

SLS Symposium on Nanostructures and Nanoparticles

Tuesday, May 13, 2014

10:00 to 11:45, WBGB/019

10:00 Surface sensitive measurements on the nanometer scale by means of grazing emission X-ray fluorescence

Yves Kayser, J.-Cl. Dousse, P. Hönicke, J. Hoszowska, M. Pajek, J. Szlachetko, and J. Sá

10:30 Lithography at Beyond EUV for the Future of the Semiconductor Industry

Nassir Mojarad, M. Vockenhuber, J. Gobrecht, and Y. Ekinici

11:00 Coffee

11:15 Mechanism of Gold Nanoparticle formation and aggregation using in-situ SAXS measurements

Jun Han and Andreas Menzel

Surface sensitive measurements on the nanometer scale by means of grazing emission X-ray fluorescence

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The grazing emission X-ray fluorescence (GEXRF) technique allows for surface-sensitive studies with nanometer-scale accuracy in the depth direction by measuring the intensity variation of an X-ray fluorescence (XRF) line with the grazing emission angle. The probed depth scale varies between a few nanometers and several hundreds of nanometers and depends pronouncedly on the grazing emission angle at which the XRF signal is detected. The reasons are the refraction of the fluorescence X-rays at the sample surface interface and the implicit long emission paths within the sample matrix. The surface sensitive character of GEXRF is especially useful for the non-invasive study of sample systems of interest for the micro-electronics industry where progresses made over the last years relied, among others, on the down-scaling of device sizes.

In this perspective, the detection limits of GEXRF for different trace impurities on Si wafer surfaces were investigated. Further applications were depth-profiling measurements on the dopant distribution in low-energy ion-implanted Si and Ge wafers and on Al-layered Si wafers with nominal film thicknesses varying from 1 to 150 nanometers. The deposited Al surface layers were characterized in terms of layer thickness, layer density, oxidation and surface roughness. GEXRF can also be used for the characterization of nanoparticles on the top of wafer surfaces in terms of shape and size and offers as well sensitivity on the core and shell thickness of alloyed core-shell nanoparticles of interest for catalysis.

Usually the intensity variation of the considered XRF line with the grazing emission angle is assessed in a series of sequential measurements. Recently it was shown that the angular intensity dependence of the XRF signal can as well be measured at a single position of the sample detector arrangement by using an angular dispersive arrangement based on a position-sensitive area detector. This scanning-free approach is especially of interest if the grazing emission geometry is to be combined with other scanning-based techniques, e.g., X-ray absorption (XAS), and potentially also, because of its single-shot characteristics, for surface-sensitive time-resolved in-situ experiments.

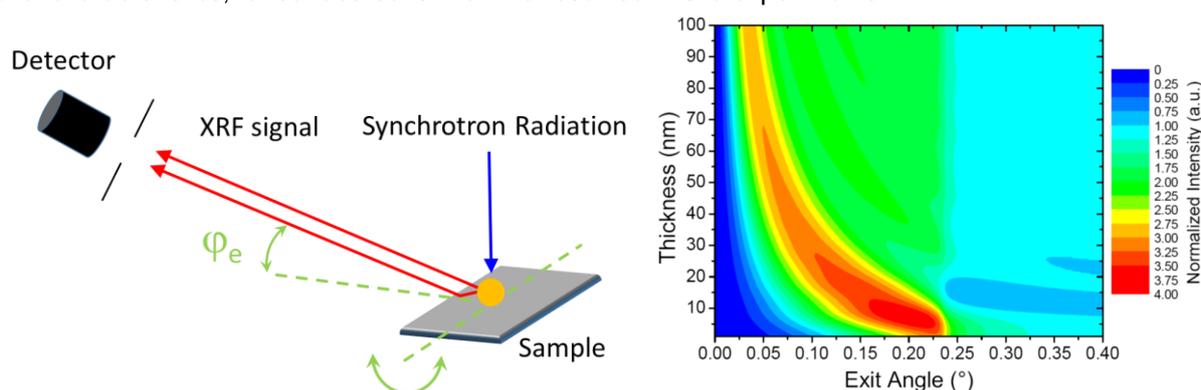


Figure 1: The principle of GEXRF consists in recording the intensity dependence of the XRF signal on the grazing emission angle in the angular range around the critical angle. In the right hand panel the sensitivity of the GEXRF intensity profile for the Pt $L\alpha_1$ X-rays on the diameter of spherical Pt particles on the top of a Si surface is shown.

References:

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- Y. Kayser, J. Szlachetko, D. Banaś, et al., Spectrochim. Acta B 88, 136-149 (2013).
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Lithography at Beyond EUV for the Future of the Semiconductor Industry

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Extreme ultraviolet (EUV) lithography at 13.5 nm wavelength has been considered as the main candidate for reaching the future technological nodes of the roadmap of the semiconductor industry. Lithography at this wavelength is expected to be the semiconductor industry's main patterning scheme for the next decade, after which it reaches the resolution limit. Afterwards, reduction of the wavelength to 6.x nm wavelength, coined as Beyond EUV (BEUV), is the main candidate for photon-based lithography at sub-10-nm resolutions.

We present lithography at 6.5 nm wavelength for patterning structures with half-pitch (*HP*) smaller than 22 nm. We quantify BEUV lithography performance by evaluating crucial parameters such as critical dimension and line-edge-roughness, and comparing them with EUV lithography at 13.5 nm. We, moreover, discuss the contribution of different physical limitations, such as shot noise and flare that might hinder the utilization of BEUV for fabrication at the diffraction limit.

