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

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The outstanding chemical, electrical, and optical properties of silicon dioxide have made it ubiquitous in science and technology. The ability to create SiO₂ nanostructures of well-defined geometry would broaden its range of applications even further, in particular in the chemical, electrokinetic, and biomedical realms. Atomic layer deposition (ALD) is especially suited to nanostructuring, since its kinetics are controlled by surface chemistry rather than mass transport from the gas phase. However, reports on the ALD of silica are few and far between in the open literature to date. All published reactions suffer from some weakness: a corrosive by-product or catalyst, poor reproducibility, or impurities in the deposited film. Herein, we describe a practical ALD process for SiO₂ that overcomes such limitations.

Based on the NH₄-catalyzed hydrolysis of tetraethoxysilane (Si(OEt)₄), chemical intuition dictates that a triethoxysilane bearing an aminoalkyl moiety be readily hydrolyzed without any external catalyst. The basic functionality will stabilize the strong Si–O bonds, a phenomenon that can be called “self-catalysis” to emphasize the fact that one chemical species is both substrate and catalyst. Subsequent oxidative cleavage of the tethered moiety should afford a silanol, amenable to further reaction with aminoalkyltriethoxysilane molecules. Accordingly, a three-step reaction sequence based on 3-aminopropyltriethoxysilane, water, and ozone (O₃) can be envisioned for the ALD of SiO₂ (Scheme 1).

Scheme 1. Proposed reaction steps in one cycle of SiO₂ ALD from H₃N(CH₃)₂Si(OCH₂CH₃)₃, H₂O, and O₃. a) Anchoring: surface hydroxy groups cleave Si–OEt bonds of the silane under self-catalysis by the pendant amino group (green), causing chemisorption; b) hydrolysis: remaining ethoxy groups are removed self-catalytically; c) oxidation: the aminoalkyl arm is removed by ozone; d) completion of the cycle: Si–OH groups are left; the initial chemical identity of the surface has been regenerated after addition of one SiO₂ unit.

Indeed, a SiO₂ film is deposited onto a sapphire substrate (heated to 150°C) when a reaction cycle consisting of consecutive exposure to gaseous H₃N(CH₃)₂Si(OEt)₃ (heated to 100°C), water (60°C), and O₃ (ca. 10% in O₂) is carried out repeatedly. The film thickness depends linearly on the number of reaction cycles, with a growth rate of (0.6±0.1) Å cycle⁻¹ (Figure 1). The growth rate remains constant (within uncertainty) for substrate temperatures varied between 120 and 200°C, silane pulse times between 1 and 5 s, and silane exposure times between 7 and 30 s (Figure 2). That the deposition is unaffected by such variations in the main experimental parameters demonstrates that it is controlled by surface chemistry rather than by gas–solid mass transfer and thus establishes its genuine ALD nature.

The deposited SiO₂ films are pure, as determined by X-ray photoelectron spectroscopy (XPS, Figure 3). In the depth profile, the atomic ratio Si/O is constant at 1:2, and the carbon...
and nitrogen impurities are below the detection limit of 0.3 at.%. Additionally, film thickness and refractive index were determined by spectroscopic ellipsometry (see Figure S1 in the Supporting Information). The spectra recorded for the polarization of a light beam after interaction with the films show multiple interferences arising from reflection at the interfaces. The line-shape analysis yields refractive indices in excellent agreement with literature values for bulk SiO₂ (Δν ≤ 0.008) and thereby confirms the very high chemical purity for the deposited film.

The ALD reaction is amenable to the preparation of nanoobjects when applied to structured substrates. Figure 4 displays the results obtained with porous anodic alumina membranes as template.[8] Ordered arrays of parallel tubes are obtained. Electron microscopy (SEM, TEM) shows smooth walls with constant thickness up to an aspect ratio of 500. Electron diffraction indicates a glassy structural state of SiO₂.

The novel ALD method is particularly advantageous in practical terms. The silane precursor is a liquid at room temperature, with sufficient vapor pressure under moderate heating. It is noncorrosive, only mildly sensitive to moisture but sufficiently reactive, and commercially available at modest cost. The temperatures required for precursors and substrate lie within the range accessible to most ALD reactors. Finally, the growth rate is quite high ("ideal" ALD reactions: ca. 1 Å cycle⁻¹).[6]

The favorable growth rate can be traced back to the small size of the silane precursor molecule and its well-behaved chemistry.[9] The strength of the Si–OR bonds of tetraalkoxysilanes (ca. 420 kJ mol⁻¹)[10] renders them inert to hydrolysis in uncatalyzed conditions, both in solution[11] and in gas-solid reactions.[5] In an ALD method based on an alkoxysilane precursor, two steps involve the breaking of a Si–OR bond by a hydroxyl (OH) group and therefore require acidic or basic catalysis: 1) the chemisorption of the silane onto a hydroxy-terminated surface, and 2) the subsequent reaction of water with surface-bound Si(OR)₂ moieties (1 ≤ x ≤ 3). The presence of a basic amino group on a nonhydrolyzable alkyl tether in H₃N(CH₂)₃Si(OEt)₃ allows reactions (1) and (2) to happen without added catalyst. This self-catalytic effect, arising from the coexistence within one molecule of the Si–O bonds and the –NH₂ group, causes the moisture-sensitivity of H₃N(CH₂)₃Si(OEt)₃, which contrasts the stability of tetraethoxysilane and of alkylamines towards water.

Simplifying the SiO₂ process further and circumventing the hydrolysis step (Step b) in Scheme 1) by relying exclusively on oxidation is not possible. We have observed no ALD deposition from the reaction Si(OEt)₄ + O₂, in
accordance with the inert behavior of Si(OR)$_4$ towards surface hydroxy groups in uncatalyzed conditions.

In conclusion, a robust and practical method is now available for the preparation of SiO$_2$ thin films and nanostructures by ALD. The high purity of the deposited solid film, the outstanding control over its thickness, and the ability to coat nonplanar substrates make this process the ideal candidate for the preparation of bioactive, catalytic, or electrokinetic nanotubes and of optical microresonators. The quite low temperatures (120–200°C) are also attractive for thermally fragile (e.g., organic) substrates. We are currently exploring such directions of research.

Our novel SiO$_2$ ALD overcomes the inertness of the Si–O bond by tethering a catalytic amino group in the vicinity of the chemical bonds to be activated; this group is then removed after it has carried out its function. Organic chemists would call it an activating group, and indeed, the self-catalytic effect is conceptually similar to some tools used routinely in the complex preparative schemes of organic chemical synthesis (activating groups, protecting groups, neighboring-group effects). Inspiration drawn from the versatile preparative approaches used by chemists may be fruitful in solid-state physics.

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[7] In contrast, for most other gas–solid deposition techniques, for example chemical vapor deposition (CVD), pulsed-laser deposition (PLD), molecular beam epitaxy (MBE), and plasma sputtering, the growth rate is proportional to the (local) partial pressure of the gaseous precursors or reactants.