varying the phases via different annealing procedures, the exchange bias strength as well as the hardness of the hysteresis loops is varied. These results provide important information for the manipulation of the exchange bias and the magnetic hardening effect in transition metal oxide NPs, which could be useful for applications in data storage or spintronics.

# Edge sensitive *in-situ* GT-XPCS of slot-die coated nanoparticle thin films

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X-Ray Correlation Spectroscopy (XPCS) is a useful tool to investigate the dynamics and the morphology of hard and soft condensed matter. Via XPCS, it is possible to probe short length scales ( $< 100$  nm) and long time scales ( $> 10^{-4}$  s). To obtain information about the underlying dynamics, the correlations of the scattered intensity (speckle pattern) in a time series is investigated. In our approach, we use XPCS to investigate slot-die coated thin films *in situ* in grazing incidence transmission (GT) geometry to gain insights in the underlying processes of thin film formation near the substrate edge. For printing, an up-scalable printer setup is used and as a model system a colloidal suspension is examined. These suspensions are widely used to investigate lattice growth, which is a technologically important research topic (e.g. programmable matter). As a model system for colloidal suspensions, silica nanospheres are used. To investigate transitions inside the drying nanoparticle coating, characteristic diffusion times and two time correlation functions are extracted. To model the GI data it is necessary to consider the distorted wave born approximation (DWBA), which considers multiple reflection and refraction events inside the thin film. The GT signal lacks the presence of reflection from the substrate and is therefore more straight forward to model via the simpler born approximation (BA). These two different scenarios can be used to further examine the robustness of the different modelling approaches and their impact on the extracted dynamics.

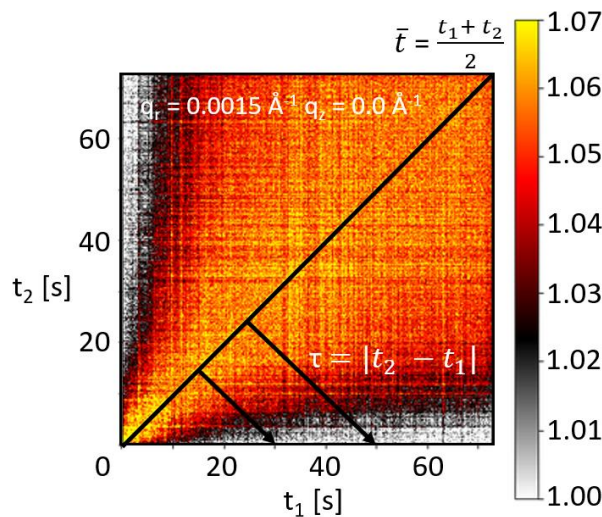


Figure 1: Two-Time Correlation function of ‘aging’ behaviour in drying of multilayer silica thin film near the substrate edge.

# What is the initial stage of degradation mechanism for perovskite solar cells?

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Mixed organic-inorganic hybrid perovskite solar cells have shown a promising future because of their outstanding photoelectric performance. Solution processing makes it possible to achieve low-cost manufacturing of these solar cells. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) reached the champion value of 25.2 % [1], making this technique competitive with commercial silicon solar cells. Despite all these advantages, the application of PSCs is currently limited by combining high performance and operational stability because PCE of PSCs can degrade due to presence of temperature, light, humidity and oxygen [2]. In addition, the rapid developing progress in the fabrication of PSCs has not accompanied the development of start-of-the-art characterization methods. Current degradation research on PSCs is performed by simple current-voltage measurement. Therefore, it is necessary to introduce new characterization tools for analyzing the degradation mechanisms of PSCs. We investigated initial stage degradation processes of different device architectures of PSCs under illumination condition with in-situ grazing incidence wide-angle X-ray scattering (GIWAXS) and grazing incidence small angle X-ray scattering (GISAXS) [3]. With this approach, we are able to follow the evolution of characteristic structures and of the inner morphology under illumination. After understanding the degradation mechanisms for different device architectures, potential solutions could be found to suppress the degradation.

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# Conformal Polymer Thin Films with Polymer brushes

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Polymer brushes are thin films consisting of polymer chains, which are tethered with one end to a solid surface. At high grafting densities (number of grafted chains per surface area), repulsive forces between neighbouring chains lead to chain stretching and a brush conformation is obtained. These thin films arouse interest from a theoretical, fundamental and applied science point of view. While their theoretical understanding is very advanced, it is commonly very difficult to verify these theoretical predictions and explain phenomena like roughness correlation. Polymer brushes form conformal layers, in which the structure of the underlying substrate is copied to the free film surface. This phenomenon of conformality has previously been investigated for spin coated polymer films.[1] However, conformal spin coated films are metastable and will relax during annealing, whereas in polymer brushes the conformality is assumed to be persistent. This property polymer brushes could be used for stable surface coatings with a locally defined layer thickness. Polymer films with an overall thickness down to a few nanometres can show a large relative deviation in local film thickness due to interfacial roughness between polymer layer and substrate. In polymer electronics, like organic light emitting diodes however, a constant quality across the entire diode is required.

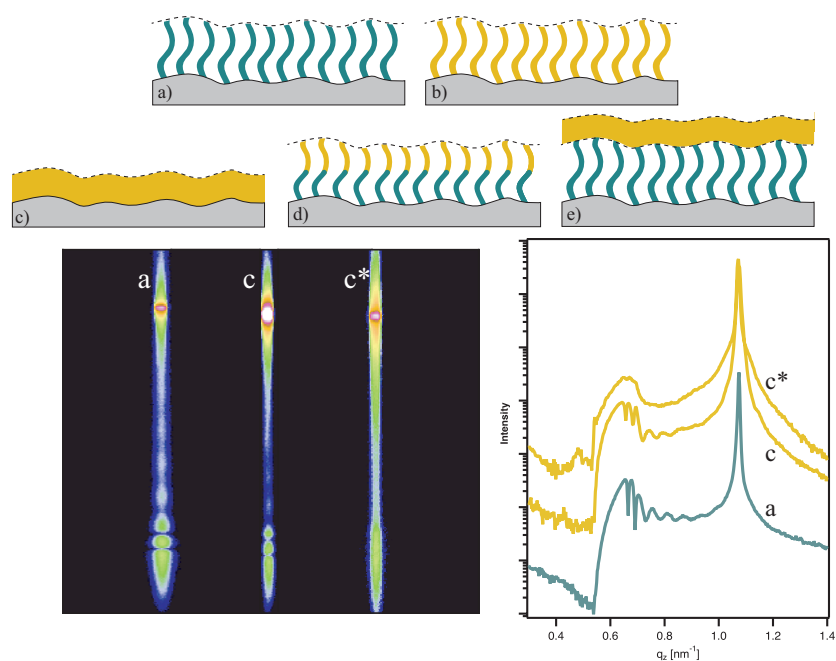


Figure 1: Polymer thin films for studies on roughness correlation with GISAXS detector images and  $q_z$ -line cuts of PMMA-brushes (green, a) and spin coated PS-films (yellow, c) before and after annealing (c\*).

Recently we were able to prepare polymer brushes and spin coated films with PS and PMMA, as shown in figure 1, to compare the surface structure and roughness correlation before and after annealing. Roughness correlation of polymer brushes was investigated with Grazing Incidence Small Angle X-ray Scattering (GISAXS), which is a powerful tool to analyse interfaces of polymer thin films. The GISAXS data clearly show oscillations in  $q_z$ -direction between Yoneda peak and specular peak, proving that the polymer layers have a locally correlated layer thickness. We observed that roughness correlation is an intrinsic property of polymer brushes.

