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Atomic Layer Deposition: How a small country can be big in nanolayers

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ALD@NL day

Friday November 6, 2020

The aim of this national event is to bring researchers, technologists and other people interested in ALD together to learn about the latest developments in research, development and manufacturing.
The day will feature presentations and also provide ample opportunity for networking.

Please reserve the date!

Please preregister to receive updates on the event:

www.AtomicLimits.com/ALD-NL-day

ALD in the Netherlands

Concept preview

preview

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Atomic layer deposition in the Netherlands

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

preview

ALD – a truly enabling nanotechnology

And how the Netherlands contributed to its wide spread application

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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preview

Atomic layer by atomic layer

Atomic layer deposition (ALD) is vapor-phase deposition technique in which thin films are deposited atomic layer by atomic layer (figure 1) [1,2]. This is done by repeating cycles in which carefully chosen reactants are dosed to a surface in an alternating fashion. Typically, one can distinguish two half-cycles A and B that are separated by purge steps: half-cycle A consists of dosing a precursor to the surface that deposits the main constituent of the film whereas half-cycle B consists of dosing a co-reactant that turns the precursor into the material of choice and reestablishes the starting surface. Next a new cycle can be carried out and the process can be repeated until the targeted thickness of the film is achieved.

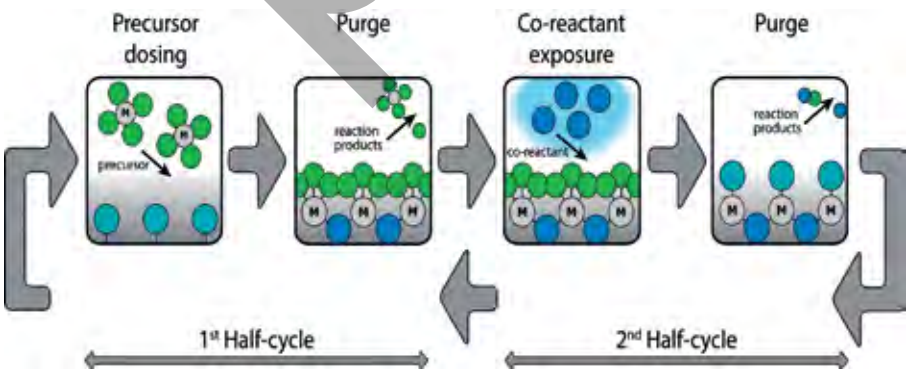

Figure 1 Schematic representation of an ALD cycle. By repeating the cycle, nanolayers can be prepared atomic layer by atomic layer until the targeted thickness is reached [8].

ALD processes rely on surface chemical reactions that are self-limiting. This means that for an ALD process the surface reactions in every half-cycle self-terminate because either the reactive surface sites have been reacted away or are not available anymore otherwise. The fact that the surface reactions are self-limiting means that the 'growth per cycle' is independent of the dosing time as long as sufficient precursor or co-reactant is dosed. This is typically verified by measuring saturation curves in which the growth per cycle is monitored as a function of dosing and purge times.

The number of ALD processes is continuously being extended but the prototypical ALD process is the one for Al_2O_3 which consists of the alternating dosing of $Al(CH_3)_3$ as precursor and H_2O as co-reactant. In half-cycle A $Al(CH_3)_3$ reacts with –OH surface groups leading to adsorbed $-Al(CH_3)_x$ and in half-cycle B the H_2O reacts with $-CH_3$ surface groups reestablishing a –OH covered surface with an Al_2O_3 atomic layer deposited. In both half-cycles CH_4 is the volatile reaction product released.

In most cases the processes are carried out in ALD reactors under low vacuum conditions and with the A and B half-cycles alternated as a function of time. Yet also ALD processes under atmospheric conditions exist whereas the half-cycles can also be alternated in the spatial do-

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.

