TEM-Based Metrology for HfO\textsubscript{2} Layers and Nanotubes Formed in Anodic Aluminum Oxide Nanopore Structures

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Nanotubes are fabricated by atomic layer deposition (ALD) into nanopore arrays created by anodic aluminum oxide (AAO). A transmission electron microscopy (TEM) methodology is developed and applied to quantify the ALD conformality in the nanopores (thickness as a function of depth), and the results are compared to existing models for ALD conformality. ALD HfO\textsubscript{2} nanotubes formed in AAO templates are released by dissolution of the Al\textsubscript{2}O\textsubscript{3}, transferred to a grid, and imaged by TEM. An algorithm is devised to automate the quantification of nanotube wall thickness as a function of position along the central axis of the nanotube, by using a cylindrical model for the nanotube. Diffusion-limited depletion occurs in the lower portion of the nanotubes and is characterized by a linear slope of decreasing thickness. Experimentally recorded slopes match well with two simple models of ALD within nanopores presented in the literature. The TEM analysis technique provides a method for the rapid analysis of such nanostructures in general, and is also a means to efficiently quantify ALD profiles in nanostructures for a variety of nanodevice applications.

1. Introduction

To a significant extent, the promise of nanotechnology may well be realized in devices and nanostructures that employ: 1) pattern definition through nanofabrication (typically, increasingly challenging lithography); 2) self-alignment, in which conventional processes of material addition or subtraction can be used to form more complex three-dimensional (3D) structures; and 3) nature’s tendency toward self-assembly. Both pattern definition and self-alignment are already hallmarks of the most advanced micro- and nanoscale technologies today, such as in complex semiconductor devices and circuits, where the watchword is to maximize self-alignment in relation to tiny patterns formed by difficult lithographic steps whose number should be minimized.\cite{rubloff2007,son2008,son2009}

Substantial attention and effort in nanoscale science and technology is aimed at exploiting self-assembly, a pathway with potential to reduce the complexity and cost of pattern definition.

One intriguing example is the combination of nanopore self-assembly in anodic aluminum oxide (AAO) formation together with electrochemical deposition of materials into the AAO pores in a self-aligned manner to form nanotube or nanowire structures. By using appropriate polymeric materials in nanopore arrays, fast electrochromic displays have been demonstrated, where the short distances required for ion diffusion in the nanostructures enable higher frames-per-second rates...
Researchers have also used atomic layer deposition (ALD) as an alternative self-alignment process to form nanotubes or nanowires in AAO,\[^{6-9}\] thus taking advantage of the unprecedented capability of ALD for thickness control (at the atomic scale) and conformality in the most demanding circumstances (aspect ratios of the order 100:1 or more, i.e., depth/width). ALD is a gas-phase deposition technique that utilizes self-limiting chemistry to control film thicknesses down to the atomic scale. It employs alternating reactant exposures of two precursors, which react on the surface sequentially to build thin films atomic layer by atomic layer. ALD proves to be an effective technique for the deposition of conformal films into high-aspect-ratio nanopores. However, conformality along the entire length of the pore is still a challenge in ALD due to diffusion limitations, although this problem can be alleviated in part by increasing exposure times during deposition runs.\[^{6,8,10,11}\]

While the perfection required in such ALD nanostructures depends on the application, measuring geometrical profiles and tolerances will be crucial to most if not all applications. For example, wall-thickness profiles of ALD nanotubes may well determine breakdown voltages and leakage current in energy-capture or -storage devices, while also determining the efficacy of nanoparticle drug-delivery systems built from such nanotubes. Metrology of 3D nanostructures will therefore be crucial to a variety of device applications as well as to optimizing ALD processes. This is, however, a difficult challenge.

Herein, we report an approach for the efficient metrology of high-aspect-ratio nanostructures and its application to nano-device structures employing ALD. It capitalizes on AAO templates for ALD nanotube fabrication, template dissolution, and subsequent transmission electron microscopy (TEM) imaging of the nanotubes, and algorithms for rapidly determining wall-thickness profiles along the nanotube axis. For HfO\(_2\) ALD nanotubes formed in AAO templates, we find that the resulting thickness profiles are in agreement with two prior models for ALD conformality. The approach demonstrated here presents a useful means for analysis of ALD process performance in nanostucture applications, as well as a more general method for metrology in some classes of relatively symmetric nanostructures.

