History of atomic layer deposition and its relationship with the American Vacuum Society

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History of atomic layer deposition and its relationship with the American Vacuum Society

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This article explores the history of atomic layer deposition (ALD) and its relationship with the American Vacuum Society (AVS). The authors describe the origin and history of ALD science in the 1960s and 1970s. They also report on how the science and technology of ALD progressed through the 1990s and 2000s and continues today. This article focuses on how ALD developed within the AVS and continues to evolve through interactions made possible by the AVS, in particular, the annual International AVS ALD Conference. This conference benefits students, academics, researchers, and industry practitioners alike who seek to understand the fundamentals of self-limiting, alternating binary surface reactions, and how they can be applied to form functional (and sometimes profitable) thin film materials. The flexible structure of the AVS allowed the AVS to quickly organize the ALD community and create a primary conference home. Many new research areas have grown out of the original concepts of “Atomic Layer Epitaxy” and “Molecular Layering,” and some of them are described in this article. The people and research in the ALD field continue to evolve, and the AVS ALD Conference is a primary example of how the AVS can help a field expand and flourish. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4816548]

I. INTRODUCTION

This article describes the growth of the atomic layer deposition (ALD) field from a historical context, including early work on molecular layering (ML) performed in the Soviet Union in the 1960s and the invention of atomic layer epitaxy (ALE) processes and reactors in the 1970s. The article also discusses work during the 1980s and 1990s that illustrates how the field transitioned from ML or ALE to atomic layer chemical vapor deposition (ALCVD) before the term ALD became widely recognized. We also discuss how the field continues to evolve, producing advances in plasma ALD, spatial ALD, molecular layer deposition (MLD), sequential vapor infiltration, and other emerging techniques.
ALD became commercially important in the early 2000s when the semiconductor industry adopted ALD for manufacturing of high performance complementary metal oxide semiconductor transistors. As this wave of interest began, the AVS community recognized the potential of the field. This article recounts how a group within the Thin Film Division (TFD) worked to re-establish the previous ALE international conference and attract active research groups from around the world.

The article also describes several areas that have emerged from the basic ALD concept. These examples suggest that there may be many other advances and new directions yet to be defined. The well-organized and committed staff and leadership within the AVS continue to provide opportunities for other new fields to assemble and grow. We would like the history of ALD within the AVS to provoke and embolden others to try new experiments to expand scientific communication and community in other future developing fields.

II. EARLY YEARS OF ATOMIC LAYER PROCESSES

The ALD thin film deposition technique was originally developed by Dr. Tuomo Suntola and co-workers (Jorma Antson, Sven Lindfors, Arto Pakkala) in the mid-1970s. The motivation for developing the ALD technology was the need for high-quality thin films in electroluminescent (TFEL) flat-panel displays. At that time, the method was called ALE. The first experiments were carried out with elemental zinc and sulfur source materials. The word “atomic” in the name derives from the original use of elemental atomic sources. The word “epitaxy” derives from the Greek roots *epi*, meaning “above,” and *taxis*, meaning “in an ordered manner.”

Soon thereafter, it became clear that molecular precursors were required for more general deposition and to expand the materials selection. Some researchers using molecular precursors referred to the process as molecular layer epitaxy (MLE) to distinguish the use of molecular precursors from the use of elemental sources. By 1980, ALE technology was successfully advanced and Suntola and his team were able to produce TFEL displays at the industrial scale by ALE using manganese-doped zinc sulfide luminescent layers and aluminum–titanium oxide dielectrics. This work was performed at Lohja Oy, which later became Planar International. Planar is now known as Beneq.

Many ALD reactors were proposed and utilized during these formative years. Figure 1 shows an original reactor design from Suntola described in one of his early patents. This design moved the substrate between different reactant sources in an early version of spatial ALD. Figure 2 is a picture of Sven Lindfors in 1978 with one of the early hot wall tube ALD reactors. This reactor design was a predecessor to many of the hot wall viscous flow reactors in operation today. Figure 3 is a photograph of Jarmo Skarp in 1985 standing next to a Planar P1000 reactor used in TFEL display production at Lohja Oy. The key to the success of ALD was the development of production-worthy cross-flow batch ALD equipment. These reactors facilitated the introduction of molecular precursors to a number of substrates simultaneously in a short time.

