Surface Structuring

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Nanoscale Structuring of Surfaces by Using Atomic Layer Deposition

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Controlled structuring of surfaces is interesting for a wide variety of areas, including microelectronic device fabrication, optical devices, bio(sensing), (electro-, photo)catalysis, batteries, solar cells, fuel cells, and sorption. A unique feature of atomic layer deposition (ALD) is the possibility to form conformal uniform coatings on arbitrarily shaped materials with controlled atomic-scale thickness. In this Minireview, we discuss the potential of ALD for the nanoscale structuring of surfaces, highlighting its versatile application to structuring both planar substrates and powder materials. Recent progress in the application of ALD to porous substrates has even made the nanoscale structuring of high-surface-area materials now feasible, thereby enabling novel applications, such as those in the fields of catalysis and alternative energy.

1. Introduction

Atomic layer deposition (ALD) is a gas-phase method that allows the deposition of conformal thin films with monolayer-precision film thickness.[1–4] As illustrated in Figure 1 a, two or more reactants (precursors) are fed into the reaction chamber in an ABAB scheme, separated by time. To ensure a self-limited reaction terminating at a complete monolayer, all the precursors have to react with the substrate surface, but must not react with themselves, with chemisorbed reaction products, or with a reaction by-product. To remove the precursors and by-products from the gas phase as well as desorb the multilayers after reaction, the chamber is pumped or purged with an inert gas. The scheme in Figure 1 a corresponds to an idealized ALD cycle in which a monolayer is deposited. By repeating this cycle, films thicker than a monolayer can be obtained. Unlike other deposition methods, it is feasible with ALD to deposit large areas and high-aspect-ratio (i.e. for a cylindrical pore, a large value for the pore length/diameter ratio) substrates such as powders or porous membranes without blocking the pores (see Figure 1 b).[5] It should be mentioned that a single ALD cycle of a metal oxide typically does not provide a complete monolayer of the oxide film.[1,6]

The described process is the basis of all ALD methods. It is referred to as thermal ALD and has mainly been employed for the deposition of metal oxides as well as other materials such as noble metals and nitrides.[7] In addition to this, other methods have been developed, such as plasma-enhanced

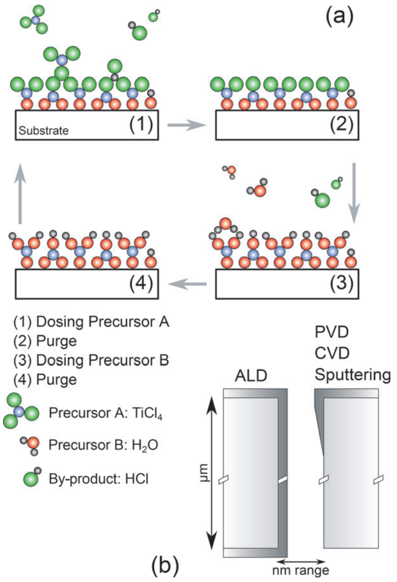

Figure 1. a) Example of an ideal thermal ALD cycle of metal oxide with two precursors starting at a hydroxylated substrate. b) Deposition of high-aspect-ratio substrates by ALD compared to common deposition methods that result in pore blocking. PVD: physical vapor deposition, CVD: chemical vapor deposition.

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ALD (PEALD) and spatial ALD (SALD).[1] PEALD uses a plasma to create precursor radicals, which allows the deposition of other materials, such as non-noble metals, nonmetal elements, nitrides, and carbides.[7] To obtain very high deposition rates, SALD uses separated precursor zones with a moving substrate between them. Both methods have been very useful for planar substrates, but are not yet applicable to porous materials.

