Chemical
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A Kinetic Model for Step Coverage by Atomic Layer Deposition in Narrow Holes or Trenches**

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Highly conformal coatings can be deposited inside narrow features, such as holes, using complementary self-limiting reactions of two vapors with a surface. A simple theory is developed for the conditions needed to deposit coatings with uniform thickness in narrow holes of arbitrary cross section. Two conditions are found to be necessary: 1) certain minimum amounts of vapor must be supplied, and 2) a certain minimum product of vapor pressure and its exposure time at the entrance to the hole. The theory is in good agreement with data from the reaction of hafnium dimethylamide vapor and water vapor to form hafnium dioxide films that are completely conformal in holes with an aspect ratio of 43. The theory provides simple scaling laws to predict the conditions needed to coat holes with other aspect ratios.

Keywords: Atomic layer deposition (ALD), Hafnium dioxide, Kinetic models

1. Introduction

Conformal coatings play an increasingly crucial role in a wide variety of technologies. For example, in microelectronics, films of insulators, conductors, diffusion barriers, adhesion layers, etch stops, and protective layers must be placed inside holes and trenches that are being made narrower and deeper every year. Aspect ratios (defined for a hole as the ratio of length to diameter) of five to ten are used today, while aspect ratios an order of magnitude larger will be used in the near future for devices such as trench capacitors in semiconductor memories.[1] In filtration and gas separation systems, conformal coatings can be used to reduce pore sizes in a highly controlled way.[2] Conformal coating processes can spread catalysts efficiently over the surfaces of supports with high surface area.[3]

Physical vapor deposition methods, such as evaporation and sputtering, have limited ability to coat structures with high aspect ratios. Some CVD reactions can coat or even fill holes with high aspect ratios. For this reason, CVD is being increasingly used in microelectronics. However, not all CVD reactions are conformal; conformal CVD reactions must have their slowest, rate-limiting steps on the surface of the growing film, rather than in the gas phase. Particularly high aspect ratios can be coated conformally by a CVD method in which two complementary reactant vapors are supplied to a surface in alternating pulses. In this way, their reactions are forced to be entirely on the surface, since they never meet in the gas phase. This method of deposition is commonly known as atomic layer deposition (ALD).[4]

In order for an ALD reaction to give 100 % step coverage, three separate conditions must be met:

1. *Chemistry*: The chemistry of the two reactants must be suitable. In particular, each of the two reactants must undergo a self-limiting reaction with the surface covered with the reaction products from the other reactant. These reactions must be fast, complete and irreversible, and after each reaction is complete, no further reaction must occur between any excess reactant and its own reaction products on the surface. The reactants and by-products must be sufficiently volatile at the deposition temperature that no physical adsorption occurs. The reactants and volatile reaction by-products must not etch the film. Meeting these chemical conditions is a matter of choosing the right reactants. In this paper, we will show that the ALD reaction of hafnium dialkylamides with water appears to meet all of the required chemical criteria for achieving highly uniform coatings.
2. *Stoichiometry*: A large enough dose of each reactant must be supplied so that the stoichiometric amount of material is available for deposition over the entire surface, including the flat surface and the interior surface of holes in the substrate, as well as all of the inside surface of the reaction chamber that is exposed to the vapors. The stoichiometric calculation is just the straightforward counting of the molecules going into the reaction. The stoichiometric dose is not necessarily determined by the maximum number of reactive sites; the bulky ligands on most ALD precursors usually prevent complete saturation of all reactive sights.

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3. *Kinetics*: The doses of each reactant vapor must be present at the entrances to the holes for a long enough time so that the reactant reacts with the entire interior surface of the holes. The kinetics of the depositions are limited by the diffusive flow of molecules down the hole, rather than the surface reactions that occur on a much faster time scale. We treat this diffusion for the case of molecular flow, in which the mean free paths of the reactant molecules are much larger than the diameter of the holes.

The paper begins with a brief account of the stoichiometry, resulting in a minimum amount of each reactant that must be supplied to cover the surfaces. Then kinetic theory is applied to the diffusion of the reactants, yielding a simple formula for the exposure time during which the reactant vapor must be supplied to the entrance to a hole. We then test the theory against ALD experiments depositing uniform hafnium oxide coatings inside very narrow holes with aspect ratios up to 43.