The ALD principle, where surface reactions follow a binary sequence of self-limiting half-reactions, was first published under name “molecular layering” in the early 1960s by Prof. S. I. Kol’tsov from Leningrad Technological Institute. These experiments were conducted under the scientific supervision of Prof. V. B. Aleskovskii. The concept of molecular layering was first proposed by Prof. V. B. Aleskovskii in his Ph.D. thesis published in 1952. Based on the early publications from Kol’tsov and Aleskovskii, the

![Fig. 1. Schematic picture of an ALE reactor from early Suntola patent in 1977 where the substrates (14) rotated between the sources (13a and b). Image from T. Suntola and J. Antson, U.S. patent 4,058,430 (1977).](image)

![Fig. 2. (Color online) Sven Lindfors in 1978 next to an early hot wall tube ALD reactor.](image)

![Fig. 3. Jarmo Skarp in 1985 standing next to a Planar P1000 reactor used in TFEL display production.](image)
work was initially motivated by the desire to modify the surfaces of sorbents and catalysts. They were able to quantify the reaction between TiCl\textsubscript{4} and Si–OH groups on silica gel by titration and colorimetry. The product stoichiometry indicated reaction of 3 Si–OH groups with TiCl\textsubscript{4} producing (Si–O)\textsubscript{3}–Ti units and one Ti–Cl. They later showed\textsuperscript{2} that the Ti–Cl group density scaled with the amount of Si–OH present in the initial gel, so that less Si–OH led to more Ti–Cl\textsubscript{2} units. Further work published in 1969 described the sequential exposure of TiCl\textsubscript{4} and water to form TiO\textsubscript{2}.\textsuperscript{3} The reaction scheme from that publication is reproduced here in Fig. 4.\textsuperscript{4} Earlier work on this topic may also be available.\textsuperscript{5} In the 1969 article, the authors report that the initial reaction between TiCl\textsubscript{4} and Si–OH tends to involve 3 Si–OH, forming one Ti–Cl, whereas after the first water step, the second TiCl\textsubscript{4} exposure reacts with 2 Ti–OH, forming Ti–Cl\textsubscript{2} groups. A planar thin film was not produced or evaluated.

The early literature on ALD technology in the 1970s was comprised primarily of patents.\textsuperscript{4} The principle demonstrated that a compound material thin film (e.g., ZnTe) could be formed by exposing a surface to alternating exposures of elemental constituents (Zn and Te vapors).\textsuperscript{6} The ability to control the film growth was verified by a number of techniques including X-ray photoelectron spectroscopy.\textsuperscript{6} By controlling the substrate temperature above the Zn and Te sublimation temperature but below the vaporization temperature for the ZnTe compound, the Zn atoms impinging on the surface would form stable bonds only with Te, and Te would bond only with Zn. The sequential ALE approach (referred to in the 1980 publication as “atomic layer evaporation”) provided good quality polycrystalline films over a wider range of deposition temperatures compared to the more common co-deposition molecular beam epitaxy (MBE) method. The better growth by ALE was ascribed to improved surface species transport during ALE, where species are able to optimize their bonding without being hindered by elements impinging on the surface.

Because TFEL display manufacturing by Lohja Corporation was the only industrial application of ALD for a long time, ALD research was largely focused on EL materials. The early publications dealt with characterization of ZnS ALD films\textsuperscript{7} and ZnS:Mn EL devices.\textsuperscript{8} The old publications did not provide many details of the ALD process. For example, the nanolamine structure of the superior aluminum–titanium oxide (ATO) dielectrics widely used in the early 1980s was revealed only in the 1990s.