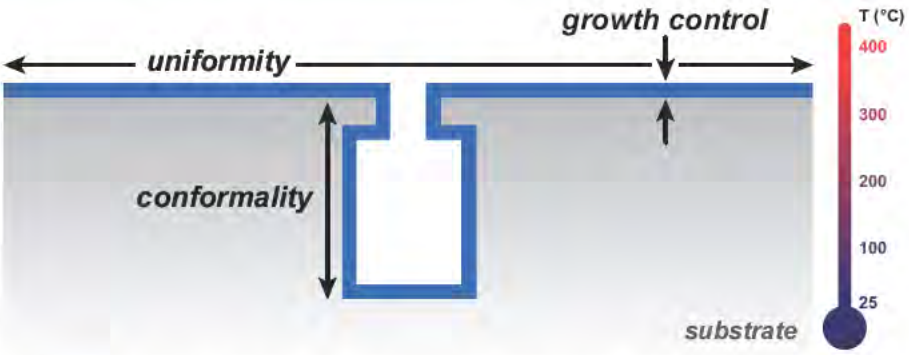

Figure 2 Illustration of the merits of ALD: precise thickness control, excellent uniformity over large substrates, unparalleled conformality over 3D structures, all possible at relatively low temperatures [2].

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.

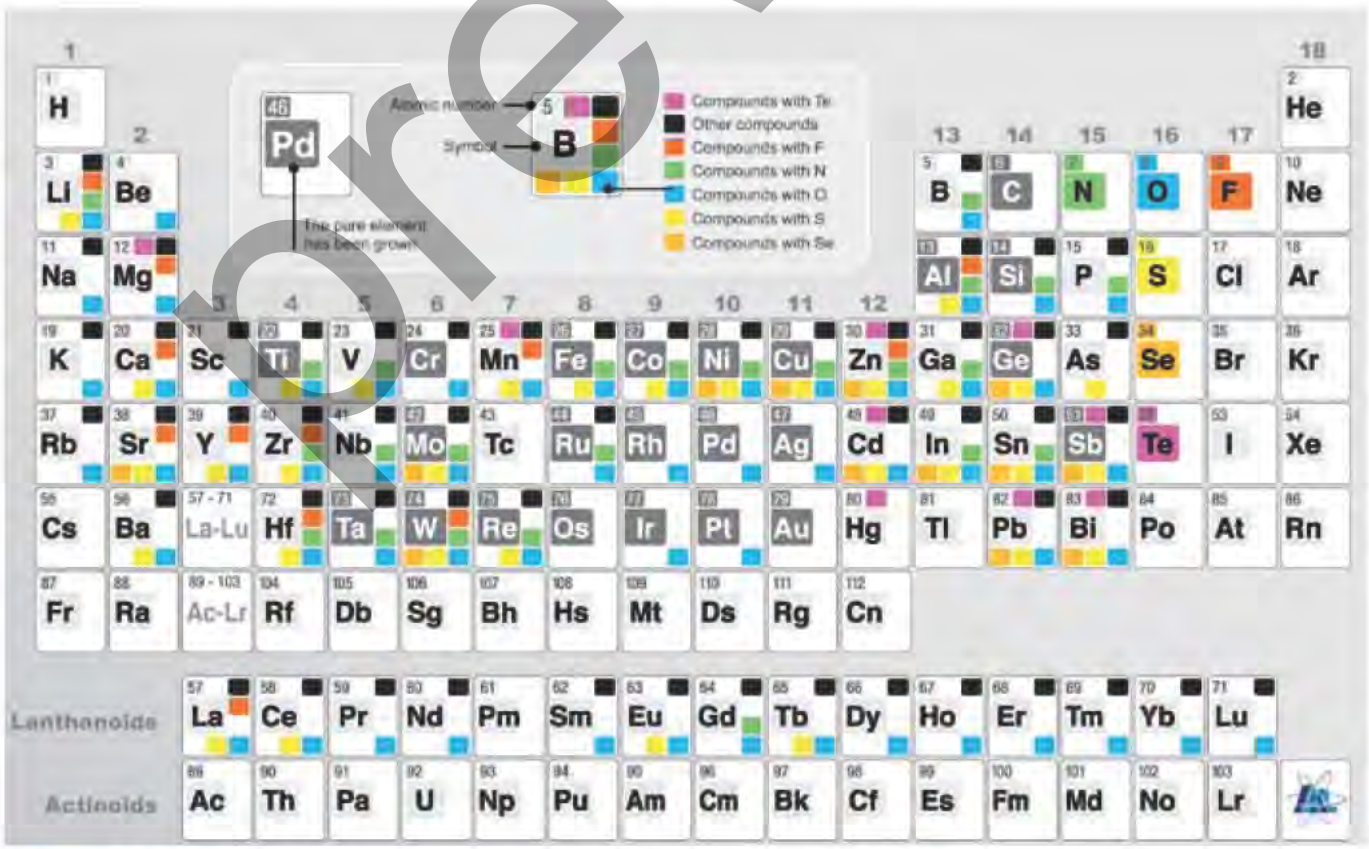

Figure 3 Periodic table illustrating the materials that have been synthesized by ALD [9].