2. Stoichiometric Requirements for 100 % Step Coverage

In an ALD reaction, the reactants are supplied in alternating doses to the surface. Only a certain maximum amount of each reactant can be chemisorbed onto the surface from each dose; this is what is meant by a self-limiting reaction. For the specific ALD reaction that we are studying in this paper, we find that only a saturation dose $S_{Hf} = 2.5 \times 10^{18}$ molecules of $Hf(NMe_2)_4$ vapor can be adsorbed on a square meter in the first half of the cycle, as shown in Equation 1.

$$\mathrm{Surface(OH)_2 + HfL_4(g) \longrightarrow SurfaceO_2HfL_2 + 2\,HL(g)} \quad (1)$$

L is an alkylamide ligand, such as dimethylamide, $-N(CH_3)_2$. If more than 2.5×10^{18} molecules per square meter are supplied, this excess material does not chemisorb onto the surface, and any unreacted or physisorbed molecules will be pumped out of the chamber by the vacuum pump. Similarly, only a saturation dose $S_0 = 5 \times 10^{18}$ molecules of water can be chemisorbed on a square meter in the second half of the ALD cycle, as shown in Equation 2.

$$\mathrm{2\,H_2O(g) + SurfaceO_2HfL_2 \longrightarrow SurfaceO_2Hf(OH)_2 + 2\,HL(g)} \quad (2)$$

At the end of these two self-limiting reactions, 2.5×10^{18} molecules of solid HfO_2 have been uniformly deposited on each square meter of surface, as measured by Rutherford backscattering (RBS) from the deposited film. This amount of film corresponds to 0.1 nm thickness per cycle. To within the accuracy of our experiments, the yield of these reactions is 100 %, in that every hafnium or oxygen atom entering the reactor as part of the saturation dose of a reactant becomes part of the film (impurities (carbon and nitrogen) were not detected in the RBS). In practice, a slight excess (about 10 %) over the saturation dose of each reactant is used, in order to make sure that all parts of the surface are saturated.

The amount of each reactant needed to cover an entire surface is given by the saturated surface density per cycle (S) times the entire surface area to be coated, including the substrate (its flat surface and the interior surface of any holes in it), as well as the interior surface of the reactor chamber. Deposition also takes place on part or all of the back surface of planar substrates by diffusion through the narrow space between the back of a substrate and the holder on which it is resting.

The area of the flat substrate surface and the reactor surface is straightforward to measure. At 100 % step coverage, the same number of atoms will also be deposited on the bottom of the hole, so for accounting purposes the bottoms of the holes can simply be included in the flat area, no matter how many holes are present.

The interior area of the vertical surface of a hole is given by the product of its perimeter (p) and its depth (L) so the vertical surface of a hole accumulates the following number of atoms per cycle (N_{walls}) as shown in Equation 3.

$$N_{walls} = S(Lp) = S\left(4A_{hole}\frac{Lp}{4A_{hole}}\right) = 4SA_{hole}a \quad (3)$$

Equation 4 gives the definition of the “aspect ratio” of a hole with cross-sectional area A_{hole}.

$$a \equiv \frac{Lp}{4A_{hole}} \quad (4)$$

For a hole with circular cross section, the aspect ratio reduces to the ratio of its length to its diameter. The area of the vertical walls of a hole (Lp) is simply given by the cross-sectional area of the hole times its aspect ratio (a) multiplied by 4. The stoichiometric amount of reactant required to coat substrates conformally inside holes increases linearly with a of the holes.

3. A Kinetic Model for the Diffusion of Reactants

3.1. Deposition onto a Flat Surface

How fast do the precursor molecules deliver their atoms into the film? Even if a stoichiometrically sufficient number of atoms enter the reactor chamber, a certain minimum amount of time will be needed before they can be deposited on the entire surface of a patterned substrate. We estimate this minimum exposure time from fundamental principles.

For ideal ALD reactants, each chemisorption reaction has 100 % sticking coefficient on a surface previously satu-

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rated with the other reactant, until the reactant reaches its saturation coverage and then its sticking coefficient drops abruptly to zero.