Ideally, the described ALD process leads to a homogeneous film covering the complete surface. Such films are of interest for applications in many different areas. In industry, ALD has grown in popularity for the fabrication of semiconductors and is used to deposit passivation layers to microelectronics and jewelry.[8] Current research topics include optical elements,[9,10] high-*k* dielectrics,[11] reduction of the pore size of membranes,[12] homogeneous depositions on mesoporous powders,[13,14] catalysis,[15] and alternative energy applications.[16]

This Minireview is organized as follows: In Section 2 we discuss the potential of ALD for the nanoscale structuring of planar substrates using area-selective ALD (nanopatterning). The use of ALD for nanostructuring of powder samples is illustrated in Section 3, with a focus on catalysts. In Section 4, we briefly review the current state of ALD-based structuring of high-aspect-ratio and complex-shaped substrates and present perspectives for potential future developments.

2. Nanopatterning of Planar Substrates

In conventional methods for the fabrication of devices, structuring is achieved by a top-down approach based largely on lithographic techniques and etching, which represents the main limitation to downscaling.[3,4,17] ALD, as an alternative bottom-up technique, allows surfaces to be structured by area-selective deposition. ALD is a powerful technique for the deposition of thin films on flat surfaces that is based on cycles of self-limiting chemical reactions between gas-phase precursor molecules and a solid surface, thereby providing homogeneous coatings on arbitrarily shaped materials with control over the atomic-scale thickness. The principle of area-selective ALD is illustrated in Figure 2. If precursor molecules come into contact with two chemically different (patterned) regions on the surface, for example, hydrophilic (OH-terminated) and hydrophobic (H-terminated) regions, they may adsorb only onto the hydrophilic domains, thereby leading to nucleation. By repeating the ALD cycles, self-patterned films will be formed. Thus, during this process the original surface pattern is transferred to the final film.

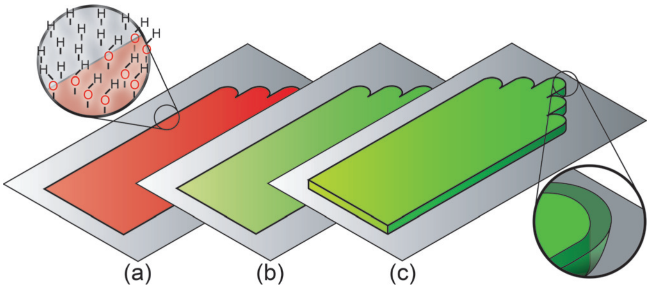

Figure 2. Concept of area-selective ALD. A substrate containing chemically different surface regions, for example, hydrophilic and hydrophobic (a), reacts selectively, for example, at the hydrophilic regions through self-saturated reactions (b), thereby leading to the formation of a patterned film (c). The enlarged area shows the broader real edge compared to the ideal edge. The red and green areas represent the initial and modified substrate surfaces, respectively.

A variety of lithographic processes, such as conventional lithography and microcontact printing (soft lithography), have been employed to obtain such patterned surfaces. For example, in the latter, a patterned elastomer, such as poly(dimethylsiloxane) (PDMS), can be used as a stamp, mold, or mask to transfer the pattern to substrates. In all cases, the substrate is patterned by area-selective immobilization of molecules, thus making the substrate chemically inert towards the ALD reactants. As illustrated in Figure 3, Park et al. processed such a PDMS-patterned substrate by ALD to deposit thin titania films.[18] After removal of the PDMS master and chemical etching, a titania pattern on scales from hundreds of nanometers to micrometers was obtained. Although only demonstrated for TiO_2, this approach is expected to work similarly for other materials. By using standard lithographic methods, substrate patterning typically in the micrometer and, as illustrated in Figure 3, sometimes in the sub-micrometer regime can be achieved.

In the following, we discuss examples of patterning in the nanometer region. Biercuk et al. employed an electron-beam ALD process, in which a film of poly(methyl methacrylate)

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Nicolas Sobel obtained his BSc and MSc in Applied Physics at the University of Applied Sciences RheinMain, Germany. During his MSc he focused on vacuum and fuel-cell technologies. Since March 2012, he has worked at the Technische Universität Darmstadt in the group of Prof. Christian Hess. In his PhD studies, he developed a thermal ALD system to deposit metal oxides mainly on porous substrates such as ion-track-etched membranes and mesoporous powders.