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# Surface-Controlled Crystal Alignment of Naphthyl End-Capped Oligothiophene on Graphene: Thin-Film Growth Studied by In Situ X-ray Diffraction

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The thin-film microstructure of small  $\pi$ -conjugated molecules dictates their electronic and spectral properties. [1] Two-dimensional materials, such as graphene, can be used as a surface template to control the crystal alignment and growth of the small molecules during fabrication of thin-film devices. [2] However, the effect of the surface quality on the growth behavior is not well understood. Here, the microstructure, morphology and growth of 5,5'-bis(naphth-2-yl)-2,2'-bithiophene (NaT2) thin films deposited on two types of graphene surfaces are reported. Grazing incidence X-ray diffraction (GIXRD) and atomic force microscopy (AFM) measurements demonstrate that the NaT2 crystal structure and orientation depend strongly on the underlying surface and surface quality, with the molecules predominantly lying-down on the graphene surface (face-on orientation) and standing nearly out-of-plane (edge-on orientation) on the Si/SiO<sub>2</sub> reference surface. *In situ* GIXRD measurements show that the time dependence of the intensity of the (111) reflection from the crystalline edge-on phase does not intersect zero at the onset of the deposition, indicating that an initial wetting layer, corresponding to 1-2 molecular layers, is formed at the surface-film interface. The surface-controlled crystal alignment demonstrated here provides insight into the complex dynamics of small molecule growth for graphene-based thin-film devices.

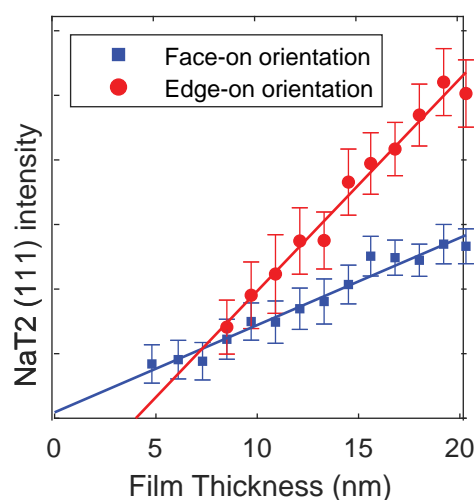


Figure 1: Integrated intensity of the NaT2 (111) reflection as a function of nominal film thickness measured during deposition on custom-made graphene substrate.

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# GIWAXS study of Phase Separation in Non-Fullerene Organic Solar Cells

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The device performance of bulk-heterojunction solar cells strongly depends on the donor and acceptor properties, the phase separation in the absorber layer and the formation of a bicontinuous network. In the case of polymer:fullerene solar cells this phase separation is well known. However, little is known about the phase separation in polymer:non-fullerene acceptor solar cells. Due to the chemical similarity of the conjugated polymer donor and the organic non-fullerene acceptor structural analysis by methods such as conventional transmission electron microscopy and atomic force microscopy is difficult. Complementary surface-sensitive methods such as grazing-incidence small- and wide-angle scattering help to get a deeper understanding of the phase morphology in such systems.

Here we report on a grazing-incidence wide-angle X-ray scattering (GIWAXS) study on such polymer:non-fullerene acceptor solar cells using the Anton Paar SAXSpoint 2.0 instrument [1]. GIWAXS measurements revealed that the conjugated polymer and the non-fullerene acceptor show a face-on orientation in the pristine films as well as in the blend films.

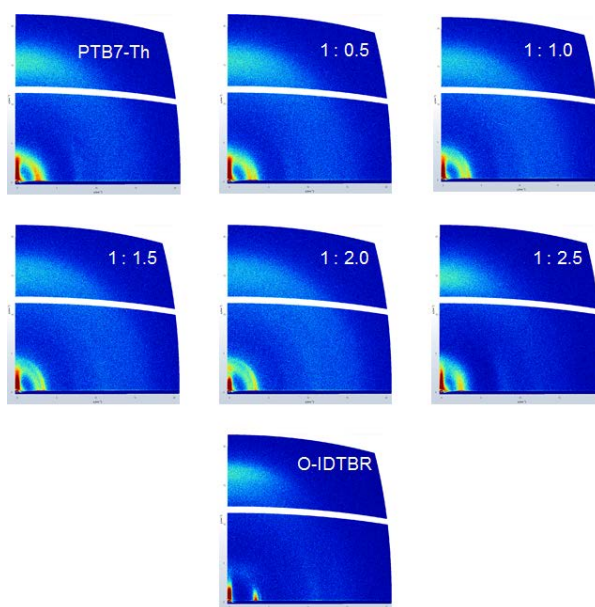


Figure 1: 2D GIWAXS patterns for the pristine PTB7-Th and O-IDTBR films and the binary blends (PTB7-Th:O-IDTBR)

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# Charge transport properties of mesoporous $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin-films

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Perovskite oxides have been the focus of intense research in the fields of heterogeneous catalysis and energy conversion as an alternative to noble metal catalysts. Their tolerance towards doping and composition changes enables tuning of their physicochemical properties towards specific catalytic processes.

Especially the electro catalytic properties have been investigated, revealing a correlation between the filling of the  $e_g$ -orbitals and catalytic performance in various electrochemical reactions (e.g. oxygen reduction (ORR) and evolution (OER))[1]. More recently, however, an appreciable involvement of oxygen vacancies next to transition metal centres in the catalytic reaction has been suggested[2,3]. Textural modification may thus improve not only the electrochemically active surface area, but provide additional surface oxygen vacancies as catalytic centres.

In our work we investigate the charge carrier transport in mesoporous  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  thin-films with pore sizes of 20 nm and 25 nm as a model system. The small grain size and high surface curvature suggests high concentrations of surface defects, which can act as catalytic centres. Impedance spectroscopy at varying oxygen partial pressures is employed to analyse the defect chemistry of the thin-films, while XPS measurements reveal the surface composition relevant for catalytic processes.

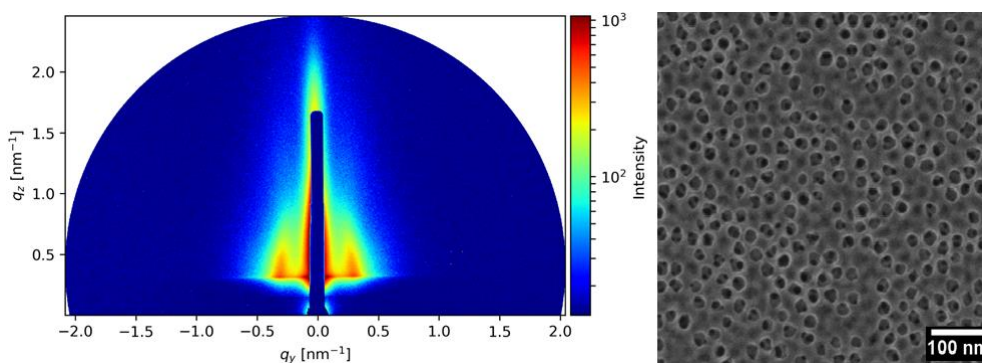


Figure 1: GISAXS measurement and SEM image of the investigated mesoporous thin film of  $\text{LaMnO}_3$ .