### 1.1. Nanopore Metrology

Traditional techniques that attempt to experimentally measure thin films deposited in nanopores or trenches employ scanning electron microscopy (SEM) or TEM, which require lengthy sample preparation that typically involves sample cross-sectioning. Nanopores are especially difficult to cross-section due to their one-dimensional shape and small diameter. Ideally, the cross-sectional cut for a nanopore should be along the center axis of the nanotube to obtain an accurate measurement of sidewall film thickness along its full length. If the cut is not aligned with the pore axis, wall-thickness data can be skewed as a result of the pores’ cylindrical character. If the cross-sectional cut is off center, film-thickness measurements will be larger than the actual film thickness. In most of the literature, nanopores are imaged by cutting a bulk nanoporous film parallel to the nanopore axis and then searching along the face of the cross section to find pores that have been cut along their specific axis. Gordon et al. imaged a thin film deposited in elliptical pores deep-etched into silicon by cleaving the silicon along a natural crystallographic axis and imaging with a dual-beam SEM–focused ion beam system, which allowed for further in situ cutting of the sample.\[^{12}\]\[^{13}\] Elam et al. imaged a thin film deposited in nanoporous AAO by embedding the film in epoxy and polishing perpendicular to the nanopore axis. This allowed for accurate measurement of film thickness within the pores at different depths in SEM. However, to obtain a highly resolved thickness profile for the full length of a pore would require many iterations of polishing and SEM imaging for a single sample.\[^{6}\] Employing traditional SEM cross-sectioning techniques for the characterization of films deposited along the full length of nanopores is possible, but proves to be time consuming and depends on the researcher’s ability to apply cross-sectional cuts accurately along high-aspect-ratio structures.

### 1.2. ALD Conformality: Modeling and Experiment

There have been several studies in the literature which attempted experimentally and/or theoretically to understand the film deposition characteristics in nanopores or trenches.\[^{6,8,10-14}\] Gordon et al.\[^{11}\] developed a simple theory that could generate conditions for which full step-coverage could be attained within narrow high-aspect-ratio holes. This simple theory depends on the exposure time and partial pressure of the precursor species, which limits conformality (deep penetration into the nanopore) in the ALD process. The theory predicts the expected partial pressure \(P\) and time \(t\) required to achieve full step-coverage in a pore for a given aspect ratio. Assuming a cylindrical pore with one open end:

\[
(Pr)_{\text{total}} = S \sqrt{2 \pi m k T} \left[ 1 + \frac{19}{4} t + \frac{3}{2} a^2 \right]
\]  

where \(S\) is the saturation dose, \(m\) is the molecular mass, \(k\) is Boltzmann’s constant, \(T\) is the temperature during exposure, and \(a\) is the aspect ratio of the nanopore.

This equation applies to whichever precursor limits conformality or penetration into the pores. Which reactant is the limiting precursor depends on the precursor’s molecular mass \((m)\), the size of the exposure dose \((i)\), and the partial pressure of the precursor during exposure \((P)\). For example, from our experiments we can calculate the aspect ratio \((a)\) depending on \(P\), \(t\), \(m\), and \(S\) for the separate precursors, water and tetrakis(ethylmethylenamino)hafnium (TEMAH). For our experimental parameters (see Section 5) we estimate the aspect ratio of a pore for which TEMAH can fully coat to be about 30:1, while the aspect ratio of a pore for which water can coat is about 90:1. So for our experiments TEMAH is limiting the depth to which the ALD films can penetrate into the nanopores.

Larger pressures and exposure times will allow the reactant to penetrate deeper into the nanopores, whereas a larger molecular mass will hinder its ability to enter a nanopore. To
fully coat the AAO nanopores in our experiments (4 μm in depth, 60 nm in diameter, aspect ratio ≈ 70), the exposure time of TEMAH would have to be increased from 0.6 to ≈ 2 s.

As the model deals with submicrometer diameters with gas pressures around 1 Torr, the mean free path of the molecules within the gas is much larger than the diameter of the pore. Therefore, the assumption was made that gas diffusion within the pores could be modeled by molecular flow in which there are no gas-phase collisions. Researchers backed this theory with experimental evidence by depositing HfO₂ by ALD into high-aspect-ratio holes etched in silicon. The holes for which the ALD precursor exposure times were higher than the value generated by the model exhibited full step-coverage, but those with times lower than this value exhibited incomplete coverage, with thinning regions in the deeper portions of the pores.

