Spatially controlled atomic layer deposition in porous materials

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We describe a technique for depositing materials at controlled depths within porous substrates based upon the passivating effect produced by one precursor to prevent the adsorption of a second precursor. For example, a surface exposed to trimethyl aluminum is not reactive toward diethyl zinc. This effect, combined with Knudsen diffusion in which the precursor exposure times dictate the depth of penetration of the deposited layer, enables spatially controlled "stripe coating" within porous supports. We demonstrate ZnO stripes in anodic alumina and model the results using Monte Carlo simulations. Etching is identified as a potential problem for certain precursor combinations. © 2007 American Institute of Physics. [DOI: 10.1063/1.2822897]

Atomic layer deposition (ALD) is a thin film growth method using alternating, self-limiting reactions between gaseous precursors and a solid surface to deposit materials in an atomic layer-by-layer fashion.[1] These attributes allow highly conformal and uniform films to be deposited on complex, three-dimensional substrates such as aerogels,[2] powders,[3] and anodic aluminum oxide (AAO) membranes.[4] Functionalizing these porous substrates by ALD enables the synthesis of nanostructured catalysts.[4,5] Previously, ALD has been used to completely infiltrate porous substrates yielding uniform catalyst coatings on all interior surfaces. However, there are some advantages to applying the catalyst only at specific, controlled locations within the porous substrate. For instance, localized regions of different catalytic materials assembled in a specific sequence along the walls of a nanopore (i.e., "stripes") could afford precise control over a multistep catalytic process.

In the past, patterned ALD has been accomplished only on planar substrates.[6,7] In this article, we describe a method that enables patterned ALD in porous substrates at controlled depth locations. This method uses the passivating effect of one ALD precursor to prevent the chemisorption of a second precursor applied in a subsequent exposure. For instance, after a hydroxylated surface has been exposed to trimethyl aluminum (TMA), this surface will be unreactive toward the chemisorption of diethyl zinc (DEZ). Infiltration of nanoporous materials occurs via Knudsen diffusion so that the reactive sites tend to fill in order starting from the pore entrance.[8] Consequently, the pore entrance can first be reacted using a subsaturating TMA exposure. During the subsequent DEZ exposure, the DEZ will only adsorb on the interior pore surfaces further down from where the TMA was applied. The TMA and DEZ exposures can be followed by a saturating H_2O exposure to form the corresponding metal oxides and repopulate the surfaces with hydroxyl groups. By repeating this $TMA/DEZ/H_2O$ sequence, a ZnO stripe is formed in which the depth location and width are controlled by the durations of the TMA and DEZ exposures, respectively.

This procedure has been demonstrated using AAO membranes. The AAO membranes were prepared[9] with a pore diameter of 56 nm and a membrane thickness of 75 μm. A masking process[5] was used to preserve an aluminum ring around the perimeter of the AAO membrane allowing a gas-tight connection using face-seal fittings. During coating, the membranes were installed in a custom fixture to ensure that the precursors only contacted the membrane from one side. ALD was performed at 150 °C in a custom viscous flow reactor[10] using alternating exposures of DEZ/H_2O and TMA/H_2O to form ZnO and Al_2O_3, respectively. Titanium tetrachloride/H_2O and vanadium oxytriisopropoxide/H_2O_2 were used to form TiO_2 and V_2O_5, respectively. The ALD timing sequences can be expressed as (t1-t2-t3-t4-t5-t6) where t1, t3, and t5 are the exposure times for the first, second, and third precursors, respectively, and t2, t4, and t6 are the corresponding purge times with units in seconds.

Stripe-coating experiments were performed in AAO membranes using TMA as a masking agent to prevent subsequent DEZ adsorption. The duration of the TMA exposure was varied while keeping all other sequence times constant. 20 ALD cycles were performed using the sequence $TMA/DEZ/H_2O$ with the timing sequence (t1-5-4-10-5-15) using t1=0.5, 1.0, and 1.5 s. The coated membranes were then cleaved, embedded in silver epoxy, polished flat, and carbon coated. Elemental maps were acquired using a Hitachi S4700 scanning electron microscope with a field emission gun electron beam source and energy dispersive analysis of x-ray (EDAX) detector. The EDAX signals yield elemental concentrations averaged over ~20–100 AAO pores.

