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Pt-Al₂O₃ Dual-Layer ALD Coating in High Aspect Ratio Nanopores

Running heads. Pt-Al₂O₃ ALD in Nanopores

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Abstract. Functional nanoporous materials are promising for a number of applications ranging from selective biofiltration to fuel cell electrodes. This work reports the functionalization of nanoporous membranes using atomic layer deposition (ALD). ALD is used to conformally deposit platinum (Pt) and aluminium oxide (Al₂O₃) on Pt in nanopores to form a metal-insulator stack inside the nanopore. Deposition of these materials inside nanopores allows adding extra functionalities to nanoporous materials such as anodic aluminium oxide (AAO) membranes. Conformal deposition of Pt on such materials enables increased performances for electrochemical sensing applications or fuel cell electrodes. An additional conformal Al₂O₃ layer on such Pt film forms a metal-insulator-electrolyte system, enabling field effect control of the nanofluidic properties of the membrane. This opens novel possibilities in electrically controlled biofiltration. In this work, the deposition of these two materials on AAO membrane is investigated theoretically and experimentally. Successful process parameters are proposed for a reliable and cost-effective conformal deposition on high aspect ratio 3D nanostructures. A device consisting of a silicon chip supporting an AAO membrane of 6 mm diameter and 1.3 µm thickness with 80 nm diameter pores is fabricated. The pore diameter is reduced to 40 nm by a conformal deposition of 11 nm Pt and 9 nm Al₂O₃ using ALD.

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1 Introduction

In recent years, the interest for novel functional and well-controlled nanoporous materials has grown extensively [1-5]. Nanoporous materials possess a number of interesting features. At the nanoscale, the increased surface-to-volume ratio ($\sim l^{-1}$) enhances the interaction between liquid analytes or electrolyte and the device surface. In addition, the porosity,

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ϵ , increases the effective surface area of the macroscopic material ($\sim \epsilon$). The porosity also increases the line length of triple phase (solid, liquid, gas) interfaces ($\sim l^{-1/2}$).

The increased surface-to-volume is an advantage for surface governed phenomena, such as molecular transport in nanofluidics, largely governed by the surface charges via the electrical double layer (EDL) [6-8]. The increased effective surface area improves surface limited phenomena, such as overpotential losses in electrodes [9, 10] and the increased line length of the triple phase interface allows increasing the current density in fuel cells [11] or the sensitivity in gas- and biosensors [12-16].

In addition to these intrinsic features, embedding functional capabilities in or on these materials will further enhance their interest. In nanofluidic channels, the EDL thickness can be tuned with the choice of the nanopore wall material, the ionic strength and the pH to obtain a specific transport regime [17], but functionalized nanopores are promising for adding an external control on the EDL without the need of changing any of the bulk properties of the material system, as shown by Martin *et al.* [18] and Karnik *et al.* [19, 20]. In biosensing, biofiltration, and drug delivery applications, functional nanoporous materials can also provide better selectivity, controllability and efficiency [21-26]. In DNA and proteomic analysis, functional nanopores represent good candidates for faster and highly parallelizable analysis [27-29]. Although the transport of biological species through nanoporous membranes has already been largely studied and reviewed [30-32], many technological challenges remains to better control and apply these technologies. The difficulty is to provide such nanoporous structures with the required functionality and dimensions.

In the context of functional nanoporous materials, anodic aluminium oxide (AAO) and porous silicon are of major interest because their manufacturing is relatively low cost and is well suited for up scaling [33-37]. These materials can now be produced with a high level of control, in terms of pore density and size, over a full wafer area or even larger and they can be transformed to make freestanding membranes [38-40]. AAO membrane, especially, represents an interesting substrate for the fabrication of functional nanoporous material. AAO structures have been functionalized using atomic layer deposition (ALD) [41-45], among other techniques, as recently reported by Banerjee *et al.* [46], who made use of AAO defined nanopatterns, functionalized with a metal-oxide-metal multilayer, to form a regular array of nanocapacitors and Gu *et al.* [47] who formed nested semiconductor/metal nanotubes using ALD.

