Spatial atomic layer deposition: a route towards further industrialization of atomic layer deposition

Citation for published version (APA):

DOI:
10.1116/1.3670745

Document status and date:
Published: 01/01/2012

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 15. Nov. 2021
Spatial atomic layer deposition: A route towards further industrialization of atomic layer deposition

Paul Poodt
TNO, P. O. Box 6235, 5600 HE, Eindhoven, The Netherlands

David C. Cameron
Advanced Surface Technology Research Laboratory (ASTRaL), Lappeenranta University of Technology, Prikaatinkatu 3E, FI-50100 Mikkeli, Finland

Eric Dickey
Lotus Applied Technology, 1050 NW Compton Drive, Hillsboro, Oregon 97006

Steven M. George
Departments of Chemistry & Chemical Engineering, University of Colorado, Boulder, Colorado 80309

Vladimir Kuznetsov
Levitech BV, Versterkerstraat 10, 1322 AP Almere, The Netherlands

Gregory N. Parsons
Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695

Fred Roozeboom
TNO, P. O. Box 6235, 5600 HE, Eindhoven, The Netherlands, and Eindhoven University of Technology, P. O. Box 513, 5600 MB, Eindhoven, The Netherlands

Ganesh Sundaram
Cambridge NanoTech Inc., One Kendall Square, Suite B7301, Cambridge, Massachusetts, 02139

Ad Vermeer
SoLayTec BV, Dillenburgstraat 9g, 5652AM, Eindhoven, the Netherlands

(Received 29 August 2011; accepted 29 November 2011; published 14 December 2011)

Atomic layer deposition (ALD) is a technique capable of producing ultrathin conformal films with atomic level control over thickness. A major drawback of ALD is its low deposition rate, making ALD less attractive for applications that require high throughput processing. An approach to overcome this drawback is spatial ALD, i.e., an ALD mode where the half-reactions are separated spatially instead of through the use of purge steps. This allows for high deposition rate and high throughput ALD without compromising the typical ALD assets. This paper gives a perspective of past and current developments in spatial ALD. The technology is discussed and the main players are identified. Furthermore, this overview highlights current as well as new applications for spatial ALD, with a focus on photovoltaics and flexible electronics. © 2012 American Vacuum Society. [DOI: 10.1116/1.3670745]

I. INTRODUCTION

Atomic layer deposition (ALD) is a thin film growth technique based on the sequential exposure of a substrate to self-limiting surface half-reactions. ALD is currently being used commercially by the semiconductor industry to form metal/high-k gate oxide stacks for field effect transistors, capacitors for dynamic random access memory devices, as well as in the thin-film magnetic head industry to form gap dielectrics. Recently, ALD has raised interest from new application areas, such as photovoltaics and organic electronics. Applications where ALD has displayed added value include surface passivation layers in crystalline silicon solar cells, buffer layers in CuInGa(Se,S) (CIGS) as an alternative to chemical bath deposition (CBD) CdS, and moisture diffusion barrier layers for OLEDs and thin film photovoltaics. These applications; however, require high-throughput and low-cost production techniques to make them economically viable. Unfortunately, these prerequisites are considered to be the weak points of ALD. One way to increase the throughput of an ALD system is to do batch processing, but this is not always compatible with the in-line processes often used in the before mentioned applications. A significant reduction of the cost of ownership of ALD processes and equipment must be realized to make ALD economically viable for these new applications.
Spurred by these new opportunities for ALD, several “new” approaches to ALD have been recently proposed and developed to meet this challenge. Many of these approaches share a common feature: spatial separation of the half-reactions, and can be summarized under the term “spatial ALD.” This paper overviews the development of spatial ALD, the approaches and progress to date. Furthermore an overview of potential new applications of spatial ALD will be given.