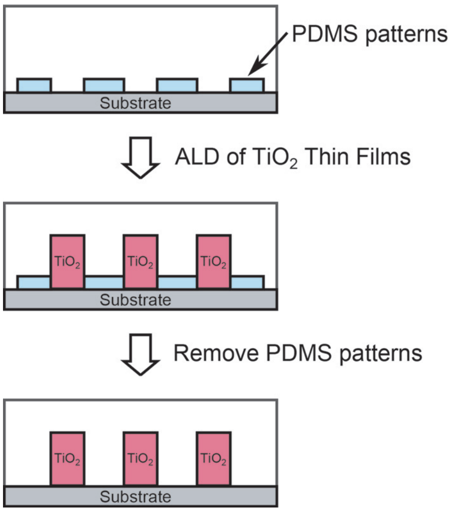

Figure 3. Schematic procedure for fabricating patterned TiO_2 thin films by ALD on PDMS-patterned Si substrates. For further details, see the text. Reproduced from Ref. [18] with permission.

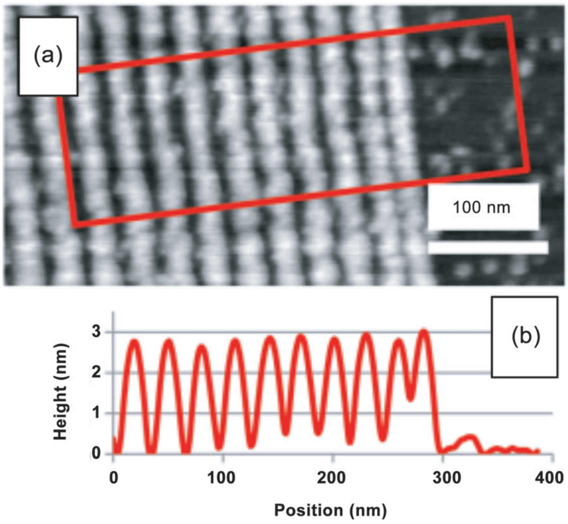

Figure 4. a) Atomic force microscopy (AFM) image of TiO_2 nanostructures on Si surfaces fabricated by scanning tunneling microscopy (STM) lithography. b) Cross-section of the rectangle in panel (a). Reproduced from Ref. [24] with permission.

(PMMA) was spun on a SiO_2/Si substrate and patterned by electron-beam lithography (EBL).[19] A subsequent ALD deposition yielded hafnium oxide structures with feature sizes of about 80 nm. Whitney et al. used nanosphere lithography (NSL) to pattern a Si substrate with triangular Ag nanoparticles (side length 90 nm)[20] before successively depositing Al_2O_3 by ALD selectively onto the Ag nanoparticles. Considering the growing interest in plasmonic nanostructures, this approach is very promising, for example, for the formation of coated SERS (surface-enhanced Raman spectroscopy) substrates with increased thermal stability and biocompatibility. By patterning a self-assembled monolayer (SAM) of octyldecyltriclorosilane (ODTS) by EBL, Huang et al. deposited isolated TiO_2 lines with widths of less than 30 nm onto SiO_2/Si substrates.[21] By using a similar approach starting from a SAM of ODTS but performing the patterning step by oxidation atomic force microscopy (AFM) lithography, Prinz and co-workers formed ZrO_2 and PbS nanostructures with approximately 40 nm resolution.[22,23] Recently, scanning tunneling microscopy (STM) tip-based lithography was developed and applied for the fabrication of TiO_2 nanostructures on Si surfaces.[24,25] Patterning was performed by local stimulation of a hydrogen-terminated Si surface, thereby leading to unpassivated Si areas. After partial oxidation, ALD was selectively carried out on those areas from which hydrogen had previously been removed. By using this approach a lateral resolution of approximately 15 nm was achieved (Figure 4). Recently, electron-beam-induced deposition (EBID) has been combined with ALD to fabricate high-quality Pt nanostructures, thus making this technique a competitor to EBL, but without the need for resist films.[26]