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# Ordering of ZnPc:F<sub>n</sub>ZnPc evaporated blends

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The electronic energy levels of phthalocyanines can be shifted without changing the optical gap by substituting hydrogen with fluorine atoms. Schwartz et al. [1] have recently demonstrated that by mixing zinc phthalocyanine (ZnPc) and its octuply fluorinated counterpart (F<sub>8</sub>ZnPc) in different ratios, the ionisation energies of blends can be linearly shifted thus enabling band tuning in organic electronic devices. Band tuning offers an accessible and versatile way of e.g. ensuring energy level alignment with metal contacts or minimising voltage losses in organic photovoltaic heterojunctions.

In this work, we present a grazing incidence wide angle X-ray scattering (GIWAXS) study of vacuum thermal evaporated pure and mixed films of ZnPc and F<sub>8</sub>ZnPc highlighting structural changes for different blend ratios. We find that films of fluorinated molecules display higher lattice spacings and a more isotropic distribution of grain orientations compared to unsubstituted molecules. We relate these microstructural changes with device performance studies and measurements of the external quantum efficiency of organic photovoltaic devices.

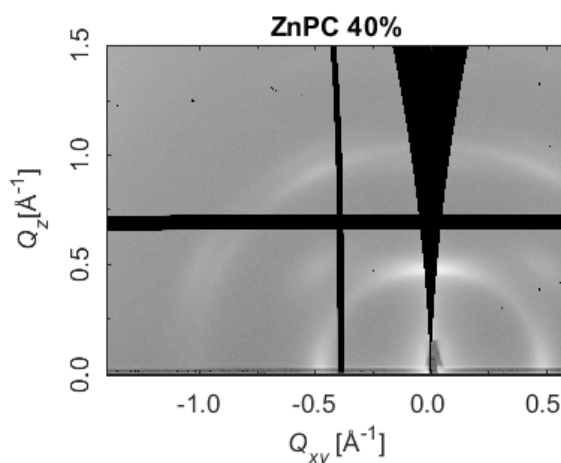


Figure 1: GIWAXS 2D reciprocal map of ZnPc:F<sub>8</sub>ZnPc evaporated film with a blend ratio of 40:60.

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# Classifying Grazing Incidence X-ray Scattering Patterns via Convolutional Neural Networks

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Nano-structured thin films have a variety of applications, such as antireflecting coatings for solar cells, waveguides, gaseous sensors, and piezoelectric devices. Grazing-incidence small-angle X-ray scattering (GISAXS) has become a key technique to determine the morphologies of such thin films. One of the main challenges is to determine the structure information encoded in the data based on scattering patterns alone. We propose a computational scheme that learns the structure of well-defined layers of nanoparticles from GISAXS patterns. We explore this class of thin-film materials in terms of physics-based simulation models and experimental data and apply convolutional neural networks to the simulated data to obtain the encoded information of the morphology. Our classification models categorize millions of simulated scattering patterns with success rates over 94%. In addition, we show how these data-driven models have the potential to decrease analysis time of real scattering patterns from experiments.

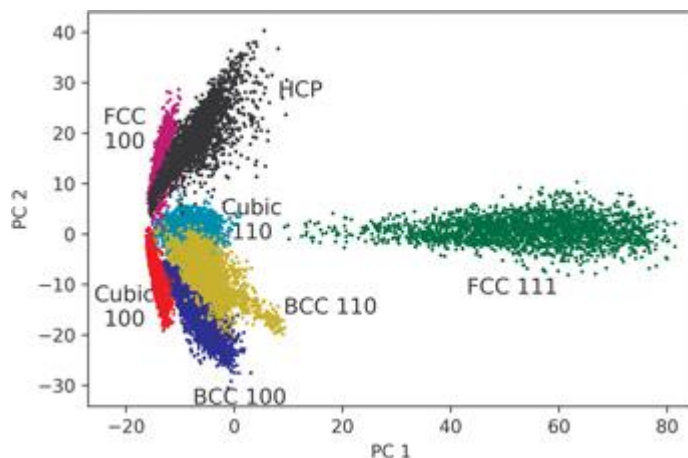


Figure 1: PCA of the final fully connected layer of the trained CNN. We see a distinct gap between the components of the BCC / Cubic structures and the FCC structures. PCA allows us to see how the CNN is learning to classify the different crystal structures.

# Picosecond pump-probe GIXRD/scattering setup at the Austrian SAXS beamline at the ELETTRA

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We present a new setup for picosecond pump-probe X-ray scattering at the Austrian SAXS beamline at the Elettra-Sincrotrone in Trieste [1]. A high-power/high-repetition-rate laser system (Pharos, Light Conversion, Lithuania) has been installed on site, delivering UV/VIS/IR femtosecond pulses [2] in-sync with the Elettra storage ring. Data-acquisition is achieved by gating a multi-panel detector (Pilatus3 1M, Dectris, Switzerland), capable of discriminating the single X-ray-pulse in the dark-gap [3,4] of the Elettra hybrid filling-mode. We further describe specific aspects of laser- and detection-synchronization, on-line beam steering as well protocols for spatial and temporal overlap of laser and X-ray beam. The capabilities of the setup are demonstrated in GIXRD conditions by studying a heat-transfer in an In/Al/GaAs superlattice structure where the transient temperature in the corresponding layers was evaluated from the shift of the diffraction peak positions [1]. The flexible layout of the setup is also compatible with transmission geometry, required for liquid samples, allowing for studying picosecond dynamics of biologically relevant compounds at their natural conditions or alternatively to implement fast T-jump experiments in liquid.

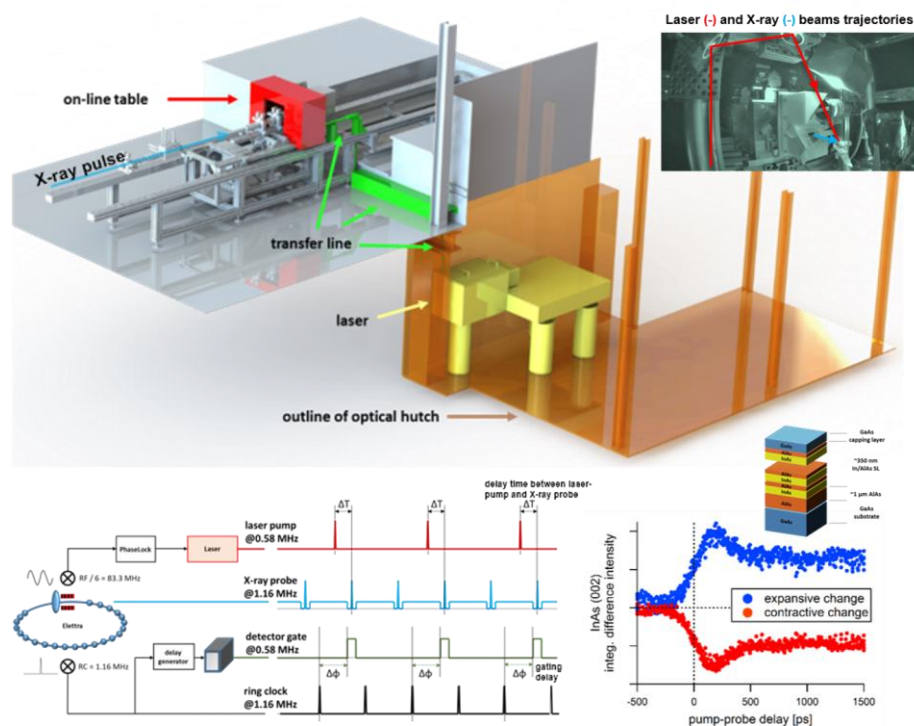


Figure 1: (Top) Sketch of the laser infrastructure implemented at the Austrian SAXS beamline for pump-probe experiments. (Bottom, left) Synchronization scheme of electronic and optical components to the storage ring time-base. (Bottom, right) Transient heat-transfer in an In/Al/GaAs superlattice structure.