II. SPATIAL ALD

The difference between conventional temporal ALD and spatial ALD lies in the manner that the precursors are delivered to the substrate (see Fig. 1). In conventional ALD the precursors are dosed into a chamber sequentially, separated in time by a purge step [Fig. 1(a)]. In spatial ALD, the precursors are supplied continuously, but in different physical locations [Fig. 1(b)]. Thus there are (at least) two zones where, in the presence of a substrate, a half-reaction can take place. If the substrate is present in such a half-reaction zone for a sufficiently long period of time, a saturated monolayer will form from precursor A. Then, the substrate is moved to the second half-reaction zone, where the ALD cycle is completed to form one ALD monolayer. Alternatively the substrate position could be fixed and the gas supplies could be moved, or some combination of the two. To obtain thicker films, this sequence has to be repeated for the desired number of cycles.

The main advantage of spatially separating the half-reactions is that the purge steps between the precursor dosages in conventional ALD become obsolete. As a consequence, the available net deposition rate is no longer limited by the accumulated individual cycle step times, but by the time required to move between half-reactions zones. Of course the ultimate limit depends on the kinetics of the specific reaction involved, but this can be of the order of a few milliseconds when using planar substrates. For substrates with more complex topographies (e.g., trenches), required exposure times will scale dictated by transport limitations at the feature scale, similar to conventional ALD.

The main essence of ALD lies in decoupling the (at least) two independent half-reactions, which requires a complete separation of the precursors with no intermixing precursors whatsoever. In conventional ALD this is achieved through the use of purge steps in between the half reactions. In spatial ALD, the half reactions are separated using a combination of physical barriers and continuously flowing purge streams to prevent the interdiffusion and mixing of the precursors.

In conventional ALD, deposition will not only take place on the substrates, but on the reactor walls as well. Furthermore, the purge steps in between the half reactions will remove any surplus precursor from the reactor, making it unavailable for incorporation into the deposited film. This results in an inherently poor precursor utilization efficiency, constraining the ability to employ costly precursors for large scale applications. In spatial ALD, the separation of the reaction zones combined with barriers to prevent mixing ensures that precursors never reside in the same reactor volume. As a consequence, the only place where deposition will take place is on the substrate and no parasitic deposition on the reactor walls will occur. A significant reduction of precursor consumption and consequently the cost of ownership can be achieved, depending on the specific design, mode of operation and desired deposition rate of the various spatial ALD concepts.

Summarizing, the three main characteristics of spatial ALD are: (1) physically separated half-reactions zone, (2) movement of the gas injector head and/or substrate, and (3) a barrier between the half-reaction zones to prevent precursor mixing.

A. Early developments

Although there have been several recent developments in spatial ALD, the original idea was already patented in 1977 by Suntola et al. They described the concept of spatially separating the half-reactions, with separate precursor inlets and exhausts. In their patents, the authors describe the use of shields of inert gas for separating the half-reaction zones, where the gas shield width should be designed wide enough to prevent any diffusion and cross-reactions between the precursors.
Jusung Engineering (Korea) also developed a spatial ALD reactor, quite similar to Suntola’s concept. They used a rotating injector with, at least, four arms in a sort of windmill construction; two for supplying each precursor separately and two arms in between supplying inert gas acting as purge steps. This concept has been commercialized as their Cyclone reactor, but publicly available information is limited.

B. Lotus Applied Technology

Lotus Applied Technology (Hillsboro, USA) has developed a spatial ALD reactor for flexible substrates, operated in a roll-to-roll mode. In this approach the flexible substrate is woven back and forth between two precursor zones separated by an inert gas zone in a serpentine configuration (Fig. 3). Differential pressure and pumping is used to prevent precursor migration into the purge zone. Process pressure is generally about 2 mbar, similar to that used in conventional pulse-based ALD. This approach was originally published in 2007, with the first experiments beginning in 2008 in a 100 mm research reactor. Initial work was done using well-known water-based thermal processes (Al₂O₃ from TMA + H₂O, TiO₂ from TiCl₄ + H₂O). The first results, including results for full roll-to-roll processing were published in 2009. To overcome processing speed limitations related to desorption of excess physisorbed water following water precursor exposure, plasma-based processes were employed beginning in 2009, and this has remained the focus of technology development.