preview

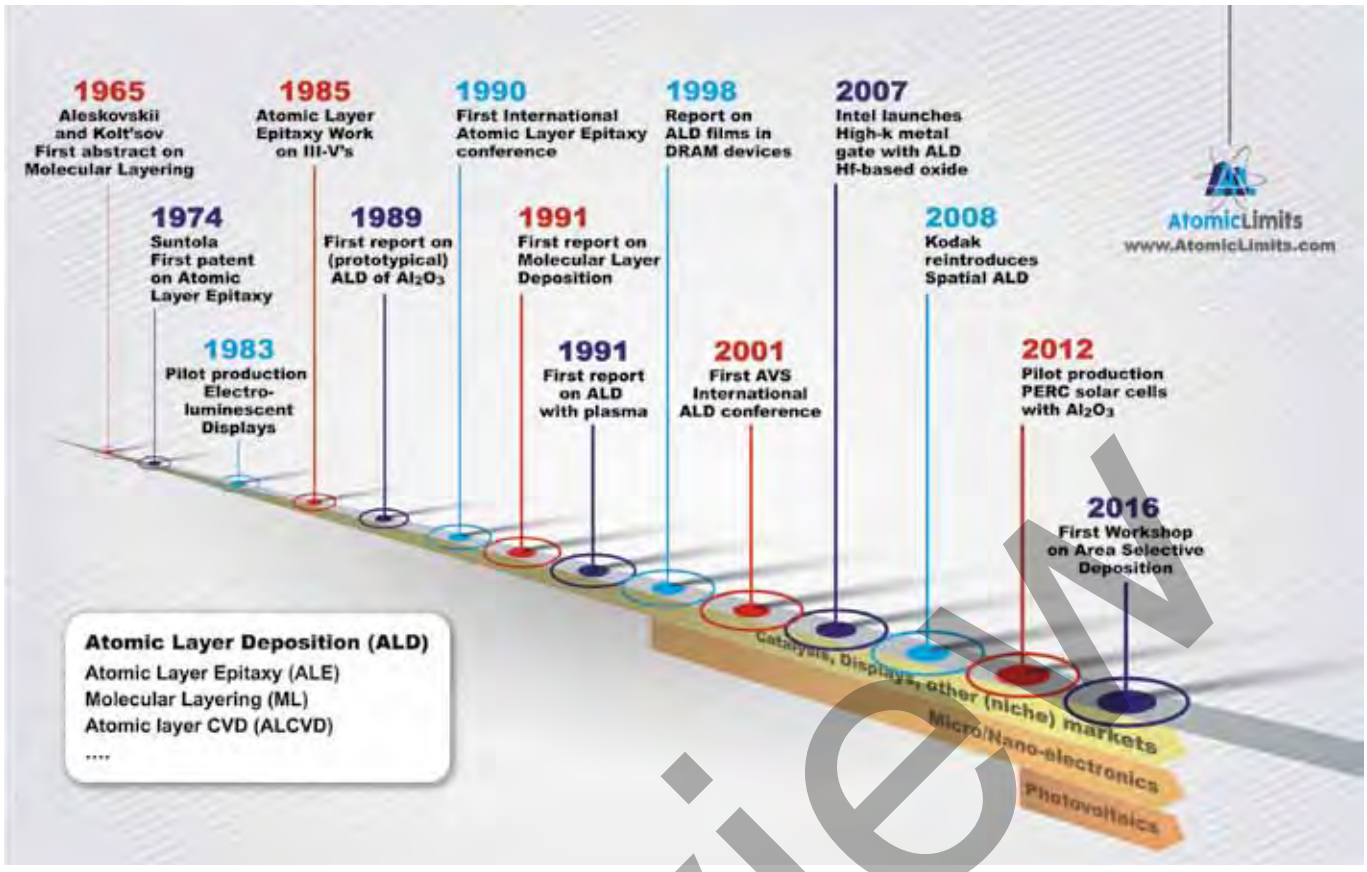

Figure 4 Timeline highlighting some remarkable events in the history of ALD.