Alternatively, nanoscale features are accessible by patterning approaches based on nanometer-sized objects or topological structures to selectively passivate the substrate, by employing either colloidal crystals or nanopillars.[27,28] By using the self-assembly of silica spheres to form colloidal crystals, Bae et al. used the corresponding chemical patterns (sizes: 94, 79, 52 nm) for ALD of TiO_2 nanodiscs.[27] Reducing the feature size further, Liu et al. employed S-layer proteins (found in the cell envelope of bacteria) as a template, which reassembled on a silicon substrate to form 2D arrays with ordered pores of nearly identical sizes (9 nm).[29] As shown in Figure 5, ODTS was utilized to selectively react with the

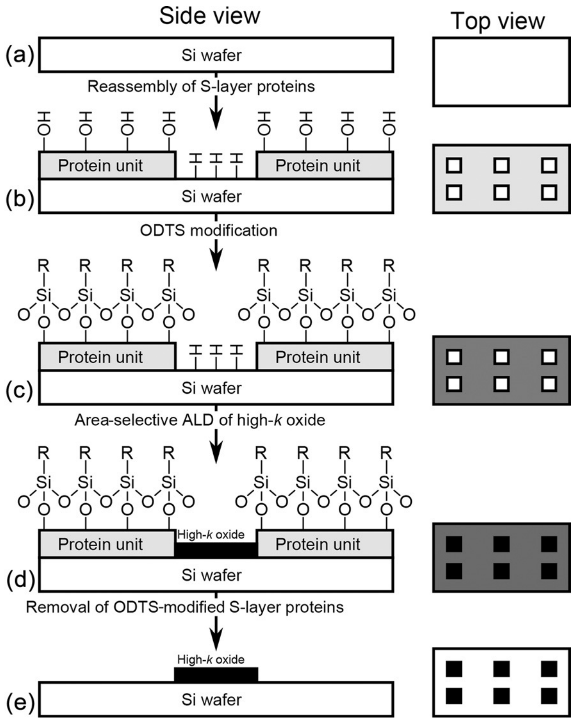

Figure 5. Schematic side and top views illustrating the procedure for generating periodic nanopatterns on a Si substrate by using a nanotemplate of S-layer proteins combined with an area-selective ALD process. Modified from Ref. [29] with permission.

S-layer proteins but not with the Si surface exposed through the pores defined by the proteins, thereby allowing area-selective ALD of hafnium oxide in the pores. By using this approach, periodic HfO_2 nanopatterns with a feature size of approximately 9 nm were achieved. As the Si surface is H-terminated, this study shows that the deposition of oxides using ALD does not necessarily require the presence of hydroxy groups. It is worth mentioning, that ALD of oxides has also been demonstrated on metal surfaces (HfO_2 on Cu).[30] In a more recent study, Alaboson et al. used self-assembled organic monolayers of 10,12-pentacosadiynoic acid (PCDA) to form well-ordered domains on graphene to template the growth of ALD-deposited oxide nanostructures such as ZnO and Al_2O_3 with a resolution of less than 10 nm.[31] It should be mentioned in this context that the molecular structure of the self-assembly is guided by the symmetry of the underlying honeycomb lattice of graphite and thus strongly depends on the surface properties of the substrate.

