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Special issue on Atomic Layer Deposition
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This special issue of the NEVAC blad is completely devoted to the method of atomic layer deposition (ALD). Initially the occasion for this special issue was the 20th International Conference on Atomic Layer Deposition, which includes the 7th Workshop on Atomic Layer Etching. This ALD/ALE2020 conference was scheduled to take place in Ghent, Belgium this year from June 28 to July 1. However due to the COVID-19 pandemic this conference was changed into a smaller online event, which is extremely unfortunate as the conference is held in Europe only once every four years. Yet, having no ALD conference in the lowlands is even one reason more to highlight the substantial ALD activity in the Netherlands through this special issue.

At our technical universities, there is a lot of research on ALD with many researchers involved. The academic research has also contributed to several breakthroughs of ALD, e.g. in technology development and in extending the application range. The ALD research at the universities has also sparked many industrial activities in the field of ALD, although companies also spotted the interest in ALD from the market themselves. Yet, the extensive know-how and deeper understanding of its basics have certainly stimulated and advanced the rapid pickup of the technique in industry. Currently there are quite many companies – a disproportionally high number compared to other countries – that have business in the field of ALD. Especially in the field of spatial ALD – a method to enable ALD for high volume manufacturing, also for applications outside those in semiconductor technology – the Dutch industry has been pioneering and is very strong. The many industrial ventures are also illustrated in this special issue through the advertisements of such companies.

We hope that this special issue gives a clear view of the method of ALD, its application areas, the cutting-edge research involved, and its future perspectives. Perhaps your interest is triggered, and you might even participate in the online version of the ALD/ALE conference this year. But note that we are also planning to organize a national meeting on ALD: ALD@NL. This meeting will take place on Friday November 6 and more information can be found elsewhere in this issue. But mark your calendar first!

Guest editors
Bart Macco & Erwin Kessels
Atomic layer deposition (ALD) is a method to precisely deposit high-quality nanolayers of all kind of materials. As such, it is a true nanotechnology which – among a multitude of other applications – enables the fabrication of the integrated circuits in your smart phone. In this introductory article, the method of ALD and its merits are briefly introduced. Also its history is presented in a nutshell and it is discussed how our country has played a vital role in the research and development of ALD and its widespread use now and in the future.

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main by translating the substrate with respect to the reactant injection positions. This is called spatial ALD.

**Unique selling points**

The self-limiting surface reactions that characterize ALD provide the method with its very important merits (figure 2). First, they lead to a very well-defined amount of material that is deposited per cycle. This growth-per-cycle is very reproducible from cycle to cycle but also independent of ALD reactor when working at the same substrate temperature. The self-limiting surface reactions also make the method surface-controlled instead of flux-controlled. This means that an excellent uniformity can be reached even for very large substrates and also that an unparalleled conformality (also referred to as ‘step coverage’) of the films can be obtained when the substrates have a demanding surface topology (e.g. surfaces with trenches, vias, pillars, packed particles, etc.). Especially through the latter aspects ALD distinguishes itself from the common flux-controlled techniques such as chemical or physical vapor deposition. A key merit of ALD is also that the processes commonly take place at reasonably low substrate temperatures. The temperature is typically well below 450°C, commonly around 200°C and in some cases as low as 25°C. ALD processes involving a plasma as co-reactant – plasma-assisted ALD – are typically well-suited to prepare films at low temperatures [3,4]. Moreover, ALD can be described as a ‘soft deposition’ technique as it typically leads to much less surface damage than physical vapor deposition techniques that involve energetic ions.

The number of ALD processes developed has grown vastly over the years and at this stage many materials can be deposited by ALD: oxides, nitrides, sulfides, tellurides, selenides, fluorides and metals. The periodic table in figure 3 shows which materials have been reported in the literature although it should be mentioned that not all ALD processes are straightforward to apply or viable for high volume manufacturing.

![Figure 2](image_url) **Illustration of the merits of ALD:** precise thickness control, excellent uniformity over large substrates, unparalleled conformality over 3D structures, all possible at relatively low temperatures [2].

![Figure 3](image_url) **Periodic table illustrating the materials that have been synthesized by ALD [9].**
A brief history

Although ALD has only become very popular in the last decades, the method is not new at all. The first patent filed dates back to 1974, but even before the Finnish inventors Suntola and Antson disclosed their work there was already some related activity on molecular layering in Russia. Figure 4 shows a timeline highlighting some main developments over the years [5].

Focusing on the role that the Netherlands played, a couple of important activities that contributed to the popularity of ALD can be mentioned:

A first notable fact is that the first report on plasma-assisted ALD originated from researchers from the Philips Research Laboratories in 1991 [3]. Later, from 2003 on, plasma-assisted ALD was really boosted by the research carried out at the TU/e. Nowadays, about 1/3rd of all ALD production tools are plasma-assisted ALD tools with a major application of plasma-assisted ALD in nanopatterning combining lithography, ALD and plasma etching [4].

One of the leading global manufacturers of ALD tools for the semiconductor market is the Dutch company ASM [6]. They were among the first to recognize the potential of ALD and through the acquisition of the Finnish company Microchemistry in 1999 they acquired a lot of ALD know-how. It is a public secret that ASM was a main partner of Intel in their efforts to replace SiO2 by HfO2 as gate dielectric in chips (since 2007).

Besides the semiconductor industry, the solar cell industry has also embraced ALD in high-volume manufacturing since 2012. The pioneering TU/e research on surface passivation of silicon by ALD Al2O3 nanolayers has contributed to this largely [7]. Currently also other applications of ALD in solar cell manufacturing are actively being considered and the TU/e has also had a pioneering role in the application of ALD in the production of perovskite solar cells.

The interest of solar cell industry in Al2O3 sparked the development of spatial ALD tools for high volume manufacturing. TNO and the companies Levitech and SolayTec where pioneers in the development of such tools that are currently used in production and which can reach a throughput up to 6000 solar cell wafers per hour. Also other Dutch companies started to work on spatial ALD such as VDL, Smit Thermal Solutions, SALDtech and SALD. These work on emerging applications of ALD such as batteries and displays.

Dutch researchers have also spearheaded other ALD approaches, application fields and related technologies that expected to have their breakthrough in a couple of years. This includes ALD on powders (TUD); hot-wire ALD (TU); ALD on and for 2D materials (TU/e); area-selective deposition by ALD (TU/e) and atomic layer etching (ALE), the etch-counterpart of ALD.

The articles in this special issue will give more insight in these ALD research activities in the Netherlands and provide a perspective on current and future applications of ALD.
Erwin is a professor at the TU/e where he initiated the research on ALD in 2003. Among many other things, he has contributed mainly to the breakthrough of plasma-assisted ALD and the use of ALD in solar cell manufacturing.
Plasma-assisted Atomic Layer Deposition

High-volume manufacturing and new opportunities in research

The usage of plasma as a reactant in atomic layer deposition processes started out as a niche process but in the meantime had its breakthrough in high-volume manufacturing in nano-electronics. Understanding the processes in plasma ALD is challenging but the knowledge in the Netherlands on plasma science, surface science and the ALD end-applications are a perfect foundation for a globally leading position in this field.

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Plasma-assisted Atomic Layer Deposition

Atomic layer deposition (ALD) is a processing technique that has been widely adopted for the growth of nanometer-scale films of a variety of materials. Besides the control at small length scales, there are also increasingly stringent requirements on material properties and limits on processing temperature. Therefore, a strong research effort into ALD has been present for the past few decades to improve and extend ALD processes. New chemistries are being sought continuously and the use of a plasma as one of the steps in ALD has been a common method to extend the processing capabilities of ALD [1,2]. Plasma ALD differs from thermal ALD by the use of a plasma as the reactant (e.g., an O₂ plasma instead of H₂O exposure to grow oxides). Interestingly, plasma ALD – which originally started as a niche method to expand the capabilities of ALD – has become an enabling technology in high-volume manufacturing and a large field of study [3]. Currently, its use in high-volume manufacturing is dominantly for patterning, but it is now also considered for masking and barrier layers, gate spacers, and low temperature encapsulation layers. Furthermore, plasma ALD and related methods are expected to be a prominent part of atomic-scale processing techniques envisaged for emerging developments.