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# Mechanism of Block-copolymer self-assembly during spin coating revealed by ultrafast in-situ GISAXS

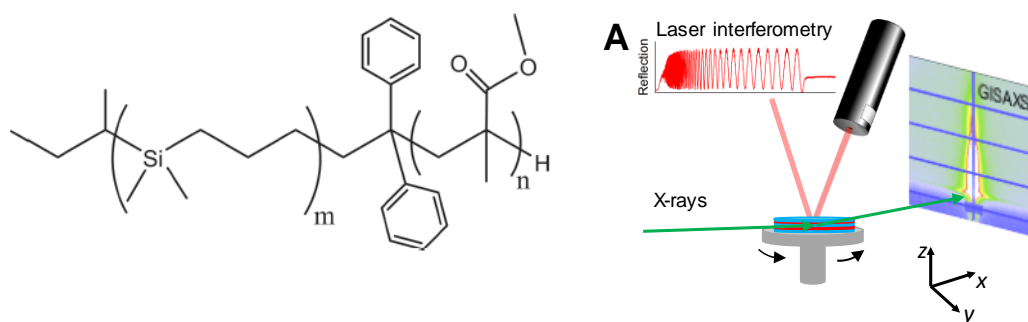
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Periodic structures of nanometer length scale obtained by block copolymer (BCP) self-assembly in thin films constitute a versatile platform for technological applications such as data storage, lithography, nanostructured membranes, sensors or solar cells.[1] Different methods including dip coating, spin coating, ink-printing and slot-die coating can be employed to process BCP in thin films. Among them, spin coating is one of the most versatile technique to process nanostructured block copolymer thin films finding numerous applications in emerging technological fields such as nanolithography or organic electronics. Despite the apparently simple use of the spin coating process, the mechanism of phase separation and structuring that polymeric systems undergo during spin coating can be rather complex and follow a multistage process.

In this contribution we have used a recently developed combined laser/X-ray setup [2] to perform in-situ synchrotron grazing incidence X-ray scattering (GISAXS) experiments during block copolymer structuring. In particular, a poly(1,1-dimethyl silacyclobutane)-b-poly(methyl methacrylate) (PDMSB-b-PMMA) BCP has been studied, showing fast self-assembly behavior. By tuning the processing parameters, this polymer is able to form highly oriented out-of-equilibrium lamellar structure, characterized by an extremely low degree of disorder. In order to elucidate the mechanism of formation of such a highly ordered structure, we have performed simultaneous laser interferometry and GISAXS experiments with millisecond time resolution during spin coating from THF solution. Our results show a multistage process (comprised of five different stages) where the formation of transient micellar phases are clearly visible.[3] These short-living micellar phases undergo subsequent growth and coalescence and their assembly during spin coating is the key step to reach highly ordered structures. Our observations are partially in line with what has been recently reported in literature, [4] but present novel features previously never observed experimentally in ultrafast BCP phase separation.



**Figure 1.** (left) structure of the PDMSB-b-PMMA block-copolymer. (right) Experimental setup used for in-situ laser and GISAXS experiments.

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# Tracking structural heterogeneities arising from colloidal precursors in hybrid perovskites thin-films

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A colloidal nature of perovskite precursors [1] used for film fabrication is suggested, and phenomena such as glass-transitions, crystal twinning, and growth instabilities are explored in order to explain diffusion-limited self-organization of thin films. Morphological and structural heterogeneities within thin films are identified to be a consequence of deposition through dynamic precursors, far from thermodynamic equilibrium. The significance of such a finding suggests that perovskite films possess soft properties, implying there exists a delicate balance between entropic and enthalpic contributions towards the free energy of the dynamically changing system, which needs to be regulated for controlling film morphology; which has been established as a crucial prerequisite for improving solar cell performances.

Further, local crystallographic characteristics of two exemplary perovskite systems are mapped. The compositions include thin films of a stoichiometrically pure MAPbBr<sub>3</sub> and a mixed hybrid perovskite (MAPbBr<sub>3</sub>)<sub>0.50</sub>(FAPbI<sub>3</sub>)<sub>0.50</sub>. Local heterogeneities emerging at the nanoscale were discovered, making it possible for the first time to map individual crystallites of solution-processed thin films and pinpoint local sites of degradation within the two prototypical materials making it possible to draw correlations between chemical identities of perovskites and heterogenetic morphological tendencies.

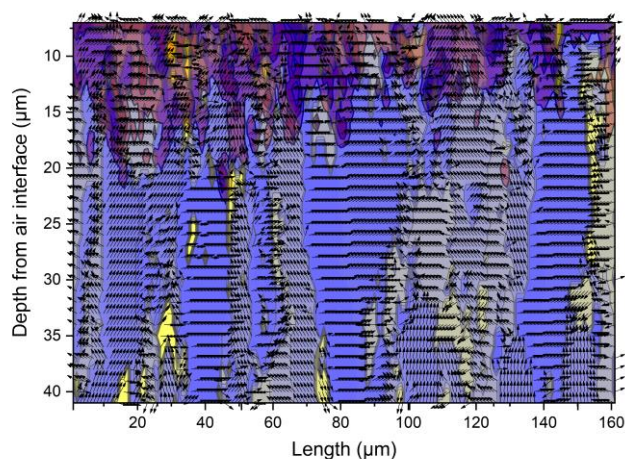
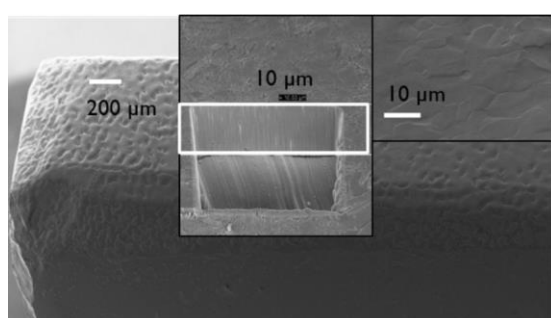


Figure 1: Cross section of distributed nanostructures from spray deposited hybrid perovskite (left) and nanodiffraction mapped heterogeneities (right).

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# Surface dynamics of solids upon high-intensity laser irradiation investigated by grazing incidence X-ray scattering

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The motivation for this study is to understand the nanoscale structures in solid density plasmas [1]. We are interested in the surface dynamics of solids upon high intensity laser excitation in picosecond and nanometer spatial in-plane and in-depth resolution. Therefore access to the density profile of the surface is needed which is realized by multilayer samples. X-ray reflectivity at grazing incidence is a suitable tool to get information on surface density with nanometer depth sensitivity, but is not practical for dynamically changing samples we want to probe here. Therefore we performed a single-shot GISAXS [2] experiment at the SACLA FEL facility in Japan. Employing X-ray photons of 8.81 keV we fixed the incident angle to  $0.64^\circ$  and recorded the scattered signal on an area detector with  $2\theta$  resolution adapting various time intervals between laser excitation and X-ray beam. We demonstrate that changes in the scattering signal are visible for different time steps up to 6 ps. By proper analysis relying on distorted wave born approximation (DWBA) [3] we can get access to the full dispersion profile of the sample during the first 6 ps and see the ultrafast evolution of the density profile including compression and expansion due to laser excitation. This leads to important indications for a deeper understanding of laser-matter interaction processes.