The ZnS:Mn based TFEL displays were monochrome (yellow–black) and the development of multicolor displays came next. Different rare earth doped ZnS and alkaline earth sulfides were studied between 1985 and 2000.\textsuperscript{9} The primary problem was the blue phosphor. Some thiogallate materials were studied, but it was soon concluded that the project scope was not sufficient to identify highly efficient inorganic blue material for TFEL displays. In addition, alternative dielectrics were sought, and although the ATO remained in the TFEL displays, this research laid the groundwork for future exploitation of ALD in microelectronics.

Interest in ALE for elemental semiconductors as well as III–V and II–VI compound semiconductors began to rise in the early 1980s. Groups reported ALE (or MLE) of silicon and gallium arsenide and other III–V compounds using different metal precursors.\textsuperscript{10,11} Most of the emphasis was on alkyl compounds.\textsuperscript{10,12} Good results were reported for epitaxial growth. However, the overall success was limited and there were no reported commercial applications. ALE did not bring obvious benefits over the traditional MBE and metal organic vapor phase epitaxy methods. Consequently, the activity in this ASE area diminished in late 1990s. The interest in III–V compounds and alkyl precursors did lead to the discovery in 1989 of what has become the most popular and most widely studied ALD process, viz., Al\textsubscript{2}O\textsubscript{3} ALD using trimethylaluminum and water.\textsuperscript{13}

Microchemistry Ltd. was founded in late 1987 as a research company of Lohja Oy and Neste Oy. An image of a mousepad used to promote Microchemistry Ltd. is shown in Fig. 5. The image on this mousepad was the well-known picture of a conformal Al\textsubscript{2}O\textsubscript{3} ALD film on a trenched silicon wafer by Ritala et al.\textsuperscript{14} Neste Oy was an oil company interested in using ALE for solar energy and catalysis applications including polymerization and hydrogenation. The catalyst research widened the scope of ALE to modification of high surface area materials like silica and alumina. In this work, the surface area reacted with molecular precursors approximated that of a football field.\textsuperscript{15} Understanding the nature of the reactive sites on the silica and alumina surfaces

$$3 \text{Si–OH} + \text{TiCl}_4 \rightarrow \text{Ti–Cl}_2 + 3 \text{HCl}.$$  

$$\text{TiCl}_3 + \text{H}_2\text{O} \rightarrow \text{Ti–OH} + \text{HCl}.$$  

![Fig. 5. (Color online) Photograph of promotional mousepad distributed by Microchemistry, Ltd. showing the excellent conformity of Al\textsubscript{2}O\textsubscript{3} ALD on a trenched silicon wafer.](Image 324x125 to 552x301)

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to be coated was important to select the correct molecular precursors to achieve active catalysts.

At Microchemistry, Ltd., ALE was successfully used to uniformly saturate 1 kg of mesoporous silica with a Zr precursor. In the late 1990s, a large scale-up for ALE catalysts was obtained using a circulating fluidized-bed reactor at Neste Oy. Precursor saturation was successfully demonstrated for the production of 17 kg of a silica modified alumina catalyst. The main interest of Neste Oy was in catalytic materials for oil refining. However, Neste Oy was not a catalyst manufacturer, and they decided that ALE would be too expensive to manufacture catalysts at the 1000s of kilogram scale needed for large-scale reactions, such as hydrogenation. The team did recognize, however, that ALE was well suited for manufacturing small amounts of tailored catalysts. The work on ALE for catalysis was, however, halted in the late 1990s, and Microchemistry, Ltd. changed its focus toward ALE processes and equipment for semiconductor applications.

ALE conference activities started in 1990 when the first International Symposium on Atomic Layer Epitaxy was organized in Helsinki. The symposium series was biannual and was scheduled to cycle through Europe, Asia, and America every 6 years. However, only four symposia were organized between 1990 and 1996. The programs of these ALE symposia had a strong emphasis on epitaxial films and compound semiconductors. Polycrystalline and amorphous films were studied only by a few groups.

Interest in ALD increased in the late 1990s and 2000s, driven strongly by silicon-based microelectronics. ALD was recognized to have the greatest potential for producing very thin, conformal films, with very accurate control of the film thickness and composition at the atomic level. The need to scale down microelectronic devices continues to be a major driving force for growing interest in ALD. The fundamental studies on group IV oxides in the early 1990s can be viewed as first steps to the use of hafnium-based ALD materials as gate dielectrics in metal-oxide field effect transistors. The hafnium-based ALD materials became the industry standard starting in about 2007.