Figure 1 shows the Zn $L\alpha$ EDAX maps versus the TMA exposure time. The Zn signal appears as a stripe, which shifts to greater distances and also narrows with longer TMA exposure times. Clearly, the TMA serves as an effective mask for the subsequent ZnO growth because ZnO does not deposit on the outer portions of the AAO pores that have been exposed to the TMA. Previously, self-assembled monolayers (SAMs) of long-chained, hydrophobic alkanes such as docosyltrichlorosilane (DTS) have been used as masking agents for selective ZnO ALD.[6] However, the DTS SAM can only
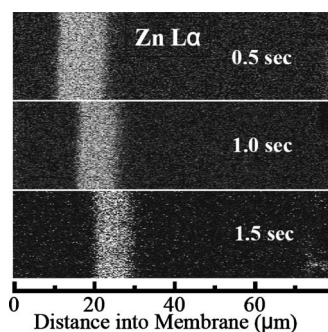
FIG. 1. EDAX elemental maps for Zn $L\alpha$ following deposition of ZnO stripes in AAO varying only the TMA exposure time.

be patterned on a flat surface, while our method allows selective ZnO ALD on three-dimensional structures.

Figure 2(a) shows line scans generated by integrating the EDAX maps in Fig. 1 along the lateral dimension parallel to the AAO pores. Figure 2(b) shows the results of Monte Carlo simulations[8] of the ZnO stripe coating experiments using the same timing sequences as those in Fig. 2(a). These simulations modeled the AAO pores as a one-dimensional array and followed the trajectories of individual TMA and DEZ molecules. Knudsen diffusion was modeled as a one-dimensional random walk of hop length d, the local pore diameter. After each hop, a molecule could react on an empty site with a probability equal to the reactive sticking coefficient 10^{-3}. Each trajectory continued until the molecule reacted or exited the tube.
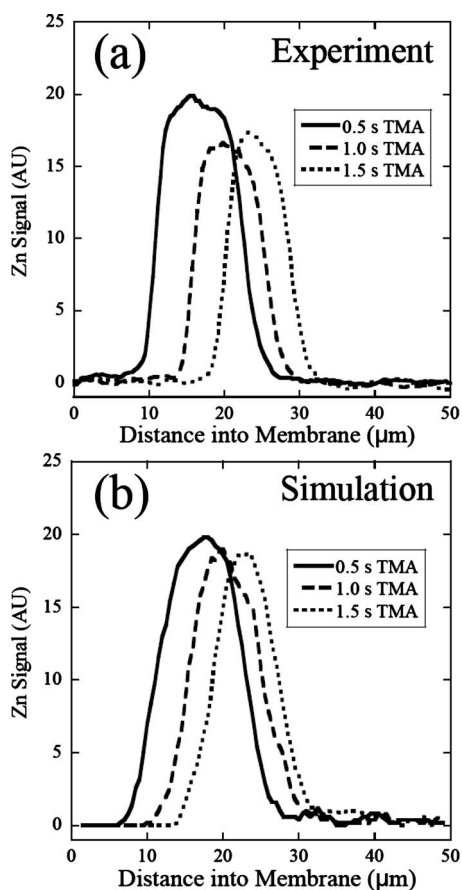

FIG. 2. Experimental (a) and simulated (b) Zn $L\alpha$ line scans for ZnO stripes in AAO corresponding to the elemental maps in Fig. 1.
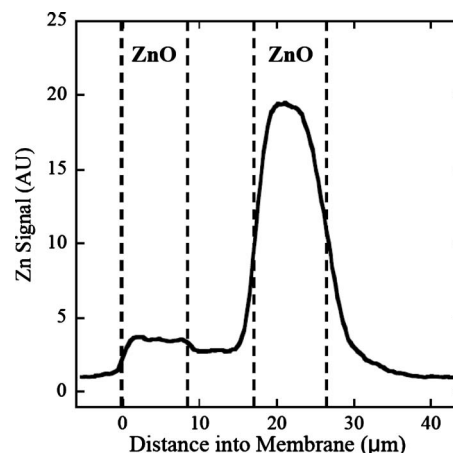

FIG. 3. Zn $L\alpha$ line scan following attempted two-stripe ZnO coating in AAO. Dashed lines indicate expected locations of Zn stripes.

The simulations agree well with the experimental results. In particular, the simulations confirm that the ZnO stripes narrow with increasing TMA exposure times. Analysis of the Monte Carlo simulations reveals the origin of this effect. Using longer TMA exposures, the masked region extends farther into the nanopores causing a smaller fraction of the DEZ molecules in each cycle to encounter an empty site before exiting. Because fewer DEZ molecules react, the ZnO stripe narrows.