3. Nanoscale Structuring of Powder Materials

As a very versatile ALD-based technique for nanoscale structuring, molecule-templated ALD has been introduced to create nanocavity-containing layers (Figure 6).[32] First, a sacrificial template is grafted onto the surface. Then, using ALD, a film is deposited around but not over the template. Finally, the template is removed thermally or by ozone treatment to reveal the original substrate surface. The dimensions of the cavity structures are defined by the size and geometry of the template molecule. As templates, *p-tert*-butylcalix[4]arene (CAL), adamantanecarboxylic acid, and di-*tert*-butylcatechol have been employed for deposition on alumina and titania surfaces. The resulting cavities are less than 2 nm in all dimensions (cavity volume $< 10\,nm^3$). However, even smaller template molecules with dimensions < 1 nm may be envisioned, such as 2-*tert*-butyl-3,3-dimethylbutanol. The density of the cavities can be controlled through the amount of template initially deposited. In the case of the above template molecules, cavity densities are not expected to be limited by the density of hydroxy groups on the surface but rather by the size of the template, that is, by steric effects. For example, the density of hydroxy groups on commonly used commercial titania P25 is specified as $4.6\,OH\,nm^{-2}$. This gives a maximum surface density of about $1\,CAL\,nm^{-2}$ (assuming consumption of all the surface hydroxy groups by linkages to CAL), which corresponds approximately to the cross-sectional area of CAL.

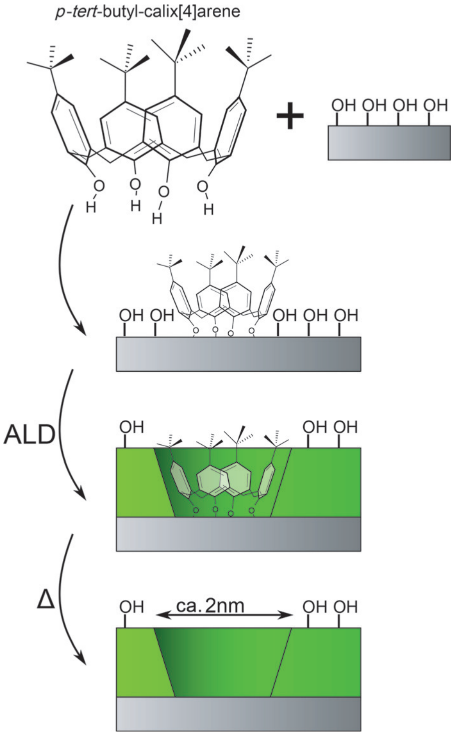

Figure 6. Molecule-templated ALD for the creation of sieving layers with nanocavities. For further details, see the text.

It should be stressed that the molecule-templated ALD approach offers broad applicability with regard to substrate materials as, in contrast to the lithography-based procedures for surface structuring, it is not limited to planar substrates. Furthermore, the underlying oxide and ALD film composition can be chosen independently. In the original work by Canlas et al.,[32] sieving layers of Al_2O_3 with nanocavities were deposited on a TiO_2 substrate and used to increase the selectivity for reactant-selective photocatalytic oxidations and transfer hydrogenations. However, as a result of its flexibility, this approach enables shape selectivity to be added to a wide range of materials. One example is the selection between similarly sized molecules in the range of a few nanometers, which would be too large for zeolite pores and too small to be separated by mesoporous materials.

As indicated in the previous paragraph, ALD has been shown to be a powerful tool for the controlled structuring of materials for energy applications, such as (photo)catalysts, solar cells, or batteries. As an example, we discuss in more detail the application of ALD to catalysts, as new ALD approaches for nanoscale structuring of catalyst surfaces have recently been introduced. For the other areas we refer to recent reviews.[33,34] It is known that the nanostructuring of surfaces plays an important role in catalyst synthesis.[35] The potential of ALD for the development of advanced catalysts is illustrated for supported metal nanoparticles used for many commercial reactions such as petroleum refining, Fischer–Tropsch synthesis, the water-gas shift reaction, and automobile exhaust-gas treatment. In particular, ALD-based strategies achieve stabilization of the catalytic active sites by preventing metal agglomeration.[36–39] To this end, ALD can be employed to apply oxide coatings (e.g. Al_2O_3) with atomically controlled thickness. To ensure the accessibility of the metal nanoparticles, the protective overcoat needs to be porous (Figure 7). Porosity within the ALD overcoat can be generated by high-temperature treatment, organic porogens, or selective growth.[36,38] For example, Liang and coworkers showed that porous Al_2O_3 films can be formed on Pt nanoparticles by alternating deposition cycles of trimethylaluminum (TMA) and ethylene glycol followed by calcination to remove the organic molecules.[39] In this context, silica-supported Pt nanoparticles (prepared by ALD) coated with