Before considering the case of a hole or trench, we consider the simpler case of the kinetic description of ALD on a flat surface. Kinetic theory gives the impingement flux (*J*) onto a surface (number of molecules crossing a plane from one side per unit time and unit area) as shown in Equation 5.[5]

$$J = \frac{P}{\sqrt{2\pi m \mathrm{k} T}} \tag{5}$$

P is the partial pressure of the precursor near the surface [Pascal = N m^{-2}], *m* is the molecular mass [kg], k is Boltzmann's constant [1.38×10^{-23} J K^{-1}], and *T* is the temperature [K]. The time (*t*) required for the vapor to supply a saturation dose (*S*) is then given by Equation 6.

$$t = \frac{S}{J} = \frac{S\sqrt{2\pi m \mathrm{k} T}}{P} \tag{6}$$

The product of the precursor partial pressure and the time (*Pt*) is a useful measure of the amount of exposure the surface has had to the precursor vapor. From Equation 6, the exposure required for saturation of a flat surface is given by Equation 7.

$$Pt = S\sqrt{2\pi m \mathrm{k} T} \tag{7}$$

We measure the saturation exposure for $Hf(NMe_2)_4$ to be $S = 2.5 \times 10^{18}$ molecules m$^{<M-2>}$. Assuming that its vapor is monomeric, its molecular mass is 5.88×10^{-25} kg. We consider a substrate temperature $T = 200$ °C = 473 K. Substituting these values into Equation 7 gives a value for *Pt* of 3.9×10^{-4} Pa s. A common non-SI unit used for quoting exposure is the Langmuir = 10^{-6} torr s. Hence, a value for *Pt* of 3×10^{-6} torr s is also 3 Langmuir. This means that this reaction could be completed either by exposure to 1 torr for three microseconds, or 1 mtorr for three milliseconds, or 6 mtorr for 0.5 ms, etc. Numerically, the Langmuir is a conveniently sized unit, in that fast surface reactions saturate after a few Langmuir of exposure. For the water vapor reaction with a surface previously saturated with hafnium dimethylamide, the saturation exposure of water was found to be 1.3 Langmuir.

It is important to emphasize that these calculations assumed a 100 % probability of reacting with the surface. Any real reaction will have less than 100 % reaction probability, so the required exposure will be higher than these calculated values, which can be taken as lower limits to the actual required exposures.

Using a quartz crystal microbalance, we have estimated that the reaction probability for hafnium dimethylamide on a water-saturated surface is at least 7 %.[6] Thus not more than about 3/0.07 = 43 Langmuir of exposure is required to saturate this reaction on a flat surface. This limit is based on the size of the microbalance sensor used, so that the actual saturation exposure could be significantly lower than 43 Langmuir (but more than 3 Langmuir). No matter where the correct value lies within this range, this is an extremely fast ALD reaction.

The exposure time required to saturate a flat surface will also generally be increased by diffusion and convection times within the volume of the reactor. Reactor-scale modeling is needed to estimate these delays in delivering the precursor.

3.2. Diffusion and Deposition Inside a Hole

We assume that there is negligible depletion of either precursor from the gas just outside the hole, because of sufficiently high concentration of precursors, fast gas-phase diffusion within the reactor volume, and rapid flow of the precursor vapor over the flat surface. For the experiments reported below, the samples were placed near the vapor entrance to the reactor, so depletion effects can be neglected. In practical cases where depletion is significant, a conservative estimate of the exposure needed for 100 % step coverage can be obtained by assuming that the vapor concentration is reduced to the value remaining after reaction is complete (the concentration in excess of that needed for depositing on all surfaces).

We assume that the precursor molecules move by molecular flow (no gas-phase collisions) within the hole. This is a realistic assumption for sub-micrometer diameters and gas pressures around 1 torr, since the mean free paths are much larger than the hole diameter. Molecules hitting an already saturated surface are assumed not to physisorb at all, and to immediately return to the gas phase in a random direction, distributed according to the usual cosine law for re-emission of molecules from a surface. Vapor by-products from the chemisorption reactions are assumed not to re-adsorb onto the surface, not to etch the film, and not to play any further role in the process.

With these assumptions, we can estimate the minimum exposure required to provide 100 % step coverage of film on the inside surface of a hole below a flat surface. Deposition is of course occurring on the flat surface as well as inside the hole. However, the reactions become saturated more quickly on the flat surface than inside the hole, since the molecules need more time to diffuse down the hole in order to reach the lower portions of the hole. The top portion of the hole becomes coated and saturated first, and then the reaction progresses further and further down the hole. This is because the molecules first diffuse along the already-saturated upper portion of the hole, and then react at their first opportunity: their first collision with the as-yet-unsaturated lower portion of the hole.

