In situ x-ray fluorescence measurements during ALD on flat substrates and in nanoporous catalyst support materials

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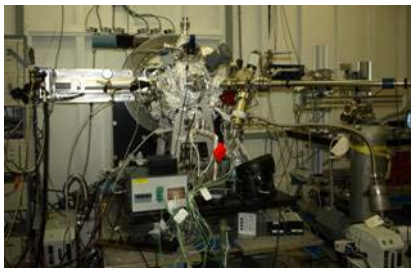
Due to its ability to produce conformal coatings, ALD has become an interesting candidate for functionalizing porous materials, particularly in the field of catalysis. In recent years, the ALD modification of anodic aluminum oxide membranes with pore diameters of tens of nanometers has been investigated in detail [1]. However, few efforts were made to coat pores with diameters < 10nm. In the present work, we demonstrate that synchrotron based in situ x-ray fluorescence (XRF) measurements can be used to monitor the incremental increase of deposited material during each ALD cycle, even on flat Si substrates (figure (a)). Secondly, using this in situ XRF technique, we prove that ALD can be used to deposit TiO_2 into meso- (~6nm) and microporous (<1nm) films and powders.



Zeotile-4 (ZT-4) and Silicalite-1 (S-1) material were spin coated as thin films onto SiO_2 substrates. The ZT-4 films had a porosity of 60% and contained mesopores (~6nm) in addition to micropores. The S-1 films had a porosity of 35% and contained only micropores. The films were coated with TiO_2 ALD from TDMAT and H_2O in an UHV chamber installed at the National Synchrotron Light Source at Brookhaven National Laboratory. After every deposition cycle, we measured the Ti XRF intensity. From the experimental data we obtained information on the growth per cycle on flat Si substrates and in nanoporous films. We found that TDMAT molecules with a diameter of ~0.7nm can penetrate into micropores with diameters somewhat smaller than 1nm. Furthermore, saturation of the growth rate in these porous films was proved.

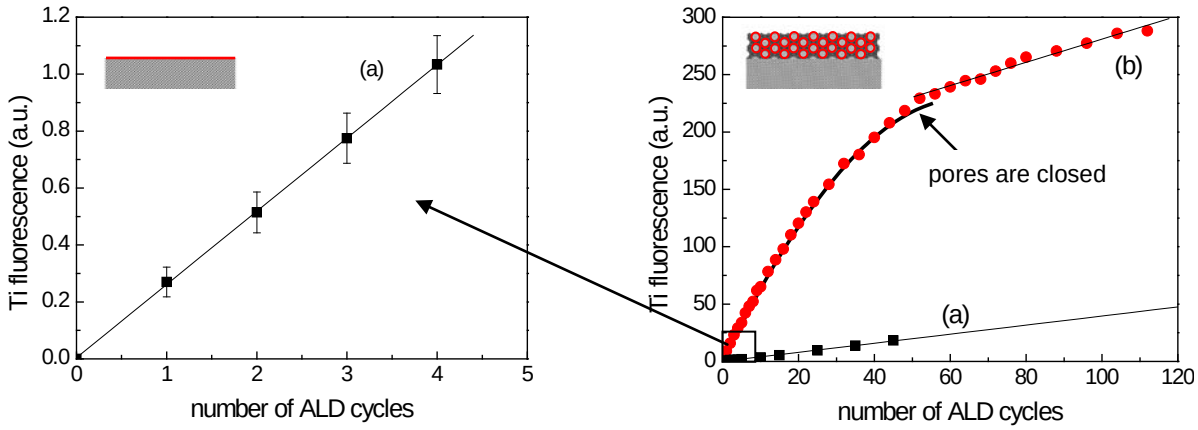


Figure: Ti XRF intensity (Ti Kα peak area normalized to the intensity of the incident beam) as a function of the number of ALD cycles recorded during deposition of TiO_2 on a flat Si substrate (a) and in a ZT-4 film with 6nm mesopores (b). As expected, much more material is deposited in the porous film. After 55 ALD cycles, the pores are completely filled and deposition proceeds on a 'flat' surface (characterized by linear growth). The results were in good agreement with calculations (bold solid line).

In addition, we show that Al_2O_3 ALD can be used to introduce catalytic activity in the originally inactive ZT-4 powder, as demonstrated by the catalyzed hydroconversion of decane.

[1] J. W. Elam, D. Routkevitch, P. P. Mardilovich, and S. M. George, Chem. Mater., 15, 3507 (2003).