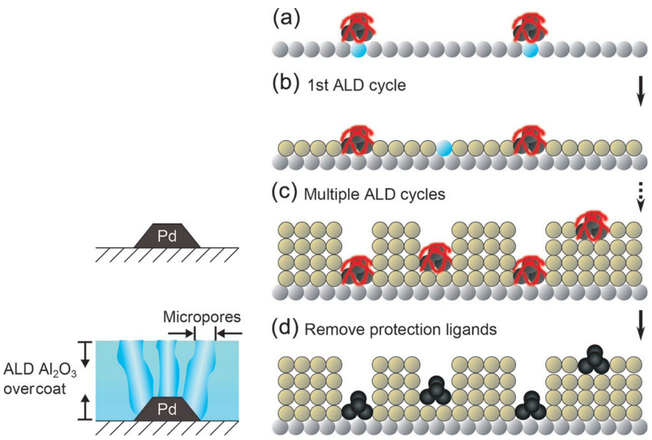

Figure 7. Left: Schematic model of a porous oxide overcoat for protecting metal nanoparticles. Right: Strategy for stabilizing nanoparticles by using an ABC-type ALD process: a) An initial support surface with nucleation sites is exposed to a volatile metal precursor A to form metal nanoparticles with some of the ligands retained (red curves). b) Reagents B and C are added to form a new support surface. c) Multiple ABC cycles form new support surfaces and metal nanoparticles protected by ligands. d) The protective ligands are removed to activate the metal nanoparticles. Modified from Refs. [37,38].

similarly synthesized Al_2O_3 films with defined porosity clearly demonstrated size-selective behavior in the liquid-phase hydrogenation of *n*-hexene versus *cis*-cyclooctene.[40] In the "selective growth" approach the metal nanoparticles are masked by organic molecules prior to ALD treatment. Subsequent oxidation removes the organic template but leaves the oxide overcoat.[36] It can be envisioned that further optimization of the use of organic porogens or the "selective growth" method will result in control over the size and shape of the pores, which may add shape selectivity to the functions of catalysts in the future.

In addition to the application of protective overcoats and nanoparticle synthesis, ALD has been used for the nanoscale synthesis of stabilized, uniform metal particles. This strategy for nanoparticle stabilization is illustrated on the right of Figure 7. First an initial support with nucleation sites is exposed to a volatile metal precursor to form metal nanoparticles with some of the ligands retained (red curves) (a). In subsequent steps, the nanoparticle is stabilized through multiple ALD cycles (b and c). Finally, the protective ligands are removed to activate the metal nanoparticles (d). Lu et al. applied this approach to the controlled synthesis of alumina- and titania-supported Pd nanoparticles.[41] They reported the synthesis of Pd nanoparticles with a very narrow size distribution of around 1 nm over a broad range of Pd loadings (0.7%–6.6% for Pd on Al_2O_3).

More recently, ALD strategies have been developed to synthesize supported bimetallic nanoparticles, which are of great interest for (electro)catalytic applications. In this case, ALD is used to selectively grow a secondary metal on the primary metal particle, but not on the support, thereby allowing the controlled formation of core–shell and well-mixed alloy nanoparticles (PdPt, PtPd, RuPt, and RuPd).[41–44]

4. High-Aspect-Ratio and Complex-Shaped Substrates

Many material properties and applications depend on geometrical shape or structure. In particular, porous substrates take advantage of their high specific surface and a specific pore-size distribution to confine liquids or gases, or allow unique interactions between substrates and electromagnetic waves. Unfortunately, in many cases the available porous materials do not have the required specifications in terms of chemical resistance or temperature stability. Coating is a straightforward way to alter the surface and thus change the properties. Unlike wet-chemical or continuous coating methods such as CVD, ALD is able to preserve the geometry of the substrate. However, despite the self-limiting nature of the ALD process, homogeneous deposition with growing aspect ratio is still a challenge and has been performed only on a laboratory scale so far.