Breakthrough into high-volume manufacturing

Around 2009 there were initial indications in the open literature for plasma ALD of SiO₂ to become a vital method for self-aligned patterning [4]. Besides the patterning techniques using multiple lithography steps, which can suffer from image placement limitations, there was a lot of interest in self-aligned techniques. For these techniques, the alignment of the individual patterns to each other is inherent to the technique and not affected by image placement. In Self-Aligned Double Patterning (SADP) a spacer is deposited conformally over a patterned mandrel. After anisotropic etching of the top and bottom parts of the spacer, and subsequent mandrel removal, the resulting pitch is half of the original pitch. Nowadays, SADP is indispensable among producers of logic and memory devices due to the repetitive patterns used which are relatively easy to produce by SADP. A key requirement for SADP has been the conformal deposition of the spacer material (typically SiO₂) to have accurate sidewall thicknesses which are needed for accurate reproduction of the desired pattern [4]. The spacer deposition typically has to occur at low temperature [5]. Thermal ALD of SiO₂ is challenging and generally requires high temperatures, while plasma ALD of SiO₂ is a facile process [6,7]. Interestingly, the use of ALD for self-aligned patterning has become the biggest of all the individual ALD markets and here the main process used is plasma ALD of SiO₂. EUV has become available as a possible alternative, but costs and throughputs are still prohibitive to replace most process steps [8]. To this end, plasma ALD is also used for self-aligned quadruple patterning (SAQP) as shown in figure 1 [5,9,10]. For SAQP, the doubling of the pattern resolution is carried out similarly as in SADP, by basically performing SADP twice. Since aligned deposition occurs twice and the resulting features are smaller, the requirements on the ALD processes are even stricter for SAQP compared to SADP and the drive for usage of plasma ALD is even bigger.
**New opportunities in research**

Plasma ALD is typically performed with a wide range of different plasma species present near the surface. But the variety of species present makes it very complex to predict what happens in the ALD process and what needs to be done to optimize or improve the process. Figure 2 illustrates some of the effects and mechanisms considered important in plasma ALD [3]. Radicals are generally considered as one of the key growth species as they are numerous and highly reactive. Radicals can be lost through recombination (e.g., O radicals recombining back into O₂) which predominantly occurs at surfaces at typical pressures. Ions, although less numerous than radicals, are considered as a contributor to the plasma ALD process due to their possible high kinetic energy. The flux and energy of radicals, ions, electrons, and photons depend on plasma input power and pressure and are typically not easily measured or predicted which makes it difficult to understand their exact roles.

Nevertheless, more insight into the relevant processes has been obtained. Studies from Eindhoven University of Technology have shown that photons can play a crucial role in the formation of device defects [11]. For ions in plasma ALD the typical energies and fluxes have been determined, and a first insight into the role of ions has been obtained by studies in which the ion energy was enhanced by RF substrate biasing [12-14] i.e., substrate-tuned biasing and RF biasing, have been implemented in a remote plasma configuration, enabling control of the ion energy during plasma-assisted atomic layer deposition (ALD). Figure 3 shows some of the effects on material properties identified that occur due to increased ion energies by applying substrate biasing. These effects indicate that ions can have a strong role in ALD surface reactions and can be used to tailor film properties or eventually cause damage. It is known from sputter and etch literature that ions can cause damage, although the energies and fluxes present during plasma ALD are typically lower [11,14,15]. Due to the limited lifetime of plasma species, the ease of conformal deposition has been a concern in plasma ALD. Figure 2 highlights key parameters on which con-
formality in plasma ALD depends and illustrates the directionality of ions and the isotropic nature of radicals going into 3D structures. Conformality for plasma ALD is much better understood than in the past, on the basis of both experimental results and theoretical models. For radical-driven processes, conformal deposition can be achieved as long as enough radicals are provided to compensate for radical recombination [16,17]. Recent studies at Eindhoven University of Technology have revealed that for plasma ALD of SiO₂ and TiO₂, even aspect ratios up to ~900 can be coated due to the low recombination probabilities involved [18]. Such studies are good examples of how fundamental understanding can lead to new and even unexpected capabilities for plasma ALD. Many technical and fundamental questions remain regarding the effect of plasma species on ALD surface reactions. For example, how do the fluxes and energies of plasma species affect the ALD chemistry and what are their exact roles?

Are there any synergistic effects such as known from plasma etching, and how do they work? In devices, the ALD layers are often close to sensitive interfaces, where the challenge is to deposit a high quality ALD film without negatively affecting the interface. Although there is a concern of damage even from remote plasmas, there are many cases where plasma ALD has been used to the benefit of such sensitive devices. Understanding all these processes should allow for better design of plasma ALD systems and in general, the understanding of radical and ion processes and surface interaction is expected to benefit a whole range of atomic scale processing techniques required to allow upcoming applications.

References:
Plasma-assisted ALD

Harm is an Atomic Scale Segment Specialist for Oxford Instruments. In addition, he is part-time Assistant Professor at TU/e. His main contributions relate to understanding and development of plasma ALD (e.g., conformality, substrate biasing and growth of nitrides).


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Hot-Wire assisted ALD

Another example of radical-enhanced atomic layer deposition

Hot-wire assisted atomic layer deposition (HWALD) belongs to the so-called radical-enhanced deposition methods, and is an alternative to plasma enhancement. By using a heated filament ('hot wire'), HWALD enables formation of reactive species (radicals) at low substrate temperatures, however without the generation of energetic ions and UV photons as by plasma. This makes HWALD a purely chemical technique, similar to thermal ALD, still enabling higher deposition rates due to the presence of radicals. This paper discusses the merits of HWALD and gives examples of HWALD of pure metallic tungsten films.

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Merits of HWALD
Over the past decades, atomic layer deposition (ALD) has become a recognized player in the field of film processing. With a few exceptions, single-element films such as metals and semiconductors, are rather difficult to deposit using purely thermal ALD processes [1,2]. Plasma-Enhanced ALD (PEALD), also called radical-enhanced ALD (REALD), can be a solution for growing single-element materials. Hydrogen-based plasmas have been reported to enable the deposition of Ru, Pt, Si, Ge and Al [1,3,4,5]. Several limitations however make PEALD less attractive. Plasma can potentially damage the sample under treatment; it may involve numerous chemical reactions and exposure of the surface to ions, radicals, atoms, and UV photons. Controlling the growth and properties of such a deposited film may be far from trivial.

Hot-wire ALD (HWALD) is a novel technique that has the potential to overcome the mentioned limitations of PEALD, still using energy enhancement to form reactive species at low substrate temperatures.

HWALD employs a heated filament to catalytically crack molecular hydrogen (H₂) or ammonia (NH₃) into atomic hydrogen (at-H) and nitrogen-containing radicals. It is well established that molecular hydrogen can dissociate upon adsorption on a W filament surface at high temperatures [6]. However, whether such-generated at-H can be delivered to the substrate without recombining has to be confirmed experimentally. The actual presence of at-H at the wafer surface can be proven by, for example, etching silicon (Si) or tellurium (Te) surfaces [7,8]. For the latter, it is reported that volatile tellurium hydride (H₂Te) can form already at room temperature through the reaction between at-H and solid Te film. Note that Te cannot be etched by molecular hydrogen [9]. Real-time monitoring of the Te-thickness, while introducing hydrogen gas via the hot-wire setup, was therefore able to prove both the generation and the delivery of atomic hydrogen from the HW to the substrate. As demonstrated experimentally, at-H could be successfully delivered to the wafer substrate when the HW was both out of and in line of sight with the substrate positions [10].

As for dissociation of NH₃ on a hot W filament, it is known that mainly NH₂ radicals and at-H are produced [11]. The formation and delivery of NH₂ radicals from the HW source to the substrate can among others be investigated by studying the nitridation of a Si surface upon exposure to the radical source. Earlier we looked into the effects of placing the HW both out of and in line of sight with the substrate [10]. The real-time monitoring of Si nitridation by spectroscopic ellipsometry (SE) indicated the formation of nitride film merely when placing the HW in the line of sight. There seemed to be a large depletion of NH₂ radicals while experiencing collisions with the reactor walls.

HWALD deposition setup
The home-built HWALD reactor is schematically shown in figure 1. The reactor consists of a big-volume (several liters) cold-wall outer chamber and a small-volume (approx. 24ml) hot-wall inner chamber. The in-situ SE enables moni-
Hot-Wire assisted ALD

monitoring of the deposition process in real time at the center of the wafer. A tungsten filament is installed on the side, just 2-3cm away from the wafer. The HW is heated to 1500-2000°C and the proximity of the HW affects the substrate temperature, setting the lower temperature limit to approx. 170°C for the wafer surface. In this experimental setup, there is no direct line of sight between the hot wire and the substrate. When H₂ gas is introduced via the HW, at-H can be generated by catalytically cracking the gas. The other precursors are supplied via the lateral gas inlets. Although the at-H flux has to diffuse around the corner to be delivered to the substrate, it does not recombine, as experimentally demonstrated by the Te etching experiments [10].