ALD is a technique that allows for the deposition of extremely conformal coatings on complex 3D nanostructures [48-52]. It is a self-limiting technique based on the deposition of a single atomic layer at a time by dissociative chemisorption of a precursor molecule on the surface.

A large panel of materials can now be deposited with ALD, even metals [53]. The advantage of ALD over conventional fabrication methods is the high deposition uniformity with a digital atomic control of the film thickness. ALD of noble metals is however a challenging process because of their low precursor reactivity on some surfaces, which makes the film growth initiation more difficult and because of a poor thermal stability of the precursor compound [54-56]. Despite these challenges, ALD of noble metals is particularly interesting because of the catalytic properties of these materials. Platinum (Pt), in particular, is often desired as catalyst in electrochemical applications ranging from fuels cells to biosensors [57-63]. This also explains why Pt precursor for ALD is one of the best studied of all the available noble metal precursors after Ruthenium [64, 65].

ALD of dielectric materials on metals, such as Al_2O_3 on Pt, might also suffer from similar film growth initiation problems. Little research has covered this topic to date.

For the reasons stated above, very promising functional nanoporous material can potentially be fabricated with a combination of AAO membrane and ALD. The deposition of "Pt-only" can be used to fabricate large surface area of porous electrode with a very controlled and low loading of the catalyst.

The deposition of a dual layer, i.e. metal-oxide, by conformal ALD deposition of a dielectric layer over the metalized nanopores, allows isolating the metal from its surrounding environment, such as an electrolyte to form a metal-insulator-electrolyte structure, also called nanofluidic transistor [19]. Such a device allows for a field effect control of the EDL thickness at the oxide-electrolyte interface by applying an external potential [66]. Potential applications range from biopolymer nanofiltration [18, 19, 67-76] and sensing [29, 77] to energy harvesting and fuel cell applications [78-81].

However, to fabricate these two types of device some challenges must be overcome: Pt must be successfully deposited inside narrow nanopores; a dielectric, e.g. Al_2O_3 , must also be subsequently deposited conformally on the Pt inside the nanopores. These challenges are addressed in this work.

Here, the ALD deposition of thin Pt and Al_2O_3 films is performed to functionalize large-area (6 mm diameter) through-hole AAO nanoporous membranes. The presented results can also be applied to other nanoporous materials. In this work, Pt is deposited in through-hole nanopores by thermal ALD. The deposition of Al_2O_3 on Pt in nanopores is also studied. The deposition rates on different substrates of interest have also been studied. Recipe parameters for the deposition of Pt and Al_2O_3 have been tuned to obtain a uniform coating inside the nanopores and are presented. These recipe parameters allow for a successful and cost-effective deposition by minimizing the use of relatively expensive precursor material. The subsequent and successful coating of the Pt layer with an additional layer of Al_2O_3 is reported. The results demonstrate the potential of ALD for the functionalization of nanoporous material for electrochemical and nanofluidic applications.

2 ALD in nanopores

ALD relies on a cyclic process, which is generally composed of four subsequent steps performed in a semi-vacuum environment: 1: a pulse of the precursor gas is introduced into the reactor chamber and the gas molecules chemisorb on the substrate surface until saturation; 2: the reaction chamber is purged with neutral argon gas to remove the excess of precursor gas and to leave an atomic monolayer of precursor molecules on the substrate surface; 3: a pulse of the reactant gas is introduced in the chamber, which reacts with the chemisorbed precursor molecules, forming an atomic monolayer of the reaction product; 4: the excess of reactant gas and the reaction products are purged out of the chamber to prepare for the next cycle. Two ALD techniques exist: thermal and plasma-based ALD. For Pt deposition, the later offers faster nucleation but creates larger grains [82], which renders this technique unsuitable for deposition in small pores. For this reason, thermal ALD is used in this work.

Figure 1. a) Schematic illustration for the modelling of a pore during ALD deposition. The spheres represent the precursor gas molecule forming a progressing monolayer until saturation of the pore surface. b) Schematics of the dual layer deposition on the nanoporous AAO membrane, c) Final device schematics. d) and e) Definition of the cross-sections and viewing direction for SEM and TEM imaging.