Elam et al.[6] studied the ALD of Al₂O₃ and ZnO in the high-aspect-ratio pores of AAO membranes. The membranes had pores with diameters of 65 nm, depths spanning the full thickness of 50 μm, and open ends on either side of the membrane. Plain-view SEM images of the bottom, top, and middle of the Al₂O₃ templates deposited by ALD showed a dependence of film conformity on exposure time. The film thickness recorded from the middle of the template at some depth within a pore varied with exposure time when compared to the thickness recorded near the top and bottom of the template. The ZnO deposited by ALD in AAO membranes showed similar results. Zinc elemental maps of the cross-sectional profiles of the membranes created by an electron microprobe revealed smaller amounts of Zn near the center of the AAO cross section for shorter exposure times.

A simple Monte Carlo simulation was also submitted to explain variations with the step-coverage due to insufficient exposure times in both the Al₂O₃ and ZnO cases. The model assumed that molecular transport within the pores was governed by molecular flow and that the coatings reacted in a self-limiting manner characteristic of ALD. The model sectioned a cylindrical pore into an adjustable number of subsections or elements. Each element can be reacted with a finite number of precursor molecules depending on its surface saturation. Two random-number generators were employed in the model, one governing the random walk of sets of reactants within the pores and the other governing the reaction of the sets to available unreacted elements of the pore. Once a set of reactants reacts with one of sectioned areas (elements), the cylindrical diameter of that section is decreased and the section is no longer available for further reaction during the current cycle. As the length of each step in the random walk of the reactants decreases with decreasing local diameter, this modeling technique gives a dynamic picture of molecular flow and how it relates to the ALD of thin films within nanopores. In both Gordon’s and Elam’s studies, experimental measurements of thickness trends along the depth of a nanotube were not extensively explored.

1.3. Our Approach

Our approach was developed in order to measure thin films deposited in nanopores without extensive cross-sectioning. This was achieved by the use of AAO as a nanoporous template. One of the novelties of using AAO in this research is its ability to be removed by dissolution, thus releasing deposited materials into solution. This novelty is exploited in the template-based synthesis method[7,15–17] to create nanotubes, nanorods, and carbon nanotubes with very uniform structures and manufactured in high density. AAO films can be structured to comprise cylindrical nanopores with uniform dimensions (15–300 nm in diameter) distributed in a dense hexagonal array. Anodization conditions, including voltage, temperature, and type of electrolytic solution, direct pores to self-assemble perpendicular to the substrate with control over pore depth and diameter.[18–22] Different deposition techniques applied to AAO membranes, including surface sol–gel,[23,24] electro-deposition,[25] electroless deposition,[26] and gas-phase deposition,[27] have yielded nanotubes and nanorods with uniform sizes and dimensions through the template-based synthesis technique.

Herein, a simple and robust methodology is put forward that details how to experimentally measure template-synthesized nanotubes processed by ALD. HfO₂ films were deposited by ALD onto AAO templates, which contained pores that were ≈ 4 μm in depth and ≈ 60 nm in diameter. TEM images of single nanotubes from this sample were obtained and analyzed by using image analysis code based on a simple geometric model. Experimentally recorded trends for multiple nanotubes are presented as an example of this image analysis technique. These trends are then compared to results from the recreated theoretical models outlined above and originally reported by Elam et al.[6] and Gordon et al.[11]

1.4. Cylindrical Assumption

Nanotubes produced by the template synthesis method in AAO have a cylindrical shape, characteristic of the pores in which they are formed. This cylindrical shape can be seen in the SEM and TEM images in Figure 1. After ALD to form nanotubes in the pores and subsequent dissolution of the AAO template, amorphous HfO₂ nanotubes (Figure 1c) appear in the TEM image as long rectangular ribbons with dark edges running along their lengths. The edges are attributed to the higher material density at the walls. At one end the nanotubes display a broadened structure reminiscent of the head of a nail, which is caused by the ALD HfO₂ material deposited on the top surface of the AAO between its nanopores. At the other end the nanotube, the walls thin due to the somewhat reduced deposition deeper into the AAO nanopore, indicative of deviation from perfect conformity (e.g., from depletion effects within the nanopore). Assuming that the nanotubes take on the shape of a cylinder, the thickness over which an electron would have to travel at any given point along a cross-sectional line of length L perpendicular to the nanotube axis is:

