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Enhancing the platinum atomic layer deposition infiltration depth inside anodic alumina nanoporous membrane

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Nanoporous platinum membranes can be straightforwardly fabricated by forming a Pt coating inside the nanopores of anodic alumina membranes (AAO) using atomic layer deposition (ALD). However, the high-aspect-ratio of AAO makes Pt ALD very challenging. By tuning the process deposition temperature and precursor exposure time, enhanced infiltration depth along with conformal coating was achieved for Pt ALD inside the AAO templates. Cross-sectional scanning electron microscopy/energy dispersive x-ray spectroscopy and small angle neutron scattering were employed to analyze the Pt coverage and thickness inside the AAO nanopores. Additionally, one application of platinum-coated membrane was demonstrated by creating a high-density protein-functionalized interface. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4904398]

I. INTRODUCTION

Functional nanomembranes are in great demand for applications ranging from catalysis and fuel cells to bioseparations and biosensors.¹⁻⁵ In general, these materials are fabricated by surface modification of the nanoporous membranes. One such class of nanomaterials is based on nanoporous anodic aluminum oxide (AAO), shown in Fig. 1. AAO has been used as a template to create functional nanomembranes using methods such as electrodeposition, sol-gel, and chemical vapor deposition.⁶ In particular, atomic layer deposition (ALD) has emerged as an important technique to fabricate high-quality AAO-modified nanomaterials because of its ability to conformally coat the high-aspect-ratio (AR = length/diameter) structures.^{7,8} Contrary to the physical and chemical vapor deposition techniques, which deposit thin films at the top of the substrate, ALD forms a thin film on the surface by a substrate-mediated, self-limiting chemical reaction.⁹ The interfacial reaction between the substrate and the precursor allows the material to infiltrate inside the structures instead of aggregating on the top of the substrate.

ALD has been demonstrated as an effective technique for the conformal coating of metal oxides inside high-AR AAO structures, but only limited penetration depth has been achieved inside high-aspect nanostructures when ALD is used with metals.⁷ The most common commercial metal available for ALD is Pt, which undergoes the following binary reaction (unbalanced equation) of an organometallic precursor, trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe₃), and O_2 in alternative cycles:^{10,11}

$$Pt(s) + O_2(g) \to Pt - O_x \tag{1}$$

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$$CH_{3}C_{5}H_{4}Pt(CH_{3})_{3} + Pt - O_{x}$$

$$\rightarrow Pt(s) + CO_{2}(g) + H_{2}O(g) + byproducts.$$
(2)

In this work, both precursor residual time and process temperature were investigated to understand and improve Pt coatings along the pore length of these membranes. The Pt ALD was carried out in a thermal mode, and the coated AAO membrane was characterized by scanning electron microscopy (SEM)/energy dispersive x-ray spectroscopy (EDX) and small angle neutron scattering (SANS) to determine the Pt coverage and thickness inside the nanopores.



FIG. 1. (a) Schematic illustration of the cross section of an anodic aluminum oxide (AAO) nanoporous membrane with pores open on both sides; (b) a representative top view scanning electron micrograph of an AAO membrane.

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II. EXPERIMENT

A. Atomic layer deposition

The ALD experiments were performed on an Oxford FlexAL* reactor in thermal mode. This reactor operates under a turbopump maintained base pressure of $\sim 1 \ \mu$ Torr. Pt precursor, trimethyl(methylcyclopentadienyl)platinum(IV) [MeCpPtMe₃] (Sigma Aldrich, St. Louis, MO), was heated at 70 °C for delivery into the ALD process chamber. The residence time of MeCpPtMe3 precursor in the process chamber was varied from 1 to 320 s and the substrate (electrode) temperature was varied from 200 to 500 °C. The coating process chamber pressure was at 32 Pa. A longer purging duration of 30 s was used in the ALD pulse sequence (Pt precursor dosepurge-O₂ dose-purge) to avoid the possibility of chemical vapor deposition reactions. Ar was used to purge the precursor lines. The AAO membranes were kept on a custom-built tripodal support for transport of precursors from both sides of the membrane during the ALD coating process.

