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Supporting Information

A Practical, Self-Catalytic, Atomic Layer Deposition of Silicon Dioxide

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Experimental details

Materials. A-plane sapphire substrates were purchased from CrysTec. 3-Aminopropyltri-ethoxysilane was obtained from Sigma Aldrich and used without further purification; it was handled under inert atmosphere. Water was purified using a Millipore system. All ALD precursors were kept in Swagelok stainless steel bottles and degassed before used. A stream of ozone was obtained as a mixture with dioxygen in 10% nominal concentration from a generator by OzoneLab.

Atomic layer deposition. ALD was carried out in a Savannah system from Cambridge Nanotech operating with Ar (40 mL/min) as carrier gas. The precursors 3-aminopropyltri-ethoxysilane, water and ozone were maintained at 100°C, 60°C, and room temperature, respectively. Substrate temperatures between 120 and 200°C were explored with similar results; 150°C was chosen as the standard temperature for planar substrates. One ALD cycle was defined as follows:

Duration / s	Designation	silane valve	H$_2$O valve	O$_3$ valve	Pump valve
2	*silane pulse*	Open	Closed	Closed	Closed
7	*silane exposure*	Closed	Closed	Closed	Closed
18	*purge*	Closed	Closed	Closed	Open
1	*water pulse*	Closed	Open	Closed	Closed
7	*water exposure*	Closed	Closed	Closed	Closed
18	*purge*	Closed	Closed	Closed	Open
0.2	*ozone pulse*	Closed	Closed	Open	Closed
7	*ozone exposure*	Closed	Closed	Closed	Closed
13	*purge*	Closed	Closed	Closed	Open

Nanotubes. Self-ordered anodic alumina membranes were prepared with pores of 40 nm according to established procedures,[1,2] and used as templates for the subsequent deposition of SiO$_2$. For ALD, all exposure and purge times were increased to 30 s and purges to 20 s; the substrate was held at 200°C. Samples for cross-sectional SEM were prepared by etching the barrier layer of alumina in chromic acid followed by a reactive ion etching step using CHF$_3$ in order to open the bottom end of the silica tubes. TEM samples were prepared by dissolving the matrix in chromic acid, rinsing the resulting suspension of tubes to neutrality, then evaporating a droplet of it on a TEM sample holder consisting of a holey C film on a Cu grid.

Ellipsometry (Figure S1). We describe the change of polarization state of a light beam after reflection on the sample by the ratio ρ of complex reflection coefficients r_p and r_s for p- and s-polarized light, respectively,[3]

$$\rho = \frac{r_p}{r_s} = \tan \Psi \, e^{i\Delta}$$

where Ψ and Δ are the ellipsometric parameters. These parameters depend on the photon energy, angle of incidence, layer structure, and dielectric function of each layer. The spectra were recorded in the spectral range from 0.75 to 4.5 eV for angles of incidence of 60° and 70°, and analyzed according to a layer stack model. The layer stack model consists of a sapphire substrate and a thin SiO$_2$ film. The dielectric function of sapphire was

1. Masuda, H.; Fukuda, K. *Science* **1995**, *266*, 1466-1468.
2. Nielsch, K.; Choi, J.; Schwirn, K.; Wehrspohn, R. B.; Gösele, U. *Nano Lett.* **2002**, *2*, 677-680.
3. Azzam, R. M. A.; N. M. Bashara, N. M. "Ellipsometry and Polarized Light", 1977: North-Holland Pub. Co., Amsterdam.