\[
L = 2 \sqrt{b^2 \left( \frac{1 - \left(\frac{x-a}{b} \right)^2}{a^2} \right)} - \sqrt{d^2 \left(1 - \frac{(x-a)^2}{c^2} \right)}
\]

where a is the horizontal outer radius, b is the vertical outer radius, c is the horizontal inner radius, and d is the vertical inner radius.
radius (see Figure 2). This equation is plotted in Figure 3 for the case of an ideal cylinder and an elliptic cylinder. The two plots are overlaid on cross sections that are indicative of the nanotube’s cylindrical nature. For the case of an ideal cylinder, parameter $a$ should be equal to $b$, and parameter $c$ should be equal to $d$. For the case of a film deposited in an elliptical-shaped pore, the parameter equivalencies for an ideal cylinder would not hold true. However, as a result of the uniform deposition provided by ALD, the wall thickness of the elliptic cylinder created within this type of pore should be uniform, and therefore wall thickness would be equivalent to $(a-c)$ which would be equivalent to $(b-d)$. The parameter $L$ can be correlated with image darkness associated with loss of electron transmission through more material. In both cases in Figure 3, thickness profiles show that the thickest portion of each cylinder corresponds to the edge of the inner surface and the thinnest portion of the cylinder corresponds to its outer edge on either side of the cylinder.

### 1.5. Bright-Field TEM

Bright-field TEM imaging records the intensity of electrons transmitted through a thin sample, so that darker areas indicate thicker or denser regions along the beam direction. As suggested by Figure 3, this permits nanotubes to be imaged as two-dimensional projections along the beam axis. For polycrystalline samples, intensity differences in bright-field images are due not only to scattering losses associated with sample thickness but also to electron diffraction by the crystal lattice. Depending on how a crystal is oriented with respect to the beam, it will diffract more or fewer electrons, thus leading to a darker or brighter intensity in the image for the area of the crystal. In our experiments, the low temperature associated with the ALD process renders all HfO$_2$ films amorphous, so that crystal diffraction mechanisms do not contribute to the image. The amorphous character of the nanotubes was confirmed by SAD patterns taken during the course of the TEM experiments (inset of Figure 1d). For amorphous and compositionally uniform samples, since the atoms in the material have no order, orientation of the sample with respect to the beam does not matter either. Thus, the number of electrons passing through the sample will only be a function of the thickness of the deposited film. It is this property of the transmitted electrons in amorphous, thin materials that is exploited for our analysis.

### 1.6. Image Analysis

The simple geometric model outlined above can assist in the analysis of nanotubes imaged in bright-field TEM. Application of this model to experimental intensity profiles can yield information about the dimensions of the nanotubes, such as inner and outer diameter and wall thickness. An image of an amorphous HfO$_2$ nanotube is shown in Figure 4. An intensity profile was taken perpendicular to the central axis of

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**Figure 1.** a) SEM image of the cross section of an AAO template showing the vertical profile of the nanotubes, b) top view SEM image of an AAO template, c) TEM image of HfO$_2$ nanotubes made by depositing HfO$_2$ by ALD into AAO templates followed by template dissolution, and d) TEM image of a single HfO$_2$ nanotube; inset: selected-area diffraction (SAD) pattern.

**Figure 2.** Cross section of an elliptic cylinder.
the nanotube, with intensity data averaged over a 10-nm portion along the nanotube’s length. The plot in Figure 4 shows the data retrieved by the intensity profile. The data consist of averaged (along the 10-nm length of the profile) 8-bit grayscale values with respect to the position along the profile. If we apply the cylindrical model to the imaged nanotube, we can denote the inner-diameter edge of the nanotube as the thickest part, and therefore the intensity values recorded in that area should be the lowest. Likewise, the outer-diameter edge corresponds to the thinnest part in the profile, and therefore the intensity values should be the highest or equivalent to the background of the image. Therefore, the distance along the x axis between where the data first meet the background and where the first minimum in the data occurs is equivalent to the wall thickness of one side of the nanotube. Similarly, the other sidewall thickness is equivalent to the distance between where the second minimum in the data occurs and where the data meet the background again. The wall thickness of the upper sidewall is 10.2 nm, while that of the lower sidewall is 10.5 nm for the example in Figure 4.