C. ASTRaL

At the Advanced Surface Technology Research Laboratory (ASTRaL) of Lappeenranta University of Technology (Finland), another spatial ALD concept for depositing on flexible substrates has been developed. They have chosen to pass the flexible web around a large rotating drum adjacent to the various gas inlet and purge zones. A schematic of this process is shown in Fig. 4(a).

As a vehicle to explore the issues concerning the operation of such a system, such as uniformity, gas flows, gas separation, etc., they have carried out initial experimental work using a system based on the same design ideas except that, for simplicity, a continuous web is not used. Instead, a flexible substrate is fixed to the surface of a rotating drum and sequentially passes through the precursor and purge gas zones which are separated by exhaust zones. One rotation of the cylinder is equivalent to one ALD cycle. This system is the Beneq TFS200R ALD tool and a photograph of the reaction chamber is shown in Fig. 4(b). A more detailed description is given in Ref. 12. Experimental depositions with this system have shown that the process behaves as a conventional ALD process in that the deposition rate per cycle saturates as the precursor flow rate is increased, reaching approximately 1 Å/cycle for the TMA/water process for Al₂O₃ at a temperature of 100 °C.
D. Cambridge NanoTech

Cambridge NanoTech (Cambridge, USA) is developing their own spatial ALD concept, referred to as zone separated ALD. This concept is based on a manifold/cell design [see Figs. 5(a) and 5(b)] involving the operation of the cell under choked flow conditions. Under these conditions gases are supplied via the manifold to the input side of the cell under choked flow operation at atmospheric process pressure. Choked flow operation is beneficial in that variations in the process pressure will have no impact on the flow through the cell.

Aside from the design of the cell, this zone separated has involved integrating the cell into a prototype architecture to facilitate characterizing the performance of the unit [Fig. 5(c)]. The cell and manifold are mounted on top of the pressure vessel and are covered in insulation material. The precursor and exhaust lines are similarly insulated. The yellow cabinet, shown on the left in Fig. 5(c), houses the precursors, flow controllers, pressure gauges and a variety of manual and pneumatic valves that enable system operation.

III. CLOSE PROXIMITY SPATIAL ALD

In the aforementioned applications, the separation between the precursor half-reaction zones is ensured by a relatively large physical distance between the half-reaction zones, in combination with zones of an inert gas as a diffusion barrier. An alternative approach to ensure precursor separation is by using a very close proximity of the substrate to the precursor injector (<100 μm). In such a concept, illustrated schematically in Fig. 6, the reactor has separate zones exposing the precursors one by one to a substrate that moves underneath the reactor. Between and around the reaction zones, there are shields of inert gas again to separate the precursor flows. When operated properly, these gas shields can act as gas bearings, facilitating virtually frictionless movement between reactor and substrate. When a gas-bearing is used, the distance between the reactor and substrate can be minimized and made very accurately and controllable of the order of several tens of micrometers. These small gap heights combined with the resulting high flow rates in the gaps form excellent diffusion barriers with relatively narrow widths. An additional benefit of using gas-bearings is that they completely seal off the reaction zones, making the

![Fig. 4. (Color online) (a) Schematic drawing and (b) photograph of the Astral spatial ALD reactor. The flexible substrate is mounted on a central drum and rotated past several precursor injectors, separated by inert gas and exhausts. Reprinted with permission from Chem. Eng. J. 171, 345 (2011).](image1)

![Fig. 5. (Color online) (a) Schematic drawing and (b) photograph of Cambridge Nanotech’s zone separated ALD manifold and cell. (c) Photograph of a prototype 150 mm zone separated ALD cell integrated into a system.](image2)
reactor completely independent of the environment, enabling operation under atmospheric pressure conditions.

