ESRF	**Experiment title:** Atomic layer deposition: unraveling process-structure relationships	**Experiment number**: MA-4987
Beamline: ID15A (C02)	**Date of experiment**: from: 26 October 2021 at 08:00 to: 28 October 2021 at 08:00	**Date of report**: 21 December 2021
Shifts: 6	**Local contact(s)**: Stefano Checchia	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists): Proposers: Jolien Dendooven[1] (*), Stefano Checchia (LC), Christophe Detavernier[1]; Participants: Ruben Blomme[1] (*), Lowie Henderick[1] (*), Rahul Ramesh[1] (*); [1]Ghent University, Krijgslaan 281/S1, 9000 Gent, Belgium

Report:

Atomic layer deposition (ALD) is a thin film deposition method offering atomic level control over the film thickness and exceptional conformality on complex 3D supports. ALD is performed at relatively low temperatures and, in the case of oxides and phosphates, often yields amorphous materials. However, the atomic scale structure of the as-deposited amorphous thin films is largely unknown. Here, we aimed to access the local- and medium-range order of atoms in ALD-grown thin films by means of pair distribution function analysis of grazing incidence X-ray total scattering (GI-PDF) measurements. To this end, several series of samples were prepared at the users' laboratory at Ghent University and brought to the ID15A beamline.

Experimental.

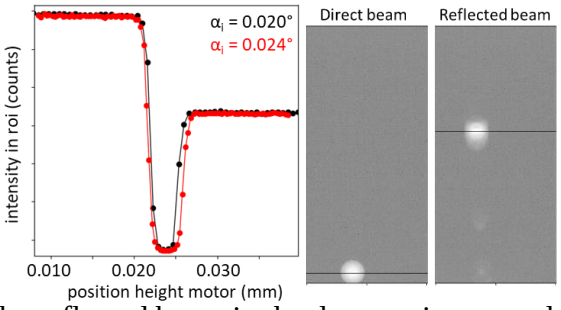
Sample preparation. Four sets of ALD-prepared samples have been investigated: (1) RuO_2 samples, (2) VO_x samples, (3) Ni phosphate samples, and (4) Pt samples. The first three sets of samples comprised (*i*) amorphous thin films grown by employing different ALD growth conditions and (*ii*) crystalline thin films obtained by post-deposition annealing. The fourth set of samples consisted of a series of samples with different Pt loading (by varying the number of applied ALD cycles). The deposits in this case are known to be 3D nanoparticles instead of a 2D film. Most of the thin films and nanoparticles were prepared on 1 cm x 1 cm fused quartz slides. The RuO_2 layers were grown on Si wafer. For the measurements, the samples were mounted (using double sided tape) on a PEEK disk which was fixed on a small goniometer (see picture on the right). Only part of the sample was positioned on the PEEK; the other, suspended part was positioned in the beam such that no PEEK is irradiated, as this would give rise to unwanted background scattering.

Beamline configuration. Total scattering experiments employing a grazing incidence geometry are an emerging approach to study thin films, and the present experiment concerned one of the first applications at the ID15A beamline. To focus the beam to a size of 2.5-3 μm (V) by 6 μm (H), the 64 keV beam is attenuated and refractive lenses are positioned in the beam path 3 m before the sample. Slit systems and a pinhole closer to the sample are inserted to reduce background scattering. Sample alignment was done by making use of a CMOS imaging detector while data were acquired with the Pilatus3 X CdTe 2M diffraction detector.

Results.

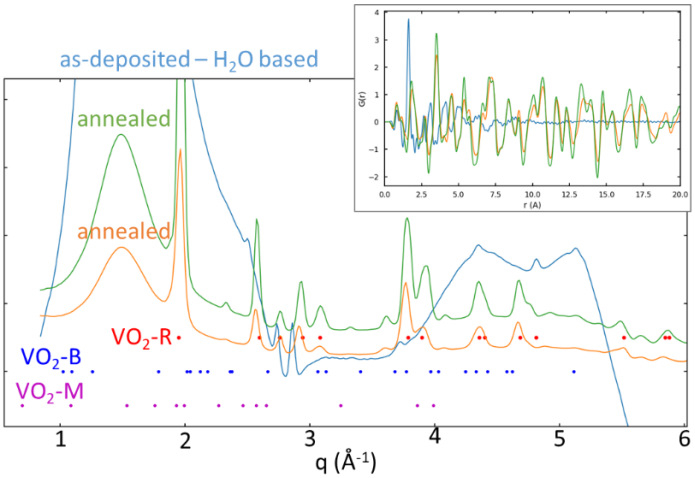
Sample alignment procedure. Following the optimization of the beamline to define a microfocused beam, a considerable part of the beamtime was spent on refining the sample alignment procedure. While aligning the first samples easily took several hours, the alignment time per sample was significantly reduced to ca. 20 minutes by the end of the campaign. A first step in the alignment concerned manually adjusting the knobs on the small goniometer such that the tilt and height of the sample, as seen on a camera screen, are visually aligned parallel to the diffractometer horizontal plane. Then, with unfocused beam and open slits, we looked for the "shadow" of the sample on the imaging detector and further adjusted the tilt and height of the sample based on this image. Next, with focused beam, the height of the sample was varied while monitoring the intensity in the region where

