In Situ Characterization of ALD in Mesoporous Thin Films by Grazing Incidence Small Angle X-Ray Scattering

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Mesoporous materials are of interest to a broad range of applications such as the development of optical, electronic and sensor devices, and catalytic surfaces. For many of these applications, the interior surface of the porous material needs to be functionalized. ALD has become an attractive technique for tailoring porous materials because of its ability to produce conformal coatings.[1] We present a synchrotron-based *in situ* characterization of TiO_2 ALD in mesoporous titania thin films by means of x-ray fluorescence (XRF) and grazing incidence small angle x-ray scattering (GISAXS).

GISAXS is a powerful technique for the morphological characterization of nanoscopic features (particles, pores, granules) at surfaces, at buried interfaces or in thin films. In the case of mesoporous thin films, the technique can reveal information on the ordering and spacing of the pores. A GISAXS experiment consists of measuring the diffuse scattering around the specularly reflected beam at a fixed incident angle. A typical dynamical feature of diffuse scattering is the Yoneda peak, i.e., an enhancement of the scattered intensity at the exit angle which equals the critical angle of the scattering medium.

Porous titania films containing ink-bottle shaped mesopores with ~3nm wide pore necks were coated with TiO_2 ALD in an UHV chamber installed at the National Synchrotron Light Source at Brookhaven National Laboratory. XRF and GISAXS measurements were performed every 1 and 2 ALD cycles, respectively. Fig.1 shows the GISAXS spectrum measured on the uncoated titania film. The clear interference pattern revealed an anisotropic pore structure in the film, in accordance with an electron tomography study of the porous film. During ALD of TiO_2 in the mesopore network, the critical angle of the material was probed *in situ* using GISAXS (Fig.2). During the first ca. 24 ALD cycles, the critical angle, which is proportional to the square root of the average electron density of the mesoporous thin film, increased gradually, indicating film densification. Thereafter, the critical angle remained constant, meaning that the density of the film no longer changed. This result is in agreement with *in situ* XRF data showing the amount of Ti atoms deposited in the film.[2] This work demonstrates that both XRF and GISAXS are suitable for *in situ* monitoring the filling of mesoporous thin films by ALD.

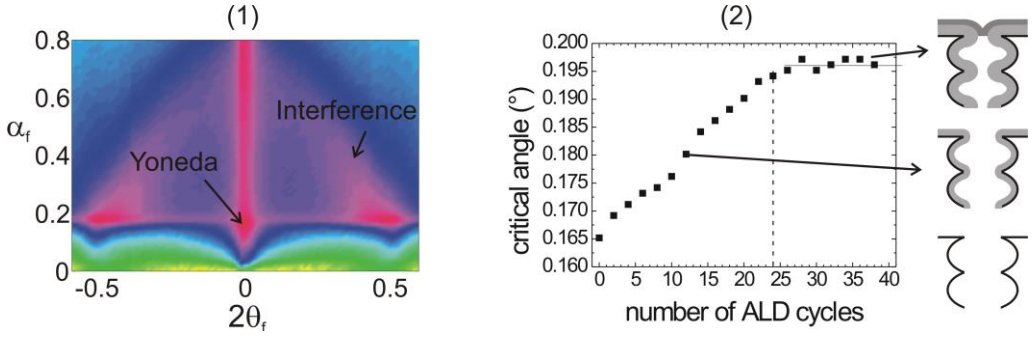

Fig. (1) GISAXS spectrum measured on a mesoporous titania film. (2) Evolution of the critical angle of a mesoporous titania film during TiO_2 ALD, as measured by *in situ* GISAXS.

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