

## Blocking the Lateral Film Growth at the Nanoscale in Area-Selective Atomic Layer Deposition

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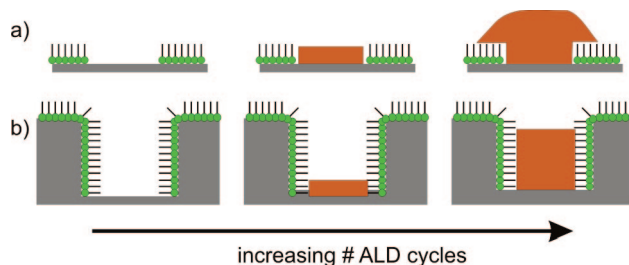
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Atomic layer deposition (ALD) is an inorganic film deposition technique based on the sequential use of self-terminating gas–solid reactions.<sup>1</sup> By its nature, ALD facilitates straightforward control of the film thickness with nanometer precision. Another unique feature of ALD is the conformal growth of films on substrates of virtually any shape. A recent example showing the reliability and economic potential of ALD is the fabrication of gate dielectrics in Intel's latest microprocessors, in which extremely thin and pinhole-free films are required.<sup>2</sup>

In ALD research, one of the current challenges is to develop techniques for area-selective film growth at the nanoscale, preferably independent of the deposited film thickness. The objective is to limit the film growth to certain areas of the substrate, whereas to avoid film growth on the remaining parts.<sup>3</sup> The selectivity in ALD growth is usually obtained by patterning of polymer films or self-assembled monolayers (SAMs) making the substrate chemically inert toward the ALD reactants. Mostly the patterns of the SAMs for area-selective ALD are obtained using lithography, leading to lateral inorganic features typically in the micrometer range and sometimes in the submicron range. To further reduce these feature sizes, one must use patterns of smaller sizes, which is challenging with standard lithographic techniques. Recently Bae et al. reported the formation of nanoscale features down to 66 nm by area-selective ALD in which the self-assembled monolayer was patterned using 2D colloidal crystals.<sup>4</sup> An interesting and important observation from their data is that the obtained inorganic structures are all significantly wider than the size of the pattern in the self-assembled monolayer from which they were made. Although the ALD film thickness was only about 7.5 nm, the lateral feature sizes before and after ALD changed significantly, respectively, from 52 to 66 nm, from 79 to 85 nm, and from 94 to 128 nm. It can be expected that, for thicker inorganic films, the features grow more and more in a lateral direction.

A plausible reason for the lateral increase in feature size is as follows (see Figure 1a). The alkyl tails of the self-assembled monolayers make that part of the substrate inert for the ALD reactants. During the first few deposition cycles, the growth is well-limited by the self-assembled monolayer and the first inorganic layers will be deposited only onto the bare substrate. However, the situation changes when the height of the deposited inorganic film exceeds the height of the self-assembled monolayer (~2 nm). In that case the growth will not be area-selective anymore near the interface where the already deposited inorganic film meets the end of the alkyl tails. Near that interface, the ALD reactants are able to adsorb on the inorganic film. This way the inorganic/alkyl interface will gradually migrate sideways with increasing number of ALD



**Figure 1.** (a) Conventional area-selective ALD in which the substrate is planar and contains patterns of self-assembled monolayers. With increasing number of deposition cycles there occurs also sideways film growth originating from adsorption of ALD reactants on the previously deposited ALD film. (b) Blocking the lateral ALD growth independent of deposited film thickness by combining surface modification and topographical features.

cycles. In other words, the inorganic film is not confined anymore to the original pattern of the SAM and the lateral dimension of the film will increase when more ALD cycles are carried out.

Our concept to prevent lateral ALD growth also at the nanoscale consists of combining the surface modification with topographical structures (see Figure 1b). In case the bottom parts are not modified, while the topographical structures are modified with, e.g., alkyls, then ALD growth will occur only at the bottom. With increasing number of cycles, there will be only material deposited on the previously deposited film. Thus, growth only occurs in height and not laterally. While the conventional area-selective ALD is based mainly on a chemical barrier for ALD growth, our new concept in addition provides a physical barrier from the topographical structures.

