Diffusion Phenomena in Atomic Layer Deposition

Mato Knez*,[1,2,3]

[1] Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany
[2] CIC nanoGUNE Consolider, Tolosa Hiribidea 76, 20018 Donostia-San Sebastian, Spain
[3] Ikerbasque, Basque Foundation for Science, Alameda Urquijo 36-5, 48011 Bilbao, Spain
*E-Mail: m.knez@nanogune.eu

Abstract:

Atomic layer deposition (ALD) is a mature technology for the deposition of conformal thin films. During the ALD process or in a post treatment, a variety of diffusion phenomena can occur which can deteriorate the desired product, but also can be used to fabricate materials or structures in a novel way. This article reviews some of the observed diffusion processes and strategies to make use of those.

1. Introduction:

The design of nanomaterials with various shapes and dimensions has seen many diverse strategies in the past years. Although the common goal is to manufacture nanoscale structures, particles, wires, etc., the anticipated application determines the quality and the way in which the structures are built. The ways include self-organization or wet-chemical growth as cost-efficient strategies, but also lithographic methods for large scale structuring as more demanding ones, particularly if electron beam lithography is applied.

The enormous variety of strategies and synthesized materials makes it challenging to overlook those and one can easily get the impression that for every aimed purpose the properly fitting nanostructure can be synthesized. In many cases, however, a rational combination of the desired shape and functionality cannot be achieved. In such cases, often template-based approaches are applied, where a given structure is modulated in its functionality either by means of coating with another functional material of choice or even by structural replication. Among the ways to functionalise such nanomaterials, especially atomic layer deposition (ALD), plays an increasingly important role as this method enables the deposition of extremely thin coatings, still maintaining structural fidelity.

ALD is a vacuum-based coating technology, which is derived from chemical vapour deposition (CVD), with one distinct technical difference: The occurring chemical reaction is separated into two half-reactions in which initially the first chemical precursor (usually a reactive metal compound) chemisorbs to any available surface site of the substrate and subsequently, after a purging step, the second precursor (water, oxygen, diverse plasmas, etc.) is injected to react with the adsorbed species. In this way, line-of-sight deposition is avoided and a controlled growth of the coating on the Å-scale is achieved simply by repeating the deposition cycle. The precision in coating thickness and conformality made ALD meanwhile an important method-of-choice for functionalisation and even replication of nanomaterials, especially in those cases where the materials have extremely complex shapes and aspect ratios [1, 2].

The coating of materials to add or replace functionalities appears straightforward for the most cases in which ALD is applied. Nevertheless, frequently side reactions can occur, intentionally or unintentionally, which alter the structural or physical properties of the resulting material. Such alterations may not always be desired, but if they are chemically and physically understood, they offer an additional degree of freedom to manipulate materials in a controlled way.

This non-exhaustive review will show some examples on how diffusion phenomena can be beneficially used to manufacture shapes and materials by ALD coating or by post-coating processing. Examples regarding interfacial diffusion, surface diffusion, diffusion/migration through coatings, and diffusion of precursors into the substrates during coating processes will be presented and discussed.

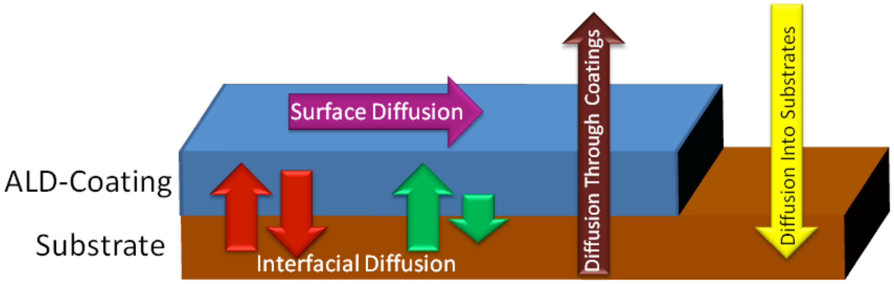


Figure 1 Schematic overview of the various possible diffusion phenomena occurring during ALD coatings or during post-processing.