the direct beam hits the imaging detector. For a sample that is perfectly parallel to the beam, the intensity as a function of the sample height should be marked by a step; with the width of the step defined by the X-ray beam height. When the incidence angle is slightly positive, total reflection occurs during the height scan, resulting in a step immediately followed by a dip in intensity in the 'direct beam region' on the detector (see figure). The width of this dip increased with increasing tilt angle, due to an increase in projected sample height (10 mm · sin(α_i)). Based on the position of the reflected beam in the detector image and the sample-to-detector distance, we calculated the incidence angle that gave rise to the reflected spot. By taking images at various grazing angles and repeating the calculations, we confirmed the correct interpretation of the observed spots, allowing us to select the tilt corresponding to the target incidence angle. The sample height was further optimized by scanning the height and monitoring the intensity in a region of the detector image where the reflected beam should appear; the target height being the one for which this intensity reached a maximum.

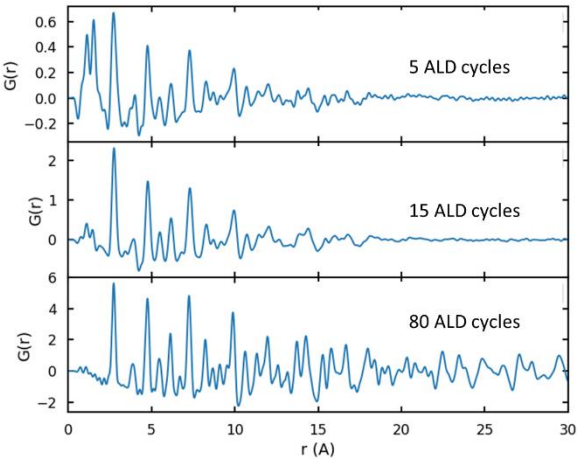


Data processing. 2D scattering images were recorded for several incidence angles, below and close to the theoretical critical angle of the thin films. At each angle, 4 images at different detector positions were recorded, allowing us to average and add intensity to the otherwise 'dead' module gaps in the image. The sample-to-detector distance and the direct beam position were determined based on a transmission measurement of a Cr_2O_3 calibration sample. Data reduction was carried out in PyFAI, yielding intensity as a function of q. Measurements of a blank quartz sample and without sample were also acquired for background substraction purposes. It was found that adding a lead shield at the exit side of the lens system reduced parasitic scattering in the data.

Initial results. **<u>VO_x thin films.</u>** ALD of VO_2 with the TEMAV precursor can be achieved with H_2O or O_3 as the second reactant, yielding amorphous thin films based on lab XRD. When annealed in O_2/He (P_{O2} few Pa), the H_2O-based film immediately crystallizes into the VO_2-R phase, while the O_3-based film first crystallizes in VO_2-B, and then VO_2-R. This suggests a different atomic scale structure for the as-deposited films. Unexpectedly the H_2O-based film displayed weak diffraction signals (see figure). Peak identification and PDF analysis are ongoing. No diffraction peaks were seen in the pattern for the as-deposited O_3-based film. In fact, in the PDF analysis, it turned out to be hard to discern the scattering of the film from the background originating from the substrate.



<u>RuO_2 thin films.</u> Also the as-deposited RuO_2 thin film that was X-ray amorphous in a lab-based XRD instrument displayed diffraction signals, which could be linked to metallic Ru. Based on XPS results however, the majority of the film should be RuO_2. PDF analysis will be carried out and atomic distances will be compared to both Ru and RuO_2 references. We are currently looking into masking of the Si diffraction spots to obtain a cleaner 1D pattern in q-space first. **<u>Pt nanoparticles.</u>** Here, we aimed to explore the feasibility of studying low Pt loadings with GI-PDF. Good quality PDFs could be obtained (see figure), even for the sample grown with only 5 ALD cycles for which the number of Pt atoms per surface area is expected to be lower than a theoretical monolayer. This illustrates a high potential of the GI-PDF method to study nucleation phenoma during metal ALD in the ultralow loading regime. (<u>Ni phosphate thin films.</u> Analysis ongoing.)



Conclusion and outlook.

While in-depth analysis of the data is ongoing, GI-PDF at ID15A is demonstrated to be a valuable approach to study ALD-grown thin films. In future measurements, the sample alignment should be further optimized to reduce as much as possible the contribution of the quartz substrate in the data. We believe the contribution may be caused by the beam hitting the front edge of the sample. Therefore, a larger sample size would be desired and/or the beam should hit the sample closer to the back edge of the sample.