Low-resistivity tungsten by HWALD

Many studies have dealt with deposition of metallic thin films for applications in semiconductor devices [12]. Tungsten (W) vias have been conventionally used to provide inter-level contacts between metal layers in metallization schemes. The downscaling of device dimensions and the increase of the scale of integration pose stringent demands on the W film conformality, uniformity and especially the step coverage in high aspect ratio (HAR) structures. Therefore, ALD is rapidly strengthening its position as a method to industrially deposit thin W films.

Successful ALD of W has been reported by using WF₆ gas and different reducing agents, for example, disilane [13], silane [14] and B₂H₆ [15]. The reducing agents form an intermediate sacrificial layer (i.e. silicon (Si) or boron (B), respectively), which can be turned into W while reacting with WF₆. However, deposition of Si or B in those cases is hardly limited to 1-monolayer (ML) formation, thereby compromising the self-limiting nature of ALD. It may additionally leave Si, B and fluorine (F) impurities inside the films, resulting in a higher-resistivity W [15].

Recently, we carried out studies on HWALD of W from WF₆ and at-H. In a first ALD half-cycle, WF₆ gas was introduced to the inner reactor chamber shown in figure 1, chemisorbing on the substrate surface in a self-limiting fashion. After the purge, in the subsequent half-cycle, the HW generated at-H was introduced, reacting with the adsorbed WF₆ groups, forming HF (byproduct) and thereby reducing the surface to pure metallic W. The WF₆/purge/at-H/purge sequence was repeated multiple times to achieve a required film thickness. This process demonstrated high-purity α-phase W films with a low resistivity of 15 µΩ cm [16], lower than that could be achieved with dedicated PEALD techniques. From figure 2, one might conclude a good conformality of the film thickness in HAR structures, which is the main hallmark of ALD.

Figure 1  Schematic representation (cross-section) of the HWALD reactor used in this study to deposit tungsten films.

Figure 2  Low-resistivity α-phase W film deposited by HWALD in trenches with an aspect ratio of 20. The thin continuous W film, covering the surface, can clearly be seen by the contrast difference. Good conformity of the film thickness proves the ALD nature of the process. Both InLens and energy filtered backscattering (EsB) images are shown.
Area-selective deposition (ASD) increasingly attracted attention over the past several years, to enable nanoscale patterning and further downscaling of device dimensions. The most common approach to area-selective ALD is to provide a molecular mask (a ‘resist’ layer) of self-assembled monolayer (SAM) materials [17] or polymers [18], to disable deposition over the covered areas. An alternative approach is to take advantage of differences in nucleation on various surfaces for a given ALD process, the so-called inherent substrate-dependent growth. Only a few results have however been reported utilizing the inherent nucleation delay [19], presumably due to the difficulty of finding and combining the required chemical properties of ALD precursors and deposition substrates.

We demonstrated inherent area-selective ALD of low-resistivity α-phase W films by utilizing HW ALD from sequential pulses of atomic hydrogen (at-H) and WF6 at a substrate temperature of 275ºC [20]. The HRTEM image of figure 3 revealed the presence of deposited W only on top of the pre-grown W, with no measurable deposition on the SiO2 surface. We further demonstrated selective growth of W by HW ALD on cobalt (Co). Under the optimized process conditions, HW ALD W could be selectively grown to a thickness of at least 20-40 nm on patterned W/SiO2 and Co/SiO2 surfaces. Moreover, no nucleation was observed on TiN and Al2O3 surfaces after an exposure up to 1000 HW ALD cycles, potentially giving a W layer of at least 10-20 nm on the proper surface with no growth on TiN and/or Al2O3.

References

Figure 3  Cross-sectional HRTEM images of a patterned substrate with pre-deposited CVD-W and thermal-SiO2 areas. Figure 3a clearly confirms the selective growth of HWALD-W on CVD-W, without nucleation on SiO2. Note the triangular-shaped ‘ears’ (bottom-left) which appear at the interface between CVD-W and SiO2, and indicate the lateral overgrowth of HWALD-W at the edges. Figure 3b is a zoomed in image of a selected area of figure 3a, confirming the polycrystalline nature of HWALD-W and visualizing the interface with CVD-W.
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Atomic layer deposition (ALD) is an excellent technique to make nanostructured particles: particles of which the surface is either covered by an ultrathin film or by nanoclusters, with applications in, for example, energy and health. ALD is suited to produce such nanostructured particles with very high precision. Using specialized reactors, we can produce large amounts of particles, even up to the ton-scale. This enables the application in a broad range of products including Li-ion batteries, pharmaceuticals and fuel cells.

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Nanostructured particles
Solid particles – small pieces of solid material – are all around us: sand, sugar, cement, pharmaceutical powders, etc. Particles or powders are also applied in many production processes. Sometimes, the powder itself is the end product, but also many engineering materials require particles as building blocks. Examples are limestone powder in concrete and carbon black particles in rubber tires. For a number of the global grand challenges we are facing, such as the supply of sustainable energy, providing clean drinking water, and advanced pharmaceuticals tailored to the patient, advanced materials will play a key role. With the rise of nanoscience, many novel nanostructured materials with superior properties have been proposed. They are often based on nanostructured particles (particles with orderly arranged elements at the nanoscale) as their building blocks. There are seemingly opposing demands when manufacturing nanostructured particles for such applications: on the one hand, we need precision at the nanoscale, while at the same time large quantities are required to fulfil the market needs. Atomic layer deposition (ALD) is a technology that can very well combine nanoscale precision and large-scale production [1].

Applying ALD to particles
When applying ALD to particles, we can get either a continuous film on the outside of the particle or the growth of islands (figure 1). For research purposes, some grains of powders could be put on a wafer or in a holder, and be coated in a regular ALD reactor. However, when some more material needs to be coated, it is much more attractive to apply a tailored reactor. In the early days of ALD, often packed beds have been applied: a vessel filled with a stagnant mass of particles, through which the reactant gases are blown. This has the disadvantage that the contacting between particles and reactant is not optimal, and that it is hard to remove the reaction heat. These days, more often reactors with moving particles are used, either by rotating the reactor vessel or by ‘fluidizing’ the particles [2]. We use the latter approach: we fill a column with the powder we aim to coat, blow an upward flow of nitrogen through it to ‘fluidize’ the powder: the particles become suspended in this gas flow. Then we add the reactants A and B alternatingly to the nitrogen flow (figure 2). We found that in this way we are able to coat the surface of all particles in a very homogeneous way. Even when the base particles are nanoparticles, this proves to work. In that case, the particles
form large, very open agglomerates in which the surface area of the individual particles is still very well reachable. So we are actually not fluidizing individual nanoparticles, but rather nanoparticle agglomerates. Unlike most ALD processes, we operate our fluidized-bed reactors at atmospheric pressure: most of the gas in the reactor consists of nitrogen, to which we add small amounts of ALD reactant [1].

**Application examples**

Broadly speaking, two different aims can be achieved with applying ALD to particles. We can provide them with a protective coating, to shield them from the outside environment. We can also give them an additional functionality by introducing a second material. With these approaches, we have already obtained very good results in several areas. A first one is in improving batteries: everyone will have the experience that after some time, the battery capacity of a laptop or mobile phone is going down. We have been showing that by coating the particles that form the cathode of Li-ion batteries, the lifetime of these batteries can be greatly enhanced (figure 3a) [3]. In pharmaceutics, you typically would like an active compound to dissolve very slowly in the patient’s body: a sudden high peak value is often quite unhealthy, and can cause severe side-effects. Coating pharmaceutical powders with ALD slows down the dissolution (figure 3b). In addition, we found that these coated powders stay stable for a longer time when storing them, and flow more easily when processing them [4]. A third application is in fuel cells: they rely on the scarce, expensive metal platinum. Using ALD, you can spread the platinum much more evenly, greatly enhancing its activity (figure 3c). This enables reducing the amount of platinum needed. This last example is not limited to fuel cells, but can be applied to all kind of catalysts [5].

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**Figure 2** Schematic of ALD in a fluidized-bed reactor. Particles are suspended (‘fluidized’) in an upward nitrogen flow; the ALD reactants are alternatingly added to this flow, leading to the coating of each individual particle.