2. Interfacial Diffusion

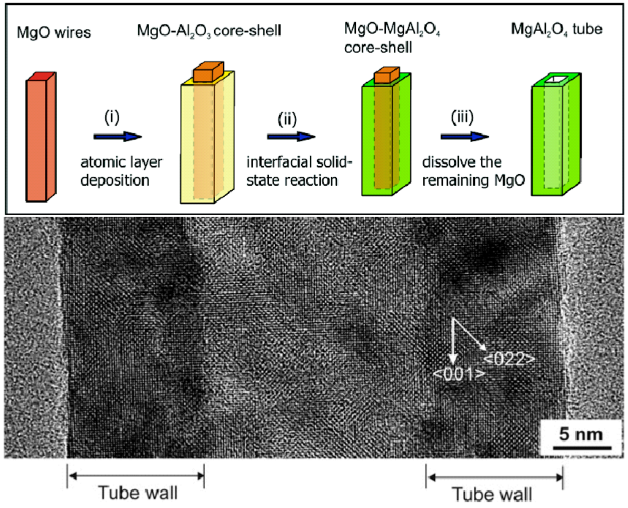
Most ALD-deposited materials require processing temperatures between 150 °C and 250 °C and thus are far below temperatures required for inducing solid-state diffusion reactions from a thermal point of view. Therefore, coating of a template will in most cases result in a core-shell structure with a relatively sharp interface between the two materials. Nevertheless, even at those temperatures a slight intermixing of the coating with the substrate is possible. The solid state diffusion will become more pronounced if energy is applied to the system, for example by means of heating. In this case, the mobility of the constituting parts of substrate and coating will induce interpenetration in both directions, eventually leading to a new compound. This diffusion is dependent on several factors, most importantly the chemical and physical nature of the materials, the annealing temperature, and the annealing duration. In a simple case, the diffusion of material at the interface will be mutual, meaning that the materials diffuse in both directions with similar velocity and quantity.

ALD allows coating of materials in a very precise way. Most of the ALD processes deposit binary oxides like Al_2O_3, ZnO, TiO_2, etc. If needed for specific purposes, ternary compounds or even higher order compounds can be deposited [3], but the selection of materials is rather sparse and the processes in many cases become complicated. Often, such processes combine two or more individual ALD processes into one. Since multiple precursors are required and in many cases the thermal deposition windows of the individual processes may not be compatible with each other, it becomes very difficult to find parameters good enough for a reasonable growth control. Material diffusion during the deposition or induced by post process thermal treatment can be beneficially used to obtain such compounds in an alternative way. The key benefits of ALD are maintained, since individual (e.g. binary) compounds can be grown very conformally with controlled thickness and the resulting mixed compound still shows a coating with good structural fidelity.

A number of such interfacial diffusion reactions have been reported to take place either at the boundary of the ALD coating to the substrate or between two subsequent ALD coatings. An early study [4] showed that ALD coating and subsequent annealing of Al_2O_3 on Si induces inter-diffusion of the Al and Si species. A follow-up work [5] described that at the interface between Al_2O_3 and Si a mixed phase of Al_2O_3 and SiO_2 forms with variable composition. Further materials with a variable composition have been obtained from Al_2O_3/HfO_2 [6] and Ru/TaN [7] systems,

igure 2 Upper image: Schematics of the fabrication process of $MgAl_2O_4$ spinel tubes. Lower Image: igh magnification TEM image of a part of the single crystalline spinel tube. Figures adapted with ermission from [8]. Copyright 2006 by the Institute of Physics Publishing.

although it is difficult to assign the intermixing to diffusion phenomena as in both cases the coating thickness was very small. Considering that an individual ALD cycle is usually not covering a complete monolayer [3] so that some surface sites will remain unoccupied, it is natural to assume that those sites will possibly be occupied in the next half-reaction, resulting in a mixed compound driven by the surface reactivity rather than diffusion.