We attempted to create a two-striped membrane using the pulse sequence and timing: DEZ/TMA/DEZ/H_2O (1-2-2-5-8-16-10-20). This treatment should produce two distinct Zn stripes of approximately equal intensity. The resulting Zn line scan is shown in Fig. 3. Contrary to the expectation, only one prominent Zn stripe is observed in the interior while the Zn stripe at the membrane inlet is greatly reduced. Furthermore, Zn is seen in the masked region between the two stripes. To understand this behavior, we conducted *in situ* quadrupole mass spectrometry measurements[11] using a similar ALD pulse sequence. During the TMA pulses that followed DEZ pulses, we observed signals at $m/e = 94$ and 79 (Fig. 4) with an intensity ratio corresponding to dimethyl zinc, indicating that Zn is etched from the membrane inlet during the TMA exposures. The dimethyl zinc can then react
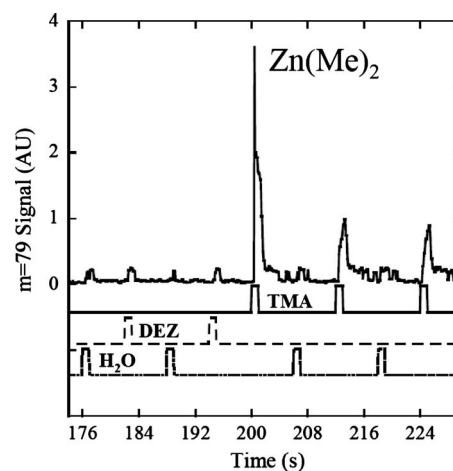

FIG. 4. Dimethyl zinc $m/e = 79$ signal vs time measured by *in situ* quadrupole mass spectrometry during DEZ/TMA/H_2O pulse sequence. Traces at the bottom of plot indicate the times when the labeled reactant pulses occurred.

with surface hydroxyl groups and deposit Zn between the stripes, as observed in Fig. 3. Etching of Zn by TMA has been observed previously.[12] This behavior may result from the larger formation enthalpy of Al_2O_3 (-845 kJ/mol Al atoms) compared to ZnO (-353 kJ/mol Zn atoms). This finding illustrates that some precursor combinations are not suitable for ALD stripe coating.

Using TMA as a masking agent, we have formed stripes of ZnO, TiO_2, and V_2O_5 at controlled depth locations within AAO membranes. We anticipate that this method is general and other precursors could be used as masking agents. We have also applied this method to other nanoporous supports including spherical silica gel particles. This technique will enable the fabrication of nanoporous membranes to catalyze sequential reactions.

[1] M. Ritala and M. Leskela, in *Handbook of Thin Film Materials*, edited by H. S. Nalwa (Academic, San Diego, 2001), Vol. 1, p. 103.

[2] J. W. Elam, J. A. Libera, M. J. Pellin, A. V. Zinovev, J. P. Greene, and J. A. Nolen, Appl. Phys. Lett. **89**, 053124-1–053124-3 (2006).

[3] S. Haukka, E. L. Lakomaa, and T. Suntola, in *Adsorption and its Applications in Industry and Environmental Protection Volume I: Applications In Industry*, edited by A. Dabrowski (Elsevier, New York, 1999), Vol. 120, pp. 715–750.

[4] M. J. Pellin, P. C. Stair, G. Xiong, J. W. Elam, J. Birrell, L. Curtiss, S. M. George, C. Y. Han, L. Iton, H. Kung, M. Kung, and H. H. Wang, Catal. Lett. **102**, 127 (2005).

[5] P. C. Stair, C. Marshall, G. Xiong, H. Feng, M. J. Pellin, J. W. Elam, L. Curtiss, L. Iton, H. Kung, M. Kung, and H. H. Wang, Top. Catal. **39**, 181 (2006).

[6] M. Yan, Y. Koide, J. R. Babcock, P. R. Markworth, J. A. Belot, T. J. Marks, and R. P. H. Chang, Appl. Phys. Lett. **79**, 1709 (2001).

[7] A. Sinha, D. W. Hess, and C. L. Henderson, J. Electrochem. Soc. **153**, G465 (2006).

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

[9] G. Xiong, J. W. Elam, H. Feng, C. Y. Han, H. H. Wang, L. E. Iton, L. A. Curtiss, M. J. Pellin, M. Kung, H. Kung, and P. C. Stair, J. Phys. Chem. B **109**, 14059 (2005).

[10] J. W. Elam, M. D. Groner, and S. M. George, Rev. Sci. Instrum. **73**, 2981 (2002).

[11] J. W. Elam, A. B. F. Martinson, M. J. Pellin, and J. T. Hupp, Chem. Mater. **18**, 3571 (2006).

[12] J. W. Elam and S. M. George, Chem. Mater. **15**, 1020 (2003).