**Figure 3** Application examples of particles coated with ALD. a) Coated cathode particles give Li-ion batteries a longer lifetime (test at 60°C to boost aging). b) Coated pharmaceutical particles dissolve more slowly, preventing peak concentrations in the patient’s body. c) Lowering the temperature during ALD leads to smaller Pt particles on a carbon support: this increases the activity of the platinum.
Scale-up
In our lab, we typically produce a few up to 100 g of the coated particles using our lab-scale fluidized beds. This could also easily be done in larger fluidized beds to produce kilograms or even tons of material, when this process is taken to industry. The exact amount needed will strongly depend on the specific application. However, the production in fluidized beds is batch-wise with respect to the particles (one amount after the other), while in many industrial processes, continuous production is preferred. We have also been developing an approach for that: the so-called pneumatic transport reactor. In this reactor, the particles are blown through a long tube, and the precursor is added along the way [6]. This indeed leads to a continuous flow of nanostructured particles. Delft IMP (which stands for Delft Intensified Materials Production), a spin-off company from our research group, is working on further scaling up this approach for various gas-phase coating processes. They are located in tech incubator YES!Delft, and have a reactor that can produce more than 100 kg of coated particles per day. Delft IMP is currently working on taking this to the ton-scale.

References
Driving innovation at the atomic scale

Atomic Layer Etch
- Ultra low damage
- High selectivity
- Ultra accurate depth control
- Process solutions for GaN, AlGaN, Si, SiO₂ & 2D materials

Atomic Layer Deposition
- Conformal coating
- Low damage plasma
- Solutions for a wide variety of materials:
  - High-k dielectrics e.g. Al₂O₃ & HfO₂
  - Dielectrics e.g. SiNₓ & SiO₂
  - Conductive materials e.g. TiN, NbN, Pt

PlasmaPro® 100 ALE & FlexAL® cluster.

25 nm wide Si trenches etched to 110 nm depth. 150 cycles. HSQ mask still in place.
Conformal coating of 15:1 trench structure using high-rate SiO₂ plasma ALD.

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Over the last decade, solar energy has boomed with an annual production already exceeding 140 gigawatts. This market is dominated by crystalline silicon cells, for which innovations at the nanoscale have been key to enabling higher cell efficiency at low cost. Atomic layer deposition is very much present in the research for nanolayer innovations, as ALD provides a platform to prepare these nanolayers with atomic-level precision and control. Meanwhile, nanoscale ALD layers are also deployed at the gigawatt scale, with Dutch companies and universities playing a pioneering role in scaling up. In this perspective article, I will show where ALD nanolayers can be found in the solar cells you buy today, and which future innovations are expected.

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Over the last decade, solar energy has boomed with an annual production already exceeding 140 gigawatts. This market is dominated by crystalline silicon cells, for which innovations at the nanoscale have been key to enabling higher cell efficiency at low cost. Atomic layer deposition is very much present in the research for nanolayer innovations, as ALD provides a platform to prepare these nanolayers with atomic-level precision and control. Meanwhile, nanoscale ALD layers are also deployed at the gigawatt scale, with Dutch companies and universities playing a pioneering role in scaling up. In this perspective article, I will show where ALD nanolayers can be found in the solar cells you buy today, and which future innovations are expected.

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process simplifications and potentially raising efficiency. A prime example of such contacts are stacks of tunneling SiO\textsubscript{x} and doped poly-Si (see figure 3, left), which are already popping up in the newest commercial solar cells. Also here ALD Al\textsubscript{2}O\textsubscript{3} can be used, but for a very different purpose than in a PERC cell: Al\textsubscript{2}O\textsubscript{3} appears to be an excellent source of hydrogen, which can diffuse from the Al\textsubscript{2}O\textsubscript{3}, through the poly-Si, to the SiO\textsubscript{x} tunnel layer. Here it binds to remaining interface defects, thereby improving passivation and significantly boosting cell voltage [9,10].

ALD layers themselves can also be used as passivating contacts. These include various metal oxides such as titanium oxide (TiO\textsubscript{x}) electron contacts, and molybdenum oxide (MoO\textsubscript{x}) hole contacts, see figure 3. Such materials are – as far as manufacturers disclose – not in production yet, but have already shown efficiencies in the range of 22-24% and I wonder where they will end [11,12].

Silicon-perovskite tandem cells: New opportunities for ALD?

One application that definitely deserves to be mentioned is the silicon-perovskite tandem cell, where the fields of silicon
Bart is a postdoctoral researcher at the TU/e where he specializes in developing novel ALD nanolayer solutions for crystalline silicon solar cells.

### Concluding remarks

To conclude, I think that ALD is a great technology to explore novel nanolayers, owing to the large materials library [15] and its excellent control over film deposition at the atomic level, while at the same time being a relevant technology at the gigawatt scale. ALD for photovoltaics is a highly active and exciting research field, and I am curious to see which innovations will make it to the solar cells of tomorrow.

### References

3. P. Poodt, this issue of NEVAC blad.
4. PV Magazine [online], pv-magazine.com/2019/06/29/the-weekend-read-atomic-layer-deposition-storms-market-for-perc
13. PV Magazine [online], pv-magazine.com/2020/01/30/tandems-cells-approaching-30-efficiency
14. M. Creatore, this issue of NEVAC blad.
15. ALD database [online], www.atomic-limits.com/alddatabase

Figure 3 Illustrative false-color electron microscope images of ALD nanolayer cross-sections of various new uses in passivating contacts.

Figure 4 Schematic cross-section of a typical silicon-perovskite tandem solar cell. Not to scale.
Over a relatively short period of about ten years, organo-metal halide perovskite solar cells have gained a widespread attention in the photovoltaic community, with a current record efficiency of over 25%. This accomplishment is the result of both fundamental understanding of the perovskite absorber itself (e.g. crystal growth, chemical composition and opto-electronic properties) and improved design and engineering of the device architecture. In this respect, the adoption of atomic layer deposition has been particularly alluring, specifically for the design and engineering of charge transport and passivation layers. In this perspective I reflect on the state-of-the art of ALD processing for perovskite solar cells and on the opportunities and challenges yet to be met.

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Atomic layer deposition for photovoltaics
ALD $\text{Al}_2\text{O}_3$ surface passivation of crystalline silicon (c-Si) surface defects is the only case of ALD integration in PV high volume manufacturing [1]. However, ALD has been widely explored also in thin film PV technologies such as CIGSe, organic PV and dye-sensitized solar cells (DSSC) [2]. Also organo-metal halide perovskite solar cells (PSCs) represent an exciting R&D playground to explore the well-known ALD merits of precise control in chemical composition, thickness and conformality of layers. What was perhaps considered just a hype early in 2010, is now the objective of intensive research, which has enabled to reach a photovoltaic conversion efficiency (PCE) of 25.2% this year [3]. The excellent PSC opto-electronic properties potentially allow photo-conversion efficiency values close to radiative limits [4]. The hybrid organic/inorganic chemistry $\text{ABX}_3$ [5] of perovskite enables tuning its band-gap in the range of 1.55-2.3 eV, with tangible opportunities for tandem architectures. Starting from 2014, ALD has permeated the field of PSC technology by focusing on the several challenges to be met by this PV technology to become mature and ready for commercialization. Moreover, ALD demonstrated to deliver conformal, electrically continuous thin films, whereas wet chemistry approaches would generally lead to films with pinholes, responsible for short circuit pathways in the cell.

Engineering a CTL/perovskite heterojunction requires, however, to go beyond the ALD merits of conformality and uniformity. A primary consideration is the energy level alignment: the electron transport layer (ETL) should have a conduction band (CB) aligned with or slightly lower than the CB level of the perovskite, whereas the hole transport layer (HTL) should have a valence band
(VB) aligned with or slightly higher than the VB level of the perovskite absorber. In parallel, both transport layers should block the injection of the charge counterparts. The extensive literature of the last five years has focused primarily on TiO₂ and SnO₂ as ETLs [9,10] and NiO as HTL [11,12]. The Fermi level position and hence the work function of transport layers and the offsets with respect to the energy level of the perovskite absorber can be tuned significantly by the specific ALD process (plasma ALD vs. thermal ALD), substrate temperature (figure 1) and post-treatment (e.g. annealing as shown in figure 2a). ALD SnO₂ is presently the material of choice in single junction p-i-n configuration and in the top perovskite cell in tandems [13], because it highly contributes to cell performance stability under thermal stress and humidity exposure. It also serves as buffer layer, protecting the sensitive organic layers underneath from the sputtering process of the top contact. Oxford PV-The Perovskite Company announced a certified world record for a 1cm² c-Si/perovskite tandem of 28% [14]. Although no details were disclosed on the cell design, it can be expected that the ALD SnO₂ plays a major role in the tandem architecture. Recently, Solliance and its partners demonstrated a glass/glass encapsulated perovskite module (figure 3), where ALD SnO₂ plays a major role in promoting the cell performance stability [15].