The line profile analysis method detailed above can be used to create a rapid characterization method for ALD conformality in high-aspect-ratio nanopores. Line profiles can be taken in succession along the whole length of a nanotube giving variation of outer diameter, inner diameter, and film thickness with respect to length from top to bottom. The outer diameter of the nanotube is defined by the AAO template in which it is formed. Thus, for an AAO template with constant pore diameters along its whole depth, the nanotubes created should have constant pore diameters. To realize the rapid characterization method for ALD conformality, a Matlab routine was developed. First, an image of a nanotube (similar to the image in Figure 4a) is inputted into the program and the user draws a multisegmented line through the center axis of the nanotube. The user also inputs various parameters, such as the number of data points, data-point separation, and area of the cut for which the wall thickness is measured. The Matlab routine will then take the user inputs and output a graph of thickness versus nanotube length.

All nanotubes measured by this method were isolated, broken-off pieces of a larger bulk nanotube film, to avoid inaccuracies that might arise from nanotubes stacked closely together in an image. Even though we do not know exactly where each nanotube broke off from the bulk film, we can still estimate their aspect ratio using images which contain bunches of nanotubes that are intact from top to bottom (Figure 1c). These nanotubes have an approximate length of 1500 nm and a thickness of about 60 nm, that is, an aspect ratio of 25:1. This is consistent with the prediction (above) from Gordon’s model that our experimental ALD process parameters should achieve conformality only to an aspect ratio of about 30:1.
1.7. Beyond the Cylindrical Assumption

Experimentally we cannot assume that the nanotubes will always maintain a cylindrical shape. Nanotubes with thin-film gradients along their lengths often look as if their outer diameters increase as their wall thicknesses decrease. We believe this is an artifact of the drying process, in which surface tensions cause thin-walled nanotube portions to deform to an elliptical shape or flatten and collapse. The nanotube’s inner and outer diameters are both equally affected by deformation in this manner during drying. During this deformation the inner and outer diameters of the nanotube should be equally affected. Depending on the thickness and properties of the film the collapse can be full or partial. A full collapse is characterized by the cylinder being completely flat with no access to its inner cavity. A partial collapse is characterized by the center part of the film collapsing but leaving cavities near the edges of the nanotube. In the case of a partial collapse, measurement methods should still hold true, since a quasi-cylindrical edge should still be available for measurement.

Another artifact that could be of some importance is the differential strain built in by the process, particularly differential thermal expansion from cooling after ALD. Since the thermal expansion coefficients \( \alpha \) in our case (substrate Al2O3 and film HfO2) are similar, and our ALD process is carried out at a relatively low temperature \( T \) (200 °C), the strain \( \varepsilon \) of the HfO2 nanotubes due to stress relief upon release from the AAO template was estimated using the standard relation:

\[
\varepsilon = (\alpha_2 - \alpha_1) \Delta T
\]  

This suggests only a tiny change in dimension (0.009%) due to the difference in thermal expansion coefficients of HfO2 (\( \alpha_1 = 1.31 \times 10^{-6} \text{ C}^{-1} \)) and Al2O3 (\( \alpha_2 = 1.89 \times 10^{-6} \text{ C}^{-1} \)) that will occur upon cooling from the ALD growth temperature of 200 °C to room temperature.\(^{[27]}\)

Variation of the inner diameter with depth into the AAO pore is governed by the ALD process. The number of cycles of ALD as well as the film thickness per cycle will define the inner diameter of the nanotube. Wall-thickness measurements are simply made by subtracting the outer diameter from the inner diameter and dividing by two. This measurement should be free from any artifacts caused by the collapse of the cylinder in thinner sections, since, as stated previously, the inner and outer diameters of the nanotube should be equally affected. Also, the wall-thickness measurements should not be affected by the brightness of the electron beam when the image was taken, or by any nondestructive post-processing image adjustments (i.e., gamma, brightness, contrast, etc.). The minima in the data will always outline the inner diameter of the nanotube and the maxima will always outline the outer diameter of the nanotube.