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 SiO_2 by HfO_2 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 Al_2O_3 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 Al_2O_3 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.

preview

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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.

preview

ALD on particles

Scalable production of nanostructured materials

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].

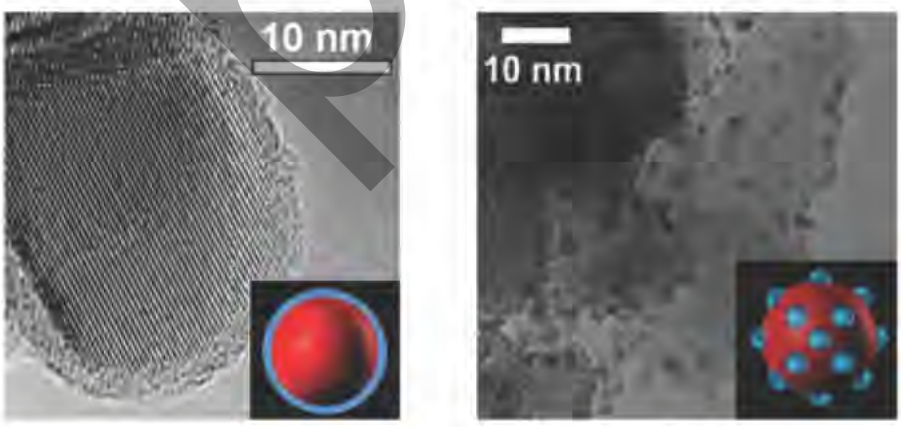

Figure 1 Particle morphology photographs obtained by transmission electron microscopy. In both cases, titania nanoparticles are coated by ALD: left with alumina giving film growth, right with platinum giving island growth. The insets give a simplified sketch of the morphologies.

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

preview

Atomic Layer Deposition for crystalline silicon solar cells

Innovate at the nanoscale, deploy at the gigawatt scale

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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preview

ALD is already big in the solar industry

Without argument, the biggest success story for ALD in solar cells deals with ALD aluminum oxide (Al_2O_3). This material has enabled to boost silicon solar cell efficiency in so-called PERC structures, and as such it is present in most of the solar cells sold today. The key characteristic of a PERC cell is an Al_2O_3 nanolayer at the back side. For a concise summary of the function of this Al_2O_3 layer, see the box and figure 1.

About 15 years ago, together with IMEC, our Plasma & Materials Processing group at the Eindhoven University of Technology pioneered ALD Al_2O_3 for surface passivation, and an absolute efficiency gain of >1% was demonstrated in PERC cells in 2008 [1,2]. This really sparked industrial interest, and nowadays the lion's share of commercial silicon solar cells are PERC-type. The Netherlands played a strong role in scaling up this technology, with companies such as SoLayTec and Levitech developing spatial ALD Al_2O_3 solutions [3]. Besides spatial ALD, nowadays also batch ALD is becoming big in solar. Giving a number, LeadMicro stated that they have supplied over 30 GW of batch ALD passivation systems, which translates to about 6 billion silicon wafers per year [4].

Beyond Al_2O_3: New ALD nanolayers

Over the last decade, many other new nanolayers have been explored for silicon solar cells, summarized in the timeline in figure 2 [5]. Clearly, ALD has played a central role in this exploration. A potentially better performance and new functionalities are the motivation for exploring new materials. I will highlight a few of these materials, with a focus on recent work at the TU/e.

Our current research is focused on two new passivation materials we recently discovered: ALD phosphorus oxide (PO_x) and zinc oxide (ZnO) [6,7]. Both materials are abundant, inexpensive, and yield state-of-the-art passivation on n-type silicon. ALD PO_x passivation layers are of interest as they are the 'positive twin' of Al_2O_3. Like Al_2O_3, they yield very low defect density interfaces, but they exhibit a very strong fixed positive charge. Whereas the negative charge of Al_2O_3 makes it suitable for the passivation of p-type surfaces, the positive charge in PO_x explains its excellent passivation of n-type surfaces. ALD ZnO is also a new passivation material that gives state-of-the-art passivation of n-type silicon, but it is unique in the fact that it is a conductive passivation layer. Because of this unique aspect, this passivation layer can potentially also help in transporting current out of the solar cell, and we are currently exploring new cell designs that can leverage this additional conductivity.