Thermal ALD is a process that is based on dissociative chemisorption of the precursor by a reactant at the surface [83]. An extensive study of various precursors for different materials has been carried out by George [84] and Puurunen [53]. The deposition rate for thermal ALD is typically 0.1-1 Å/cycle [56], which allows for a very controlled deposition [53]. This technique is therefore an excellent method for adding functionality to complex 3D nanostructures. During film growth, the saturation dose, S_s , is typically 10^{15} (molecules cm^{-2}) [85-87]. This depends on the material surface, on the pressure applied and on the gas, as the chemisorption of the first few monolayers of gas or vapour molecules depends on weak surface forces.

For a successful ALD deposition in nanopores, it is necessary to ensure the saturation of the whole surface, including deep inside the pores, with the precursor or reactant molecules. This requires that the exposures (pulse 1 and 3 in the ALD cycle) are sufficiently long to allow gas diffusion into the nanopores. An arbitrary duration would result in an only partially covered pore wall, if too short, or in a waste of precursor/reactant gas, if too long [88].

Models for determination of the required exposure for coating the pores have been presented by Gordon *et al.* [85] and Adomaitis *et al.* [89]. Adomaitis considers the transition probability of the precursor molecules passing through the pores and confirmed that the simpler model of Gordon is a very good approximation and remains valid for the case of open-ended pores.

The molecular flux at the pore opening is given by: $J_0 = \frac{P}{\sqrt{2\pi mkT}}$ (mol m⁻² s⁻¹), where P is the precursor partial pressure, k is the Boltzmann's constant, T, is the processing temperature, m is the molecular mass (kg) of the precursor. The coating with the precursor molecules saturates the surface from the top and this saturation front moves down into the pore as time increases, as illustrated in Figure 1. The reduction of the flux, $J(\ell)$, at a distance ℓ in the pore is accounted for by using the Clausing factor $CF = 1 / \left(1 + \frac{3\ell p}{16A_{\text{pore}}}\right)$, where p is the perimeter of the pore, A_{pore} is the cross sectional area of the pore. The exposure (pressure $\times$ time) needed to saturate the surface is given by: $\delta = P \cdot t = \int_0^L \frac{P \cdot S_s \cdot p}{J(\ell) A_{\text{pore}}} d\ell$. After integration, the exposure required for sidewall coverage can finally be expressed as [85]:

$$\delta = S_s \sqrt{2\pi mkT} \frac{p}{A_{\text{pore}}} \left(L_{\text{pore}} + \frac{3pL_{\text{pore}}^2}{32A_{\text{pore}}} \right) \text{ (Langmuir, L),} \quad (1)$$

This equation is often corrected with a sticking coefficient, α , as denominator to account for non-ideal saturation of the surface, where α is expressed as the percentage of the surface covered with a monolayer of precursor. However, no exact value of the sticking coefficient has been reported for Pt to date. α has also been reported to vary with the temperature [91]. It is also important to note that nucleation delay occurs for some materials before the formation of the first monolayer [90]. This nucleation delay is known to be particularly long for Pt [90].

The model does not take into account the successive reduction of the pore diameter with the increase of ALD cycles. Therefore, the exposure needs to be slightly increased to alleviate the effect of non-ideal conditions and to ensure that the entire surface is covered with a monolayer during each ALD cycle to obtain a uniform film growth [92].

Finally, this model predicts that the pulse and purge times should be equal. However, this is not the case. The purging cycle must ensure that any non-chemisorbed molecules or any reaction products present in the reactor are removed to make the surface clean and suitable for the next reaction and to ensure the self-limiting surface growth process [93, 94]. Deshpande *et al.* [95] discuss the atomic layer deposition of hafnium oxide on flat wafers and report the unequal time co-relation (about 1:15) between pulse time and the purge time. Similar behaviour can be expected here. Due to the high aspect ratio of the AAO nanopores, this pulse/purge ratio is expected even higher in this work.