A better evidence for interfacial diffusion of materials is given by controlled post-coating thermal treatment. A good example is the formation of $MgAl_2O_4$ spinel nanotubes, square shaped in their cross-section, after annealing of MgO nanowires coated with Al_2O_3 (see figure 2) [8]. The inter-diffusion of Mg^{2+} and Al^{3+} at elevated temperatures leads to the formation of the spinel. The remaining MgO core was removed wet chemically. The uniqueness of this procedure is reflected in the resulting single crystalline nanotubes, although the initial Al_2O_3 coating was amorphous. Individual processes for MgO and Al_2O_3 deposition are available and a combination thereof may be achieved. Nevertheless, it is hardly imaginable that such a combined process would lead to single crystalline structures, even after annealing. Such an attempt was tried with the combination of a $SrCO_3$ and TiO_2 process to obtain a $SrTiO_3$ film [9]. Indeed, crystalline $SrTiO_3$ formed after annealing at 650-900 °C, although not being single crystalline.

However, not all diffusion processes result in single crystalline structures. In another case, a solid-state interfacial diffusion reaction after ALD coating was used to produce a mixed phase of $CoO/ZnCo_2O_4/ZnO$ [10]. The intention of this experiment was to synthesize thin layers of ferromagnetic materials, which appeared to be unsuccessful for this material combination. Nevertheless the experiment shows another couple of binary oxides which undergo interfacial diffusion.

The lack of single crystallinity may be considered a drawback, but in fact it is not. Frequently, just the material composition is of importance and grain boundaries, especially if the film thickness is very low, may even improve some physical characteristics like the conductivity. This is, for example, the case of yttria-stabilized zirconia (YSZ). This compound is used as electrolyte in solid oxide fuel cells (SOFCs). Ginestra *et al* [11] have shown that after depositing multilayer structures of Y_2O_3 and ZrO_2 and annealing up to 950 °C in an oxygen atmosphere, a mixed compound can be produced which outperforms bulk YSZ in terms of conductivity. As reason for the good conductivity, the small grain size, and the multitude of grain boundaries are proposed.

Some material combinations show a very special case of interfacial diffusion. If a material flux in one direction across the interface cannot be compensated with an equal material flux in the counter direction, this can be compensated with a unidirectional flux of vacancies which accumulate to voids on one side of the interface. This unequal material flux is called Kirkendall effect [12, 13] and is known for decades in metallurgy. In nanoscience, this effect was often used for the synthesis of hollow nanomaterials [14]. On ALD based systems, the Kirkendall effect was observed on three material combinations: Fe_2O_3/ZnO [10], SiO_2/ZnO [15] (mediated by Au migration) and Al_2O_3/ZnO [16].

In the former case, at the interface of ALD deposited Fe_2O_3 and ZnO upon annealing at 600 °C and 700 °C, voids are observed as well as the formation of a $ZnFe_2O_4$ spinel. The resulting film exhibits ferromagnetism after the spinel formation, which was not observed in the as-deposited bilayer. The most research effort has been, however, invested in the Al_2O_3/ZnO bi- or multilayer system, which results in the formation of a $ZnAl_2O_4$ spinel [10, 16-24] and voids. In all those cases, upon annealing, Zn^{2+} diffusion into the Al_2O_3 layer occurred, leaving hollow area behind. The interesting aspect of making use of the Kirkendall effect is the possibility to convert bulk to shell. It becomes possible to produce nanochannels in various shapes, dependent on the morphology of the ZnO. In the very simple case of ZnO nanowires, the transformation leads to spinel nanotubes [16, 23], which can even have higher order hierarchy [24]. Rippled ZnO nanowires will result in peapod-like structures of ZnO embedded in $ZnAl_2O_4$ [17], and coiled nanofibres in helical nanotubes [22].