The role of ALD charge transport metal oxides is by now quite established in the perovskite cell architecture. However, the metal oxide/perovskite interface suffers from the presence of defects (figure 1c). This is also the case of metal oxides...
Interface engineering by ALD

developed by other deposition methods. Interface defects are responsible for non-radiative charge recombination pathways, which hamper the PSC technology to reach the full thermodynamic potential of the absorber and deliver a PCE approaching 30% [16]. In this respect, the organic layers PCBM and PTAA [17] are not only excellent charge transport layers, but they also passivate the trap states at the perovskite surface. Therefore, it is not surprising that these layers are often found in PSC architectures in combination with ALD metal oxides (figures 1b and 2b).

As it can be expected, ALD of Al₂O₃ (figure 4a) and other wide-gap metal oxides, is subject of a wide investigation for the passivation of the perovskite surface states. Although several studies [18,19] have shown its successful implementation in terms of PCE enhancement, improved stability against humidity and decrease in hysteretic behavior, in-depth understanding on the perovskite/Al₂O₃ interface is taking off only now [20,21].

Current challenges and new opportunities for ALD for hybrid perovskite PV

Defective interfaces. The earlier addressed explorative character of the research on metal oxide/perovskite interfaces has had limited implications so far: it is sized to the specific interface under investigation and findings cannot be extended towards universal conclusions. This is partly because ALD charge transport layers are not yet included in systematic studies along with traditionally adopted organic transport layers and solution-processed metal oxides. Methods studying interface recombination processes should be applied also to ALD metal oxide/perovskite interfaces to quantify the non-radiative interfacial recombination losses; to benchmark the ALD route (and possibly unravel its new merits) with respect to other technologies; to develop new strategies to ‘heal’ defective interfaces.

ALD processing directly on organo-metal halide perovskite? So far, any attempt to develop ALD CTL directly processed on top of the perovskite has delivered rather disappointing PCE values. Next to the control on parameters such as substrate temperature and processing time, this research field requires efforts to generate insights into the surface reactions between the ALD chemistry (precursor and co-reactant) and the chemically challenging nature of hybrid

**Figure 3** Glass/glass encapsulated perovskite module with an aperture area of 100cm² and efficiency above 10%, developed by Solliance Solar Research and collaborators [15]. The module withstands 1000 hrs continuous illumination at 1 Sun, 1000 hrs exposure to high humidity and 50 thermal cycles from -40 to 85°C. The thermal ALD SnO₂ (TU/e) plays a major role in protecting the perovskite absorber during the thermal test. Acknowledgement for the photograph: Niels van Loon (Solliance Solar Research).

**Figure 4** Thermal ALD Al₂O₃ on perovskite [18,20]. a) High-angle annular dark field scanning TEM image of a perovskite/Al₂O₃/HTL interface. Acknowledgement for the TEM: dr. M.A. Verheijen (Eurofins EAG & TU/e). b) Differential IR spectra with increasing number of ALD cycles of Al₂O₃: the negative features represent species which are abstracted during interaction of the perovskite with the TMA precursor. Positive absorption features indicate Al₂O₃ growth. c) Proposed reaction mechanism between the perovskite surface and ALD chemistry (trimethylaluminum and H₂O) according to IR and XPS measurements.
Novel ALD chemistries and ALD merits for perovskite PV. Molecular Layer Deposition (MLD) can contribute to the expansion of the toolbox of atomic scale processing for perovskite PV. Recently, it has been demonstrated that self-assembled monolayers (SAMs) deliver (non-radiative) lossless interfaces with perovskite absorbers [22]. MLD offers the opportunity to recreate (and possibly emulate) the SAM chemistry, but then avoiding spin-coating or dipping procedures. Finally, ALD has been extensively acknowledged for delivering superior moisture and (O₂) permeation barrier layers for several applications, e.g. organic LEDs and organic PV. Surprisingly, this merit has not been exploited yet into its full potential to address the perovskite environmental instability. A last note concerns with the increasing interest into perovskite PV implementation in the built environment, e.g. in windows. The necessary compromise between conversion efficiency and transparency offers intriguing opportunities to further expand the atomic scale processing toolbox towards selective growth of mesoscopic perovskite structures on spatially functionalized ALD CTLs.

These research directions represent only a selection among the several opportunities, which I foresee developing in the field of ALD interface engineering for perovskite PV.

References
1 W.M.M. Kessels, this issue of NEVAC blad; B. Macco, this issue of NEVAC blad.
3 Efficiency chart [online], www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20191106.pdf
5 In ABX₃, A usually refers to one of the following cations or a mixture of them: CH₃NH₃⁺, HC(NH₂)₂⁺ and Cs⁺. B corresponds to Pb²⁺ and/or Sn²⁺ and X to a mixture of I⁻, Cl⁻, Br⁻.
7 ALD applications in the field of PSCs include charge transport and passivation layers, charge blocking layers, transparent conductive oxides, and moisture permeation barrier layers. Also, ALD was originally applied to PSCs grown on mesoscopic scaffolds and, later, to PSCs in thin film architecture. In this perspective, I focus only on the first two applications and to PSCs in thin film architecture.
8 The n-i-p configuration refers to the perovskite absorber being synthesized on top of the electron transport layer (ETL), with the hole transport layer (HTL) completing the device. The p-i-n refers to the inverted order, where the perovskite is synthesized on top of the HTL and the device is completed by the ETL.
17 PCBM (serving as ETL) is the common abbreviation for the fullerene derivative [6,6]-phenyl-C₆-butyric acid methyl ester. PTAA (serving as HTL) is the common abbreviation for poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine].
Large-area and flexible electronics could potentially benefit tremendously from the advantages of ALD over other deposition techniques. These applications, however, require deposition on large areas and on flexible substrates at deposition rates unattainable with conventional ALD. For this purpose, spatial ALD has been developed, which relies on spatial instead of temporal separation of precursor exposures. In this article, the pivotal role of the Dutch spatial ALD community is highlighted, and several examples of current challenges in spatial ALD are discussed.

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Spatial Atomic Layer Deposition

In the past decade, ALD has become a mainstream deposition technique in the microelectronics industry because of its excellent performance in terms of film quality, thickness control, uniformity and step coverage. For the same reasons, the use of ALD is of interest for other application areas as well, including large-area and flexible electronics. Examples include buffer, transport and conductive layers in thin-film solar cells, thin-film encapsulation and oxide semiconductors in OLED displays, as well as passivation layers and electrolytes for (solid state) Li-ion batteries. Although the examples mentioned are quite diverse, they share common aspects that clearly differentiate them from microelectronics; in order to keep the costs of mass production low and the throughput high, these applications require deposition on large areas or on flexible substrates at high deposition rates. Mainstream ALD equipment is typically designed for processing 300mm wafers, either in single-wafer or in batch mode, where typical deposition rates are in the order of nanometers per minute. It would be very difficult to adapt these tools to handle the very large substrates used in e.g. OLED display manufacturing (up to 1.5m x 1.85m), or roll-to-roll systems that can handle 1.3m wide foils at tens of meters per minute web speeds. Therefore, a different way of doing ALD than the usual time-sequenced, low-pressure methods currently employed is required. One possible solution is Spatial Atomic Layer Deposition (SALD) [1]. Just as in conventional ALD, in Spatial ALD the substrate is exposed to individual precursors sequentially, but instead of separating precursor steps in time, the precursors are spatially separated in precursor zones through a so-called injector or deposition head. To prevent mixing of precursors and to avoid CVD, these zones are confined by inert ambient zones, for instance a vacuum, a gas shield, or a gas bearing [1]. The ALD cycle is completed by moving the substrate with respect to the injector head from one zone to the other, which is repeated until the desired thickness is achieved. Moving the substrate or injector can be done by e.g. translation or rotation. With the reaction rates generally being very high and without the need for purging a reaction chamber between the precursor steps, the effective deposition rates achieved can be in the nm/s range [2], allowing high-throughput processing and the deposition of relatively thick films. Furthermore, spatial ALD does not require a low-pressure environment and can be operated at atmospheric pressure. The injector head itself can be engineered to very large sizes allowing for deposition on large area substrates.

