Atomic Layer Deposition for the Conformal Coating of Nanoporous Materials

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ABSTRACT
Atomic layer deposition (ALD) is ideal for applying precise, conformal coatings over nanoporous materials. We have recently used ALD to coat two nanoporous solids: anodic aluminum oxide (AAO) and silica aerogels. AAO possesses hexagonally ordered pores with diameters d~10 nm and thicknesses L~70 microns. The AAO membranes were coated by ALD with successive layers of Al2O3, TiO2 and V2O5 to fabricate catalytic membranes. SEM, TEM and EDAX analysis of the membranes demonstrate that the ALD layers uniformly coat the extremely high aspect ratio (L/d~104) AAO pores. These catalytic membranes show remarkable selectivity in the oxidative dehydrogenation of cyclohexane. Additional AAO membranes coated with ALD Pd films show promise as hydrogen sensors. Silica aerogels have the lowest density and highest surface area of any solid material. Consequently, these materials serve as an excellent substrate to fabricate novel catalytic materials and gas sensors by ALD. In this study, both thin film and monolithic aerogels were coated by ZnO ALD and the properties of the aerogels were investigated as a function of the coating thickness.

INTRODUCTION
Atomic layer deposition (ALD) utilizes a binary reaction sequence of self-saturating chemical reactions between gaseous precursor molecules and a solid surface to deposit films in a monolayer-by-monolayer fashion [1]. These attributes make ALD an ideal method for applying precise, conformal coatings over nanoporous materials. In this manuscript, we describe recent work exploring the ALD coating of two nanoporous solids: anodic aluminum oxide (AAO) and silica aerogels. AAO membranes are synthesized by the anodization of aluminum metal [2], and consist of well-ordered hexagonal arrays of open pores with diameters d~10 nm and thicknesses L~70 microns. Silica aerogels are fabricated by the supercritical drying of a silica sol-gel [3] and consist of a randomly inter-connected network of fine filaments and particles. The AAO and silica aerogels have been successfully coated using ALD methods with a variety of oxide films including Al2O3, TiO2, V2O5 and ZnO as well as metallic Pd films. The ALD coated AAO and aerogel materials were characterized by SEM, TEM, EDAX, XRD ellipsometry, optical absorption and four-point probe conductivity measurements.

The ALD/AAO materials are being employed as mesoporous catalytic membranes and gas sensors. The catalytic membranes were fabricated by applying successive coatings of Al2O3, TiO2 and V2O5 onto AAO membrane supports. These catalytic membranes show high selectivity for the oxidation dehydrogenation. Additional AAO membranes coated with ALD Pd exhibit fast response and high sensitivity for hydrogen detection. Silica aerogels have the lowest density and highest surface area of any solid material. Therefore, these materials are excellent templates for preparing novel catalytic materials and sensors by ALD. In these initial studies, monolithic (bulk) and thin film silica aerogels were coated by ZnO ALD and the physical properties of the resulting ZnO/SiO2 materials were investigated as a function of the ZnO coating thickness.
EXPERIMENTAL

Anodic aluminum oxide (AAO) membranes with hexagonally ordered arrays of nanopores with diameter \(d=40\) nm and thickness \(L=70\) micron were prepared by a two-step anodization procedure [2]. Aluminum sheets were electropolished in a solution of perchloric acid and ethanol and anodized in 0.3M oxalic acid at 3 °C for 24 h. Freestanding AAO membranes were obtained by selectively etching away the unreacted Al in saturated HgCl\(_2\) solution and then immersing in 5.00 wt% phosphoric acid at 30.0 °C for 65 min to remove the barrier layer. Bulk aerogels with a density of 10 mg/cm\(^3\), and a surface area of 350 m\(^2\)/g were prepared by supercritical drying of a silica sol-gel using the procedure described in reference [3]. Thin film aerogels were prepared using the same procedure by first applying the sol-gel between two flat SiO\(_2\) surfaces.

The ALD was performed in a viscous flow reactor [4] using the reactants and temperatures given in Table 1. The reactant pressures, exposure times and purge times were increased relative to the values necessary to coat flat surfaces to allow diffusion of the gaseous reactants into the high aspect ratio pores of the AAO and aerogel materials [5]. The AAO membranes and aerogel materials were analyzed using scanning electron microscopy (SEM), energy dispersive analysis of x-rays (EDAX), transmission electron microscopy (TEM), x-ray diffraction (XRD) optical absorption, and four-point probe resistivity.

Table 1. Precursors and deposition temperatures for ALD film growth.

<table>
<thead>
<tr>
<th>ALD Film</th>
<th>Metal Source</th>
<th>Oxidant/ Reductant</th>
<th>Deposition Temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>Trimethyl Aluminum (TMA)</td>
<td>H(_2)O</td>
<td>177</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>Titanium tetrachloride (TiCl(_4))</td>
<td>H(_2)O</td>
<td>100</td>
</tr>
<tr>
<td>V(_2)O(_5)</td>
<td>Vanadyl oxytriisopropoxide (VOTP)</td>
<td>H(_2)O(_2)</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>Diethyl zinc (DEZ)</td>
<td>H(_2)O</td>
<td>177</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd hexafluoroacetylacetonate (Pd(hfac)(_2))</td>
<td>HCOH</td>
<td>200</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