A very interesting aspect of the Kirkendall-based transformation is the possibility to delaminate films initially bound to each other. Formation of interconnected voids in 2D was observed on planar and V-shaped multilayer structures [17], but this was even more expressed in the case of multilayer coating of fibres [21]. The thickness control of the ZnO layers is of critical importance as the ZnO needs to be completely consumed. In multilayered alternating alumina/ZnO films, the Zn^{2+} can diffuse bi-directionally and result in isolated spinel layers forming tube in tube structures (see figure 3). With the thickness precision of the ALD layers and the resulting high crystallinity, one may envision this procedure being attractive for numerous applications. Freestanding thin films are, for example, very interesting for application as support for TEM investigation.

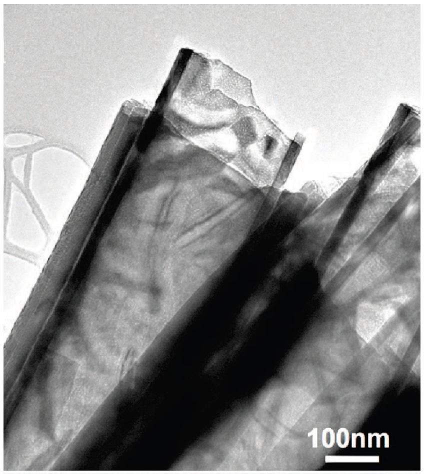


Figure 3 Typical TEM image of $Al_2O_3/ZnO/Al_2O_3$ microtubes (~18/10/44 nm) annealed at 700 °C for 12 h. Broken tubes clearly reveal physical separation and delineation between the inner and outer spinel tubes. The image confirms increased roughness of the spinel layers along the

length of the tube, on the surfaces adjacent to the Kirkendall voids. Image adapted with permission from [21]. Copyright 2009 by the American Chemical Society.

One should, however, be aware that not every void formation relies on the Kirkendall effect. ZnO or CuO nanowires coated with a titania film also form voids upon exposure to UV light either in aqueous environment [25] or simply by storage at ambient laboratory conditions [26]. The voids are a result of photocatalytic etching of the bulk nanowires by the titania shell and not by the diffusion of ZnO into the shell as can be deduced from the fact that the resulting nanotube does not contain Zn after completion of the ZnO removal.

3. Surface Diffusion

The ALD process is often seen in a static model: precursor chemisorbs at the substrate surface and reacts with the counter precursor in the next half reaction. However, reality is in most cases more complicated. The adsorption of the first precursor will initially be of physical nature (physisorption) which goes hand in hand with surface diffusion until a reactive surface site for chemisorption is reached. The diffusion tendency of the precursor is dependent on several factors, among them the chemical nature of the substrate which is often related to the process temperature, the dissociation ability and the binding energy of the resulting precursor/substrate complex, and the differences in the surface free energy of the two materials, the substrate and the coating [27, 28, 29]. The surface diffusion may occur in two stages of the ALD process: i) the first precursor may diffuse on the substrate during the first pulse/purge period, or ii) the product may diffuse after the pulse of the second precursor. An exact judgement of the diffusion tendency of either of those species, the dissociated precursor or the product, is sometimes difficult. However, a rough estimation can be made if one considers the Pauling electronegativity (X_M) of the molecules/atoms. Fu and Wagner [30] explained this in more detail on the example of metal atom adsorption on TiO_2 surfaces. Metals with $X_M > 1.9$ (e.g. noble metals) will show a tendency to adsorb to Ti-sites of the surface, while metals with lower X_M will preferentially bind to oxygen sites. Keeping this in mind, it is not astonishing that noble metal ALD on dielectric substrates will lead to cluster and island formation as the metals upon reaction with the second precursor may easily diffuse on the substrate to find defective sites, kinks, or steps where an interaction with the metal site of the substrate instead of the oxygen site can occur. Consequently, the initial metal seed keeps on growing with each ALD cycle, since this surface site is preferential for further growth rather than the dielectric substrate. The island growth can be beneficially used for the formation of metal nanoparticles by ALD [31]. The particle size can even be controlled with the number of ALD cycles with very high precision. Figure 4 shows an example of Pt nanoparticles grown on $SrTiO_3$ nanocubes by ALD [32]. Within the initial 5 ALD cycles one can observe that surface diffusion leads to nanoparticle coalescence (figure 4 c) and to a decrease of the surface to volume ratio (figure 4 d). Such access to fine tuning of the particle sizes opens new ways for the synthesis of supported catalysts.