Dynamic random access memory devices (DRAMs) that require increasingly more complex three-dimensional capacitor structures comprise another critically important application area for ALD. The first news that ALD was used in DRAM production came out in 1998. Today, DRAM dielectric materials are typically ZrO$_2$–Al$_2$O$_3$–ZrO$_2$ nanolaminates produced by ALD. ALD continues to increase its importance not only in microelectronics but also in many emerging areas. The selection of materials that can be prepared by ALD, the number of metal precursors, and the number of ALD processes are reported to be 160, 300, and 780, respectively. These numbers will grow as researchers advance the performance of current devices and continue to create new application areas.

### III. AVS AND THE INTERNATIONAL ALD CONFERENCE

During the 1990s, when the International ALE Conferences were occurring every 2 years, several talks and posters related to ALD and ALE were given at the AVS Annual Symposia. A few presentations were in sessions organized by Surface Science, Electronic Materials, and the Thin Films Divisions. A session on Advanced Thin Film Formation Chemistry was organized by Greg Parsons for the 1999 Annual AVS Symposium in Seattle. There were three ALD-related talks: one on plasma-enhanced ALD for interconnects from Steve Rossnagel at IBM and two thermal-ALD talks on W/WN and SiO$_2$/Al$_2$O$_3$ from Steve George and his students from the University of Colorado. In addition, Hyeongtag Jeon from Hanyang University in Seoul gave a poster on TiN ALD. During the poster session, Hyeongtag Jeon, Steve George, and Greg Parsons began discussions on ways to bring attention to “Atomic Layer Chemical Vapor Deposition.” Greg Parsons was the newly elected Chair of the TFD for 2000. The three of them decided to meet again at the TFD dinner that week to develop a session for the following year.

The 2000 AVS Symposium in Boston had two TFD sessions on Atomic Layer Chemical Vapor Deposition, with the lead invited paper given by Mikko Ritala of the University of Helsinki. During this time, there was significant concern by the AVS Board of Directors regarding the future of the TFD, which had been declining in submissions and attendance at the AVS Annual Symposium. The combined need for new TFD activity and interest in ALCVD led the TFD to propose an AVS Topical Conference Workshop on ALCVD that would be separate from the AVS Annual Symposium. At that Boston meeting in late-October, the group decided to hold the Workshop in the coming spring to be chaired by Steve George. There was also some discussion that night about holding a meeting in Korea. The decision was made that if the spring ALD meeting was successful, Korea would be considered for a follow-on meeting in 2002 or 2003.

The 2001 ALD meeting was targeted to be a small workshop of 30–50 people. Della Miller at AVS West suggested that the workshop be held in May 2001 in Monterey, CA and that it share part of the conference facility with an AVS Topical Meeting on Plasmas. The conference was designed to work on a short timescale to keep the talks fresh and up-to-the-minute. The abstracts were due less than 6 weeks before the meeting. The registration fees and other costs were kept low to break even financially while maximizing scientific discussion and interaction.

The organizers had to overcome what was thought to be a major hurdle when Steve George received a letter from a tool vendor indicating that the “ALCVD Conference” name would infringe on their copyright on “ALCVD.” After some discussion, the name was changed to the “ALD Conference” or more formally the “International AVS ALD Conference.” This change turned out to be a fortunate because “ALD” was a much better name than ALCVD. The term ALD was more general than “ALE” and better captured the majority of the work in the field that was dominated by metal oxides that were not epitaxial to the underlying substrate.

A few decisions were made prior to the ALD 2001 meeting in Monterey, CA, which have come to define the AVS ALD Conferences. Most importantly, the conference was...
designed to have a primary focus on advancing the science of thin film materials and surface formation reactions, while simultaneously improving current applications and creating new uses for the technology. Toward this goal, the 2001 meeting brought the most experienced academic researchers together with key technology leaders to discuss advances and ongoing problems. This opened the door for new learning and rapid progress in fields that would not have otherwise occurred. The focus on aligning basic scientific underpinnings with new and better applications provides continued motivation for the conference.