2. Results

2.1. Method of Data Extraction

Using the image analysis techniques discussed above, thickness profiles over the full measurable lengths of multiple individual nanotubes were made, which yielded data for film thickness as a function of depth within AAO porous membranes. As explained above, not all nanotubes obtained from the templates were fully intact from top to bottom; for example, isolated nanotubes (as in Figure 5) were sometimes shorter than those that remained as bunches (as in Figure 1c). Furthermore, one cannot rule out breakage/loss of the thinnest portion of the nanotubes. Nevertheless, thinning was readily observed near the deepest end of the examined nanotubes, and thus the rate at which the films thinned as a function of depth (or slope at the nanotube end) was fully measurable in this experiment. The thinning rate or slope is significant because it reflects the experimental parameters in ALD and the dimensions of the nanopores, and can be compared to ALD conformity models. In Figure 5, thickness versus length data are plotted for a single nanotube. These data were fitted with a sigmoidal curve:

\[
y = \frac{a}{1 + e^{-\frac{x-b}{c}}} + d
\]

using the nonlinear least-squares regression method. This curve fit assisted with singling out a region of interest within the data by providing a smooth analytical curve through the data, which helps to identify the region of decreasing thickness, that is, the portion of the nanotube which is presumably most indicative of ALD depletion. The curve fit also facilitates more quantitative investigation: specifically, its second derivative with respect to position along the length of the nanotube provides a minimum and maximum at either end of the ALD

Figure 5. Schematic image of how the data range was narrowed down to obtain a region of interest from which a linear slope could be extracted. The thickness data with respect to distance from the top to the bottom of the nanotube are fitted with a sigmoidal curve. The second derivative of the sigmoidal curve is taken, for which the maximum and minimum points define the region of interest.
depletion region (the region of prime interest), where curvature is highest in the original sigmoid fit. A linear regression was then fitted to the extracted data in this ALD depletion region, and the slope was determined from this regression as a measure of the rate of thinning for the imaged nanotube.

2.2. Comparison to Prior ALD Conformality Results

Using the semiautomated image analysis metrology described above and with these regression methods, experimental data for slope in the ALD depletion region, as well as the average nanotube wall thickness and diameter in this region, were determined (Table 1) for 16 different nanotubes fabricated from AAO templates deposited with 10 nm of HfO$_2$ under the same ALD conditions. Slope measurements were quite repeatable amongst the set of 16 nanotubes, with an average slope of around $-0.020$ and a standard deviation of 0.002 (or 10%). This is apparently the first time such slopes to indicate ALD depletion effects have been reported, which suggests that our methodology provides a valuable approach for nanotube metrology in general, and for understanding the consequences of ALD process chemistry and conformality in particular.

As an alternative, we compared these results to those generated by the kinetic simulations/models reported by Gordon et al.$^{[11]}$ and Elam et al.$^{[6]}$ We recreated each of these mathematical models for the parameters describing our experimental conditions. The areal density of reactive sites$^{[11]}$ was taken as $2.5 \times 10^{18}$ sites m$^{-2}$. A sticking coefficient of 100% was used for both models (sticking coefficients are fixed in Gordon’s model but adjustable in Elam’s model). We treated the case of a cylindrical nanopore with a diameter of 60 nm and depth of 4 $\mu$m, with the experimentally measured deposition rate of 0.1 nm cycle$^{-1}$.

Table 1. Experimentally measured slopes for 16 separate nanotubes. Experimental measurements of the slopes can be compared directly to values derived from two literature models.$^{[6,11]}$

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-0.021$</td>
</tr>
<tr>
<td>2</td>
<td>$-0.019$</td>
</tr>
<tr>
<td>3</td>
<td>$-0.021$</td>
</tr>
<tr>
<td>4</td>
<td>$-0.021$</td>
</tr>
<tr>
<td>5</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>6</td>
<td>$-0.016$</td>
</tr>
<tr>
<td>7</td>
<td>$-0.016$</td>
</tr>
<tr>
<td>8</td>
<td>$-0.024$</td>
</tr>
<tr>
<td>9</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>10</td>
<td>$-0.022$</td>
</tr>
<tr>
<td>11</td>
<td>$-0.021$</td>
</tr>
<tr>
<td>12</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>13</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>14</td>
<td>$-0.018$</td>
</tr>
<tr>
<td>15</td>
<td>$-0.017$</td>
</tr>
<tr>
<td>16</td>
<td>$-0.017$</td>
</tr>
<tr>
<td>Average</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Gordon’s model provides the depth of coverage for a single cycle [see Eq. (1)]. To obtain a slope it was necessary to iterate the model, with each cycle encountering a smaller diameter for the ALD-covered nanopore. This iteration allowed us to simulate the entire 100 cycles of our ALD experiment. Since gas kinetic flow within the nanopore is strictly molecular flow, the rate of thinning depends only on the ALD process parameters, not on the pore dimensions or number of ALD cycles. We determined the slope expected for the ALD depletion region from Gordon’s model to be 0.0196, in very good agreement with our experimentally observed value of 0.020.