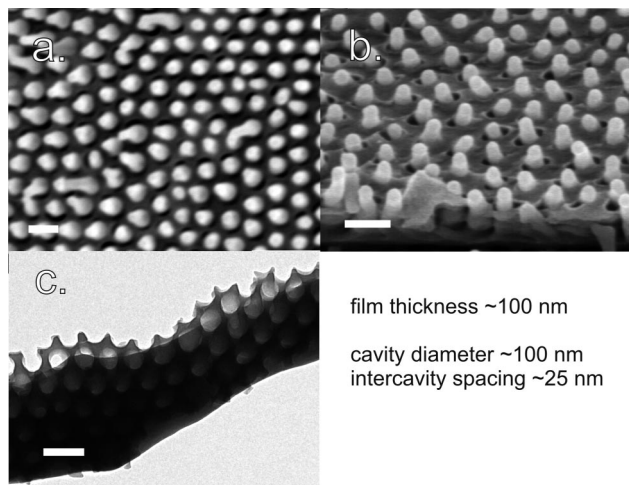
To proof this concept we have selected cicada wings, a template from nature. Cicadas are insects that have large transparent wings. The surface of the wings is covered with a hexagonally close-packed array of bottle-shaped nanopillars (Figure S1). The diameter at the pillar base is approximately 100 nm and at the top 60 nm. The height of the pillars is about 250 nm. Insect wings, like insect skeletons (i.e., cuticle), consist of a nanocomposite material composed of crystalline chitin nanofibers embedded in a protein matrix, polyphenols, water, and lipids.<sup>5</sup> In the case of cicada wings, the pillared surface is coated with a waxy layer.<sup>6</sup>

The ALD of ZnO on cicada wings results in material deposition at the bottom between the pillars, whereas there is no growth on the pillars themselves (Figure 2a,b). Other reports on templating and replicating of nanostructures deal with coating of the whole surface.<sup>7</sup> In contrast, here we coat only selective parts of the cicada wing surface with nanometer precision. The inertness of the pillars with respect to the ALD reactants is likely due to the waxy coating of the wing, providing a chemical barrier similar to the self-assembled monolayers traditionally used in area-selective ALD. The film growth starting from the bottom between the pillars indicates

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**Figure 2.** (a and b) SEM images of the cicada wing that is exposed to 600 cycles of diethylzinc/water. ZnO is only deposited from the bottom between the pillars, not on the pillars themselves. This ALD process is area-selective on cicada wings. (c) TEM image of the inorganic film that is peeled off from the sample in images a and b. The scale bars are 200 nm.

that the waxy coating is not present there and that the other cuticle components (such as chitin and proteins) can be directly accessed by the ALD reactants resulting in film growth. When the ALD-coated wing is broken, then part of the inorganic film can be peeled off (see Figure 2c). Owing to its area-selective growth, the thin ZnO film has an ordered array of holes of approximately 100 nm in diameter. The role of the waxy coating is to prevent ZnO growth on the pillars, which would otherwise lead to ZnO nanocups instead of a nanoporous ZnO film. Despite the success with ZnO, not all ALD processes are area-selective on the cicada wings. In the case of ALD growth of  $\text{Al}_2\text{O}_3$  using trimethylaluminum/water, the whole surface including the pillars is coated with an inorganic film (Figure S2), even though the number of deposition cycles is significantly less than that used for ZnO.

Even though the ZnO film in Figure 2 is very thick ( $\sim 100$  nm), ALD growth remained area-selective throughout the film due to the topographical structures of the pillars. The accuracy of the templating process is obvious as the diameter of the cavities in ZnO (approximately 100 nm) is similar to the base diameter of the pillars from which they are constructed. Also, the ZnO film between the edges of the cavities is  $\sim 25$  nm wide (= intercavity spacing) which is close to the distance between the pillars of the original cicada wing. Such small features of 25 nm in size are to our knowledge the smallest created by area-selective atomic layer deposition. The construction of such small lateral structures by ALD, even though the deposited film is multiple times thicker,

demonstrates the value of our new concept for blocking the film growth at the nanoscale.