In and around 2008 several groups have independently filed patents on gas bearing based spatial ALD concepts. These groups are Eastman Kodak (Rochester, USA),13 ASM International (Almere, The Netherlands),14 and TNO (Eindhoven, The Netherlands).15 However, Levy and co-workers from Eastman Kodak were the first to present their results.16

A. Eastman Kodak

Eastman Kodak first started with a transverse flow spatial ALD head without gas bearings. However, precursor gas separation was not optimal.17 In an improved design, the substrate is allowed to approach the head until the pressure field resulting from the gas flow hydrodynamically supports the substrate (Fig. 7). In this case, the system operates like a gas bearing and the substrate is maintained in close proximity to the coating head without the need for extremely high tolerance mechanical fixtures. The main application this group has been working on is thin film transistors where Al2O3 and ZnO are deposited with their setup.18

B. University of Colorado

The University of Colorado at Boulder (USA) has made a spatial ALD reactor similar to the Kodak design (Fig. 8). The gas source head is composed of a series of rectangular channels that spatially separate the process sequence. The substrate sits below the gas source head and is mounted to a frictionless translation table. A linear translation stepper motor was programmed to translate the substrate back-and-forth underneath the gas source head. The spacing between the gas source head and substrate is fixed and can be controlled with micron precision using micrometers. This apparatus can test how continuous atmospheric ALD depends on the gap spacing, substrate translation speed, gas flow rates, and the pressure difference between reactant and purge channels. Tests have been performed using helium as a probe gas to demonstrate that operating conditions exist where the two reactant streams do not mix.19 Reactant isolation could be maintained with a gap spacing as large as 100 μm. Al2O3 ALD films were also grown by translating the substrate relative to the gas source head.19 These model experiments revealed that fixed gap spacings using a mechanical spacer are very difficult to maintain during substrate translation.

C. TNO

For the development of their spatial ALD concept TNO combined their gas bearing technology with atmospheric pressure gas phase deposition technology. They started development on their rotary proof-of-principle reactor in 2009 and presented their results soon after.20,21

These experiments have led to the conclusion that defining the gap spacing using a gas bearing may be required for reliable ALD during sample translation.
zones are incorporated in a round reactor head surrounded by exhaust zones [Fig. 9(a)]. These zones are surrounded by gas bearing planes. The reactor head is mounted on top of a rotating substrate table [Fig. 9(b)]. The entire construction is mounted in a convection oven. Round substrates with diameters of 150 or 200 mm and (semi-)square 15.6 × 15.6 cm² wafers can be mounted. Their main focus was ALD of alumina as surface passivation layers on crystalline silicon solar cells, an activity that has been transferred to the spin-off company SoLayTec (see the next section). TNO is currently developing new tools and processes for spatial ALD for applications such as encapsulation, photovoltaics, and solid state lighting.

D. ASM International

ASM International patented a spatial ALD reactor combined with the floating wafer and conductive heating technology they developed earlier for their rapid thermal processing tools (Levitor RTP). This technology was further developed by ASM International’s spin-off Levitech, aiming at solar cell applications which will be discussed in more detail below.

IV. FIRST INDUSTRIAL APPLICATION: PASSIVATION LAYERS FOR SILICON SOLAR CELLS

An obvious application for spatial ALD is backside passivation of crystalline silicon solar cells. Silicon solar cell efficiency can be increased by applying thin Al₂O₃ films by ALD for surface passivation. Such films combine excellent chemical passivation with field effect passivation caused by a high intrinsic negative charge density fixed at the Si-Al₂O₃ interface. This implies a breakthrough in the production of high-efficiency solar cells, but also opens the way to using thinner silicon wafers, where surface passivation is of utmost importance. Here, the requirement called for is the availability of an ALD deposition technique meeting the industrial throughput requirements of ~3000 wafers/h.

The demand for a high-throughput ALD deposition tool has led to the formation of two companies developing and commercializing spatial ALD machines dedicated for depositing Al₂O₃ passivation layers on crystalline silicon solar cells: Levitech and SoLayTec. Both use a double-sided gas bearing configuration, sandwiching the solar cell wafer (Fig. 10). This concept allows for a near-frictionless movement of the wafer through ALD half-reaction zones. Both spatial ALD tools were recently compared with batch ALD and PECVD in a market survey on aluminum oxide deposition systems for passivation layers.