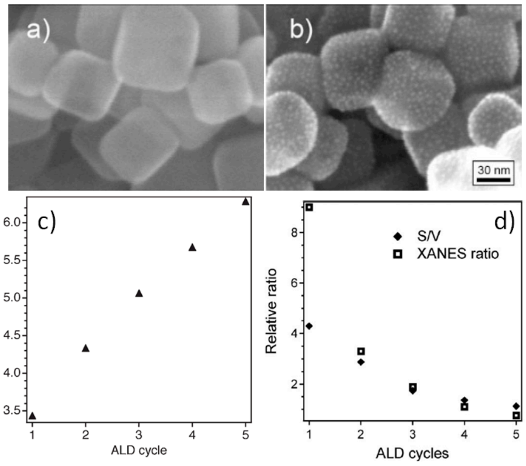


Figure 4 SEM images of $SrTiO_3$ (STO) nanocubes before (a) and after (b) coating with Pt nanoparticles using three Pt ALD growth cycles. (c) Centre-to-centre interparticle spacing (D). The linear dependence of D on the ALD cycle shows that the number density of nanoparticles is decreasing due to nanoparticle coalescence. (d) Comparison of the surface area to volume ratio (S/V) with the XANES ratio of Pt–O to Pt–Pt bonding. Images reprinted with permission from [32]. Copyright 2009 by Wiley & Sons.

Surface diffusion can also be used for post-process nanostructure synthesis. Considering CuO nanowires coated with metal oxides by ALD, one initially observes a very conformal coating. Upon reduction of the coated nanowires at elevated temperatures in a H_2 atmosphere, the CuO is reduced to Cu. This reduction to metallic Cu causes a shrinkage in volume and in parallel a de-wetting due to the high mobility of the Cu on Al_2O_3 [33]. The de-wetting at elevated temperatures together with the Rayleigh instability eventually results in the formation of Cu nanoparticle chains embedded in a metal oxide shell (figure 5).

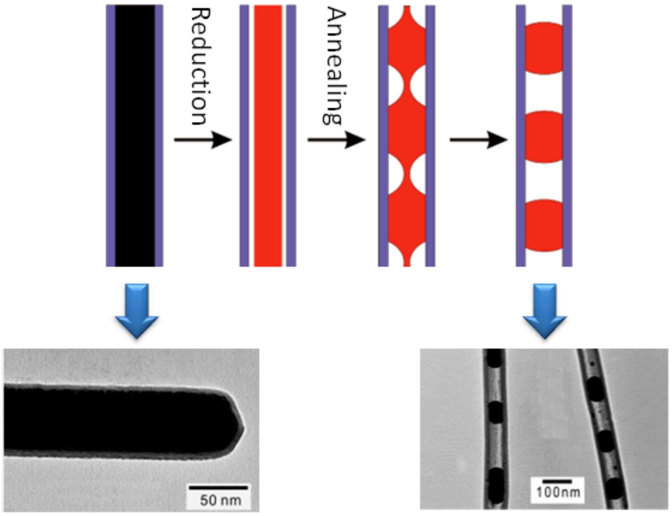


Figure 5 Schematics of the formation process of Cu nanoparticles in metal oxide nanotubes. CuO nanowires are coated with Al_2O_3 and subsequently reduced at elevated temperatures. The Rayleigh instability induces nanoparticle chain formation. Initial and final stages of the process are shown with typical SEM images. Figure adapted with permission from [33]. Copyright 2008 by the American Chemical Society.

