Nucleation, Growth and Crystallization of ALD Catalytic Oxide Layers

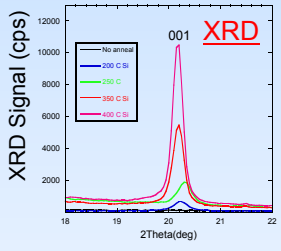
J. W. Elam[1], P. W. Klamut[1], J. E. Gerbi[2], G. Xiong[1], C. Y. Han[1], H. H. Wang[1], J. N. Hryn[1], M. J. Pellin[1]
Argonne National Laboratory[1], Argonne IL, University of Illinois[2], Urbana-Champaign IL

Abstract

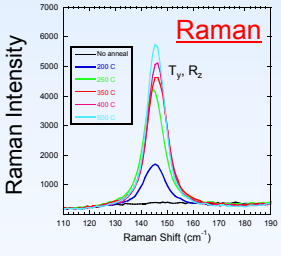
We are fabricating novel catalytic membranes by depositing ALD nanolaminate oxide layers onto anodic aluminum oxide (AAO) scaffolds. To fabricate these membranes optimally, one must address the chemistry underlying the nucleation and growth of the various ALD layers, as well as the crystallization that occurs when the membranes are heated during catalysis. In this study, the nucleation and growth of ALD Al_2O_3, TiO_2 and V_2O_5 on each other were studied, as was the crystallization of ALD V_2O_5 upon thermal annealing. ALD films prepared on planar substrates were analyzed using spectroscopic ellipsometry, x-ray diffraction, scanning electron microscopy and Raman spectroscopy. We found that by varying the underlying oxide layer, the growth rate of the subsequent overlayers could be enhanced or suppressed. These findings were confirmed using in-situ quartz crystal microbalance measurements. In addition, we found that V_2O_5 films annealed to progressively higher temperatures exhibit an amorphous to crystalline transition at a temperature that depends on the underlying substrate. Nanolaminate $Al_2O_3/TiO_2/V_2O_5$ films can be deposited on AAO to fabricate catalytic membranes of enhanced selectivity when compared with conventional powder catalysts.

Crystallinity vs. Annealing

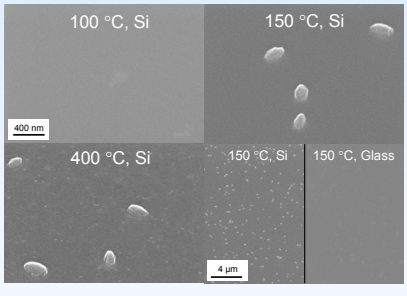
- V_2O_5 Films deposited on Si(111) using VOTP/H_2O_2 at 100°C
  - Anneal in air 60 minutes at various temperatures



Annealing Temperature (°C)	Average Grain Size (nm) (Scherer Eqn.)
200	17.3
300	14.9
400	19.3
500	23.2



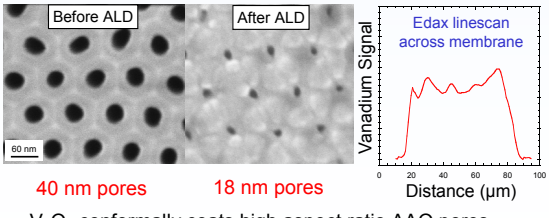
SEM



- V_2O_5 shows increased crystallinity and grain size with increasing annealing temperature

ALD V_2O_5 on AAO

- AAO membrane pore diameter d=40 nm, length L=60 µm, aspect ratio L/d=1500

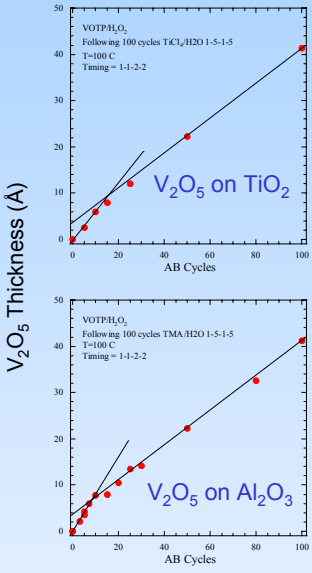


40 nm pores 18 nm pores

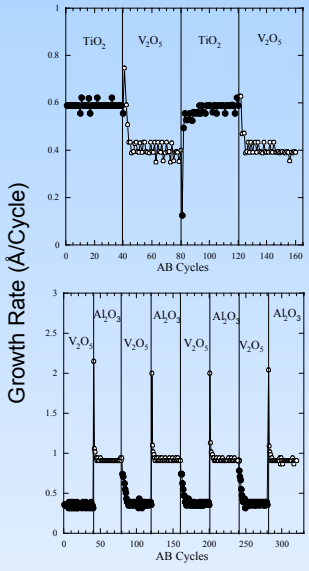
- V_2O_5 conformally coats high aspect ratio AAO pores

TiO_2/V_2O_5 and V_2O_5/Al_2O_3 nanolaminates

Ellipsometry



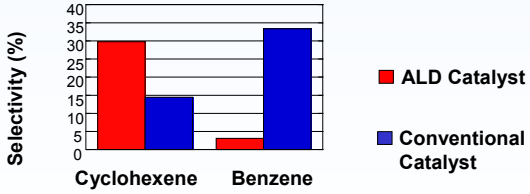
In Situ QCM



- V_2O_5 Growth enhanced on TiO_2 and Al_2O_3
- Al_2O_3 Growth enhanced, TiO_2 Growth diminished on V_2O_5

ALD/AAO Catalytic Membranes

Selective Oxidation:
Cyclohexane + O_2 → cyclohexene → benzene



- ALD catalyst shows higher cyclohexene selectivity

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