Spatial ALD in the Netherlands

Although the spatial ALD concept was already described in an early ALD patent...
by Antson and Suntola in 1977 [3], the concept was independently reinvented and further developed by several groups in the past years [1]. At present, a growing number of groups and companies worldwide are developing spatial ALD technology for a wide range of applications. The Netherlands has always been a hot spot for spatial ALD R&D. TNO (via its open innovation institutes Holst Centre and Solliance) has been active in R&D programs on spatial ALD since 2009 [4,5]. This resulted in numerous collaborations with industry and academia. Some highlights include the spin-off companies SoLayTec [6] (2010; SALD equipment for c-Si solar cells) and SALDtech [7] (2018; SALD equipment for OLED displays), collaborations with Dutch equipment companies VDL and Meyer Burger (both roll-to-roll SALD equipment) and Smit Ovens (sheet-to-sheet equipment), and collaborations between TNO and TU/e on more fundamental aspects of spatial ALD. Other Dutch spatial ALD activities include Levitech (SALD equipment for c-Si passivation; spin-off from ASM International), SALD (a recent spin-off from SoLayTec) and TU Delft (SALD on powders) [8].

**Current challenges in spatial ALD R&D**

Whereas the first applications of spatial ALD were based on simple oxides such as Al₂O₃, TiO₂ and ZnO, and on substrates of relatively small sizes (up to 300mm), today the use of spatial ALD for increasingly more demanding applications and complex materials is being explored. In many cases, the literature shows that the added value of introducing ALD layers has already been demonstrated on lab-scale for conventional ALD, but the scale-up towards industrial manufacturing still has a long way to go. One example are OLED displays where quaternary oxides like indium-gallium-zinc oxide (IGZO) have to be deposited with less than 2% variation in stoichiometry and thickness on more than 2m² glass plates at takt times of around 60s [9]. Other examples include perovskite solar cells, where ALD layers have to be deposited in a roll-to-roll mode on very sensitive substrates and at low deposition temperatures [10], and roll-to-roll ALD in highly porous substrates, such as separator membrane foils [11]. Depositing compound materials like IGZO and LiPON involves much more complex reactions than e.g. Al₂O₃. Developing SALD processes for these materials requires careful selection of suitable precursors and an in-depth investigation into the reaction kinetics. The same holds for SALD in high aspect ratio 3D and porous substrates, where the precursor reactivity and diffusivity mainly determine how deep and how fast pores can be coated [12]. Furthermore, temperature limitations imposed by the substrate, e.g. in case of polymer materials, are common in flexible electronics. For this and other reasons, the development of (atmospheric pressure) plasma-assisted SALD is actively being pursued [13]. Next to the evolution towards more complex processes and materials, also patterned deposition is gaining more attention. Because of the excellent step coverage of ALD, patterned deposition through the use of shadow masks is not feasible as it will lead to undesirable deposition under the mask. Therefore, SALD-based maskless direct patterned deposition techniques, including area selective deposition, are being developed [14].

Finally, new SALD equipment concepts are being developed that can be scaled to the very large substrate sizes and high throughputs used in industry, while keeping the investment and operational costs low. The performance of a spatial ALD tool is determined by a complex interplay of gas flows and pressures, precursor-substrate interactions, diffusive and convective transport of precursors and reaction products, substrate movement and plasma radical generation and recombination (in case of plasma SALD). Modeling, in particular fluid dynamics modeling, is an essential tool in developing and designing new SALD reactor concepts and new models are currently being developed.

**Conclusions**

Since its re-invention more than ten years ago, spatial ALD has been a subject of growing activities and importance in both the R&D community and industry worldwide. It can be expected that spatial
Spatial ALD will be adopted by more and more industries in the coming years, which requires continuous research and development, from a fundamental and from an applied research point of view. The SALD community in the Netherlands has played a pivotal role in the development of SALD because of its unique SALD knowledge value chain; ranging from fundamental research at the TU/e via applied research at TNO, up to the many equipment companies who build and sell SALD equipment to industry. This has resulted in several successes so far, like SALD for c-Si passivation and roll-to-roll SALD for barrier foils. If the Dutch SALD community keeps working together and even further strengthens their ties, it can maintain its worldwide leading position and the future for Dutch SALD will be bright and sunny.

References
4 www.holstcentre.com
5 www.solliance.eu
6 www.solaytec.com
7 www.saldtech.com
14 A. Mameli, F. Roozeboom, P. Poodt, Area-selective deposition of SiO2 based on spatial ALD with interleaved etching steps to obtain selectivities > 10nm, 4th Area Selective Deposition workshop (ASD 2019), Leuven.

Figure 3 Examples of results of advanced spatial ALD R&D conducted at TNO. a) Cross section of a perovskite solar cell with a 45nm ZnO buffer layer [16] b) InGaZnO film (100nm) deposited by plasma-assisted spatial ALD on a 30cm x 40cm glass plate with a thickness non-uniformity of 1%. c) Area selective spatial ALD of SiO2 on SiO2 (growth area) vs. ZnO (non-growth area). Interleaved etch steps are used to selectively deposit thick films [14]. d) SEM cross-section of the bottom of a 9µm deep and 90nm wide pore (aspect ratio 100:1), coated with SALD Al2O3 with 100% step coverage.

Paul is leading the spatial ALD R&D activities at TNO - Holst Centre, developing spatial ALD technology for applications in large-area and flexible electronics. He is also part-time associate professor at the TU/e and CTO of TNO’s spin-off company SALDtech.
Area-selective atomic layer deposition for bottom-up fabrication of nanoelectronics

Ever since Richard Feynman’s lecture on nanotechnology entitled *There is plenty of room at the bottom*, one of the main challenges in nanoscience has been to develop reliable approaches for bottom-up processing of materials. Despite this vision, the miniaturization of electronics in the past few decades according to Moore’s law relied completely on innovations in top-down processing. In this article, the alternative of using area-selective ALD for bottom-up fabrication is discussed. The approaches that currently exist for achieving area-selective ALD are reviewed, together with their merits and limitations.

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Motivation for area-selective ALD
The multilayered devices at the heart of every integrated circuit are fabricated by repeating deposition, lithography and etching steps for each device layer, as illustrated in figure 1. Area-selective deposition (ASD) focuses on the deposition of material only where it is needed, and thereby eliminates the need for a lithography and an etching step after the deposition [1,2]. Because of the atomic-level control of ALD and its strong dependence on the surface chemistry of the substrate, it has been considered as an ideal starting point for the development of ASD processes.

There are several different motivations for working on area-selective ALD. The early work on area-selective ALD aimed at reducing the complexity of nanofabrication and at dealing with compatibility issues [1]. When working with materials that are not compatible with conventional etching or lift-off steps, it is desired to process the material in a bottom-up fashion. These initial studies predominantly focused on the development of methods that involve patterning steps. For instance, our previous work aimed at the patterning of contacts on sensitive nanomaterials such as carbon nanotubes and graphene by a combination of e-beam patterning and ALD [3,4].

In recent years, most work on area-selective ALD is motivated by challenges in alignment for sub-5nm technology nodes [2,5]. With the downscaling of nanoelectronics, it becomes more and more difficult to align structures relative to one another during the fabrication of multilayered device structures. The alignment is typically described by referring to the parameter *edge placement error* (EPE), which is allowed to be roughly a quarter of the size of the structure (i.e. ~2nm for a critical dimension of 10nm). Area-selective ALD is currently explored for applications in self-aligned fabrication schemes. For these applications, a partially processed device structure fabricated using conventional top-down

![Figure 1](image-url) Conventional patterning relies on repetition of deposition, lithography and etching steps for every layer in a multilayered device. At the small dimensions of current and future devices, it is often difficult to align features on top of each other, which results in an edge placement error (EPE). Area-selective ALD solves alignment issues, and eliminates etching and lithography steps.
fabrication is considered that consists of different materials (figure 1). Performing ALD selectively on only one of these materials results in a perfectly aligned structure, while the costly lithography and etching steps are eliminated.

An example of such an application is the fabrication of fully self-aligned vias (FSAV) [6]. Currently, EPEs in interconnects or VIAs are a limiting factor in device reliability, for example by introducing shorts. Area-selective ALD processes for dielectric-on-dielectric deposition, considering a metal as the non-growth area, are currently being explored for the deposition of a topographical barrier that reduces the chance of shorting.