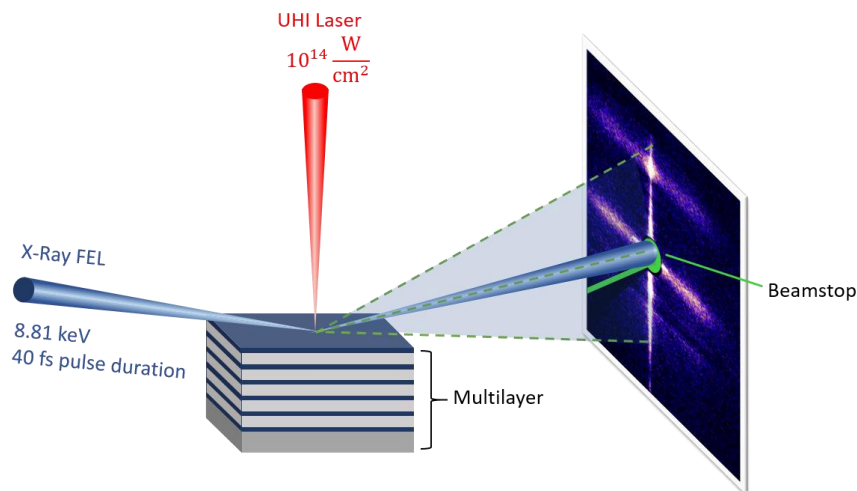


Figure 1: Experimental setup of the GISAXS experiment at the SACLA FEL facility in Japan.

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# In-situ GISAXS measurements on slot-die printed planar perovskite thin films

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Reaching minimodule efficiencies of around 17% in 2018 and 15% on ultrathin flexible substrates further improvement on scaling up of organic-inorganic metal halide perovskite based solar cells (PSCs) is needed in order to push PSCs to the commercial market.[1] Especially changing the deposition method from lab-scale spin-casting [2] to industrial compatible methods raises many questions due to the additional requirements, e.g. fast and roll-to-roll compatible deposition, low energy and low temperature processing as well as low material waste during production.[3] In principle, those requirements can be met by, e.g. (roll-to-roll) slot-die coating.[4-6] In order to control crystallization behavior for optimal film quality and power conversion efficiency we use *in-situ* grazing incidence small angle x-ray scattering (GISAXS) measurements to probe the film's nanostructure in slot-die printed planar multi-cation mixed-halide perovskite films for a p-i-n device architecture. Highly crystalline and uniform films with low defect concentrations are paramount in reaching high power conversion efficiencies in PSCs.[7-8] GISAXS and also GISANS (grazing incidence small angle neutron scattering) measurements are well suited in shedding light on the influence of temperature, ambient moisture, printing parameters and precursor composition on crystallization dynamics and crystal film quality by probing stochastically relevant large sample areas.[9-10] In this way additional insights necessary for efficient large area perovskite deposition can be gained and used for optimized printed film quality.

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# Liquid Interface Scattering at P08

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Liquid-vapour and liquid-liquid interfaces are sites of a wide range of physico-chemical processes, from biological activities at the biomembranes [1] to electrochemical reactions [2]. The structural modification at the interfaces is the key to resolve the mechanisms of such processes. At the High Resolution Diffraction Beamline P08 at PETRA III, the structures at the liquid interfaces can be resolved from Å-scales up to ~50nm, using X-ray reflectometry and grazing incidence X-ray scattering [3]. The setup also includes simultaneous X-ray fluorescence measurements to study the accumulation of elements at the interfaces. Here, we show two example studies. In the first example, the formation of superlattices by nanodiscs at the liquid-vapour interface was studied by in situ GISAXS experiments [4]. In the second example, the layer structure of lipid membranes at air-water interfaces was measured with sub-minute time resolution.

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# In Situ Studies of Organic Optoelectronic Materials

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Organic and hybrid organic/inorganic semiconductor materials show promise for opto-electronic applications including photovoltaics[1-2], flexible electronics and next generation x-ray detectors[3]. Their complex structure-performance-processing interrelationship makes it imperative to characterize the structure *in situ* under processing conditions or *in operando* with simultaneous characterization of performance. At beamline 8-ID-E of the Advanced Photon Source, the GIXS instrument supports *in situ* spin coating with simultaneous GIWAXS and optical reflectance measurements. Studies investigating the role of additives in polymer and small molecule organic photovoltaics reveal a dramatic extension of the timescale of structural evolution from seconds for casting from neat solvents up to hours with additives[1]. A versatile sample chamber incorporating a thermal stage provides a vacuum environment for GIWAXS under illumination by a solar simulator, as well as simultaneous measurement of the J-V curve of the photocurrent in the device. For perovskite thin films, GIWAXS indicates a light-induced lattice expansion that relaxes strain and improves device performance[2].

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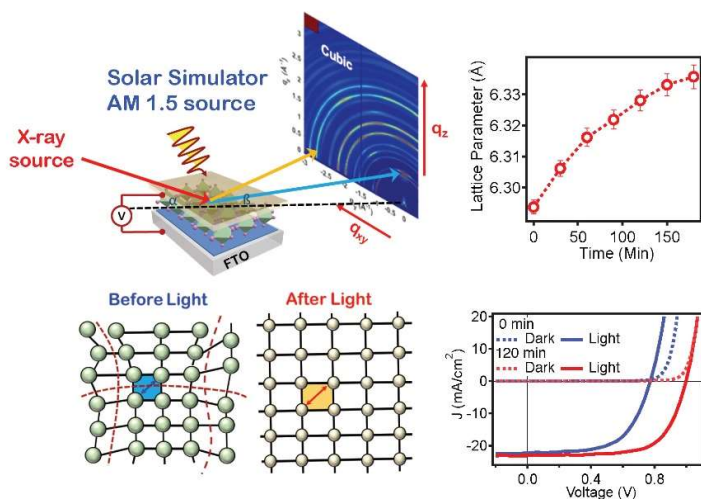


Figure 1. GIWAXS of perovskite thin films during light soaking, experimental setup (top left) and the corresponding light-induced lattice expansion effect (top right: lattice constant vs. illumination time), which leads to curing defects and relieving of lattice strain (bottom left) and as a result an increase in the open circuit voltage of a solar cell (bottom right).

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# Monitoring nanostructural transformations during drying of industrially relevant clearcoats from waterborne latex particles by in-situ GISAXS