3 Methods

3.1 Substrate preparation

The fabrication of porous AAO membrane on silicon substrate (Figure 1) was performed as follows. A 1- μm thick aluminium layer was sputtered onto a single-side polished 525 μm thick 4 inch Si-wafer with an initial 400 nm thermally grown silicon dioxide (SiO₂) layer. The aluminium layer was anodized to form a regular pore array of 25 nm diameter with 125 nm pitch (Figure 2. a), with the pores stretching through the whole layer thickness. The anodization was carried out by Synkera Technologies Inc., Longmont CO, USA. After anodization, the thickness of the layer increases to 1.36 μm due to material expansion during anodization.

Figure 2. Fabrication flow and SEM images of the AAO substrate at different process steps: a) and b) The AAO film is formed on a Si substrate. Cavities are etched in the substrate from the bottom and the grid is patterned on spray coated photoresist; c) and d) The grid is etched from the backside in the Si until reaching the buried SiO₂ layer. The AAO surface is protected with a photoresist layer before dicing. The inset shows the closed end of the AAO pores; e) and f) After dicing, the buried SiO₂ and the Al₂O₃ barrier layer is etched on chip level to open the AAO membrane. The inset shows the pores now open at the bottom.

The SiO₂ layer, used as hard mask, on the backside of the Si wafer was then lithographically patterned (10 μm thick AZ-9260 resist from AZ Electronic Materials) and developed (3 min, 5:1 DI-H₂O:2401 developer, Shipley Microposit) to define 6 mm diameter membrane areas. It was observed that KOH-based developer 2401 widens the AAO nanopores at a rate of 10 nm/min at room temperature.

Subsequently, the silicon was dry etched using deep reactive ion etching (DRIE) to a depth of about 440 μm (Figure 2. a). A second photolithography was performed to define the supporting grid structure, which is necessary to ensure mechanical stability of the membrane (Figure 2. a).

A spray coater was used to conformally deposit a 6 μm thick layer of photoresist (AZ-9260) in the previously formed cavities, followed by proximity exposure in the cavities to define a triangular grid with 20 μm wide and 120 μm long beams.

The wafer was then further etched with DRIE until the buried silicon dioxide layer was reached (Figure 2. c). At this point, the wafer was diced into 10x10 mm chips, each containing one membrane with the supporting grid structure suspended on top of a 6 mm diameter cavity. To protect the nanostructures while dicing, thick photoresist was spun on the top surface. After dicing, the photoresist was dissolved in acetone.

To facilitate the test of different process parameters, the next process steps were performed on chip level with the use of a carrier wafer.

At this stage, the membrane consists of three layers: the porous anodic aluminium layer, the barrier layer, which is a thin compact Al₂O₃ layer resulting from the anodization at the bottom of the pores, and the silicon dioxide layer. The chips were mounted upside-down, the AAO facing the carrier, using thermal-release tape (NWS-TS322F, Nikko Denko Corporation). The silicon dioxide layer below the Al₂O₃ layer was removed by RIE (Applied Materials Precision 5000). The Al₂O₃ barrier layer was then removed using the same machine, but with an etch gas composition of Cl₂ 20 sccm, BCl₃ 2 sccm and Ar 20 sccm at 600 W, (Figure 2. e).

SEM images of the AAO top surface before processing, and of the final AAO membrane are presented in Figure 2. b and f respectively. **Figure 2. d** shows a SEM image of the supporting grid. The insets in Figure 2. d and f show the barrier layer closing the pores and the open pores after removal of the barrier layer on the final AAO membranes. More than 50 such substrate samples were fabricated for subsequent study of ALD deposition.

For the monitoring of the ALD film growth, plain substrates for reference were also prepared. Different substrate surfaces were prepared to match that on the final porous AAO membrane surfaces, i.e. Pt film growth was studied on

Al₂O₃ surfaces and Al₂O₃ film growth was studied on Pt surfaces. Additionally, both film growths were monitored on bare Si and SiO₂ surfaces.