A valuable tradition within the conference was pioneered by Steve Rossnagel when he suggested that all presenters would be required to make their presentations from a central computer using Microsoft PowerPoint rather than from their own computer or from overhead slides. Overhead transparency slides were still common at the time. The central computer was set up to capture the presentation audio, including questions and answers, so that each presentation could be “played back” at some point after the meeting. In place of any printed proceedings, encrypted CDs with all of the complete presentations were made after the meeting and distributed to all attendees.

The technical process has evolved and been improved over time. However, this basic method has been successful for every ALD Conference to date and is expected to continue into the future. Recordings from all previous AVS ALD conferences are available from Della Miller at AVS. In 2011, the Journal of Vacuum Science and Technology A began to assemble a special issue on ALD, which was published in the January 2012 issue. Articles were based, in part, on work presented at the ALD Conference. However, the Journal of Vacuum Science and Technology A was also open for any submission on ALD-related work. A second issue was published in 2013, and this practice is expected to continue in the future.

The ALD Conference organizers in 2001 were surprised and happy when the expected 30–50 attendees became more than 200 registered attendees. However, the large numbers posed a significant problem for the available conference space. In response, a satellite room with television monitors was set up and handled the overflow attendance. Both rooms were completely full for most of the 2½ day conference, even though many attendees had to watch on TV in a separate room.

Following the ALD2001 meeting success, the TFD decided to hold a meeting in 2002 in Seoul, Korea, chaired by Hyoongtag Jeon. At about this same time, the TFD group also agreed to establish a U.S./International meeting cycle. The ALD meeting would be held in the United States in odd-numbered years and the meeting would alternate between Asia and Western Europe in even-numbered years. The ALD2002 meeting in Seoul was a great success. A picture of the conference location at Hanyang University is shown in Fig. 6. The front page of the conference abstract book for the ALD2002 meeting is displayed in Fig. 7.

In 2003, the meeting was held in San Jose, chaired by Greg Parsons. In 2004, the meeting went to Helsinki, chaired by Mikko Ritala. The goal was to make the AVS ALD meeting a truly international meeting and recognize the centers of work in the ALD field around the world. This international cycle has been successful and is planned to continue. Chairs are selected every year by a TFD ALD “steering committee” comprised of several previous chairs active in the AVS TFD.

A list of the meeting locations, chairs, and numbers of presentations and attendees is given in Table I. Starting in 2007, to recognize the importance of industry in the ALD field, conference leadership was shared by co-chairs, usually one from academia and one from industry. In 2005, a 1-day
tutorial session was added at the start of the meeting to help students and others to learn new aspects of the field. During the first several years, the meeting was a sequence of single-session topics. Starting in 2005, the conference had grown to the point where the meeting needed multiple parallel sessions. The most recent conference in San Diego had several parallel sessions and 325 presentations.

The program committee continues to debate the impact of single versus multiple sessions, oral versus poster presentations, and the value of maintaining a 3-day format. The group currently agrees to keep the meeting at 3 days plus the tutorial to better reflect the intimacy and immediacy of the original 3-day workshop. A big change from the original meeting in 2001 is the number of commercial sponsors. While sponsorships were not originally sought, many companies showed interest in participating, and sponsorships were developed for the meeting. The generous support of many sponsors continues to help the meeting maintain its visibility and livelihood.

In addition to the annual AVS ALD Conference, there are several other regional ALD conferences. The original regional meeting is the Baltic ALD Conference (BALD) held about every 2 years. The first one in 1991 was in Helsinki and was called the “Helsinki University of Technology-University of Tartu 1st ALE Meeting.” The third meeting in 1995 became the “Baltic ALD Meeting.” The name later changed to Baltic ALD, and in 2004, BALD was held in conjunction with the AVS ALD meeting in Helsinki. Other regional meetings include the Korean ALD meeting, the German ALD meeting, and more recently the Chinese ALD meeting.

