NSLS 2004 Annual Users' Meeting Workshop

Grazing Incidence Small X-ray Scattering

A workshop on Grazing Incidence Small-Angle X-ray Scattering was held on May 17, 2004 as part of the 2004 National Synchrotron Light Source (NSLS) Users Meeting. This technique, commonly referred to by the acronym GISAXS, is the surface analogue of Small-Angle X-ray Scattering (SAXS). Scientific topics discussed included thin polymer films, nanoparticles at interfaces, and semiconductor nanostructures. GISAXS measurements are sensitive to both the surface morphology and the internal structure of films, and provide information both lateral and normal to the surface on length scales extending from 1–100 nm. As a result, GISAXS provides an excellent complement to more conventional nanoscale structural probes such as atomic force microscopy and transmission electron microscopy. Moreover, GISAXS lends itself to *in situ* and real-time studies. Eleven speakers presented their results and this was followed by a discussion on ways to improve the technique and the access to GISAXS facilities.

The first speaker was Detlef Smilgies from the Cornell High Energy Synchrotron Source (CHESS). Detlef presented a short introduction on the history and applications of GISAXS. He reviewed the rapid development of the technique, starting with the pioneering measurements of Levine and coworkers in the US and Naudon and coworkers in France during the late 1980s. Detlef provided a perspective on how three different X-ray communities—SAXS, diffuse reflectivity, and Grazing Incidence Diffraction (GID)—were converging through GISAXS. In the following talk, Sunil Sinha from the University of California presented an intriguing and mesmerizing talk on the underlying scattering theory associated with GISAXS with a focus on the Distorted Wave Born Approximation (DWBA). Examples were presented where wave-guiding effects, induced by the film interfaces, significantly enhanced the small angle scattering from the particulate matter inside or on the surface of the film. In the third talk, Ian Robinson from the University of Illinois presented a stimulating talk on coherent GISAXS investigations of granular micro-structures in thin metal films, performed at the Advanced Photon Source (APS). Speckled diffraction patterns were reported for gold nanoparticles prepared by the dewetting of a thin gold film on a solid support. The shapes of the gold nanoparticles were uniquely deduced from the speckle patterns.

After a short break, Till Hartmut Metzger from the European Synchrotron Radiation Facility (ESRF) presented a captivating review on combined GISAXS and GID studies of semiconducting nanostructures, so-called quantum dots, performed at HASYLAB and the ESRF. Particular emphasis was placed on the role of strain, size and chemical composition and their relationship to the growth, which are the crucial input parameters for the understanding of the electronic and optical properties of the quantum dots. Specific examples included InAs islands on GaAs and Ge pyramids on Si, for which detailed maps of strain and composition within the quantum dots were obtained. The following speaker, Alain Gibaud from the Université du Maine, presented a visually stimulating talk on *in situ* studies of surfactant templated silica thin films at the NSLS, which included the premier of several "reciprocal space" movies. In these studies, time-resolved GISAXS measurements were carried out simultaneously with gravimetric studies during the slow evaporation of ethanol from a film containing surfactant (CTAB), silica precursor (TEOS) and water to obtain silica mesostructures. The time evolution was exploited to probe the mechanism of the self-assembly process. Prior to lunch, Thomas Russell from the University of Massachusetts gave a lively and animated presentation on the assembly of nanoparticles at the interface of two immiscible fluids. Tom noted that the nanoparticles mediate the interactions between the two fluids, thereby reducing the interfacial energy.

After lunch, Christine Papadakis from the Technical University of Munich awoke the audience with an enlightening presentation on the inner structure of lamellar diblock copolymer thin films, as studied at CHESS and the ESRF. Christine showed how poly(styrene-*b*-butadiene) films undergo a morphological transition from parallel lamellae for short chains to perpendicular lamellae for long chains. Complementary *in situ* time-resolved GISAXS measurements were presented after the injection of toluene into the sample cell, which revealed both changes in the sample thickness and the lamella orientation during swelling on a timescale of minutes. Continuing the polymer theme, Matthew Misner from Prof. Russell's group at the University of Massachusetts presented an informative talk on real time studies of block copolymer thin films at the NSLS. Results for two different systems were examined: poly(styrene-b-ethylene oxide) diblock copolymers, where the orientation of the micro domains was normal to the surface, and poly(ethylene-*alt*-propylene-*b*-lactic acid), where the orientation was parallel to the substrate. Analysis of the time-resolved GISAXS provided information on the size, morphology, and orientation of the films during solvent evaporation. In the final polymer talk, Phong Du, a student from Cornell University working with Prof. Ober and Prof. Wiesner, presented an intriguing overview of their GISAXS studies at the CHESS. Poly (styrene-*b*-ethylene oxide) structures were exploited to create silica nanostructures, making use of the silica precursor being readily concentrated in the poly(ethylene oxide) block and successive calcination. In a second project, nanosieves were prepared from cylindrical diblock copolymer films by selective photoreactions, in order to remove one block, while cross-linking the other for stability. To close out the session, Oleg Gang from Brookhaven National Laboratory presented a fascinating talk on liquid films on nano-sculptured surfaces. By varying the chemical potential difference between the liquid-vapor coexistence, small nanometer pits were filled with an organic liquid. By combining GISAXS and X-ray reflectivity at the NSLS, detailed information could be obtained on both the liquid in the pits and the thin wetting film above the surface.

After a short break, Gilles Renaud from the Commissariat à l'Energie Atomique (CEA) in Grenoble provided an inspiring whirlwind presentation of their work on real-time *in situ* investigations of the morphology, organization, and internal structure of growing metal nanoparticles on oxide surfaces in ultra-high vacuum at the ESRF. Results were presented for palladium, silver, and platinum on MgO(001) as well as for copper on alumina, gold on TiO_2, and copper and silver on ZnO. Combined GISAXS and wide-angle X-ray scattering provided a wealth of information on the growth modes and particle morphology. Quantitative information could be extracted by theoretical modeling within the framework of DWBA. In the final presentation, Jin Wang from Argonne National Laboratory gave a thought-provoking talk on the kinetics of nanocomposites obtained from both SAXS and GISAXS measurements at the APS. Jin showed that the motion of the nanoparticles is highly anisotropic.

Following the talks there was an enthusiastic discussion on the future of GISAXS methods, including the needs of the emerging community. There was wide agreement that one of the key features of GISAXS is the ability to carry out real-time, *in situ* measurements. While there are currently few dedicated GISAXS beamlines, GISAXS capabilities can often be implemented on existing SAXS or GID beamlines through the addition of a 2D detector. There was a lively discussion on CCD detectors, including the need for faster readout times. For soft matter applications, it was noted that it is often desirable to combine GISAXS with reflectivity and SAXS measurements. Simultaneous optical measurements of the film thickness can be very useful for *in situ* experiments. For hard matter applications, it was noted that it is essential to combine GISAXS measurements with GID studies in order to obtain shape and internal structural information. Finally, it was remarked that future GISAXS facilities should be user-friendly and well supported in order to open up the technique to non-specialists. ■

Acknowledgements

The workshop was sponsored by the Users Executive Committee of the National Synchrotron Light Source and Certified Scientific Software, the maker of spec X-ray software. Brookhaven National Laboratory is supported by the U.S. DOE Contract No. DE-AC02-98CH10886. CHESS is a national user facility supported by NSF/NIH/NIGMS award DMR 0225180.

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