4. Diffusion/Migration through Coatings

ALD is commonly referred to as an effective means of producing diffusion barriers. Most of the work in this field is focused on inhibiting diffusion, relevant for electronic applications to prevent the diffusion of a conductor into the dielectric (see e.g. [34]) or as moisture barrier for encapsulation of OLEDs. The conformal and pinhole-free nature of an ALD coating furthermore promises serious benefits over commonly used methods for blocking gas permeation or metal diffusion [2, 35].

In some cases, however, diffusion or migration through ALD coatings may be desired. This is primarily the case when a post-coating chemical reaction beneath the ALD layer is required. Diffusion through ALD coatings is strongly dependent on the chemical composition of the film, its crystallinity, thickness, and the nature of the molecules which are supposed to diffuse through the coating (e.g. gases or water vapour). Amorphous coatings with a thickness of a few to a few tens of nanometres are very promising for good diffusivity of small molecules, considering the results reviewed in [35]. However, Fe particles coated with 8 nm alumina in a fluidized bed reactor showed exceptional oxidation resistance, indicating an effective gas diffusion barrier [36]. The question arises whether or not the barrier is the driving force for hindering an oxidation or whether further physical effects, like the confinement and the restriction of volume expansion of Fe if oxidized to Fe_xO_y, play a role. An inverse experiment was performed by Qin *et al* [33], showing that a layer of 5 nm or 20 nm thick Al_2O_3 does not prevent the encapsulated CuO to be reduced to Cu if annealed in a H_2 atmosphere. The reduction is apparent as the system gains space after CuO is transformed to Cu which subsequently undergoes an undulation and particle chain formation based on Rayleigh instability. Another approach by the same author [37] showed that sacrificial layers, deposited between the substrate nanowires (Au in this case) and the shell could also be removed. The layers consisted of Al_2O_3 or polyimide (deposited by MLD) and were removed wet chemically or simply by annealing in the case of alumina or polyimide, respectively. It is not clear whether both ways are solely based on diffusion through the coating, but particularly in the latter case this is imaginable as a decomposition of the polymer should lead to a variety of small molecules like CO, CO_2, etc., which may easily pass the barrier.

A further way to induce transport through a compact ALD coating was shown by Yang *et al* [15]. In this work, the coating was performed with SiO_2 which at elevated temperatures shows serious fluidity. The substrate was Au-coated ZnO nanowires. The Au layer disassembled into nanoparticles which migrated through the SiO_2 to the surface in order to minimize the interface energy. Such a migration, however, will be limited to very few system combinations only.

A completely different way to achieve transport through an ALD coating was recently shown by Qin *et al* [38]. Coating of CuO nanowires was performed by molecular layer deposition (MLD) of alucone [39], an organic-inorganic hybrid material, deposited by replacing water vapour with ethylene glycol or similar organic compounds. Such inorganic-organic hybrid coatings form nanopores or mesopores upon annealing by decomposition of the organic constituent of the film [40]. Once the pores form, Cu from the core can diffuse through the coating to the outer surface if the system is annealed (see figure 6). Nanoparticles of copper oxide form on the outer surface which indicates that the out-diffusion of copper takes place much more rapidly than the in-diffusion of oxygen. This may be related to the size and the complicated pathways of the pores. An additional interesting effect is that with thicker coatings more and smaller particles are formed. An explanation for this is given with the number of pore openings which increases if the porous shell becomes thicker. More nucleation spots are available where the out-diffusing copper encounters oxygen and forms Cu_xO particles.