A. Levitech

Levitech, a spin-off from ASM International, developed a spatial ALD tool for the passivation of silicon solar cells with Al₂O₃ layers based on the ASM International concept as shown in Fig. 10(a). Silicon solar cell wafers are transported in a linear track crossing areas with precursor gas curtains. The wafers are transported between two gas bearings, levitating in between a narrow track. Figure 10(a) shows the cells of the Levitrack system. Wafers pass such a cell in ~1 s resulting in a throughput of 3600 wafers/h. The total number of ALD cells determines the final layer thickness. For the deposition of a 10 nm layer the tool length will be ~10 ms [Fig. 10(c)].

Extensive modeling was used to optimize the track performance. The track dimensions and gas flow rate are chosen such that no gas mixing occurs in the track when empty or during processing of (156 × 156 mm²) wafers. Heated top and bottom walls transfer heat efficiently to the wafers: heating up and cooling down takes place in the first and the last 60 cm of the track, respectively. The TMA evaporation rate is tuned to just reach wafer surface saturation; consequently, almost no TMA goes to the exhaust. A high-speed N₂ flow protects the back side of the wafer against Al₂O₃ deposition.

The tool has been manufactured and tested for passivation quality of atmospheric ALD layers, throughput and reliability. The results have demonstrated that the electrical charge in the deposited Al₂O₃ layer is sufficient to provide field-effect passivation. Measurements of the minority carrier lifetime show good passivation levels. Marathon runs at throughputs rates of 4000 wafers per hour showed a reliable system performance. Complete solar cells with ALD Al₂O₃ passivation layers deposited in the Levitrack reactor on 156 × 156 mm² wafers have been fabricated following existing industrial technologies (optimized for SiNx and SiOx passivation). Here, superior results were obtained with the ALD Al₂O₃ layers with thicknesses in the range 5–10 nm.
The highest efficiency obtained for n-type crystalline silicon cell was 18.3%.29

B. SoLayTec

SoLayTec, a spin-off company from TNO, have developed a spatial ALD reactor for depositing Al₂O₃ passivation layers where substrates are moved back and forth all the way underneath a spatial ALD injector head with the same width as the substrate.30,31 By using a double-sided gas bearing (below and above the substrate; Fig. 10(b)), the substrate floats virtually frictionlessly underneath the injector zones. By pulsing flows of inert gas into the substrate drive-in and drive-out zones next to the injector, the wafer can be moved back and forth without utilizing carriers. The film thickness is tuned by simply selecting the number of passages of the substrate.

The total deposition rate depends on the number of TMA and water slots that are integrated in the injector head, in combination with the number of passages of the substrate per second. Currently, each substrate passes 4 times per second through the injector head containing a single TMA slot, resulting in an effective deposition rate of ~0.45 nm/s. This allows for throughput numbers of the order of 100 wafers/h, based on a passivation layer thickness of 10 nm. However, integrating 2 or 3 TMA and water half-reaction zones is possible; thus increasing the throughput accordingly. With this tool [Fig. 10(d)], homogeneous deposits (30 nm ± 2–4% thickness variation) can be obtained over the entire area of 156 × 156 mm² solar cell wafers, with minimal backside deposition with low effective recombination velocities (~30 cm/s) for 180 μm thick p-type CZ Si-wafers, 1–5 Ωcm), but highly dependent on type, quality, pretreatment and posttreatment of the Si-wafer).32,33 Further up-scaling to industrial scale can be achieved by incorporating 10 or up to 15 injectors in parallel use, as a modular system. In this way throughput numbers over 3000 wafers/h can be obtained while keeping a relatively small footprint.

V. OUTLOOK

Several potentially new applications for spatial ALD will be discussed in this section. Some have seen already quite some development but await industrialization, others are still in a very early stage of development.