modeled according to the literature.[4] Since SiO_2 is a non-absorbing material over the range of energies considered (imaginary part of the refraction index $\kappa = 0$), we used the Cauchy approximation to describe the dependence of the real part of the refraction index, n, on the wavelength λ of the incoming photon,

$$n = A + \frac{B}{\lambda^2}$$

where the Cauchy parameters A and B are treated as adjustable. The experimental data were fitted to yield $A = 1.441(\pm 0.001)$ and $B = 3.7(\pm 0.3) \times 10^{-3}$ μm^2.
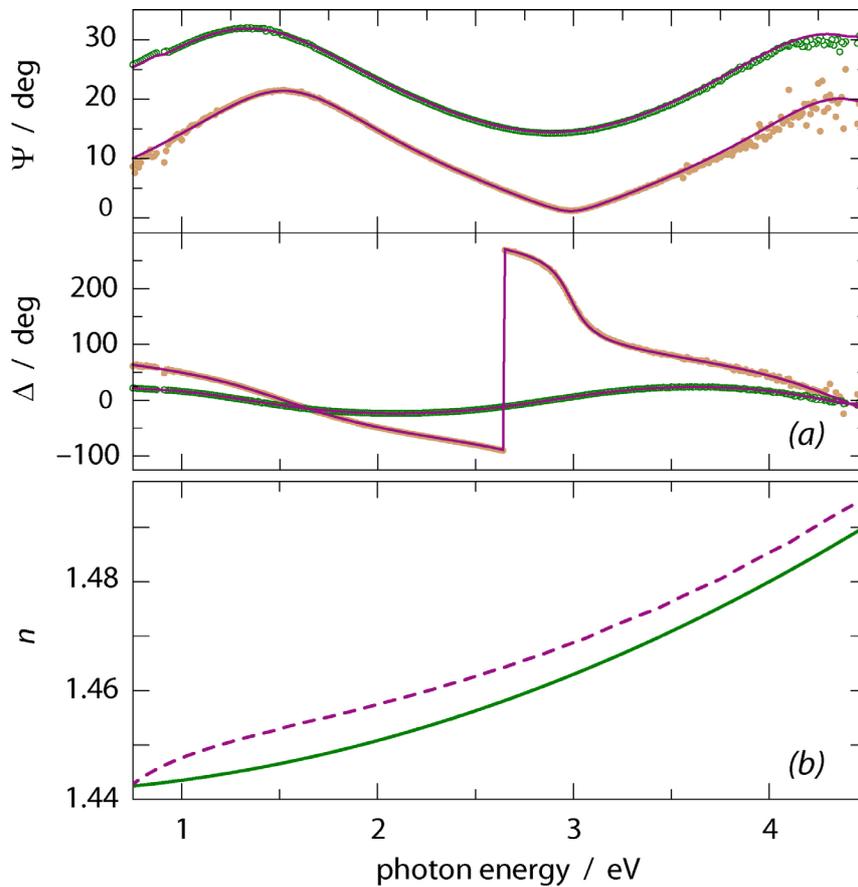

Figure S1. Spectroscopic ellipsometry of a SiO_2 ALD film on sapphire. *(a)* Experimental spectra of the ellipsometric parameters Ψ and Δ for incidence angles $a = 60°$ and $70°$ (full beige and open green circles), and fitted curves (purple). *(b)* Spectra of the refractive index n determined from the fit (green), compared with the literature for SiO_2 (dashed purple).[5]

4. Yao, H.; Yan, C. H. *J. Appl. Phys.* **1999**, *85*, 6717-6722
5. Palik, E. D. in *Handbook of Optical Constants*, Vol. 1, Academic Press, New York, **1991**.

X-ray photoelectron spectroscopy. A sample of ALD-SiO$_2$ (2000 cycles, ~120 nm thickness) on a flat sapphire substrate was used for XPS analysis. In order to determine the elemental concentrations as a function of the distance to the surface, XPS sputter depth profiles were acquired under high vacuum (3×10^{-9} mbar) on a Physical Electronics (PHI) Quantum 2000 photoelectron spectrometer. Material was etched away from the surface by a 4-kV Ar$^+$ ion beam between consecutive analyses of the elemental concentrations. An area of approximately 100 µm diameter was analyzed. Elemental concentration are given in atomic percent (normalized to yield a total of 100 at-%) using the C 1s, N 1s, O 1s, Si 2p and Al 2p photoelectron peak areas after Shirley background subtraction and using the built-in PHI sensitivity factors for the calculation. Measurements on a reference sample yield a detection limit of ~0.3 at-% for the elements considered. No C 1s and N 1s photoelectron peaks could be detected, resulting in the measurement of a 0.1(±0.1) at-% noise for both elements.