The flux of molecules into the hole can be estimated from formulae developed for the molecular flow of gases in a vacuum system. The reactive uncoated lower portion of

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the hole acts as a "vacuum pump", with the upper-coated portion of the hole playing the role of the piping leading to the vacuum pump. The geometry of the hole in this discussion is shown in Figure 1. After going a distance λ down the pipe, the flux at the flat surface is reduced by a factor (CF) given in Equation 8.[7]

$$CF = \frac{1}{1+\frac{3\lambda p}{16A}} \tag{8}$$

λ is the length of the upper portion of the hole that has already been saturated, p is the perimeter of the hole, and A is the cross-sectional area of the hole. For a circular hole, this "Clausing Factor" reduces to $[1 + (3\lambda/4d)]^{-1}$, where d is the diameter of the hole. The flux at a depth λ in a hole is then given by Equation 9.

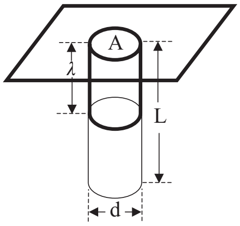

Fig. 1. The geometry of film deposition in a hole.

$$J = \frac{P}{\sqrt{2\pi m \mathrm{k} T}\left(1+\frac{3\lambda p}{16A}\right)} \tag{9}$$

This flux decreases with time as the coated length (λ) along which the precursor must pass becomes longer. The increment of time $\mathrm{d}t$ needed to coat an additional length $\mathrm{d}\lambda$ of the hole is given by the saturated surface coverage (S) times the incremental area $p\mathrm{d}\lambda$ divided by the flux (J) times the cross-sectional area (A_{hole}) of the hole, as shown in Equation 10.

$$\mathrm{d}t = \frac{Sp}{JA_{\mathrm{hole}}}\mathrm{d}\lambda \tag{10}$$

Substituting into Equation 10 the value of the flux given by Equation 9, and integrating up to the time (t) at which the reaction front reaches the bottom of the hole (where $\lambda = L$, the total length of the hole) we obtain Equations 11 and 12.

$$t = \int_0^t \mathrm{d}t = \frac{S\sqrt{2\pi m \mathrm{k} T}}{P}\frac{p}{A_{\mathrm{hole}}}\int_0^L \mathrm{d}\lambda\left(1+\frac{3p\lambda}{16\,A_{\mathrm{hole}}}\right) \tag{11}$$

$$t = S\sqrt{2\pi m \mathrm{k} T}\,\frac{p}{A_{\mathrm{hole}}}\left(L+\frac{3pL^2}{32\,A_{\mathrm{hole}}}\right) \tag{12}$$

Writing this result in terms of the aspect ratio $a = Lp/4\,A$, and multiplying by the reactant partial pressure (P) gives the exposure required for complete coating of the side walls of the hole, shown in Equation 13.

$$(Pt)_{\mathrm{sidewalls}} = S\sqrt{2\pi m \mathrm{k} T}\left[4a+(3/2)a^2\right] \tag{13}$$

After the coating of the side wall is complete, coating of the bottom of the hole takes place. The bottom area to be coated is the cross-sectional area (A) and the flux available (J) is given by Equation 9 with the length (λ) set equal to the total length of the hole (L). From this information, the exposure required for coating the bottom can then be put in the form of Equation 14.

$$(Pt)_{\mathrm{bottom}} = S\sqrt{2\pi m \mathrm{k} T}\left[1+(3/4)a\right] \tag{14}$$

Adding together the exposures from the side walls and the bottom gives the total exposure that should give complete coating of the hole, Equation 15.

$$(Pt)_{\mathrm{total}} = S\sqrt{2\pi m \mathrm{k} T}\left[1+(19/4)a+(3/2)a^2\right] \tag{15}$$

The factor $S(2\pi m \mathrm{k} T)^{\frac{1}{2}}$ is just the exposure required to saturate a flat surface, as given in Equation 7. The term $[1 + (19/4)\,a + (3/2)\,a^2]$ gives the factor by which the exposure must be increased to coat fully a hole with aspect ratio a. For example, a hole with aspect ratio 43 requires an exposure 3000 times longer than a flat surface. If the flat surface requires 3 Langmuir to be saturated by a certain reaction, then this hole requires 9×10^3 Langmuir for complete coverage.

During the course of depositing a film whose thickness is not negligible compared to the width of the hole, the aspect ratio increases. In order to achieve 100 % step coverage, it is necessary that the minimum exposure be exceeded even at the end of the deposition in the narrower coated hole. Thus the minimum exposure criterion should be calculated from the final aspect ratio of the coated hole at the end of the deposition.