Elam’s Monte Carlo model has fewer assumptions and actually simulates molecular flow within a nanopore assuming random-walk behavior of precursor molecules. The nanopore is split up into an adjustable number of sectors along its depth. Simulation of ALD was achieved by cycling of the precursor exposures in which each sector could be reacted only once in each cycle. As the number of sectors used had some effect on the outcome, the simulation was run multiple times with sector numbers of 25, 50, 75, and 100. The average slope recorded after five simulations for each sector number was $-0.0186$ with a standard deviation of 0.004. Thus, the results from Elam’s simulations also agree well with the slopes in the ALD depletion region determined from our experimental data and image analysis. Our results are apparently the strongest validation currently available for the two models.

3. Discussion

ALD, with its capability for atomic-level thickness control and conformal coverage over very demanding 3D nanoscale topography, is emerging with a major role in nanotechnology. It has already been applied to coating of nanoparticles,$^{[28-31]}$ carbon nanotube electronics,$^{[32-34]}$ and energy systems, and interest is increasing in the use of selective ALD.$^{[35,36]}$ Dozens of different ALD process chemistries have been identified,$^{[37-42]}$ which place a premium on rapid characterization and understanding of ALD process performance and material quality as realized in nanostructure devices.

The uniqueness of ALD for deposition control is derived from the self-limiting adsorption/reaction of each precursor half-cycle, which leads to both atomic-level thickness control and unprecedented conformality and uniformity. However, in reality the self-limiting behavior is not perfect, and leads to depletion effects and process complexity associated with precise precursor doses and interactions between the doses of the different precursors. While the precursor surface reactions are primarily self-limiting and thus account for the high value seen in ALD, it is the deviations from ideal self-limiting reaction that determine the ultimate performance of ALD processes, and the extreme geometries encountered in nanostructure applications push the limits of ALD process performance. The very high aspect ratio of AAO nanopores (depth/width $\approx 50–100$) at nanometer diameters illustrates this point, and it is notable that these aspect ratios are comparable to or even higher than those of state-of-the-art structures in semiconductor chips today.
Because of this, the development of new metrology approaches to nanostructure fabrication and ALD processes is critical. This is emphasized in the International Technology Roadmap for Semiconductors,[43] which underscores the need to develop new metrology techniques for sidewall thicknesses in nanostructures, as well as other methods demanded by the new materials and device geometries emerging in nanotechnology. Metrology for novel nanostructures is challenging both qualitatively and quantitatively, because ever-smaller dimensions are encountered as new device geometries are invented or achieved. Other high-aspect-ratio nanopore structures (i.e., track-etched polycarbonate membranes[44,45]) used for template-based synthesis of nanotubes could also benefit from this type of metrology.

4. Conclusions

AAO templates in combination with the deposition control delivered by ALD processes present an attractive route to nanostructure fabrication, but measurement technology to guide and control these processes is challenging. This work demonstrates three relevant metrology advances. First, by dissolution of the AAO template after nanostructure formation, the structures are freed and readily observed by TEM, without the need for difficult and painstaking work to create cross-sectional TEM samples. This is useful as part of a metrology strategy whether the intention is to manufacture free nanostructures or nanodevices retained in the AAO template.

Second, an image analysis method has been developed which semi-automates the extraction of nanotube diameter and wall thickness as a function of depth into the original nanopore. Such a spatial metrology will be important for a variety of applications, because the distribution of wall thicknesses and diameters will most likely determine important properties, such as breakdown voltage and leakage current in electrical devices, diffusion through nanotube walls in chemical or drug-delivery applications, or sensitivity when nanotubes are used as markers, for example, in diagnostic imaging.

Third, we have shown a means to extract parameters from the ALD profiles that reflect the process limitations of ALD. The deposition regime where nanotube wall thinning is observed reflects the depletion of the ALD precursor reaction deep in the nanopores, that is, a regime which will limit applicability in the more demanding nanostructure geometries. We have derived a characteristic slope parameter from fits to the deposition profiles that may be regarded as measures of the self-limiting performance of a specific ALD process. This can be compared to modeling results and may be attractive as a rapid indicator of ALD process robustness and simplicity, since better self-limiting behavior is desirable. Indeed, rapid feedback of this sort is important given the dozens of ALD process chemistries now of interest to a variety of application areas.