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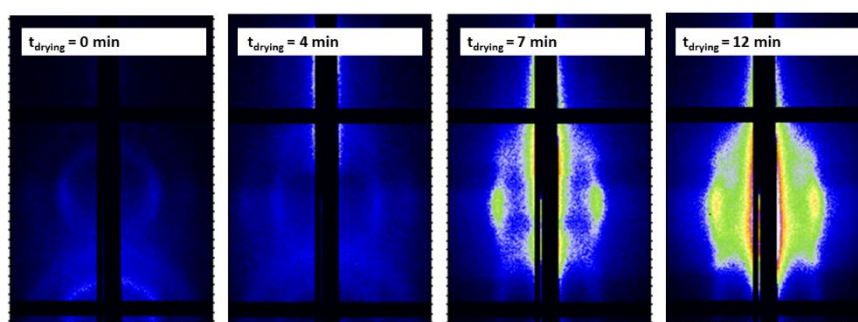
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Clearcoats made from polymer colloids are utilized as primary constituents in paints and adhesives, where a crucial property determining their performance is their efficiency in preventing solvent penetration.[1-2] This property depends directly on the structural homogeneity at the nanoscale and on the interplay between temperatures of film formation and glass transition,  $T_g$ . [3] Health and environmental regulations dictate that waterborne polymer colloid suspensions are utilized, in order to minimize volatile organic emissions during solvent evaporation right after depositing the coating (e.g. paint layer deposition). However, the complex interactions from the aqueous environment itself as well as the polymer colloid architecture (chemical composition and softness, dictated by the  $T_g$  of each polymer phase) lead to challenges in obtaining structural homogeneities at different length scales.[3] Our recent investigation of the dry micron-sized slot-die coatings from polyacrylic colloids of different architecture and softness has provided evidence of residual nanostructure, with characteristic distance ( $d^*$ ) smaller than the original particle size and even smaller ( $\ll d^*$ ) heterogeneity dimensions, anisotropically aligned across the film's cross-section and more concentrated in the upper film layer. This residual structure stems from partial particle coalescence.[4] Using the broad spatiotemporal resolution of in-situ GISAXS, we have probed here non-destructively the nanostructural evolution during water evaporation immediately after slot-die coating. We have observed distinct nanostructural variations over time depending on the exact polyacrylic colloid architecture. This is the first non-destructive demonstration of nanostructural transitions from suspensions of soft polymer colloids during the early stages of slot-die coating application, rendering the results strongly relevant for coating industry and surface science.



**Figure 1.** 2D GISAXS patterns at different drying times ( $t_{dry}$ , min), right after slot-die coating, at  $\alpha_i = \alpha_{c,polymer}$  for thick ( $30\ \mu\text{m}$ ) films of multiphase polyacrylic aqueous suspensions on sodalime glass substrates.

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# Monitoring selectivity of gold cluster growth/formation on antifouling-relevant zwitterionic thin block copolymer coatings

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Polysulfobetaine (PSB) films serve as promising antifouling coatings [1]. In addition, metal-coated thin polymer films hold also tremendous potential for antifouling and antibacterial applications [2]. However, the exact limit to how much one may tune antifouling by means of altering the block copolymer nanostructure with a metal sputtered on top of the polymer remains practically unexplored. Schwartzkopf et al. [3] have shown that sputtered gold can exhibit wetting selectivity with different affinities in each constituent of a PS-*b*-PEO block copolymer film. The correlation between gold growth and affinity to the particular polymer phase of the PSB copolymer structure and its impact on antifouling efficiency remain elusive. By in-situ microfocus GISAXS ( $\mu$ GISAXS) we present the nanostructure evolution of gold film growth on thin (<100 nm) polymer films. We compare poly (N-isopropyl methacrylamide) (PNIPMAM) homopolymer, PNIPMAM-*b*-PSB diblock copolymer and a PSB homopolymer. We inspect for potential selectivities during gold sputtering on these polymer films and potential correlation between polymer-metal nanocomposite structure to antifouling efficiency.

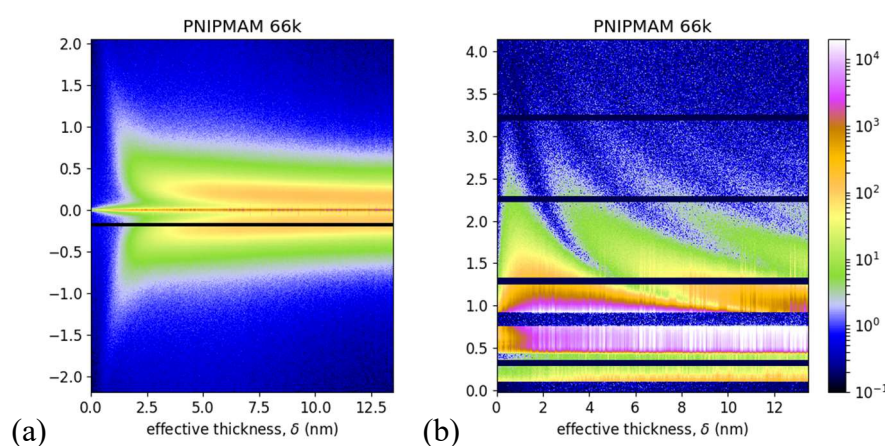


Figure 1: Mappings created from two-dimensional (2D)  $\mu$ GISAXS data of PNIPMAM 66k thin ( $\sim 70$ nm) films as function of the effective thickness,  $\delta$  ( $\delta$ ), of sputtered gold in (a) horizontal ( $q_y$ , nm<sup>-1</sup>) and (b) vertical ( $q_z$ , nm<sup>-1</sup>) directions. Intensity scale for both panels is from 0.1 to  $2 \cdot 10^4$ .

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# Electrochemically-Assisted Self-Assembly (EASA) in Ionic Liquid-templated Mesoporous Silica Films

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The use of ionic liquids (ILs) as structure directing agents in the synthesis of mesoporous silica is a novel approach with the huge advantage of the IL functioning simultaneously as co-solvent and template, but also providing an additional function to the porous structure, i.e. ionic conductivity [1]. Another novelty in the synthesis of mesoporous silica films is the utilization of electrochemically-assisted self-assembly (EASA), which upon use of surfactant-like molecules as templating agents allows rapid growth of monolithic silica with cylindrical pores oriented perpendicularly to the substrate [2]. The long-term goal of our research is to obtain monolithic, protic ionic liquid-filled and ordered mesoporous silica films to study their morphology and ion conduction property. As a first step in this direction, we have synthesized and characterized mesoporous silica films prepared via the EASA method using the ionic liquid  $C_{16}MIMCl$  as templating agent (Fig. 1). The properties of the films are compared to those of an analogous film prepared using CTAB as the surfactant instead.

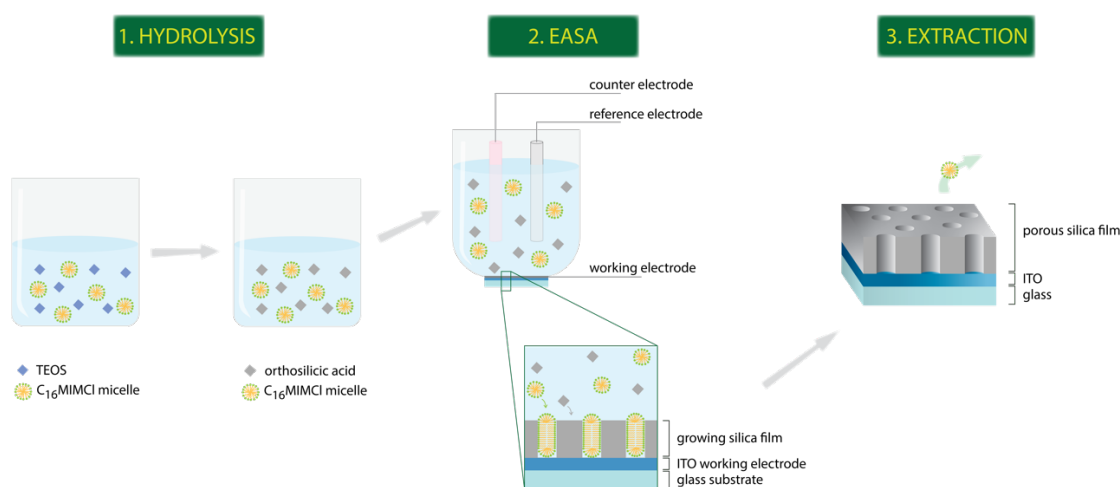


Figure 1: Schematic of the electrochemically-assisted self-assembly (EASA) method used to synthesize  $C_{16}MIMCl$ -templated silica films.