B. Materials

Whatman anopore membranes (Anodic aluminum oxide of 200 nm pore diameter and 60 μ m membrane thickness, with pores open on both sides) were purchased from GE Healthcare Life Sciences (Pittsburgh, PA). Membrane scaffold protein (MSP) was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO) and used without further purification. Thiol compounds were synthesized as discussed earlier.¹²

C. Small angle neutron scattering measurements

SANS measurements were carried out at the NG7 30 m SANS instruments at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD.¹³ The scattering data were reduced using the IGOR software package (WaveMetrics, OR) with SANS macros developed at the NCNR.¹⁴ The scattering data were normalized to the incident neutron beam, and radially averaged to obtain the scattering intensity I(q)as a function of the wave-vector transfer, $q = 4 \pi \sin \theta / \lambda$, where 2Θ is the scattering angle and λ is the neutron wavelength (6 Å). The solvent condition of 73% $D_2O:27\%$ H_2O , where the scattering from the AAO substrate was found to be minimal in previous studies,¹⁵ was used for the SANS experiments in order to highlight the scattering from the deposited thin films. The SANS data were fit with a core-shell cylinder model using IGOR with the NCNR-SANS macros to estimate the thickness of the films inside the AAO nanopores.

D. Scanning electron microscopy

All images were taken on a Zeiss Ultra 60 field emission scanning electron microscope at 10 kV using an in-lens secondary electron detector. Elemental analysis of the nanopores was performed on the AAO membrane cross-sections using an integrated Oxford EDX spectrometer and data were analyzed by INCA software. The Pt distribution inside nanopores was quantified by scanning along the axial length and recording Pt concentration in 5 or 2 μ m increments. The Pt coverage was normalized by the maximum measured Pt concentration. EDX elemental mapping was performed for qualitative information about the two-dimensional distribution of Pt inside nanopores.

E. X-ray reflectivity

X-ray reflectivity (XRR) measurements were performed at the NCNR on a D8 Advance x-ray reflectometer (Bruker) employing Cu K_x radiation ($\lambda = 1.54$ Å) and the data were analyzed using the REFLPAK software package developed at the NCNR.²³ The XRR profiles were obtained as a function of the wave vector transfer, *q* (defined above). The reflectivity represents the ratio of reflected to incident x-ray intensity. The scattering length density (SLD) represents the average x-ray scattering lengths of all the atoms divided by molecular volume. The thickness of the Pt ALD film was obtained by fitting the XRR data with a multilayer slab model. The XRR measurements were performed on two samples, and the reported error is the standard deviation of the mean.

III. RESULTS AND DISCUSSION

The molecular transport of precursor molecules inside high-AR structures such as AAO is the main challenge for successful ALD on these materials. Various theoretical models have been developed to understand ALD inside high-AR structures.¹⁶ They predict that a higher saturation dose of precursors is required for conformal ALD coating on these structures as compared to that on planar substrates. Elam et al. successfully demonstrated conformal coating of zinc oxide and aluminum oxide inside high-AR AAO membranes by increasing the precursor exposure time.⁸ We postulate that, because the Pt precursor, MeCpPtMe₃, lacks the molecular symmetry possessed by precursors of metal oxides such as trimethyl aluminum [Al(CH₃)₃],⁸ its surface reaction probability is very low.¹⁷ Thus, in this study, the precursor exposure time was extended to develop the conformal coating of Pt ALD at a commonly used process temperature of 300 °C over 200 cycles to ensure a continuous thin film.¹⁸

As illustrated in Fig. 2, Pt EDX line scans along the length of the nanopores demonstrate that increasing the precursor exposure times improves the Pt coating coverage inside the pores. At 1 s precursor exposure time, Pt only coated the surface of the nanopore membrane and there was no Pt inside the pores. As the exposure time was increased to 80 s, with each ALD cycle comprised of pulse sequences of 80 s (Pt precursor)_30 s (purging time)_50 s (O₂ precursor)_30s (purging time), the Pt film coverage increased to $10\,\mu m$ from both sides of the nanopores. However, after 80 s, subsequent increase in the precursor exposure time did not further improve the Pt film infiltration depth inside the AAO nanopores. We also tested membranes with larger pore sizes of 250 or 300 nm and found Pt infiltration depths similar to that of 200 nm AAO membranes. These results are consistent with previous reports of Pt ALD on AAO membranes.^{19–21} Additionally, this suggests that Pt ALD inside



FIG. 2. (Color online) (a) Schematic illustration of platinum (Pt)-coated AAO; and (b) relative Pt coverage inside AAO measured by EDX line scans [along the half length of the nanopores (30 μ m) from either side of the membrane] for different precursor exposure times.

higher AR structures such as AAO membranes is not a reaction-limited, but rather a diffusion-limited phenomenon.