These methods are useful in two domains. All three components are directly relevant to the understanding and control of ALD processes and their integration into specific nanodevice fabrication. Indeed, the measurements presented here provide what is likely the strongest confirmation to date of existing models for ALD conformality, including both prediction of slopes at the deepest penetration point and aspect ratios for which conformality is achieved. In addition, the first two (and perhaps the third) hold value for a broader class of nanostructures, including those made using AAO templates with electrochemical or other deposition means, and perhaps also using other kinds of templates.

5. Experimental Section

AAO procedure: A porous AAO template was synthesized by a two-step anodization method.[46] In brief, a piece of electro-polished aluminum foil (99.99%, Alfa Aesar) was anodized at 40 V and 10 °C in an electrolytic bath of oxalic acid (0.3M). In the first step of the anodization process, the foil was anodized for long enough (7 h) so that the pores were ordered and growing orthogonally with respect to the substrate. The AAO film that was created was then etched off by an aqueous mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%), leaving a pretextured and ordered aluminum surface. In the second step, the foil was anodized for a set amount of time (1 h) that defined the depth of the pores to be 4 μm. The pore diameters were adjusted to ≈60 nm using a pore-widening solution of phosphoric acid (0.1 M) at 38 °C. Membranes were not detached from the substrate before ALD processing and therefore its nanopores only had one open end.

ALD process: High-K dielectric HfO₂ thin films were deposited by alternating reactant exposures of TEMAH, that is, Hf(N(CH₃)(C₂H₅))₄ (99.99% grade, Sigma–Aldrich), as the organometallic precursor and deionized (DI) water as an oxidant. The ALD equipment consisted of a stainless-steel tube (25” in length and 3” in diameter) in a tube furnace. Precursors and nitrogen gas were introduced through one end of the reactor, while unreacted precursors and reaction by-products were exhausted at the opposite end of the tube to a rotary-vane vacuum pump. Substrates were introduced into the system through a removable flange at the exhaust end of the reactor. The wafer temperature was measured by a thermocouple to be 200 °C. During each of the self-limited half reactions corresponding to the alternating exposures of TEMAH and water, reactants were dosed to achieve full surface saturation, which resulted in excellent thickness control at the atomic level as a submonolayer of oxide was consistently deposited for each cycle.

A reservoir containing TEMAH (5 g of liquid) was placed in an incubation oven set to 105 °C to achieve a vapor pressure of approximately 2 Torr. Prior to each exposure, the TEMAH gas was fed into a 20-mL isothermal volume and TEMAH doses were controlled by timing the opening of a pneumatically actuated valve. A dose of TEMAH (0.85 μmol) was determined to be sufficient to achieve full saturation on a Si substrate located next to the AAO template. In the case of water, the vessel was kept at room temperature. Accurate water dosage was achieved by filling a 20-mL isothermal volume up to a targeted pressure monitored by a capacitance gauge, and then discharging the gas into the
reactor for a fixed amount of time. This pressure end-point control approach was required to minimize the effect of cooling of the water source over the duration of the process due to the forced vaporization of the precursor and the resulting decrease of its vapor pressure. Full saturation was achieved by filling up the volume at 7 Torr. We estimated the partial pressures of both the water and TMAH doses to be \( \approx 7 \text{ mTorr} \) from the pressure spike recorded by a downstream pressure sensor (average change in pressure over peak width).

Throughout the deposition process, a flow of nitrogen (30 sccm) was continuously fed into the reactor to maintain a reactor pressure of 96 mTorr. A growth rate of 1 Å cycle\(^{-1}\) was achieved over a 100-cycle process. Prior to each pulse, a 10-s N\(_2\) purge was initiated to ensure that unreacted precursor and reaction by-product, mainly \((\text{CH}_3\text{C}_2\text{H}_5)\text{NH}\), were adequately purged out of the reactor.

**TEM characterization:** After ALD, samples were placed in an NaOH solution (0.1 M) for 1 h, which dissolved away the alumina JEOL 2100 microscope with a LaB\(_6\) source operated at 200 keV. carbon-coated Cu TEM grid. TEM studies were performed on a with DI water, a drop of the solution was placed on a Properties Laboratory (NISP Lab).

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