4. Experimental Results on Step Coverage in Deep, Narrow Holes

Hafnium oxide was deposited by ALD on patterned substrates having holes 7.3 μm deep. The initial cross section of the holes is elliptical, with major axis about 0.30 μm and minor axis about 0.17 μm. This initial geometry corresponds to an aspect ratio of 36. After coating with HfO_2 with a thickness of 25 nm, the inside dimensions of the hole decreased to about 0.25 μm by 0.12 μm, and the aspect ratio increased to 43, corresponding to a calculated minimum exposure of 9×10^3 Langmuir.

Coatings of HfO_2 made with exposures greater than 9×10^3 Langmuir had step coverage of 100 %, in agreement with the calculations. Figure 2 shows an example of a cross section of a hole coated with 100 % step coverage using 30 × 10^3 Langmuir of exposure in each of 250 cycles. Two complete holes are shown, along with higher magnification images of the top and bottom of one of them, showing the film more clearly as a light band with a uniform thickness of 26 nm.

Exposures less than 9 × 10^3 Langmuir had less than 100 % step coverage. Figure 2 also shows examples of two films grown with exposures too small to produce 100 % step coverage, as well as an uncoated hole for comparison. The two holes coated using 2 × 10^3 Langmuir (350 cycles) were only coated along the top quarter of their length. The two holes coated using 4 × 10^3 Langmuir (250 cycles) were coated over about three quarters of their length. The uncoated holes have a thin light line along their edges, which is an artifact of the imaging by the electron microscope.

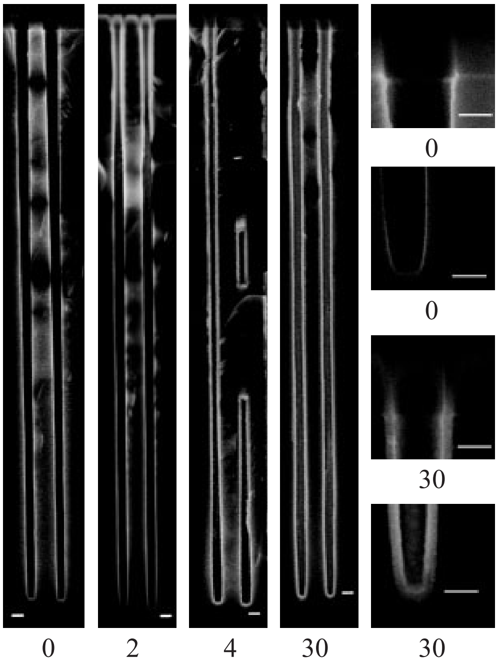

Fig. 2. Cross-sections of HfO_2-coated holes. Exposures of the Hf precursor (in thousands of Langmuir) are given under each image; each white bar is 0.1 µm long.

If we consider the requirements for coating holes with increasing aspect ratios, the additional *quantity* of precursor (required to cover the larger surface area of the sides of the hole) increases *linearly* with the aspect ratio. At the same time, the *exposure* required increases much more rapidly. For large a, exposure $\propto a^2$, the *square* of the aspect ratio. Thus fully conformal coating of holes with higher aspect ratios requires increased exposure time as well as more material to cover the larger area. The predicted exposure, according to Equation 15, needed for holes with a range of aspect ratios from 1 to 2000, is plotted in Figure 3.

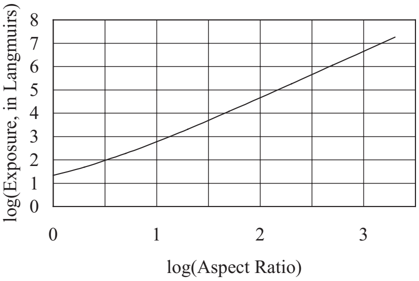

Fig. 3. A plot of the predicted exposure needed for holes with a range of aspect ratios from 1 to 2000.

5. Conclusions

Uniform coatings can be made inside holes and trenches with very high aspect ratios, using suitable pairs of reactants supplied in alternating doses of vapor. The doses must be sufficiently large to saturate each surface reaction, and the vapors must be exposed to the openings of the holes for a sufficient time. A simple formula is derived for the required exposure time. Experiments on the deposition of hafnium dioxide in holes with coated aspect ratios of 43 support the theory in showing that an exposure greater than about 9 × 10^3 Langmuir is required to obtain completely uniform coatings. This technique may be useful in making deep trench capacitors for microelectronics, as well as in other applications requiring coatings within narrow structures with high aspect ratios.