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# Characterizing Rough Multilayers by GISAS – Theory and Experiment

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Grazing incidence small angle scattering (GISAS) intensity patterns of multilayer interfaces are investigated theoretically in the large roughness approximation ( $q_z\sigma > 1$ , LRA). Distorted wave Born approximation (DWBA) theory and numerical calculations for realistic multilayer parameters reveal i) for single surfaces: the sample-plane-parallel (y-) cuts broaden with increasing out-of-plane wavevector ( $q_z$ -) transfer. For periodic multilayers of imperfect roughness replication the (y-) cut broadening is only a tendency. ii) At resonant diffuse scattering (RDS) sheets the y-cut widths exhibit local minima. iii) At a given in-plane momentum ( $q_y$ -) transfer the sample-plane-perpendicular (z-) cuts of the RDS sheets broaden with increasing ( $q_z$ -) wavevector transfer. iv) Within a given RDS sheet the z-cuts broaden with increasing in-plane wavevector transfer.

In the small roughness approximation ( $q_z\sigma \ll 1$ , SRA) effects ii), iii) and iv) can be explained by spatial frequency dependent roughness replication, however, large roughness alone may explain phenomena ii), iii) and iv) without any assumption on spatial frequency dependence and account for the otherwise unexplained increase of the diffuse scattering intensity at large  $q_z$ . Unjustified application of SRA may lead to misinterpretation of the experimental results and erroneous derivation of the in-plane and the out-of-plane correlation lengths.

Experimental GISAXS patterns of Ni-Ti periodic multilayers of period number of 25, bilayer thickness and roughness of 150 and 5-15 Å, respectively, were recorded at different grazing angles of incidence and evaluated within the DWBA using spatial frequency independent [1] and dependent [2] roughness replication models. The scattered intensity at large  $q_z$ -s is larger than expected from SRA and the RDS peaks are excessively broadened in good agreement with the present DWBA calculations using LRA.

# Gold Sputter Deposition on Polystyrene Thin Films: Influence of Molecular Weight and Template Thickness

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Nanostructured noble metal films on polymer layers are of fundamental importance in the field of organic electronics due to their unique optoelectronic, electrical and catalytic properties [1] and promise various potentials applications in solar cells, biosensors, reflective or antireflective coatings as well as in heterogeneous catalysis. Moreover, such material combinations have recently gained importance for stabilizing thin polymer films during annealing above glass temperature [2]. In order to study the effect of polymer film thickness and molecular weight we combine sputter deposition with grazing incidence X-ray scattering (GISAXS) to investigate in-situ the growth kinetics of Au on polystyrene thin films with different thin thicknesses and two different molecular weights [3-4]. We analyze quantitatively the metal nanoparticle layer growth and compare our results within the different polymer thicknesses [5]. It is mandatory to understand the influence of the growth kinetics on the metal film morphology during sputter deposition for understanding the influence of molecular weight and template thickness on Au cluster growth. For future studies the results could be compared with different homopolymers like polymethylmethacrylate.

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# Hybrid Energy Harvester based on Solar Cell and Triboelectric Nanogenerator

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Developing clean energy plays a central role in the sustainable development of human society [1]. Solar energy is one of the most promising energy sources in replacement of conventional used fossil fuels [2-3]. However, the daily and seasonal fluctuations in weather limit solar cell's applications. Integrating the solar cell with other kinds of energy harvesters in one device is a possible solution [4]. Triboelectric nanogenerator (TENG) originating from Maxwell's displacement current is a new type of energy harvesters. Due to its advantages of light-weight, low-cost, and easily fabricated, TENG attracts worldwide attention in the past years [5-6].

In the present work, a flexible hybrid energy harvester was designed and fabricated based on quantum dots (QDs). This device consists of a PbS-QD solar cell part and a polydimethylsiloxane (PDMS) based TENG part, which can harness both, solar and mechanical energy from ambient environment to generate electricity. GISAXS measurements were used to characterize the bending stability and morphology changes of the mesoscale structure. This work may have great applications in artificial intelligence and soft robots.

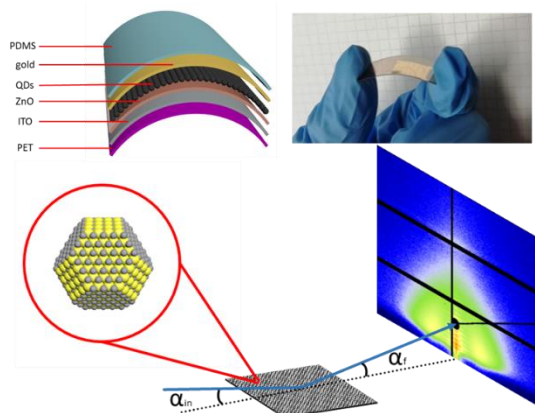


Figure 1: Top) Fabricated hybrid energy harvester as sketch (left) and in reality (right) and bottom) GISAXS measurement setup with QD layer.

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# The MiNaXS Beamline P03: Current status & future challenges

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PETRA III as a third generation synchrotron source enables new experimental opportunities using micro- and nanofocused X-ray beams. The MiNaXS beamline P03 is partitioned into a micro- (EH1) and a nanofocus (EH2) endstation, both being capable of transmission as well as grazing incidence wide- and small-angle X-ray scattering experiments [1-3]. The high temporal and spatial resolution enables deeper insights into industrial relevant coating and process technology.

The commissioned energy range of the beamline is 11.4 – 21 keV which is provided by high- $\beta$  canted 2m-long U29 undulator, a silicon (111) double crystal monochromator and a planar double higher order suppressing mirror with three different coatings (SiO<sub>2</sub>, Mo and Pd). The microfocus operates in the range of 42 x 20  $\mu\text{m}^2$  and 22 x 13  $\mu\text{m}^2$ . Even smaller microfoci (beam size down to 7 x 4  $\mu\text{m}^2$ ) were brought into operation using intermediate focusing [4]. The nanofocus end station features routinely a beam size of 350 x 250 nm<sup>2</sup> performing focusing by the system of KB-mirrors. Nanofocus end station is operated by Helmholtz Zentrum Geesthacht [3]. In front of the microfocus end station, two CRL1 and CRL2 (Compound Refractive Lenses) transfocators are located. We also commissioned one additional CRL3 in close vicinity to the sample position recently. Furthermore, we plan to parallelize the beam after monochromator by a new (CRL4) transfocator directly after the optics hutch, thereby increasing the beam transmission and compensating for the loss of its intensity due to divergence at the large distance from the source to the sample position (> 85 m).