Other instrumental techniques. Reactive ion etching of SiO$_2$ was carried out in a Si220 by Sentech. The plasma was generated with a power of 150 W under a pressure of 15 mTorr; the etching was carried out for 4 min with 20 mL/min CHF$_3$ and 5 mL/min O$_2$. SEM micrographs were taken on a Jeol JSM 6390LV or a Jeol 6340, at acceleration voltages between 2.5 and 30 kV. TEM data were collected on a Jeol JEM 1010 operating at 100 kV.

Notes

Remark concerning film thickness measurements. We found certain limitations of SEM as a method for evaluating the thickness of thin films, therefore ellipsometric data are to be considered much more reliable. The special geometry of the samples (a square edge viewed parallel to the surface) causes charging effects under the electron beam, which tend to blur the SEM image and prevent reliable measurements below a minimum thickness (approximately 15 nm on the instrument used in this study). The SEM datapoints of Figure 2 approximately fall on a straight line parallel to that defined by the spectroscopic ellipsometry measurements but separated from it by a negative offset.

Spectroscopic ellipsometry translates a direct proportionality between the number N of ALD cycles performed and the thickness d of the deposited film, without any offset.

Growth rate. The thicknesses d of the SiO$_2$ films on sapphire measured by spectroscopic ellipsometry for various numbers N of ALD cycles were fit to a straight line using a least-squares procedure. The fit to the equation $d = \zeta N + d_0$ yields the parameters $d_0 = 2$ nm, $\zeta = 0.062$ nm cycle^{-1}, correlation coefficient $R^2 = 0.996$ and standard deviations $\sigma(d_0) = 3$ nm, $\sigma(\zeta) = 0{,}002$ nm cycle^{-1}. Considering three standard deviations as the uncertainty yields a growth rate of $\zeta = 0.62(\pm0.06)$ Å cycle^{-1}. The line crosses the origin well within uncertainty, as it should, with $d_0 = 2(\pm9)$ nm.

Justification of the word "self-catalysis". In the chemical reaction presented, the available experimental evidence does not allow us to determine whether the catalytic effect of the alkylamino moiety is intramolecular or acts intermolecularly thanks to the geometric proximity of molecules adsorbed at the surface. Therefore we cannot use the term "intramolecular catalysis". Additionally, "autocatalysis" is a concept used in chemical kinetics to describe a reaction that is catalyzed by its product — thus it is not applicable to our case. These reasons force us to use the word "self-catalysis", which does exist in the literature but is often employed in a less well-defined fashion, and which certainly does not enjoy the textbook fame that "intramolecular catalysis" and "autocatalysis" have.

Other reactions attempted towards the ALD of SiO₂. George and co-workers have established the absence of ALD from the uncatalyzed hydrolysis of Si(OEt)$_4$ (reference 11 of the text). However, we attempted the reaction in our reactors as a control experiment. As expected, we were unable to observe any film growth up to substrate temperatures of 330ºC. Additionally, we sought to adapt the hydrolysis of tetraisocyanatosilane (reference 13) to our reactors and were unable to do so (also up to 330ºC). To our knowledge, this ALD reaction has not been reproduced outside of the Matsumura research group since it was first reported. We also checked the possibility of a pure oxidative route, with the ozonolysis of Si(OEt)$_4$: we observed no film growth, as can be expected when the individual steps of the surface chemistry are considered. Finally, using H$_2$N(CH$_2$)$_3$Si(OEt)$_3$ only with

ozone and without water pulse results in a drastically slower growth (approximately 1/4 to 1/3 of the growth rate described for $H_2N(CH_2)_3Si(OEt)_3 + H_2O + O_3$).