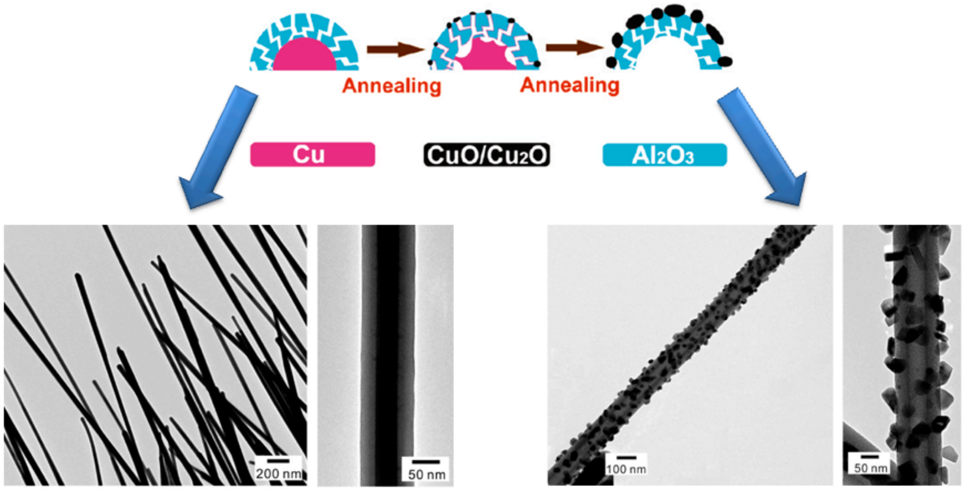


Figure 6 Schematics of the process to produce Cu_xO nanoparticles by diffusion of Cu through an ALD coating. Initially, CuO nanowires are coated with alucone. Subsequent annealing in a H_2 atmosphere

converts the alucone into porous alumina and reduces CuO to Cu. Further annealing in an O_2 atmosphere induces diffusion of Cu through the pores and a formation of Cu_xO on the pore mouths at the outer shell. Figures adapted with permission from [38]. Copyright 2011 by the American Chemical Society.

5. Diffusion of Precursors into the Substrate

The exposure of a substrate to gaseous precursors can in some cases also result in diffusion of those precursors into the substrate. This will often happen if the substrate is a soft solid, for example, a polymer. Attempts to coat several types of polymers like polystyrene (PS), polypropylene (PP), polyethylene (PE), etc. with Al_2O_3 resulted in clear evidence that the trimethylaluminum (TMA) which was used as precursor is absorbed by the polymer and induces a nucleation in the subsurface region of the polymer [41] upon exposure to water vapour. The ability of the polymer to absorb and retain TMA is dependent on its porosity or density and the functional groups the polymer exhibits. Poly(vinyl-chloride) (PVC) was shown to absorb less TMA than PP or PE. The proposed model for a subsurface nucleation was later on directly observed by TEM investigation of fibres of PP, poly(vinyl-alcohol) (PVA), and polyamide 6 (PA-6) [42]. Due to the thermal expansion of polymers, the subsurface growth is temperature-dependent [43], which is related to the enhanced diffusivity and increased free volume fraction of the polymer. The diffusion is also limited by the dose of the ALD precursor and the diffusion time. Pushing those parameters to an extreme results in a saturation of the bulk polymer with TMA which upon hydrolysis forms a monolith of porous Al_2O_3 [44].

The possibility to infiltrate an ALD precursor into a polymer together with the differences in the absorption behaviour of polymers with differing functional groups or densities opens a completely new route for nanostructure synthesis. The approach relies on the formation of domains of one polymer within the matrix of another polymer by using block copolymers [45]. Nanofibres with internal helical or doughnut-like structures were produced by confining polystyrene-*block*-poly(2-vinlypyridine) (PS-*b*-P2VP) in anodic aluminium oxide [46]. After removal from the template and selective swelling, the fibres were subjected to a ZnO-ALD process with diethyl zinc (DEZ) and water vapour as precursors. The ZnO deposited at the outer shell of the fibres, but also at the internal walls of the polymer. A removal of the polymer resulted in a structural replication by ZnO. In another series of publications, a PS-*b*-PMMA (poly methyl methacrylate) structured diblock-copolymer was processed with various ALD processes (Al_2O_3, ZnO, TiO_2, SiO_2, and W) to produce inorganic patterns resulting from the precursor diffusion through the polymer block and reaction at the interface of the polymer domains [47-49]. After removal of the polymer, the resulting inorganic nanofeatures can be used for further lithographic patterning. The concept was proven to work on a variety of substrates, among them silicon, indium tin oxide, and a Ni-Fe permalloy. The resulting structures depend on the features of the block copolymer and may resemble upstanding nanotips or even structured lines (see figure 7).