A. Spatial ALD for flexible electronics

1. Thin film encapsulation and roll-to-roll ALD

A new field of applications for spatial ALD is in flexible electronics, including flexible displays, flexible OLEDs, and flexible (organic) solar cells. Flexible electronics are slowly but surely evolving from lab-scale to industrial production. This opens up new possibilities for spatial ALD as a production technique for functional layers where conventional ALD already showed its potential in the lab, such as transparent oxide (semi)conductors [e.g., ZnO [Ref. 34]] and moisture barriers [e.g., Al₂O₃ (Ref. 4)]. A major obstacle to this development is the sensitivity of these devices towards O₂ and H₂O. For OLEDs, water vapor transmission rates (WVTRs) as low as 10⁻⁶ g/m²/day are required. The requirements for thin film solar cells are expected to be less stringent (by one or two orders of magnitude) but still beyond simple polymer encapsulation. Excellent diffusion barriers have been made from alumina by ALD, either as a single film or as part of a multilayer stack, where WVTR values below 10⁻⁵ g/m²/day have been reported. The excellent barrier properties of alumina deposited with ALD...
combined with the flexibility of the spatial ALD concept opens up the opportunity to develop a roll-to-roll spatial ALD tool for depositing barrier layers on flexible substrates for applications such as flexible OLEDs, solar cells, and displays.

Lotus Applied Technology (Fig. 3), ASTRaL (Fig. 4) and Cambridge Nanotech (Fig. 5) all have designed their spatial ALD tools specifically for roll-to-roll purposes. For Lotus Applied Technology, the near-term application target for the technology is transparent gas diffusion barriers on polymer substrates, for flexible packaging and encapsulation of flexible electronics, including thin-film photovoltaic modules and OLED displays and lighting. For the longer term, the technology lends itself well to roll-to-roll processing applications that benefit from the unique attributes of ALD, and require low cost, such as surface functionalization, active layers in flexible electronics such as gate dielectrics and semiconductors, and thin transparent conductive oxides, such as ZnO:Al. A pilot scale system, capable of coating substrates 300 mm wide by 100 m long, and up to 100 ALD cycles pass, is currently under construction.

ASTRaL is currently awaiting delivery of a complete roll-to-roll ALD system based on their technology. ASTRaL will have the capability of coating 500 mm width webs and is intended to prove the technology in a pilot-scale industrial process. Their initial aim is to study the application of ALD to paper-based products such as food packaging and labeling and also for application to plastic electronics.

Cambridge NanoTech’s zone-separated ALD work began in 2010 when they became a recipient of a FlexTech Alliance (a consortium of Flexible Electronics companies) award, to develop a Roll-to-Roll ALD system for use within the flexible electronics sector. A beta system is planned to be installed at the Flexible Display Centre at Arizona State University in 2012.

TNO is developing a roll-to-roll spatial ALD reactor consisting of a central drum that contains one or more combinations of TMA and water half-reaction zones. These zones are separated and surrounded by nitrogen gas bearings. The foil to be coated is pulled over this drum, where the gas bearing ensures that the foil is kept at a fixed distance from the surface of the drum (typically tens to hundreds of micrometers). If the foil is then moved over the drum, ALD deposition will take place, where the total thickness is determined by the rotation frequency of the drum (typically rotating counterclockwise) in combination with the translation speed of the foil.

2. Oxide based thin-film transistors

The field of oxide electronics has shown significant growth in past years, fueled to a large part by demonstrations of thin-film transistors (TFTs) based upon zinc oxide (ZnO). At Eastman Kodak, ZnO-based TFTs have been made by spatial ALD. Their spatial ALD system was used to deposit an Al2O3 film of approximately 50 nm thickness. The ZnO semiconductor layer is deposited on top of the Al2O3 dielectric using the same equipment. A final passivation layer of 30 nm thick Al2O3 is deposited under the same conditions as for the gate dielectric. These ZnO-based thin-film transistors show mobilities approaching 20 cm2/Vs and stabilities as good as any published data on this material system. The deposition system is also capable of producing very good uniformity of devices, with threshold uniformities over the area of their 5 cm wide coater of approximately 50 mV.