Al₂O₃ surfaces were prepared by ALD with a standard recipe with pulse/purge lengths adapted in this work for the deposition inside the nanopores. Pt surfaces were prepared using ALD with a recipe for deposition on a flat surface proposed by Aaltonen *et al.* [96], whose parameters are modified and tuned in this work to obtain a uniform deposition in nanopores. Silicon surfaces were etched in buffered HF, cleaned in DI water, dried with N₂ gas and transfer to the reactor within 10 min to prevent formation of native oxide. SiO₂ surfaces were prepared by wet thermal oxidation of Si.

1.2 Atomic layer deposition

For the deposition in nanopores, the deposition parameters need to be tuned to allow precursor and reactant gases to diffuse into the pores to ensure a uniform deposition, as discussed above. The deposition in this work was performed under the following conditions. The ALD reactor is a flow type reactor TFS 200 from Beneq, (Beneq Oy, Finland). The deposition of Pt results from the reaction of MeCpPtMe₃ with O₂ and the deposition of Al₂O₃ is the product of trimethylaluminium (TMA), reacting with H₂O. The molar mass of the precursor molecules is 331.9 (g mol⁻¹) for MeCpPtMe₃ and 144.18 (g mol⁻¹) for TMA. The process temperatures were 250 °C and 200 °C for Pt and Al₂O₃, respectively. For Pt, the temperature is chosen at the lower end of the temperature range, as lower process temperatures result in smaller grain films [54]. A constant nitrogen gas flow of 600 sccm and 300 sccm was used for the reactor chamber and the process chamber, respectively. The process chamber was maintained at a pressure of 1 kPa and the reactor chamber at a base pressure between pulses of 140 Pa. The precursors partial pressure is 24 Pa for MeCpPtMe₃ at 35°C and TMA is pulsed at 160 Pa at room temperature. The Pt precursor was pulsed in two phases: using only partial pressure of the precursor first and using Ar gas flow through the precursor canister in a second time to increase the flow of the precursor. The purpose of these two phases is to avoid an abrupt change in the reactor pressure during pulsing, which could otherwise lead to a non-uniform deposition. The initial diameter of the membrane pores, d_{pore} , is approximately 80 nm, the length of the pore, L_{pore} , is 1.36 μm (Figure 1), giving an aspect ratio of 17.

By applying these parameters in equation (1), we can estimate the theoretical minimum exposure necessary for a successful and uniform deposition inside the AAO nanopores. The ideal exposure, for Pt and $\alpha = 100\%$, is calculated to be 5.9×10^4 L. For hafnium oxide, values of α as low as 7% have been reported [85], indicating that low sticking coefficients ($\alpha \ll 100\%$) can be expected for Pt as well [82].

For Al₂O₃ deposition, with a sticking coefficient close to 100% [97] the ideal exposure is 0.293×10^6 L. Lower values for the sticking coefficient were reported by Dendooven *et al.* [98], which implies that the exposures obtained here are only theoretical and should serve as starting values prior to process optimization.

1.3 Experimental procedure

Starting with recipe parameters obtained from the model above, the pulse and purge durations were increased incrementally, until a conformal coating deep inside the pores could be verified by SEM imaging (Figure 3). Once the deposition could be verified with SEM images, TEM images of a sample were taken to characterize the deposition in more detail.

1.4 Film Characterization Methods

To monitor the growth inside the pores, several complementary techniques have been used. SEM images were taken with a Zeiss Gemini Ultra 55 SEM. This allowed for qualitative analysis of the top and bottom membrane surfaces (schematically shown on Figure 1. d view 1 and 3) and semi-quantitative EDX chemical analysis of the deposition along a vertical cross-section (Figure 1. d view 2). Vertical cross-sections were obtained by manual cleaving of the membranes.

TEM images were obtained on a JEOL JEM 2100 Field (HR) TEM. The samples were thinned down to about 50 nm thicknesses by ion milling which allowed imaging the deposition at horizontal cross-section at different heights along the pores (Figure 1. e view 4 and 5).

The ALD film growth was controlled and studied on the prepared reference substrates. Film thickness measurements were performed using ellipsometry (Horiba UVISSEL ER) with a spot size of about 3 mm by 1 mm to obtain an area average film thickness. The thickness was calculated using fitting models on the reference substrates. 4-point probes

sheet resistance measurements were performed on a Four Dimensions, Inc., Model 280, to monitor the conductivity of the ALD Pt layer.