Another truly hot topic in our field is passivating contacts.[8] These nanolayers passivate the silicon interface – like Al_2O_3 – but also act as contacts: they are 'membranes' that only let electrons or holes pass. This removes the need for n^+ and p^+ regions in the wafer, enabling

Interface engineering by ALD in organo-metal halide perovskite solar cells

Reflections on the state-of-the art and perspectives

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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preview

Atomic layer deposition for photovoltaics

ALD Al_2O_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 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. What is intriguing is the fact that nowadays the ALD research in perovskite PV draws the attention of the PV perovskite community in ALD (and spatial ALD). In this perspective article, which is a follow-up of the review paper published early in 2017 [6], I will reflect on the progress accomplished by ALD in the field of PSCs, but also on the opportunities and challenges yet to be met.

Interface engineering by ALD in hybrid perovskite PV: state-of-the art [7]

The early works on ALD for PSCs had primarily an exploratory character, where metal oxide charge transport layers (CTLs) were synthesized and implemented in thin film PSC cells either in n-i-p or p-i-n configuration [8]. Thin (10-15 nm) metal oxides are generally preferred to the conventional organic-based transport layers borrowed by organic PV, because of the decrease in parasitic absorption losses and series resistance in the cell. 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

Spatial Atomic Layer Deposition for large-area and flexible electronics

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].

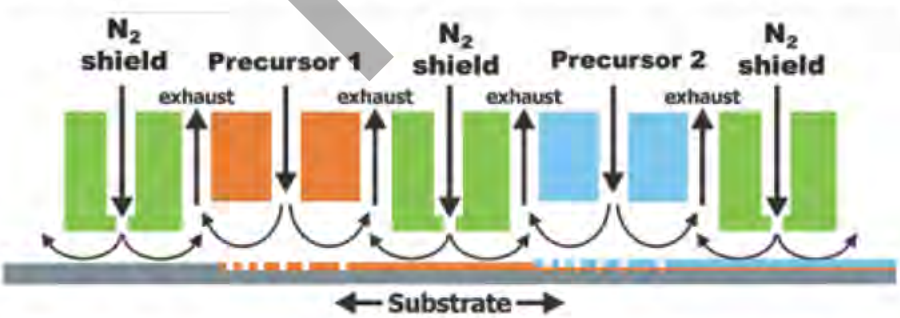

Figure 1 Schematic drawing of TNO's spatial ALD reactor concept, where the two precursor zones are separated by inert gas shields. The two half-reactions will take place subsequently to form an ALD monolayer, by moving the substrate underneath the reactor. Thicker layers are obtained by repeating the movement.

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

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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.

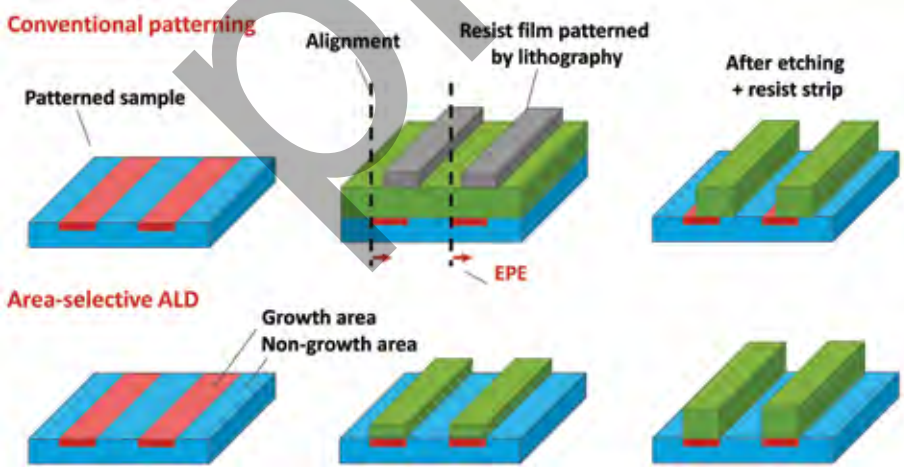

Figure 1 Conventional patterning relies on repetition of deposition, lithography and etching steps for every layer in a multilayered device. At the small dimensions of current and future devices, it is often difficult to align features on top of each other, which results in an edge placement error (EPE). Area-selective ALD solves alignment issues, and eliminates etching and lithography steps.