The mean free path of a gas, in general, is higher at low pressure because of its inverse relationship with pressure based on the kinetic theory of gases. For example, oxygen gas at room temperature under low pressure (32 Pa) will have a mean free path of ~200 μ m. We assume that under ALD process conditions (i.e., 32 Pa process pressure), the mean free path of the precursor gases is much larger than the AAO pore diameter (\approx 200 nm), which suggests that the transport of the precursor gas inside nanopores follows Knudsen diffusion,²² which is given in terms of the Knudsen permeability as follows:

$$Q = \frac{\varepsilon d}{\tau L} \left(\frac{8}{9\pi MRT} \right)^{1/2},$$

where Q is the Knudsen permeability, d is the diameter of the nanopore, L is the length of the pore, M is the precursor molecular weight, and T is temperature during deposition. In the vacuum ALD reactor, the precursor flux under Knudsen flow is pressure independent. Based on Knudsen diffusion theory, we postulated that the process temperature might also affect the precursor transport inside nanopores, and thus the infiltration depth of the Pt film.

A systematic study of Pt ALD on AAO (AR = 300) was performed by varying the deposition temperature from 200 to 500 °C, while keeping the precursor exposure pulse sequence of 80s_30s_50s_30s. No deposition was observed at 200 °C, which is consistent with the very low growth rate reported in recently published Pt ALD growth kinetics temperature dependence studies.¹¹ Increasing the deposition temperature yielded Pt deposition inside the nanopores. However, the coating depth inside the AAO pores does not increase with ALD process temperature as shown in Figs. 3(a) (EDX line scans) and 3(c) (cross-sectional EDX Pt distribution map). Rather, Pt ALD at 250 °C yielded Pt deposition into the entire length of the 60 μ m AAO nanopores, with conformal coating inside the nanopores for 20 μ m from both sides, which was significantly improved from the other higher or lower temperature conditions. Recently, Gaspard et al. also reported Pt ALD at 250 °C for conformal coating inside the nanopores of AAO membrane, albeit, with smaller AR [~16 (membrane thickness 1.3 μ m and nanopore diameter 80 nm)] using pulse sequences of 2.25 s (Pt precursor)_30 s (purging time)_1.3 s (O₂ precursor)_30 s (purging time).²¹ More importantly, they also mentioned that higher Pt precursor time is required for the increased Pt infiltration depth inside the nanopores, similar to our results. Taken together, our data suggest that conformal coating and infiltration depth of Pt inside high-AR AAO membranes via ALD depends not only on the precursor exposure time but also on the optimal process temperature.

The strikingly higher Pt infiltration depth inside AAO nanopores at 250 °C as compared to 300 °C is rather surprising, considering that there is only a 4% increase in the precursor Knudsen permeability at 250 °C. This suggests that there might be an alternative mechanism of Pt precursor transport inside the nanopores. Surface diffusion of adsorbed molecules has been a common transport mechanism for separating gases by membranes including AAO.²³ We hypothesized that surface-based diffusion of adsorbed (physisorbed) molecules to the AAO membranes might be an additional mechanism of Pt precursor transport inside the nanopores. Physisorption increases as temperature decreases,²⁴ which might be the reason for higher Pt infiltration depth inside AAO nanopores at 250 °C as compared to that at 300 °C. Conversely, at lower process temperatures such as 225 °C, the Pt ALD growth rate is comparatively low,¹¹ which does not help in increasing the infiltration depth. Our results indicate that 250 °C seems to be the optimal process temperature, which facilitated not only a good growth rate but also the transport of precursor molecules inside the nanopores, probably by both Knudsen and surface diffusion mechanisms.

To characterize the Pt thickness inside nanopores, SANS was used. Previously, electron microscopy was employed to determine the thickness of ALD thin films inside AAO membranes; however, this method requires dissolution of the AAO template for the analysis of the deposited nanostructures.²⁵ In contrast, SANS allows us to directly model the Pt film inside the AAO membrane and to calculate its thickness. Since the SLDs of Pt and AAO are sufficiently different, the scattering from the AAO was minimized by measuring the membranes in a solution consisting of 73%



FIG. 3. (Color online) (a) Relative Pt coverage inside AAO measured by EDX line scans for different process temperatures along the half length of the nanopores (30 μ m); (b) representative cross-sectional SEM image of Pt-coated-AAO (60 μ m thick AAO) for corresponding; (c) cross-sectional EDX Pt distribution map (red dots indicate the presence of Pt) inside AAO measured as a function of temperature. EDX Pt line scans and corresponding elemental area mapping indicate that, at 250 °C, Pt ALD results in maximum Pt coverage with conformal coating for a 20 μ m infiltration depth from both sides of the membrane.