Besides the focus on nanoelectronics, also some work has been performed that aims at applications in catalysis [7]. The most prominent example is to synthesize core/shell nanoparticles by area-selective deposition of a shell material on a metallic nanoparticle, with the general aim to improve the catalytic activity of the nanoparticle. Work in this direction focused predominantly on noble metals and led to the synthesis of for example Pd/Pt, Pt/Ru and Pt/FeO$_x$ core/shell particles [8].

**Approaches to area-selective ALD**

When considering the applications of area-selective ALD in self-aligned fabrication, the ALD process needs to distinguish between starting surfaces of different materials. Generally, the material on which ALD is desired is referred to as the *growth area*, whereas the material(s) on which no ALD is allowed to occur is described as the *non-growth area* (figure 1). In order to characterize an area-selective ALD process, experiments are typically conducted to investigate the nucleation behavior of an ALD process on different starting surfaces. In case an ALD process results in immediate growth on one material, while there is a nucleation delay on another material, this difference can be exploited to achieve area-selective ALD on the first material, as shown in figure 2 [5]. In ASD, selectivity is defined as the ratio of the amounts of material deposited on the growth and non-growth areas.

If only a thin layer needs to be deposited selectively, in some cases it is possible to make use of chemical differences between the surfaces of the growth and non-growth areas. For example, if an ALD precursor adsorbs readily on the growth area and experiences a significant energy barrier for adsorption on the non-growth area, such a difference can be exploited for achieving area-selective ALD. In practice, this approach only works for relatively thin layers of only a few nanometers thick, which is often not sufficient for the applications. The most common approach to obtain area-selective is ALD is to functionalize the non-growth area before the ALD process. In our research, the strategy is to implement vapor-phase correction steps during the ALD process, as illustrated in figure 3 [5]. Instead of using conventional two-step ALD processes, ABC-type ALD or supercycle ALD recipes are designed that involve the repetition of surface functionalization or cleaning steps. The focus is on using vapor-phase dosing for the correction steps, in order to develop methods that are very compatible with semiconductor processing flows.

**Advanced ALD cycles**

While there are several approaches to achieve area-selective ALD, in general the limitation is that they do not offer sufficient selectivity to allow for area-selective deposition of films with the desired thickness. In practice, there are always unintended side reactions that lead to a loss of selectivity, i.e. the initiation of ALD on the non-growth area. For example, SAMs are often not thermally stable at the temperature of deposition and degrade over time. This implies that it is not adequate to only functionalize the non-growth area before the ALD process.

In our research, the strategy is to implement vapor-phase correction steps during the ALD process, as illustrated in figure 3 [5]. Instead of using conventional two-step ALD processes, ABC-type ALD or supercycle ALD recipes are designed that involve the repetition of surface functionalization or cleaning steps. The focus is on using vapor-phase dosing for the correction steps, in order to develop methods that are very compatible with semiconductor processing flows.

An example of such an approach is to use small molecules as inhibitor [10]. While this approach relies on deactivation of
the non-growth area similar to previous work involving SAMs, the main difference is that these inhibitor molecules can be dosed during the ALD cycle instead of soaking the sample in solution before the deposition. Because of the re-application of the inhibitor molecules every cycle in an ABC-type recipe, this approach is not sensitive to degradation of the molecules, while it can also be used for a broader range of ALD processes involving for example ozone or a plasma as the co-reactant. Another example of employing an advanced ALD cycle for area-selective ALD is the combination with selective etching to improve the selectivity of ALD [11]. The implementation of an etching step (or an ALE cycle) after a certain number of ALD cycles in a supercycle recipe enables the deposition of thicker films with a high selectivity [5].

Although area-selective ALD has already been researched for over two decades, it appears that the semiconductor industry is now ready for implementing the technique. The fabrication of fully self-aligned vias is likely the first application that will be employed in high volume manufacturing [6], but there are many other applications in nanoelectronics that are currently being explored [2]. With that we are entering a new era in which the fabrication of nanoelectronics relies on both top-down and bottom-up processing.

**References**


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Adrie is an assistant professor at the TU/e since 2016. His research focuses on atomic scale processing of materials for applications in nanoelectronics, which mainly involves the development of new approaches for area-selective ALD and ALE.
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All good things come in layers
Tailoring the properties of 2D transition metal dichalcogenides by ALD

Two-dimensional transition metal dichalcogenides (2D-TMDs) are an exciting class of new materials. Their ultrathin body, optical band gap and unusual spin and valley polarization physics make them very promising candidates for a vast new range of (opto-)electronics and catalysis applications. So far, most experimental work on 2D-TMDs has been performed on exfoliated flakes made by the ‘Scotch tape’ technique. The major next challenge is the large-area synthesis of 2D-TMDs with control over their properties by a technique that ultimately can be used in industry. This article will focus on ALD for large-area 2D-TMD synthesis for application in (opto-)electronics and catalysis and will highlight the precise control over the thickness, morphology, composition and phase of the 2D-TMDs that can be obtained by ALD.

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Figure 1  High-resolution HAADF-STEM images of cross-sections of ALD-grown TiS₂ and TiS₃ and corresponding ball and stick models. TEM credit: Marcel Verheijen.
Synthesis of doped TMDs and alloys

Tunable properties such as the carrier density and the band gap of TMDs are essential for their prospective applications including nano-electronics but also photonics and spintronics. The intrinsic TMDs already offer a wide array of material properties (semiconducting, metallic, insulating) allowing the selection of a TMD that comes close to the requirements of a specific application. However, for high-performance devices and the fabrication of advanced device concepts, controllable and finely tunable properties are essential. For example, a finely tunable carrier density will be essential in the fabrication of high-performance nanoelectronics such as CMOS transistors using TMDs; control over the band gap can be exploited in photonic devices.

Tunability and control over the electrical and electronic properties of TMDs can be realized by alloying and doping these materials. These materials can be grown by ALD by repeatedly switching between different ALD processes during deposition (left panel of figure 3). Because a single ALD cycle deposits a sub-monolayer of material (figure 2a), fine mixing of the constituent materials and excellent control over the composition can be achieved by simply changing the cycle sequence. This is demonstrated by two showcases: Mo$_{1-x}$W$_x$S$_2$ alloys and aluminum-doped MoS$_2$. For Mo$_{1-x}$W$_x$S$_2$, an ALD supercycle recipe was developed in our group and we demonstrated excellent control over its composition (right panel of figure 3). We can tune the luminescence and the band gap of this alloy by changing the composition. The fundamental mechanisms responsible for this tuning can be traced back to the atomic structure of the alloy through first-principles simulations. Using a similar experimental approach, we can grow doped TMDs with excellent control over the carrier density. In the approach we developed, the carrier density of the semiconductor MoS$_2$ can be tuned between $10^{17}$cm$^{-3}$ (insulator like) up to $10^{21}$cm$^{-3}$ (near metallic), covering the range of carrier densities needed for advanced nanoelectronic device concepts.

**Figure 2**  (a) Thickness as a function of number of cycles for an ALD process for ALD of WS$_2$ [1]. (b) Transmission electron microscopy image of MoS$_2$ layers having similar thickness profiles in a high-aspect ratio trench structure [2]. Uniformity map of a 4 inch wafer covered by plasma-assisted ALD WS$_2$ measured by spectroscopic ellipsometry [1]. TEM credit: Marcel Verheijen.

**Figure 3**  (Left) Alloys can be synthesized in a highly controlled manner by ALD by using the so-called supercycle approach, where ALD cycles of the constituents (i.e. material A and B in the illustration) are performed in an alternating fashion. (Right) Measured composition and stoichiometry of Mo$_{1-x}$W$_x$S$_2$ alloys as a function of the supercycle ratio.
Tailoring the morphology

The applications of TMD layers are also governed by their morphology. When the 2D-TMD layers are aligned horizontally to the substrate surface they are promising candidates for applications in (opto-)electronics due to their high carrier mobility and sizeable bandgap. However, when the 2D-TMD layers are vertically aligned with respect to the substrate surface they expose a high density of reactive edges of the basal planes, which make them ideal for electrocatalytic applications such as water splitting [4]. We have recently shown that the use of various plasmas during the co-reactant step (plasma-assisted ALD or plasma-enhanced ALD, PEALD) can be exploited to tailor the 3D morphology of the 2D layers and in such influence the catalytic performance of these films [2]. Figure 4 illustrates that the morphology of vertically aligned 2D WS₂ layers can be varied by modulating the plasma gas composition (H₂/H₂S ratio) in the co-reactant step. This has a direct influence on the number of edge sites and consequently, the catalytic performance of WS₂ films [2].