Figure 3. SEM images of the cross-section of the nanoporous membrane. a to c is after 250 cycles Pt and subsequent 100 cycles Al_2O_3 deposition with exposures reported in **Table 1** and **Table 2**, leading to a successful deposition of both Pt and Al_2O_3 inside the nanopores. In b and c, a close-up view of a broken pore where the uniform Pt and Al_2O_3 layers can be seen. Images d to f shows the pores after 250 cycles Pt deposition only, using too short exposure resulting in an uneven and grainy deposition of the Pt in the nanopores. The grain size and density is observed to decrease from the top, d and e, to the bottom, f, of the pores.

4 Results

After successive iterations, the appropriate cycle pulse and purge times were found for deposition of Pt. This successful deposition was obtained with the recipe parameters and exposures reported in Table 1. For Al_2O_3 , a successful deposition was also obtained iteratively using parameters reported in Table 2.

The Figure 3. a to c, shows SEM images of the nanopores in a cleaved cross-section of the membrane (Figure 1. c view 2) after the subsequent deposition of Pt and Al_2O_3 . The Pt film forms a uniform layer from the top to the bottom of the pores. Figure 3. a to c shows SEM images of a broken pore in the middle of the AAO membrane height where both Pt and Al_2O_3 can be observed.

On the contrary, on Figure 3. d to f, where recipes with shorter pulse of 750 ms and 10s purge durations were used, the Pt film is not uniform along the pore depth. The deposited Pt forms bright grains instead of a uniform film, as shown with arrows on Figure 3. e, near the top of the pores, and f, near the bottom of the pores.

On the SEM images, the Al_2O_3 layer is difficult to distinguish, as it appears very transparent because of its thinness and because of the conductive Pt layer underneath. Hence, it is difficult to evaluate this layer using only SEM images. Therefore, the structures shown on Figure 3. a to c, were investigated with TEM imaging (Figure 4) to further improve the analysis of the Pt and Al_2O_3 deposition.

TEM images of horizontal cross-sections of the membrane, as shown by view 4 and 5 in Figure 1. e, at two different pore depths (very close to the bottom and in the middle of the top-half) are shown on Figure 4. b and c. These images clearly show the perfect coverage obtained for both Pt (darker) and Al_2O_3 (lighter grey) layer. The initial pore diameter of ~ 80 nm is reduced to ~ 60 nm by the deposition of the Pt layer and to ~ 40 nm after the deposition of the Al_2O_3 layer. The film thickness is measured to ~ 11 nm for Pt and ~ 9 nm for Al_2O_3 at both depths. As seen on the SEM images of Figure 3. d to f, Pt seems to nucleate in grains before forming a uniform layer. Diffraction contrast TEM and annular

dark field STEM images, not reproduced here, revealed the grains to be crystalline with an average size of less than 10 nm and interatomic plane distance of 2.6 Å.

EDX-STEM analysis was performed and confirmed the chemical composition of the two Pt and Al₂O₃ layers (Figure 4. a to c).

The deposition rate for Pt on Al₂O₃, Si and SiO₂ and for Al₂O₃ on Pt, Si and SiO₂ were measured using ellipsometry on reference flat substrates and are reported in Figure 5. a and b respectively. Once the film start growing, it is known to grow linearly with the number of cycles [51], which justifies the use of a few measurement points only to linearize the results.

Table 1. Recipe parameters for the deposition of Pt in nanopores.

Nanopore ALD recipe for Pt deposition			
Process temperature: 250 °C		Precursor source temperature: 35 °C	
Cycle steps:	Gas:	Exposure (Langmuir):	Remarks:
Precursor pulse	MeCpPtMe3	1 s	By own vapour pressure only (no Ar flow trough the source canister)
	MeCpPtMe3	1.25 s	By own vapour pressure + Ar flow through source canister
	<i>Total:</i>	2.25 s × 24 Pa = 0.405 · 10 ⁶ L	
Purge 1	Argon	30 s	
Reactant pulse	Oxygen	1.3 s × 160 Pa = 1.56 · 10 ⁶ L	
Purge 2	Argon	30 s	

Table 2. Recipe parameters for the deposition of Al₂O₃ in nanopores.