D₂O:27% H₂O. Under these conditions, the scattering from the Pt is easier to observe even though its total mass is much less than that of the AAO. This "contrast variation" technique uniquely allowed us to use SANS to measure the thickness of the Pt while attached to the AAO substrate. By fitting the SANS data to a core–shell cylinder model in which the AAO pores are hollow cylinders filled with D₂O:H₂O solution and the shell is of finite thickness representing the Pt coating (Fig. 4), a Pt thickness of ≈8 nm inside the AAO membrane was obtained. XRR was used to confirm the Pt thickness on the AAO membranes by using a mimic to Pt ALD on AAO: a planar silicon substrate was first coated with 20 nm Al₂O₃ using ALD, followed by 200 cycles of Pt ALD at 250 °C. XRR analysis (Fig. 5) indicates a Pt thickness 9.1 ± 0.31 nm on the AAO-mimic planar substrate. We attribute the differences between the XRR data and SANS data to the nonconformal Pt coverage at the middle of the AAO nanopores for



FIG. 4. (Color online) Small-angle neutron scattering (SANS) of the AAO and Pt-coated-AAO. Samples were soaked in 73% D_2O :27% H_2O to reduce the scattering from the AAO. Scattering data were fit with a core–shell cylinder model using IGOR with SANS macros developed at the NCNR to estimate the Pt thickness inside AAO nanopores. Error bars represent the standard error of the mean over the number of pixels used to average the data.



FIG. 5. (Color online) X-ray reflectivity (XRR) profiles of Pt ALD deposited on an alumina-coated substrate at 250 °C. The inset represents the x-ray SLD vs z (the direction normal to the planar substrate) obtained by fitting the XRR data.

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 \sim 30% surface area. X-ray photoelectron spectroscopy analysis confirmed that ALD-deposited Pt on the AAO membrane is metallic Pt (data not shown).

One application of these functional Pt-coated nanoporous membranes is in creating an interface for biosensing. The presence of Pt enables further modification of these nanopores by introduction of chemical functionalities via selfassembled monolayers (SAMs) of thiol molecules.¹² Other surface modification strategies such as silanization are challenging due to problems associated with hydrolysis and oligomerization. As a proof-of-concept, we further modified a Pt-coated AAO membrane with a mixed SAM containing 40% of a protein-capturing thiol and 60% of a proteinresistant thiol.³ Protein was immobilized inside the membrane using a custom-built extrusion system. As shown in Fig. 6, SANS analysis indicates that the pore thickness increases by ≈ 3 nm after immobilization of a model protein, MSP. Spectroscopic ellipsometry analysis of MSP binding on analogously prepared planar Pt substrates yielded a similar protein optical thickness of 3 ± 0.2 nm (ellipsometric thickness of the protein layer after immobilization on a SAM-functionalized Pt substrate, which has a surface chemistry similar to that of Pt-coated AAO membrane),¹² which corresponds to 400 ng/cm² protein density on these surfaces. Considering the total exposed area of the nanopores, $\approx 600 \,\mathrm{cm}^{2}$,³ functionalized AAO membranes are able to immobilize $\approx 240 \ \mu g$ of protein. Because of the higher exposed surface area provided by these functionalized membranes, protein loading is approximately two orders of magnitude greater compared to the loading on a planar substrate. This kind of surface area opens up the possibility of numerous novel applications in biosensing and bioseparations. The use of SANS enabled us to measure nonintrusively the adsorbed proteins inside the nanopores.



FIG. 6. (Color online) SANS of protein immobilized Pt-coated AAO membrane. The Pt-coated AAO membrane was chemically modified by selfassembled monolayer (SAM)-forming thiols, followed by the capture of membrane scaffold protein. Protein thickness was determined by fitting the scattering profile to a core–shell cylinder model; the average increase in the thickness of the Pt "shell" after protein immobilization was 3 nm. These functionalized AAO membranes were soaked in 73% D₂O: 27% H₂O to reduce the scattering from the AAO. Error bars represent the standard error of the mean over the number of pixels used to average the data.

IV. CONCLUSIONS

In summary, by tuning both ALD process parameters, precursor residual time and deposition temperature, we were able to achieve higher Pt infiltration depth and conformal coating (20 μ m from each side: AR = 100) inside the nanopores in high-AR AAO membranes. In particular, ours and other's²¹ results indicate that 250 °C process temperature is optimal for Pt ALD of high-AR materials. SANS measurements reveal the thickness of deposited Pt film inside nanopores. Our future efforts will focus on understanding the enhanced Pt coverage at the lower temperature of 250 °C using Monte Carlo simulations.^{8,26,27} We have demonstrated that these Pt-functionalized membranes can be further modified by organosulfur compounds for high-density loading of proteins for various biosensing applications. These membranes can also be employed for applications in the fuel cells and electrochemical sensing.

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