While vertically aligned 2D-TMDs are ideal for catalysis applications, these vertically aligned structures are undesirable for nanoelectronic applications, as they hinder charge transport and consequently raise film resistivity [5]. We developed an approach to suppress the growth of the in this case undesired 3D structures, and grow only horizontally aligned 2D layers during ALD. In this ALD process an additional plasma step (Ar or H₂ plasma) is added to the original two-step plasma-assisted process [6]. This approach reduces the density of out-of-plane structures by ~80% (figure 5c, d) and consequently, lowers film resistivity by an order of magnitude. We confirmed that the suppression of vertical 3D structures goes hand in hand with grain size enhancement together with other physicochemical effects [6].

Phase control by ALD

In addition to the 2D TMDs, there is a class of layered materials involving analogous elements, but with a transition metal to chalcogenides ratio of 3 (figure 1, right panel). These materials are known as transition metal trichalco-
Figure 5  (a) Top-view and (b) cross-section transmission electron microscopy images showing the growth of undesired 3D structures along with the desired horizontal WS$_2$ layers deposited using a regular ALD process. Corresponding (c) top and (d) cross-section images showing the suppression of the undesired 3D structures by our novel ALD process involving an additional plasma (Ar or H$_2$) step. The 3D structures can be identified by their brighter contrast in the top-view images (a) and (c). TEM credit: Marcel Verheijen.

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References
Etching with atomic-level precision

The emerging field of atomic layer etching

Following the example of ALD, its etching counterpart atomic layer etching (ALE) is currently being implemented in the semiconductor industry for the fabrication of integrated circuits. ALE enables either anisotropic or isotropic etching with atomic-level precision based on sequential and self-limiting half-reactions. This article describes the basics of ALE and its main characteristics, and briefly reviews the current status of the field. An outlook to future research is also provided.

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Etching with atomic-level precision

Similar to ALD, ALE relies on alternating exposure of a surface to two gas-phase reactants separated by purge steps, as illustrated in figure 1. In order to remove material atomic layer by atomic layer, the requirement for these reactants is that they should interact with the surface through self-limiting surface reactions. Fundamentally, etching is the process of subtracting materials and involves bond breaking to remove atoms from the surface of a solid material. This entails overcoming an energy barrier called the binding energy [1].

In the first step of an ALE cycle, a substrate material is exposed to chemically reactive species, such as gas molecules or plasma radicals. These species adsorb on the surface of the material to form a modified surface region via self-limiting reactions. As a result of the adsorption, the binding energy between the surface atoms and the underlying bulk atoms of the material is weakened, allowing the surface atoms to be removed more easily. Typically, a species that can form a volatile reaction product with the element to be etched is employed in the first half-reaction (e.g. fluorine- or chlorine-based species).

For the second half-reaction, the goal is to remove the modified surface region also in a self-limiting manner. This half-reaction often involves activation by energetic ions generated in a plasma, but can also consist of exposure to other reactant molecules, electrons, photons, or even involve a temperature ramp. Once the modified region is removed, the underlying and unmodified bulk region is revealed and ready to be removed in subsequent ALE cycles.

Two flavours: anisotropic and isotropic etching

The ability of plasmas to anisotropically etch material has been instrumental in the semiconductor industry to enable the fabrication of increasingly complex structures. Anisotropic etching is generally employed to transfer a pattern defined using lithography to the substrate, and often leads to etching of a (high aspect ratio) trench or hole in the substrate material. The anisotropic nature of etching relies on the acceleration of ions in a collisionless plasma sheath, such that the ions impinge on the substrate with a direction perpendicular to the surface. Since the seminal work by Coburn and Winters [2], it is understood that synergistic effects between plasma ions and radicals play a crucial role in obtaining a high etch rate in the vertical direction. However, now that the semiconductor industry is reaching sub-5nm dimensions, the precision has become more important than the etch rate, which led to the development of ALE processes. In ALE, the ion and radical contributions are separated in time or space in self-limiting half-reactions, allowing for the aforementioned atomic-level precision. A prominent example of an anisotropic
Etching with atomic-level precision

ALE process is to alternate between Cl₂ and Ar plasmas to etch Si [1]. The radicals from the Cl₂ plasma lead to a modified SiClₓ surface layer, which is subsequently removed by the Ar ions in the second half-reaction.

The applications in the semiconductor industry require both anisotropic and isotropic ALE processes. For example, the fabrication of gate-all-around (GAA) transistors for the 3nm node, involves defining vertical fin structures from a multilayer stack by anisotropic etching, followed by the release of individual nanosheets using isotropic etching [3]. Inspired by the surface chemistry of ALD, thermally driven processes have been developed in recent years that enable isotropic ALE. The initial studies performed since 2015 focused on surface fluorination using HF, followed by ligand-exchange reactions involving a metalorganic precursor (e.g. Sn(acac)₃, Al(CH₃)₃) as the reactant [4]. Within a few years, isotropic ALE processes for many different materials including metals, oxides and nitrides have been developed [5], which led to a renaissance for ALE research and thereby contributed to the maturing of the research field.

Characteristics of ALE

Many of the merits of ALE, shown in figure 2, are analogous to those of ALD because of the use of self-limiting half-reactions: (i) etch control with atomic-level precision, (ii) uniform etching over large-area substrates, and (iii) uniform etching over 3D topologies when considering isotropic ALE [6].

On the other hand, there are some crucial differences. Selectivity is one of the main parameters that characterizes an ALE process, which is defined in the etch community as the ratio of the etch rate of the material that needs to be removed and the etch rate(s) of other materials that are present in the device structure such as the mask layer or the underlying substrate. In the ALD community, selectivity in deposition is now also gaining more attention [7], but for deposition the term selectivity describes differences in nucleation on various starting surfaces, instead of differences in growth rates. Selectivity plays a crucial role for all the envisioned applications of ALE in the fabrication of nanoelectronics.

In order to obtain selectivity in anisotropic ALE, it is important to control the energy of the ions in the plasma. The ions need to have a sufficiently high energy such that the modified surface layer of the material of interest is removed, but not too high to avoid etching of, for example, the mask layer. Selectivity in isotropic etching can be influenced by choosing reactants that selectively react with the material to be etched [8].

Current and future research

Figure 3 also illustrates that the current work in the field of ALE encompasses two main directions as just discussed: plasma ALE for anisotropic etching, or thermal ALE for isotropic etching. Considering that achieving anisotropic ALE using thermal chemistries (i.e. without directional species) is not feasible, this leaves one category as a rather unexplored option, namely using plasma processes for isotropic ALE. This is one of the directions that we are exploring in our research at Eindhoven University of Technology. Similar to the merits of using plasma processes for ALD [9], it is expected that plasma-based isotropic ALE processes will allow for etching at lower substrate temperatures, and possibly with higher etch rates due to synergistic
The dawn of atomic-scale processing: the growing importance of atomic layer deposition and etching [online], www.atomiclimits.com/2017/07/03/the-dawn-of-atomic-scale-processing-the-growing-importance-of-atomic-layer-deposition-and-etching

effects between the radicals and ions. An example of such a plasma ALE process is employing acetylacetone (Hacac) and O₂ plasma pulses for isotropic ALE of ZnO, as shown in figure 4 [10]. The electron microscopy images taken after ALE on a ZnO-coated nanowire demonstrate the isotropic nature of this plasma ALE process.

Another important challenge we are working on is to provide a better control of the ion energy during anisotropic ALE. In conventional plasma etching and in current work on anisotropic ALE, the ion energy is controlled by applying a radio frequency sinusoidal bias voltage to the substrate, which results in a relatively broad ion energy distribution. Following the pioneering work by Wang and Wendt [11], we are exploring the use of tailored waveforms (instead of sinusoidal waveforms) in order to generate ions with a well-defined energy. This is expected to open up new opportunities for anisotropic ALE with improved selectivity and reduced surface damage.

Since the development of ALE is inspired and strongly connected to developments in the field of ALD, there is increasing attention for approaches that bring the two techniques together. This for example includes the use of ALE cycles to improve the selectivity of area-selective ALD [7], but also the application of ALE processes for the removal of native oxides or for surface cleaning before performing ALD. Instead of two separate techniques, ALD and ALE can also be considered as the main elements of the toolbox of atomic scale processing [12].

References
5. ALE Database [online], www.atomiclimits.com/aledatabase

Adrie is an assistant professor at the TU/e since 2016. His research focuses on atomic scale processing of materials for applications in nanoelectronics, which mainly involves the development of new approaches for area-selective ALD and ALE.
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