Artificial and natural polymer fibers have attracted much interest in different technological areas, including textiles, filter membranes, and medical devices.[45,46] Unlike wet-chemical or CVD coatings, ALD provides a homogeneous coating that follows the flexible movements of the fibers without cracking, for example, on cellulosic paper,[47] electrospun poly(vinylpyrrolidone) fiber mats,[48] or swelling-induced mesoporous block copolymers.[49] In the last case, thin tubes and tubular networks of metal oxides were obtained after calcination (Figure 8). For medical applications, biological compatibility, especially in the case of implantable devices, is essential, besides the technological improvement of the material. To this end, Hyde et al. used ALD to deposit $TiNO_x$ films as bio-adhesive coatings onto woven cotton fibers to enhance the adhesion of human cells to woven cotton fibers.[50] This example clearly shows the potential of ALD for surface modification to produce biocompatible cellulose and other implant materials.

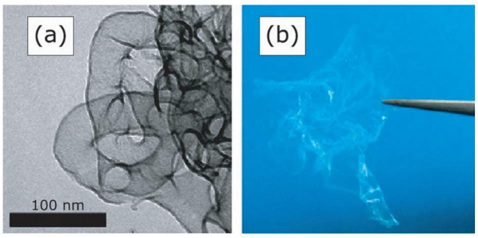

Figure 8. a) TEM image and b) photograph of swelling-induced mesoporous block copolymer obtained after 10 cycles of Al_2O_3 ALD and subsequent calcination. The interconnects are clearly visible in the TEM image. Modified from Ref. [49] with permission.

Porous membranes have a wide range of applications in separation as well as for energy conversion and storage. In particular, membranes with well-ordered pores may be used as a template for nanotubes and nanowires, which are of great interest in sensing or microtechnology applications. Separation processes depend mostly on a homogeneous and well-defined pore diameter on the micrometer and nanometer scale for particles and molecules, respectively. To this end, ALD onto porous anodic alumina and different organic membrane types has been studied. The fabrication of anodic aluminum oxide (AAO) is a straightforward process that yields a well-ordered hexagonal pore structure. The resulting membranes are chemically inert and thermally stable, but mechanically fragile. As an example, Romero et al. used ALD to deposit a 5 nm homogeneous SiO_2 film onto 60 μm long pores with a mean diameter of 35 nm by using 3-aminopropyltriethoxysilane, H_2O, and O_3 as precursors.[12] The deposited films were shown to influence the ionic transport properties. Similarly, track-etched polycarbonate (TEPC) membranes have great potential for the selective transport of ionic species or biological species through nanochannels and the development of novel nanopore sensors. For example, Li et al. deposited Al_2O_3 from trimethylaluminum (TMA) and H_2O to coat 6 μm thick membranes with a mean pore diameter of 30 nm.[51] Recently, we developed a low-temperature ALD process for the homogeneous deposition of SiO_2 onto TEPC membranes with a thickness of 30 μm and pore diameters ranging from 20 to 80 nm by using $SiCl_4$ and H_2O as precursors (both catalyzed with pyridine).[52] In contrast to AAO, TEPC is flexible even after deposition. Our studies show that the SiO_2 coating significantly improves the wettability of the TEPC membranes. After membrane dissolution, flexible SiO_2 nanotubes with a length of about 30 μm and typical aspect ratios of up to around 3000 are obtained (Figure 9, left). The right side of Figure 9 shows SEM images of representative sections of the tubes, which exhibit constant wall thickness along their entire length, thus evidencing the excellent homogeneity of the ALD process inside the SiO_2 nanochannels.