Nanopore ALD recipe for Al ₂ O ₃ deposition			
Process temperature: 200 °C		Precursor source temperature: room temperature	
Cycle steps:	Gas:	Exposure (Langmuir):	Remarks:
Precursor pulse	TMA	0.25 s × 160 Pa = 0.3 · 10 ⁶ L	By own vapour pressure
Purge	Argon	10 s	
Reactant pulse	Water vapour	0.7 s × 160 Pa = 0.84 · 10 ⁶ L	
Purge	Argon	15 s	

As expected from the properties of TMA/H₂O ALD, the Al₂O₃ film growth starts almost immediately (< 5 cycles) and continues at a rate of 1.1 Å/cycle, which are in line with earlier results [84]. However, the Pt film only starts to grow after about 125 cycles on Al₂O₃ substrates and ~160 cycles on SiO₂ substrates, with an apparent growth rate of approximately 0.8 Å/cycle. Interestingly, the Pt film growth does not fully start yet after 400 cycles on bare Si. Indeed, it was observed on SEM images that the reactivity of the Pt precursor on Si is poor resulting only in the formation of small and sparse Pt grains after 400 cycles.

Four-point probe sheet conductance measurements are presented in Figure 5. c. It was found that the Pt film starts to conduct after film growth initiation (~130 cycles). However, the conductance remains low until 250 cycles.

5 Discussion

The results in this study show the successful ALD deposition of highly conformal Pt and Al₂O₃ dual layers inside open AAO nanopores. The deposition quality is confirmed with SEM and TEM images, where a uniform film thickness is observed deep inside the pores, with the recipe parameters proposed in this work. The film thicknesses in the pores correspond to that measured on flat reference substrates, which further confirms the ALD growth mechanism and the deposition uniformity. To successfully deposit Pt deep inside the pores, the pulse duration has been increased to a total of 2.25 seconds for the Pt precursor. This is equivalent to an exposure of 0.405 · 10⁶ L. This corresponds to α = 1.46 %. To successfully deposit Al₂O₃, the cycle durations have also been slightly increased to an equivalent of 0.3 · 10⁶ L, corresponding to α = 97 % as compared with the prediction of the model. Compared to previous work

[95], the pulsing to purging time ratio for the Pt precursor was increased to 1:24, (i.e. 30s purge time) to obtain a smoother film growth inside and outside the pores.

Figure 4. TEM picture of the horizontal cross-section of the membrane, the pores extending out-of-plane for 250 cycles Pt and 100 cycles Al_2O_3 . a) and b) is a cross-section close to the bottom of the membrane. c) Cross-section in the middle of the membrane thickness.

Figure 5. ALD film growth characterization by ellipsometry and 4-point probes: a) Pt film growth starts after 125 cycles on Al_2O_3 and after ~160 cycles on SiO_2 . It does not fully start yet on pure Si after 400 cycles. b) Al_2O_3 film growth starts almost immediately, even on Pt. c) 4-points probes sheet conductance (1/ohm) measurements as a function of the ALD cycle number for Pt film on SiO_2 and on Al_2O_3 . The conductance remains low at 250 cycles. (lines are for eyes guidance only)

The growth per cycle for the Pt film, $0.8 \text{ \AA/cycle}$, is larger compared to that reported by Aaltonen *et al.* [96], $0.45 \text{ \AA/cycle}$, and Christensen [99], $0.64 \text{ \AA/cycle}$. The principal reason for this is to be found in the grain growth occurring during and just after the nucleation phase. The presence of Pt grains has been observed on the SEM and TEM images. Such grains have also been observed by Aaltonen *et al.* [96] and Shrestha *et al.* [100]. These grains are growing until coalescing into a continuous film. As consequence, until the film becomes continuous, the ellipsometry measurements provide an RMS value of the Pt thickness and explain the apparent growth rate reported. This value is however important in this work, as the deposition is done in narrow nanopores, for which clogging must be prevented. It is hence necessary to know the growth rate for the early growth phase, i.e. low number of cycles after growth initiation. It is expected to be higher due to the grain growth behaviour.