To the best of our knowledge, our results are the first demonstration of successful patterning at BEUV. This is due to the combination of our high-resolution broadband mask technology and the precise performance tool at the XIL-beamline at the SLS, which has enabled nanopatterning at the photoresist resolution limits.

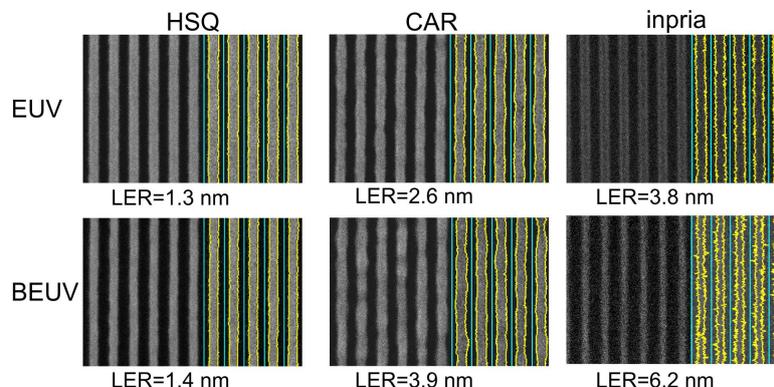


Figure 2: High Resolution Lithography at EUV and BEUV: SEM images of $HP=22$ nm line/space patterns of different photoresists exposed at EUV (top) and BEUV (bottom). Yellow lines show the analyzed profile, overlaid on the corresponding lines and the average LER is stated below each image. The photoresists we study are hydrogen silsesquioxane (HSQ), an organic chemically amplified resist (CAR), and Inpria.

References:

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- N. Mojarad, M. Vockenhuber, L. Wang, B. Terhalle, and Y. Ekinici, "Patterning at 6.5 nm Wavelength Using Interference Lithography," *Proc. SPIE* 8679, 867924 (2013).

Mechanism of Gold Nanoparticle formation and aggregation using in-situ SAXS measurements

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ABSTRACT

Gold nanoparticles (AuNPs) have been prepared by reduction of gold salts with ascorbic acid in aqueous solution with/without surfactant [1, 2]. The gold nanoplates formation process undergoing a nucleation and growth from the gold seeds to the AuNPs at the initial stages and a transformation from the AuNPs to the nanoplates in the second stage of the reaction were followed by in situ Small Angle X-ray Scattering measurements (SAXS) [3]. Modeling the scattering intensity allowed us to distinguish different stages involving nucleation, primary particle formation and particle coalescence.

The prepared AuNPs can be further stabilized and functionalized. We also investigated the stability of the complex of AuNPs with protein, bovine serum albumin (BSA) especially upon pH change by SAXS [4]. The AuNPs aggregation can be induced by BSA proteins in a relatively small pH range close to the isoelectric point of BSA. The SAXS data provided a direct evidence for aggregation of 25nm individual AuNPs occurred with an interparticle distance. The aggregation is reversible by adjusting the pH of the BSA-AuNPs solution.

A microfluidic flow-through cell for combined in-situ SAXS and UV-Vis measurements of liquid samples has been designed to have a reliable and precise measurement in continuous-flow mode. In the system, a combined spectroscopic and SAXS approach has been established and online monitor and control of flow rate, temperature and sample conditions such as concentration and pH allows studying dynamical processes in biological and soft-matter systems with changing physical and chemical conditions. The experiments of SAXS/Wide-angle X-ray scattering/UV-Vis studies of our AuNPs samples using this cell will be carried out soon to get more detailed information about the gold formation and aggregation process.

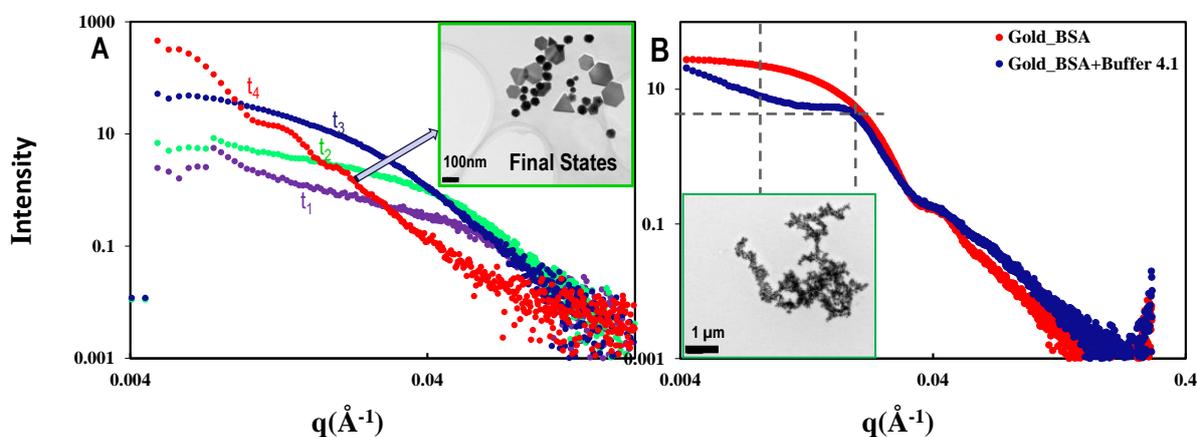


Figure 1: (A) SAXS patterns obtained during the formation of the gold nanoplates and TEM image of gold nanoplates at final state; (B) SAXS pattern of BSA-AuNPs sample without buffer and corresponding SAXS pattern and TEM image of the sample with buffer (pH=4.1).

References

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