In conclusion, we have shown a new concept to enable construction of nanoscale lateral structures by area-selective ALD. The concept is based on providing chemical inertness by surface modification combined by nanoscale topographical structures (Figure 1b). Whereas surface modification, as traditionally used in area-selective ALD, is only a chemical barrier for film growth, here we show that the topographical structures are also a physical barrier for film growth. This concept allows ALD synthesis of constructs that have lateral dimensions many times smaller than the film thickness. We have used cicada wings as a prototypical example from nature; however, this concept will be also applicable on other types of designed substrates that combine surface modification (including SAMs) with nanoscale topographies. We foresee that this concept could become a framework for construction of nanoscale parts by area-selective ALD where nanoscale accuracy of the lateral dimensions is of importance.

**Acknowledgment.** This work was supported by Academy of Finland (Decision No. 116254).

**Supporting Information Available:** Experimental procedures and SEM images of original and  $\text{Al}_2\text{O}_3$ -coated wings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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# SUPPORTING INFORMATION

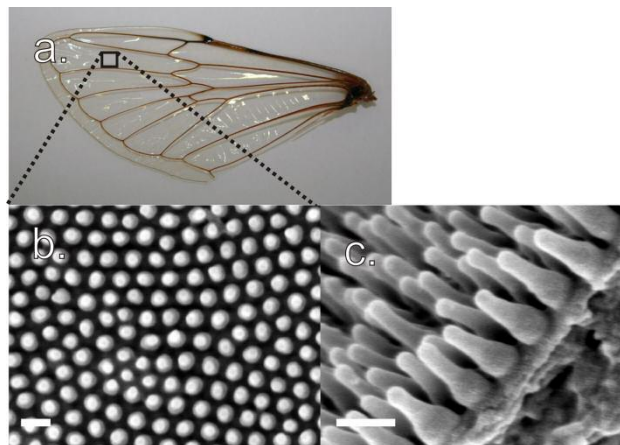
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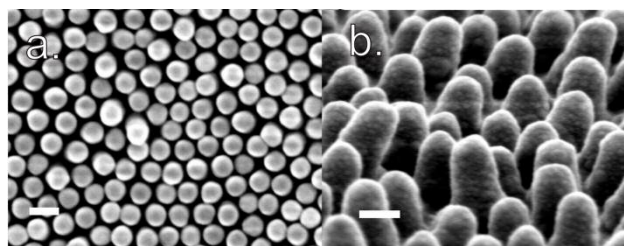
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### Experimental section

The cicada wings (*Pomponia intermedia*) were supplied from Thaibugs (Thailand). Cicada wings were cleaned in ultrasonic bath for 30 minutes with both acetone and distilled water prior to the depositions. ZnO and Al<sub>2</sub>O<sub>3</sub> depositions were performed in a flow-type hot-wall ALD reactor (MC-120 by Microchemistry Oy, Finland). Diethylzinc (Crompton GmbH, Germany) and trimethylaluminum (Witco GmbH, Germany) were used as metal precursors for ZnO and Al<sub>2</sub>O<sub>3</sub> depositions, respectively. In both cases distilled water was used as an oxygen source. Precursors were evaporated from containers kept at room temperature. Nitrogen (99.999 %) was used as purging and carrier gas. It was produced from air with a N<sub>2</sub> generator (Schmidlin UHPN 3000). Reactor pressure during the depositions was 1.2 mbar. The deposition temperature was 120 °C. In the ZnO depositions pulsing times for the precursors and purge gas were 2.5 s and the total number of reaction cycles was varied from 100 to 1200. In the Al<sub>2</sub>O<sub>3</sub> depositions precursor and purge gas pulsing times were 2.0 s and the number of deposition cycles was 120, 350 or 3500.



**Figure S1.** (a) Wing of cicada (*Pomponia intermedia*). (b+c) SEM images of the wing surface. The scale bar is 200 nm in images b+c.



**Figure S2.** (a+b) SEM images of the cicada wing that is exposed to 350 cycles of trimethylaluminum/water. This ALD process is not area-selective as it coats also onto the pillars. The scale bars are 200 nm.