B. Deep reactive ion etching

Deep reactive ion etching (DRIE) of silicon is a highly anisotropic etch process used to create high aspect ratio (20:1) features or more. DRIE was developed for the manufacture of microelectromechanical systems (MEMS) and to excavate trenches for high-density capacitors for DRAM and passive integration, and for through-silicon-vias (TSVs) in advanced 3D wafer-level packaging technology. The DRIE process of choice today is the Bosch process (Fig. 12). The Bosch process is a near-room temperature, low pressure (~100 mTorr) plasma etch process, where the etch step is divided in two separate half-reactions. The first step is etching with SF6 which is an isotropic etch. In order to minimize the lateral etching component, the etch steps are interrupted by a second step, being a sidewall passivation step by depositing a thin Teflon-like layer from C4F8. Etch or passivation
subcycle times are typically 1–10 s with 0.1–1 μm etched depth per cycle.

The similarity of this process with ALD might allow the conversion of this process from the time-divided into the spatially divided regime, similar to spatial ALD, to significantly reduce the total cycle time. A second improvement in the spatially-divided approach is the replacement of the CVD-based C₄F₈ passivation steps by ALD-based oxide (e.g., SiO₂) deposition cycles. In contrast to the C₄F₈ case the ALD-based oxide layer is self-limiting and chemisorptive of nature and less complex in its layer thickness control and thus in the anisotropy control of the total DRIE process.

C. Light management for photovoltaics and lighting

In order to increase the performance of devices such as solar cells and LEDs, functional layers can be applied on top of or below the active layers of these devices to enhance the incoupling or outcoupling of light. Examples can be mirror layers, textured front or back contacts, multilayer antireflection layers and plasmonics, typically using materials as oxides and metals. These applications often require manufacturing techniques with feature sizes of the order of tens of nanometers, for which ALD is excellently suited. However, they should be applied at low cost and industrial throughput scales (e.g., km²/yr). Here, spatial ALD can be a potential manufacturing technique as spatial ALD can cope with both aspects.

D. Textile functionalization

Fibrous materials, including natural and synthetic textiles, are important for protective and decorative function. Because of their high surface area, flexibility, ease of manufacture and low cost, research interest is growing in textile materials for biomedical systems and for applications in photovoltaic cells, transistors, or sensors. For many applications, chemically modifying the fiber surface is important to improve appearance, chemical durability, and mechanical properties. Several processes such as sol-gel or plasma treatments are known to alter surface properties of woven and nonwoven fiber mats for use in hygiene, bandages, or oil recovery functions. In addition, exposing fibers to reactive vapors is also known to alter the surface properties of fibers, especially their wetting characteristics.

Although less well known than other methods in the industry, vapor phase atomic layer deposition (ALD) is known to penetrate inside complex fibrous structures to create conformal and uniform coatings of inorganic or inorganic-organic thin films that modify the surface finish. ALD is particularly advantageous compared to wet chemical processes since ALD is highly efficient, it leaves no liquid chemical waste, and it requires no expensive thermal drying steps after coating. Recent reports by researchers at North Carolina State University show that ALD can promote wetting transitions on polypropylene and cotton fibers, and this ALD treatment can then enable more advanced functionalization.

A key factor that will limit ALD as a viable surface modification technique for textiles will be the process throughput. Most textile manufacturing proceeds via roll-to-roll, so making ALD compatible with textile processes will require movement away from batch processes. The advent of spatial ALD will be a critical enabler to help this transition happen. A recent report shows that surface-saturated Al₂O₃ and ZnO ALD can be achieved on textile materials in a reactor operating at ambient pressure, indicating that textiles can be compatible with ambient spatial ALD processes. However, we note that most of the spatial ALD tool designs developed to date are primarily focused on coating flat planar substrates (primarily flexible polymer web). For textiles the tools may require unique design features to be compatible with porous substrates where more of a “flow through” reactant delivery will likely be preferred.