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

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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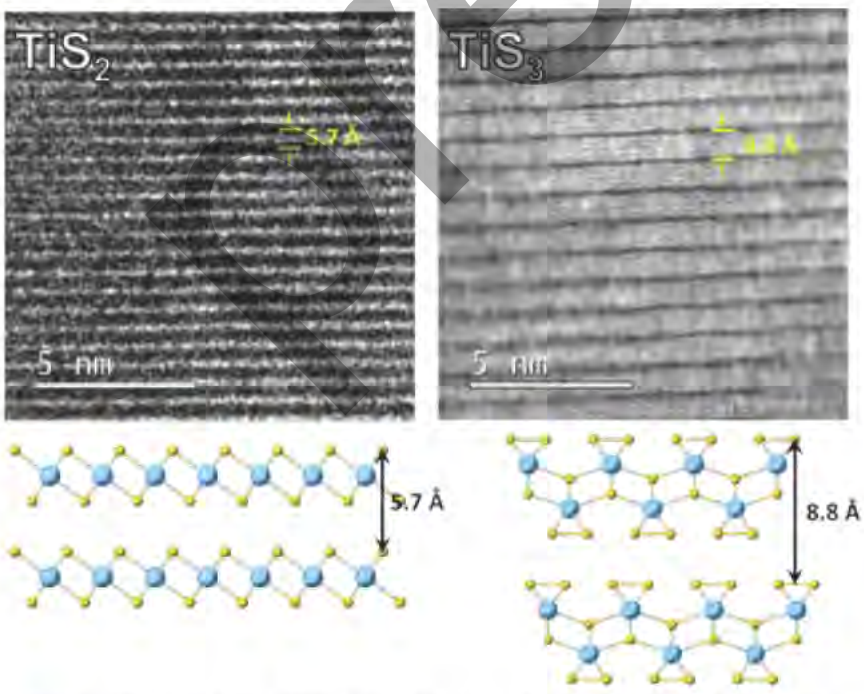

Figure 1 High-resolution HAADF-STEM images of cross-sections of ALD-grown TiS_2 and TiS_3 and corresponding ball and stick models.
TEM credit: Marcel Verheijen.

Thickness control over a large area

Similar to graphite, bulk transition metal dichalcogenides form layered structures composed of 2D layers stacked on top of one another. The chemical formula of TMDs is MX_2, where M is a transition metal (e.g. Mo, Ti, W) and X is a chalcogen (S, Se, Te). A single 2D layer (monolayer) typically consists of hexagonally arranged metal atoms sandwiched between two planes of hexagonally arranged chalcogen atoms (figure 1, left panel). When moving from bulk to the monolayer regime, the electronic band structure changes due to so-called quantum size effects, giving the 2D materials exciting new electronic properties that are not present in bulk material.

Even though layered TMDs can be obtained by techniques such as chemical vapor deposition, achieving precise control over the thickness/number of layers has remained difficult. Through its self-limiting surface reactions, ALD provides angstrom-level thickness control, making it a promising synthesis technique for controlling the number of TMD layers. In ALD the desired film thickness can be achieved by simply varying the number of ALD cycles depending upon the growth obtained per cycle, as is illustrated for WS_2 in figure 2a. A monolayer is achieved after around 10 ALD cycles [1,2]. Owing to the typical ALD characteristics, the control over thickness can be realized on both planar and high-aspect ratio 3D growth surfaces (figure 2b) over large areas (figure 2c) at temperatures below 450°C [1-3]. This makes ALD excellently suited for growing 2D-TMDs over demanding 3D electronic structures.

Review

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

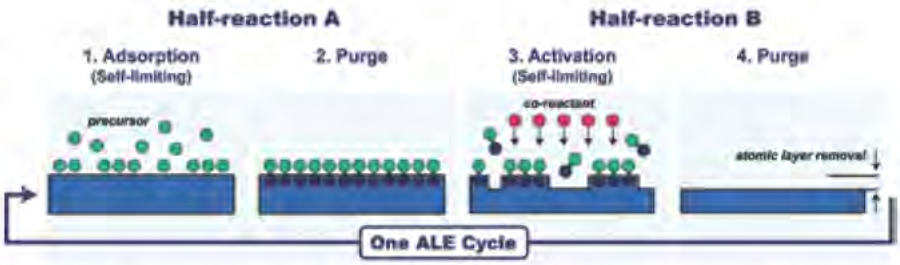

Figure 1 Schematic illustration of an ALE cycle [6]. The process consists of half-reactions involving adsorption of species and activation by a co-reactant. The etching typically occurs during half-reaction B.

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