Development of a Home-Built Atomic Layer Deposition Reactor for *In-Situ* Synchrotron GISAXS and XAS Characterization

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The high photon flux and energy tunability of synchrotron facilities provide a clear advantage for the characterization of Atomic Layer Deposition (ALD) processes. At the ALBA synchrotron, a mobile custom-built reactor has been developed to enable *in-situ* monitoring of film growth and characterization using up to now two X-ray-based techniques: Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) and X-ray Absorption Spectroscopy (XAS). The ALD reactor has been designed to be compatible with both techniques, and it can currently operate at two different ALBA beamlines (NCD-SWEET for GISAXS measurements and NOTOS for XAS) to provide complementary insights into film morphology and chemical composition.

The setup consists of a high-vacuum, pump-type reactor compatible with multiple deposition processes. It achieves a base pressure of at least 10^{-6} mbar and is equipped with a sample heater capable of reaching 1000 °C, allowing *in-situ* annealing under different atmospheres without exposing the sample. To accommodate the specific geometries required for each X-ray technique, the mobile reactor features two different configurations: for GISAXS, two CF40 flanges with mica windows allow the passage of incident and reflected X-rays, while for XAS, two perpendicularly oriented flanges with 50 µm-thick Kapton windows enable measurements covering all the beamline energy range (4.7 - 30 keV), with the fluorescence detector used (SDD with 13 channels) at 90° relative to the X-ray beam and the sample at around 30° with respect to the incident beam. Fig. 1 A shows the reactor in the GISAXS configuration at the NCD-SWEET beamline.

To validate the reactor's performance, TiO_2 thin films were deposited using titanium isopropoxide (TTIP) as a precursor in combination with water on SiO_2/Si substrates. The process exhibited a growth rate of 0.15 Å/cycle, allowing the study by GISAXS and XAS in the sub-nanometer range during the initial growth cycles. Fig. 1 B presents XANES measurements at the Ti K-edge over 1000 ALD cycles at 200 °C, revealing an increase in the XANES-edge jump intensity within the first five cycles. Since the edge jump magnitude is proportional to the TiO_2 thickness, these results indicate different growth regimes: a first stage significantly slower for 325 cycles, followed by a stage where the growth rate becomes linear. After 325 cycles, XAS measurements confirmed the formation of TiO_2 with features consistent with anatase-like coordination. The XANES features during the first 325 cycles are consistent with previously studied electronic effects in ultra-thin TiO_2 films[1]. Additionally, XAS mapping over a 20 mm x 20 mm area validated the film's uniformity.

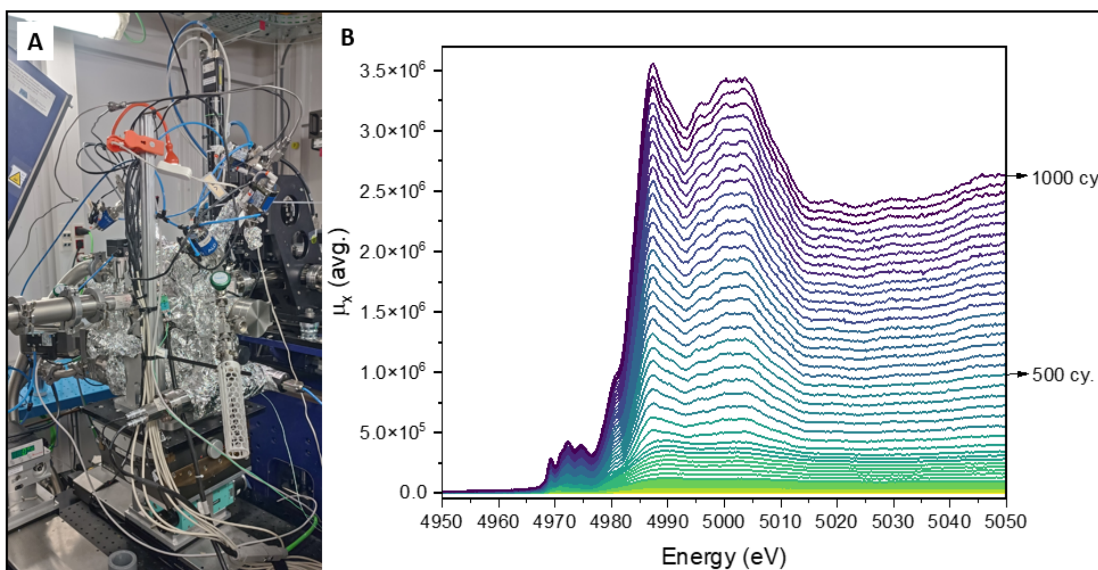

Fig. 1. (A) Picture of the ALD reactor installed on NCD-SWEET beamline in ALBA synchrotron. (B) *In-situ* Ti K-edge spectra of ALD-grown TiO_2, using TTIP as precursor, deposited at 200°C onto SiO_2/Si.

References:

[1]Tallarida, M.; Das, C.; Schmeisser, D. Beilstein J. Nanotechnol. 2014, 5, 77–82. doi:10.3762/bjnano.5.7