Real time study of local order in thin films by grazing incidence total scattering and pair distribution function analysis

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Pair distribution function (PDF) analysis has become a widely used and most effective tool to study the local structure of materials that exhibit some degree of disorder. With the increasing availability of high-energy x-ray sources equipped with large and fast area detectors, PDF has advanced into the field of *in situ* and *operando* studies. Nowadays, PDF is indispensable to follow processes in manifold bulk-type systems such as chemical reactors, electrochemical cells, mechanical testing setups, etc. More recently, the PDF technique has also been utilized to investigate thin films. Different approaches to thin film PDF have been applied, including (i) the exfoliation of the film from the substrate to grind it up into a powder [1], as well as measuring the film on the substrate in transmission under normal incidence on the surface [2]. While both of these methods are experimentally similar to bulk measurements with respect to the data collection and evaluation, they have particular drawbacks: for method (i), film-specific features such as preferred orientation may be lost and the structure modified by the mechanical treatment, and case (ii) provides an unfavorable signal to background ratio, given that the scattering from both the film and the substrate is collected and the thickness ratio is typically of the order of a factor 1000 (nanometer vs. micrometer range). In this presentation, we demonstrate the advantages of surface diffraction type PDF measurements under grazing incidence (GIPDF) to quantitatively analyze thin films with thicknesses down to a few nanometers [3]. In contrast to previous GIPDF studies, we use microfocused high energy x-rays (>60 keV) and a fast area detector to obtain high quality PDF data on the time scale of seconds to enable *in situ* and *operando* studies of thin films in real time. In a first *in situ* PDF analysis of thin film deposition [4], we followed the growth and strain evolution of sputtered platinum layers. This presentation highlights perspectives and challenges for future applications of GIPDF to *operando* and *in situ* thin film studies.

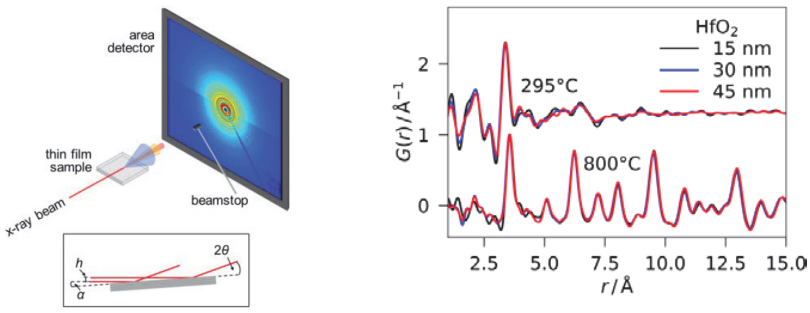

Figure 1: (left) Schematic illustration of the grazing incidence geometry, experimental setup and illumination of the sample by the x-ray beam (inset, with beam height h, incidence angle α, and scattering angle 2θ);
(right) PDFs of spin-coated HfO_2 thin films heat-treated at different temperatures to form amorphous (295 °C) and crystalline (800 °C) layers, demonstrating similar data quality for the varying thicknesses.

[1] S. R. Bauers *et al*., *J. Am. Chem. Soc.* **137** (2015), 9652.
[2] K. M. Ø. Jensen *et al, IUCrJ* **2** (2015), 481.
[3] A.-C. Dippel et al., *IUCrJ* **6** (2019) 290.
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