A common, unique feature of all these setups is the exceptionally long and flexible focal distances, 3-8 m in the case of microfocus and 8 cm in the case of the nanofocus. Therefore, varieties of *in situ* sample environments are offered at MiNaXS, e.g. nanoindenter, devices for spray deposition, sputter deposition, high pressure cell [5], etc. At the microfocus end station, we operate a flexible heavy load 5-axes system sample stage (up to 180 kg) optional equipped with an additional linear translation stage and/or a hexapod (up to 10 kg) for ensuring precise alignment of various experimental setups. We also offer additional auxiliary equipment for *in situ* measurements to our user community, e.g. microscope, heating plates, fluorescence detector, contact angle measurement device, UVVis, imaging ellipsometer, which can be used in our labs for *ex situ* sample preparation and characterization as well. Furthermore, there is also an adaptive flight-tube enabling a change of the sample-to-detector distance (from 1.5 to 8.5 m) addressing the relevant length scales ranging from Angstroms to microns. We offer several detectors, like Pilatus 300k and Pilatus 1M (Dectris Ltd.). In future, we will operate a novel, customized  $\Gamma$ -shaped Lambda 9M (X-spectrum GmbH) with a small pixel size (55 $\mu\text{m}$ ) and a 2000 fps frame rate enabling simultaneously SAXS/WAXS measurements with sub-millisecond time resolution and a Dectris Eiger X 9M at the Nanofocus Endstation. Since the amount of data is rapidly increasing during the last years, data reduction becomes tremendously important. We, therefore, offer an open-source and plugin-based software dedicated to online-and offline data analysis (DPDAK) [6].

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# Small-Angle X-Ray Scattering from Self-Assembled GaN Nanowires

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Self-assembled GaN nanowires (NWs) prepared by molecular beam epitaxy typically possess lengths of up to several microns and diameters of 20–100 nm. They elongate along the surface normal with a spread in orientations of 2–3° [Fig. 1(a)]. The aim of the present work is to study the NW diameter distribution by small-angle X-ray scattering. We analyse three different kinds of GaN NW ensembles which exhibit significantly different NW densities and diameters: (i) NW ensembles on Si with densities over  $10^{10}$  cm<sup>-2</sup> and diameters of 20–100 nm, (ii) NW ensembles on Si thinned down to 6 nm in diameter using a post-growth thermal decomposition process, and (iii) NW ensembles on sputtered Ti films that possess densities of the order of  $10^9$  cm<sup>-2</sup> and diameters of 20–50 nm.

The small-angle scattering measurements [an example is presented in Fig. 1(b)] are performed with the incident x-ray beam directed normal to the NW axis, i.e., at a grazing angle to the substrate. We avoid the complications of grazing incidence scattering by choosing an incidence angle larger than the critical angle. The analysis of the X-ray data requires development of new approaches since, unlike to the common case of small-angle scattering, the NWs are aligned. The range of orientations is, however, notably broader than the one meets in grazing incidence X-ray scattering studies of epitaxial islands, so that the characteristic features typical for scattering from these structures (like the facet truncation rods) are not directly observed. We separate the scattered intensity from NWs from all kinds of parasitic scattering caused by surface roughness, 3D islands, etc. by taking into account that an angular spread of orientations of long NWs gives rise to a cone of intensity in reciprocal space.

The facets of NWs should result in Porod's law for the intensity  $I(q)$  at large wave vectors,  $I(q) \sim q^{-4}$ . The plot of  $I(q) \times q^4$  vs.  $q$  [see Fig. 1(c)] possesses a maximum that allows us to determine the mean NW diameter directly from the measured intensity, even without a model fit. The fit provides the whole diameter distribution, which we compare with the distributions obtained from scanning electron microscopy, for the samples where the latter is possible.

Deviations of the measured intensity from Porod's law are, however, observed at large wave vectors  $q$ . We show, by rotating the sample with respect to the incident beam, that these deviations originate from the facet truncation rods, although the rods are not directly seen in the intensity distributions. The scattered intensity at large wave vectors  $q$  is maximum when the incident beam is along the facets and hence the scattering vector is along the facet normal, and minimum after a 90° rotation of the sample [see Fig. 1(c)].

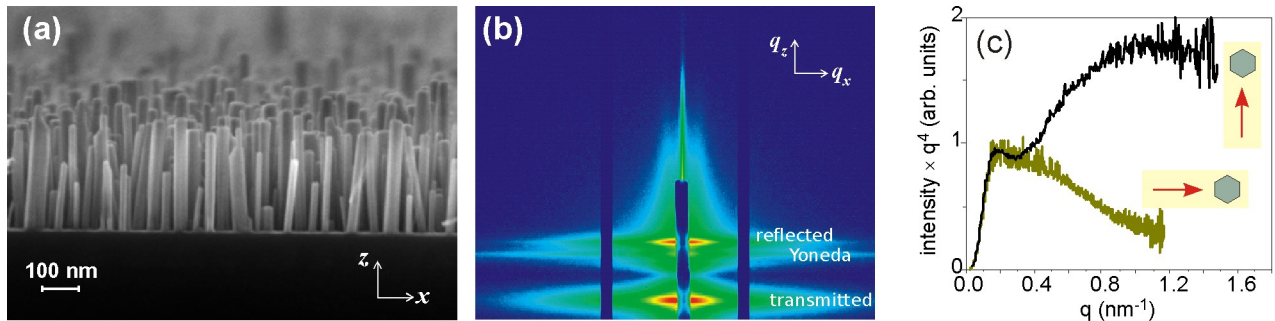


Figure 1: (a) GaN nanowires on Si, (b) SAX intensity distribution, (c)  $I(q) \times q^4$  vs.  $q$  profiles for two orientations of the sample with respect to the incident x-ray beam.

# WLAN DESY-Guest

## General Information

For guests and visitors DESY operates a guest network which can be used by Ethernet (LAN) or wireless (WIFI) after email registration.

Basically, with this network it is possible to access the internet with network-compatible devices. The guest network can be used if you connect your device to the left plug of a network socket or by using the unencrypted WIFI network 'DESY-Guest'.

## Registration and Log in Procedure

If a device is connected to the guest network (via WIFI or LAN) an IP address will be requested - usually automatically - via DHCP. After that you must register by email. It is possible to use all internet browsers to call up any **unencrypted webpage** (<http://...> **NOT** <https://...>). You will then be forwarded automatically to the web portal of the guest network.

**Note:** The 'desy.de' website can generally also be reached from non-registered guests and devices. Therefore, there will be **no forwarding** to the portal of the DESY guest network from the webpage 'http://www.desy.de'.

To register to the DESY guest network and to receive the login credentials, please click on **"Receive your credentials by EMail"**.

Fill in the fields: last name, first name and email address and accept the DESY data protection provisions. Confirm your entry details with **"Register"**. Your credentials will then be sent by email to the specified email address.

For the following **five minutes** you have limited access to the Internet to retrieve your emails and access the login data.

Return to the portal webpage of the DESY guest network (<https://guestnet-portal.desy.de>) and close the temporary connection via **"Terminate Connection"**.

You can now log in to the DESY guest network with your credentials. Fill in **"Login"** and **"Password"** and **accept** the DESY "Condition of Use". Please confirm with **"Enter"**.

For the validity of the guest network account it is required to log in once per device. After that it is possible to use this device in the guest network during the following days without a renewed log in.

**Note:** A guest network account is valid up to **10 days** and can be used with **five devices** at the same time.

## Conference Venue:

Lectures will take place in

FLASH Seminarroom;  
Bldg. 28c, 2nd floor

The tutorials will take place at:

Seminar room 456; Bldg. 25f, 4th floor and  
Seminar room 109; Bldg. 25b, 1st floor

## Preparation of the training sessions

In order to facilitate and prepare the tutorials, we would like to ask you to already install the desired software packages. We would also like to ask you to bring your own laptop/notebook.

Please visit:

<https://dpdak.desy.de>

<https://www.bornagainproject.org/>

The training data are accessible via the website (password needed, access only for participants of GISAXS2019)

## Industry Exhibition

The following companies will participate as exhibitors:

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Seminarroom;  
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Seminar room 109;  
Bldg. 25b, 1st floor

Seminar room 456;  
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