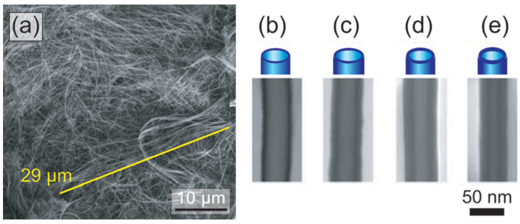

Figure 9. a) TEM image of SiO_2 nanotubes after deposition of a 10 nm thick SiO_2 film by ALD and dissolution of the TEPC membranes. b–e) STEM-in-SEM images of representative sections of SiO_2 nanotubes after deposition of a 5.3 nm (b), 10 nm (c), 14.6 nm (d), and 17.8 nm (e) thick SiO_2 film by ALD and membrane dissolution.[52]

Many catalytic applications rely on porous powders with large specific surface areas.[53] ALD has demonstrated its potential for the controlled modification of porous catalysts while preserving the structure and accessibility of the pores. This is illustrated for zeolites, which are widely used as commercial adsorbents and catalysts. Their use as an acid catalyst is based on the accommodation of trivalent species (e.g. Al^{3+}) in the Si^{4+} framework to increase the number of Brønsted sites. By deposition of Al_2O_3 by ALD, Pulinthanathu Sree et al. introduced new acid sites into zeolite Ultrastable Y (US-Y), thereby enhancing the catalytic activity.[54] N_2 adsorption measurements revealed that the accessible specific surface area of US-Y zeolite after 10 ALD cycles reduced from 636 to 533 m^2g^{-1}, while the concentration of Brønsted acid sites increased from 488 to 570 $mmol\,kg^{-1}$ with nearly a constant concentration of Lewis acid sites. Furthermore, the adsorption and desorption isotherms showed the same shape as those of the unmodified US-Y, strongly indicating an intact pore structure. However, it should be mentioned that homogeneous deposition onto high-aspect-ratio substrates is still a challenge. An important aspect concerns the deposition times, as the gas flow within the pores is governed by Knudsen diffusion in the pressure regime of most gas-phase deposition methods.

5. Summary and Outlook

This Minireview addresses the current status of the application of atomic layer deposition (ALD) to the nanoscale structuring of surfaces. The versatile application of the method to nanostructure both planar substrates and powder materials is outlined. Most studies on planar surfaces have been related to surface patterning because of its importance for applications in modern microelectronics. With the continuing trend of miniaturization, interest in bottom-up structuring using ALD will continue to increase. The application of ALD to nanostructure optical devices, based, for example, on plasmonic and photonic nanostructures, is a strongly developing field that is expected to lead to new applications. In regard to powder materials, in addition to the ongoing applications of ALD to new areas of chemistry, a variety of new ALD approaches for the nanoscale structuring of surfaces have been introduced in recent years. These include molecule-templated ALD for the formation of nanocavities as well as ALD overcoats and ALD-based synthesis for metal stabilization. The growing versatility in the use of ALD for nanoscale structuring is expected to have important implications for the development of advanced materials for applications in (electro-, photo)catalysis, (bio)sensing, batteries, solar cells, and fuel cells. Considering the recent progress in the application of ALD to porous substrates, ALD-based nanostructuring is expected to be routinely applied to high-surface area materials such as mesoporous oxides in the near future. This will open the door to new classes of materials that combine a high density of active sites with shape selectivity, features which are of great interest in many areas of chemistry, such as sorption, separation, sensing, and catalysis.

Although the application of ALD to porous substrates has progressed significantly during the last decade, an obstacle to technical applications is the small scale at which ALD processes are currently operated. Polymeric fibers, especially cellulose, are interesting cheap substrates for creating hollow tube networks. The first approaches to upscaling have been made with roll-to-roll deposition machines. Furthermore, well-ordered pores in conjunction with the properties of polymers are of great interest for many applications, but industrial-scale manufacturing will require cheap membranes (avoiding expensive track generation by heavy ions).

In terms of the technical use of ALD for the nanostructuring of (porous) powders, an important next step would be to advance from small laboratory-scale experiments to the deposition of tens of grams of substrate. That progress could be accelerated by the development of commercial reactors dedicated to the deposition of powders, as, so far, ALD manufacturers mostly provide setups optimized for wafers and other flat substrates.

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