The film growth characterization results are used to investigate the experimental value of α for Pt. Based on the measured interatomic plane distance, the ideal growth per cycle, G_{pc}^{id} , can be assumed to be approximately the same, i.e. $2.6 \text{ \AA}$. In the early growth phase, the sticking coefficient is $\alpha_{gr} = G_{pc}^{gr} / G_{pc}^{id} \approx 31\%$. Hence, the approximate theoretical minimum exposures of Pt precursor during the growth phase becomes $\delta_{gr} = 0.0197 \cdot 10^6 \text{ L}$. From these results, it can be concluded that the model can be used to adapt the proposed recipe parameters to other pore geometries, but care should be taken regarding the exact value for the sticking coefficient α and for the exact gas

partial pressure in the reactor. The model is as such mostly useful to obtain a starting value for subsequent experimental optimization.

As mention earlier, the film growth initiation can be slow for deposition of metals on oxides or oxides on metal [101, 102], resulting in long nucleation phase. This behaviour is observed here as well. The nucleation phase for Pt was observed to be particularly long (>400 cycles) on pure Si immediately after hydrofluoric acid etching. As suggested in the two previous references, it is recommended to first proceed with the deposition of a thin oxide film to help promoting the nucleation of the Pt film. Still, on SiO₂ and Al₂O₃, long nucleation phases, ~160 and ~125 cycles respectively, were observed. Hämäläinen et al. have also reported that growing of platinum film using ozone as precursor, could help improving the nucleation phase [103]. It is possible that slightly higher process temperatures could also help, although it was reported that decomposition of the precursor occurs at temperatures as low as 300 °C, affecting the self-limiting ALD [96]. The grains size is also larger at higher process temperature or when using plasma assisted ALD, impeding on the deposition in narrow nanopore. Indeed, the formation of grains during the film initiation for ALD-Pt potentially defines a lower limit to the minimum film thickness. The grains can also be the cause for the very low sheet-film conductivity at very thin Pt layer thicknesses, just after the end of the nucleation phase. Similar observation have been made about thermal ALD of Ruthenium [104]. However, the process parameters proposed in this work allowed for a successful deposition inside the nanopore with a continuous Pt film as shown in the SEM and TEM images. Nevertheless, the grain growth can also be used advantageously in the realization of ultra-high surface area Pt electrodes, while keeping a low mass loading of this expensive catalyst [101].

For Al₂O₃, film growth start almost immediately and grains were never observed. However, increased pulse and purge durations were also required to obtain uniform film thickness in the pores as compared to deposition on planar substrates. Al₂O₃ was shown to grow well on all substrates studied, also on Pt and on bare Si. The Al₂O₃ film is amorphous and very conformal, as confirmed from the TEM images (Figure 4).

6 Conclusion

The results presented in this work show the successful deposition of Pt and Al₂O₃ in AAO nanopores using ALD. Pt was deposited in nanopores using thermal ALD technique. Al₂O₃ was also successfully deposited onto Pt inside the nanopores forming metal-oxide double layer coating. Specific recipe parameters were developed and reported for the ALD of Pt and Al₂O₃ into porous substrates. SEM and TEM analysis confirmed the high quality of the deposited film. The analysis revealed the formation of grains instead of smooth layer during film growth initiation for the deposition of Pt film with inadequate process parameters and revealed the difficulty for Pt ALD in narrow nanopore.

The results show the potential of ALD to create innovative functional nanoporous materials. In this work, an AAO membrane consisting of highly parallel synthetic nanopores was realized using a scalable process. The nanopores were functionalized with ALD to become highly porous Pt electrode with potential application in integrated high sensitivity chemical sensors. The addition of a second layer of oxide, in this study Al₂O₃, transforms them into electrostatically tuneable synthetic nanopores. This opens novel possibilities for the study of nanofluidic properties as well as for the potential development of nanofluidic biosensors or novel energy harvesting applications. These successful results allow pursuing the development of novel applications in the field of electrochemical sensing and bio-nanofluidics.

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