6. Experimental

ALD depositions were carried out in a flow reactor (Fig. 4). The reactor was a stainless steel tube (length 76 cm, diameter 3.7 cm) heated in a tube furnace. Precursors and nitrogen gas were introduced into the reactor through a bored out flange at one end of the tube. Volatile reaction by-products and unreacted precursors were removed through the opposite end of the reactor with a rotary vane vacuum pump. Substrates were also intro-

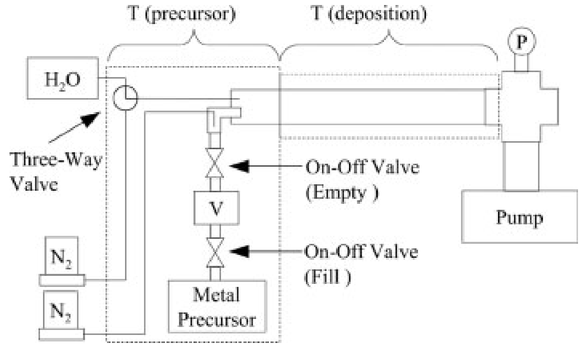

Fig. 4. Schematic diagram of the deposition system showing the location of the nitrogen mass flow controllers (N_2), the water vapor reservoir (H_2O), the metal precursor reservoir (metal Precursor), the three-way GC valve, the two on-off diaphragm valves, the metal precursor dose volume (V), the pressure measurement location (P), and the rotary vane pump (Pump) with respect to the precursor (T(precursors)) and deposition (T(deposition)) heating zones.

duced and removed from the reactor via a removable flange at the exhaust end of the reactor. The reaction zone of the reactor was 46 cm long and defined by the heated zone of the tube furnace. Both precursors were introduced at the beginning of the heated zone. A static mixer was placed along the flow path before the substrate holder. The exposed surface area in the reaction zone is the inside area of the reactor itself, the static mixer, the surface area of the substrate holder (a half round aluminum block), and the substrates themselves. This area was 944 cm^2.

Water vapor was introduced into the reactor by the action of a three-way gas chromatography (GC) valve connected to the reactor by a 0.04 mm I.D. stainless steel feed-through. The GC valve was controlled electronically and could be positioned in two states to allow either nitrogen gas (purge state) or water vapor (dose state) to flow into the reactor. The water vapor was kept at room temperature and thus had a vapor pressure of approximately 24 torr. Placing the GC valve in the dose state for 0.5 s supplied at least one μmol of water vapor. The water vapor dose was adjusted (by varying the time) so that it was twice the amount (in moles) of metal precursor.

A set volume (10 mL) of metal amide vapor was introduced into the reactor through an electronically controlled diaphragm valve (the “empty valve”). A separate electronically controlled diaphragm valve (the “fill valve”) separated the defined volume from the precursor reservoir. The entire assembly (empty valve, vapor space, fill valve, precursor reservoir) were heated in an oven to a temperature such the precursor attained a vapor pressure of at least 1.0 torr. For *tetrakis*(dimethyl amido) hafnium this precursor vaporization temperature was 60 °C. Opening the fill valve for one second (while the empty valve in closed) charged the volume between the two valves with a known volume of vapor at a known temperature and pressure. Opening of the empty valve for one second (while the fill valve is closed) emptied most (down to the reactor pressure) of this dose into the reactor. The metal precursor dose was intentionally varied between one and ten μmol as determined by the oven temperature. Nitrogen gas flow (constant during the deposition) was directed at the outlet end of the empty valve.

The total nitrogen gas flow was kept at 20 sccm and the reactor pressure was maintained at 0.2 torr. The deposition temperature was 150 °C. At least five seconds of purging was allowed between the introductions of precursors. One ALD reaction cycle is defined as one dose of the metal precursor followed by a minimum of five seconds purging, then one dose of water followed by a minimum of five seconds purging. At all times during the deposition, nitrogen flow was kept constant. During a purge, no precursors were introduced into the reactor.

The step coverage of ALD oxide layers was measured inside elliptical holes 0.17 μm by 0.30 μm by 7.3 μm deep etched in silicon. Cross-sectional images were measured by scanning electron microscope (SEM) using an FEI dual beam focused ion beam system, Strata DB235. This instrument consists of a fully digital field emission SEM integrated with a focused ion beam system. Samples were cleaved just before they were loaded in the SEM chamber to maintain fresh cross-sectional surface. To reduce significant sample charging problem caused by a non-conducting oxide layer, images were captured at the charge reduction mode, thru lens detector (TLD-C) where the detector is grounded. The applied electron beam energy was in the range 3–5 keV for most specimens.

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