AAO membranes were modified by ALD to fabricate nanoporous catalytic membranes for the selective oxidation of hydrocarbons. First, the AAO pore diameter was reduced to enhance the catalytic activity using Al\(_2\)O\(_3\) ALD. AAO membranes having an initial pore diameter \(d=40\) nm and thickness \(L=70\) micron were coated by 15 nm ALD Al\(_2\)O\(_3\) to achieve a final pore diameter of \(d=10\) nm. Plan view and cross sectional SEM images (Fig. 1) demonstrate that the very high aspect ratio (\(L/d\sim10^4\)) pores are conformally coated using ALD. TEM images of the AAO samples before and after coating with an 18 nm ALD Al\(_2\)O\(_3\) layer (Fig. 2) illustrate how the conformal ALD coatings preserve the initial asymmetry present in some of the AAO pores. Oval-shaped openings in some of the pores become more exaggerated as the pores become narrower.
After depositing the ALD Al₂O₃ coating on the AAO membrane, ALD TiO₂ and V₂O₅ coatings were deposited to serve as the catalytic support layer and active catalyst layer, respectively. In situ quartz crystal microbalance (QCM) measurements demonstrated that the ALD TiO₂ and V₂O₅ layers nucleate readily on the ALD Al₂O₃ layer as expected for hydroxyl-based growth [1]. It was necessary to coat the AAO membranes with ALD TiO₂ at 100 °C to obtain uniform, amorphous TiO₂ coatings. At higher deposition temperatures of 250 °C, the TiO₂ deposited non-uniformly as 10-50 nm anatase crystals inside of the AAO pores. Cross sectional SEM and EDAX measurements reveal that the ALD TiO₂ and V₂O₅ coatings deposited at 100 °C are uniform throughout the AAO nanopores. Catalytic testing showed that the ALD/AAO membranes were highly selective in the oxidation of cyclohexane to cyclohexene. When compared with conventional powder catalysts, the ALD/AAO membranes formed much less of the higher oxidation products benzene, CO and CO₂. We believe that the reduced contact time in the flow-through pore structure accounts for the enhanced selectivity.

AAO membranes were also coated with metal films to form gas sensors. Conformal Pd coatings with a thickness of 2 nm were deposited onto AAO membranes using alternating exposures to Pd(hfac)₂ and formaldehyde (HCOH). Cross-sectional EDAX measurements confirmed that the Pd films extended to the middle of the high aspect ratio pores, and plan view SEM revealed a nanocrystalline Pd morphology. The Pd/AAO exhibit rapid, reversible

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**Figure 1**: Plan view SEM images of AAO membrane before (a) and after (b) 15 nm ALD Al₂O₃ coating. (c) Cross-sectional SEM image after coating recorded from middle of membrane. Conformal Al₂O₃ coating extends to middle of AAO.

**Figure 2**: TEM images of AAO membrane before (a) and after (b) 18 nm ALD Al₂O₃ coating. Conformal ALD coating maintains initial AAO pore asymmetry.
conductivity changes upon hydrogen exposure and show great promise as hydrogen gas sensors with fast response and high sensitivity.

The ability to coat ultra-low density silica aerogels with conformal layers of different metal and metal oxide materials using ALD will enable the fabrication of novel gas sensors and catalysts. In this study, monolithic and thin film silica aerogels were coated by ZnO ALD [6]. Prior to the ZnO coatings, a 3 Å ALD Al₂O₃ coating was applied as a nucleation layer. SEM images of the silica aerogel versus number of ZnO ALD cycles (successive exposures to DEZ and H₂O) are shown in Fig. 3. The silica aerogels have an open, filamentous structure and the conformal ZnO coating increases the filament diameter with increasing ZnO cycles. After 80 ALD cycles, ZnO nanocrystals are visible on the surface of the coated aerogel. XRD measurements of this sample reveal hexagonal zincite. The weight change of the monolithic silica aerogels versus number of ALD ZnO cycles is shown in Fig. 4. Also shown is the Zn EDAX signal obtained from thin film aerogels versus number of ZnO cycles. The weight gain and Zn content vary quadratically with the number of cycles. This finding is surprising given the highly linear growth observed on flat substrates for ALD ZnO films. This discrepancy is explained by the increase in filament diameter demonstrated in Fig. 3. The amount of ZnO deposited per cycle varies with the square of the filament radius. Because the filament radius increases linearly with the number of ZnO cycles, the sample weight and Zn content increase quadratically.

The optical absorption and electrical conductivity of the thin film silica aerogels were monitored versus number of ALD ZnO cycles. ALD ZnO is electrically conducting and absorbs blue light, while SiO₂ is electrically insulating and optically transparent. As the aerogel becomes progressively coated by the ZnO, both the electrical conductivity and optical absorption increase.

![Figure 3: SEM images of silica aerogel versus ZnO ALD cycles illustrating progressive thickening of aerogel filaments.](https://doi.org/10.1557/PROC-876-R12.6)
Figure 4: Mass gain and Zn EDAX signal versus ZnO ALD cycles on silica aerogel. Quadratic behavior results from linear increase in aerogel filament diameter with number of ZnO cycles.

CONCLUSIONS

We have used atomic layer deposition (ALD) to apply precise, conformal coatings over nanoporous anodic aluminum oxide (AAO) membranes and silica aerogels. The ALD layers uniformly coat all exposed surfaces of the substrates including the inner walls of the extremely high aspect ratio (L/d~10^4) AAO pores. We have deposited successive layers of Al_2O_3, TiO_2 and V_2O_5 onto AAO to fabricate catalytic membranes for the selective oxidation of hydrocarbons. AAO membranes coated with ALD Pd show great promise as hydrogen sensors. Very low density silica aerogels can be coated with ALD ZnO layers to alter the aerogel properties.

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REFERENCES