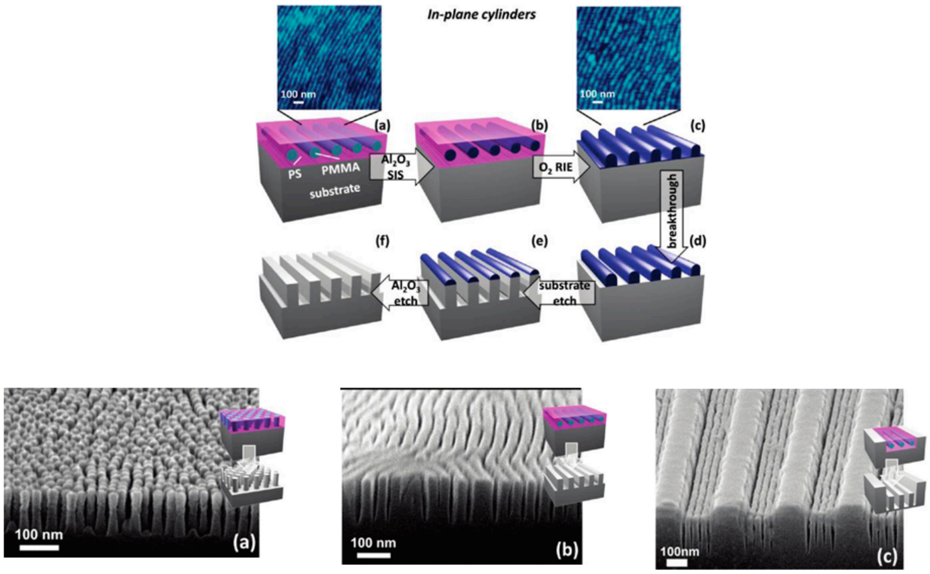


Figure 7 Upper image: Schematics of a lithographic process. The pattern is produced from diblock-copolymers and one phase reinforced with alumina by infiltration. The remaining processing steps are common lithographic procedures. Lower image: Three examples of patterns transferred from standing PMMA cylinders, in-plane PMMA cylinders, and in-plane PMMA cylinders aligned using graphoepitaxy. Images reprinted with permission from [49]. Copyright 2011 by the American Chemical Society.

As a side effect, the precursor diffusing into the polymer may also induce a chemical reaction with the substrate [50, 51]. Such chemical changes will in some cases go hand in hand with changes in the physical properties of the material. In various experiments with spider silk, collagen, or poly-tetrafluoroethylene (PTFE) as substrates, the mechanical properties of the (bio)polymers have been shown to significantly change as a direct consequence of the diffusion of precursors into the polymers and the chemical reaction between those [52-54].

6. Conclusion

Diffusion phenomena related to ALD or to a post treatment process may have significant impact on the material or structure which is subjected to coating. Diffusion of material can occur at material interfaces, at substrates, through ALD coatings, and into the substrate, strongly depending on the chemistry of the substrate, the precursors, and the deposited material. In most cases, diffusion phenomena may be considered a drawback, but the examples in the manuscript show that many beneficial aspects can be found, be it for the sake of nanochannel formation, nanoparticle synthesis, or even for producing metal-organic hybrid materials. Controlling the diffusion in various aspects may enable new ways of material synthesis and functionalisation which was already shown on a couple of examples described above. A deeper understanding of the various diffusion processes is still required in order to exploit the processes for the benefit of new functional materials and advanced technologies. Given the fact that more and more research groups from various research fields and disciplines are starting to use ALD for their particular purpose, more scientific input and novel ideas will develop in the near future and diffusion phenomena will inevitably play an important role.

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