E. New processes

Other processes than thermal ALD [e.g., plasma ALD (Ref. 56)] are possible as well with spatial ALD. Lotus Applied Technology uses an oxygen containing plasma in their reactor. However, the close proximity spatial ALD discussed earlier in this review operates at atmospheric pressure, and conventional low-pressure plasmas cannot be used. Yet, plasma ALD should be possible by allowing an atmospheric plasma source to replace one of the reactant channels in Fig. 6. Photon-assisted ALD could also be implemented by allowing radiation to pass through one of the reactant channels. A continuous flow of reactants, plasma or photons, can be defined much more easily in the spatial ALD format than in the temporal ALD format as the latter is confined to a vacuum chamber. Having the substrate at atmospheric pressure and the gas source head open to the atmosphere allows much more flexibility. In addition, low vapor pressure...
reactants could also be introduced very closely to the reac tant channel in the gas source head thus enabling deposition rates unattainable in the temporal ALD case. The closer proximity to the substrate and the much smaller volume in the reactant channel could allow a much wider range of low vapor pressure precursors as, for instance, used in molecular layer deposition.\textsuperscript{5,6}

VI. SUMMARY AND CONCLUSIONS

Although the basic concept of spatial ALD is already known for decades, the most major developments occurred in the past two to three years. A major driver for these developments is the growing demand from industry for high throughput, large area ALD equipment and processes. Surface passivation of crystalline silicon solar cells is an important example that led to the launch of dedicated spatial ALD equipment. Another upcoming application is the encapsulation of thin-film solar cells and OLED devices, both rigid and flexible. Especially the possibility of roll-to-roll spatial ALD holds promise to make ALD an established manufacturing technique for flexible electronics.

Several potentially new applications for spatial ALD have been discussed. Most mentioned applications fall outside the more traditional application domains of ALD in, e.g., microelectronics. This is probably because the throughput limitations of conventional ALD are less of an issue in the microelectronics industry. For spatial ALD to successfully enter these new application domains, new materials, processes and reactor concepts need to be developed that fit the requirements of these applications. There is a risk; however, that for more complex materials and applications there will be significant challenges for spatial ALD to overcome. For example, so far only processes for which high vapor pressure precursors are available have been developed for spatial ALD (e.g., for Al\textsubscript{2}O\textsubscript{3} and ZnO), but for many precursors the vapor pressure is limited. Furthermore, freeform and highly textured substrates might impose limitations on the applicability of spatial ALD, especially for close-proximity spatial ALD concepts.

Nevertheless, spatial ALD has experienced a strong development in the last few years and smart tailor-made solutions have been developed to overcome the technical and economic obstacles that make volume manufacturing with conventional ALD impossible. Although much more research and development is required, spatial ALD has the potential to become a disruptive manufacturing technique for a wide number of applications. The future of spatial ALD promises to be very exciting.

ACKNOWLEDGMENTS

The authors gratefully acknowledge David Levy from Eastman Kodak for supplying information and figures. ASTRAI acknowledges Tekes—the Finnish Funding Agency for Technology and Innovation and the European Regional Development Fund—for support. The work at the University of Colorado was supported by grants from Defense Advanced Research Projects Agency and from the Center for Revolutionary Solar Photoconversion, a division of the Colorado Renewable Energy Collaboratory. Cambridge Nanotech wishes to acknowledge the FlexTech Alliance for financial support of its Roll-to-Roll ALD program.

\textsuperscript{1}S. George, Chem. Rev. 110, 111 (2010), and references therein.
\textsuperscript{11}W. A. Barrow and E. R. Dickey, proceedings of the Fall Conference of the Association of Industrial Metallizers, Coaters and Laminators (AIMCAL), 2009 (unpublished).
\textsuperscript{24}J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M.C.M. van de Sanden, and W. M. M. Kessels, Prog. Photovolt. 16, 461 (2008).
41H.A. Atwater and A. Polman, Nat. Mater. 9, 205 (2010).