The International AVS ALD Conference remains the most widely attended and recognized meeting for presentation and sharing new knowledge for ALD materials, processing, and technology. The meeting promotes sharing of ideas, discussion of advances, vetting of new hypotheses, and airing of scientific controversies. Many advances that the field is experiencing can be traced to original presentations and announcements at the AVS ALD meetings. When ALD first came to AVS, the AVS tradition for promoting university/industry interaction and expanding interpersonal relations provided a basis to build a cohesive international ALD community. This strengthened and broadened the ALD community, and the synergy continues to benefit AVS and the ALD field. Several new areas of investigation have grown in importance over the past several years. A few of these are discussed in Sec. IV.

IV. EMERGING AREAS AND FUTURE DIRECTIONS

This section briefly summarizes some of the active current areas of ALD-related research that have emerged and expanded, in part, through advances shared at the ALD conference. There is significant room for further creative development to enlarge and enrich the field.

A. Plasma ALD

Work on plasma ALD, also called plasma-enhanced ALD (PE-ALD) or plasma-assisted ALD, started in 1991 when De Keijser and Van Opdorp at Philips Research Laboratories reported the use of a plasma during ALD to generate atomic hydrogen for GaAs ALD.25 The atomic hydrogen enabled growth at reduced substrate temperatures <500°C and suppressed the thermal decomposition of the Ga(CH3)3 precursor. PE-ALD developed rapidly from 2000 onwards, starting with the experiments performed by Rossnagel and co-workers at IBM studying barrier materials for Cu interconnects.26 The

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<th>Year</th>
<th>Conference</th>
<th>Location</th>
<th>Chairs</th>
<th>Oral</th>
<th>Poster</th>
<th>Total</th>
<th>Attendees</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>ALE1</td>
<td>Helsinki</td>
<td>Lauri Niinistö, Helsinki University of Technology</td>
<td>20</td>
<td>20</td>
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<td>1996</td>
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<td>2001</td>
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<td>2003</td>
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<td>Gregory Parsons, North Carolina State University</td>
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<td>AVS ALD Helsinki, Finland</td>
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<td>2012</td>
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<td>AVS ALD San Diego, CA</td>
<td>Jiyong Kim, University of Texas, Dallas; Paul Ma, Applied Materials</td>
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<td>Yoshihiro Shimogaki, University of Tokyo, Japan; Christian Dussarat, Air Liquide</td>
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<td>2024</td>
<td>AVS ALD Helsinki, Finland</td>
<td>Mikko Ritala and Markku Leskelä - Celebrating 50 years of ALD</td>
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plasma generated hydrogen radicals as reducing agents to form Ti and Ta metal films. A schematic diagram of one of their early plasma ALD reactor designs is shown in Fig. 8.26

The number and types of materials produced by plasma ALD continues to expand and now includes many metals, metal nitrides, and metal oxide films.27 A key advantage of PE-ALD is deposition at lower substrate temperature than available in thermal ALD. Plasma ALD can also (1) allow deposition of materials that cannot be deposited by thermal ALD, such as Ti and Ta; (2) deposit films with improved properties and control of the film composition; (3) work with a wider choice of precursors; (4) achieve a larger overall growth rate (i.e., a larger thickness per cycle and a shorter purge and cycle time); and (v) permit more process versatility in general.

There are many plasma ALD reactor configurations including remote plasma ALD reactors where the plasma source is positioned upstream and electrically separate from the substrate stage.28 Another form is direct-plasma ALD, where a capacitive reactant before the reactant reaches the substrate. Hot-wire ALD, photon-enhanced ALD, and UV-catalyzed ALD also use external energy enhancement. Plasma ALD with substrate biasing or direct-write ALD processes are new developments that expand the processing capabilities of "conventional" thermal ALD as well.30,31

B. Molecular layer deposition

In the early 1990s, work by Yoshimura et al. showed that organic polymide films could be formed on a surface through a sequence of vapor-surface reactions using bifunctional organic precursors including diamines and dicarboxylic acids.32 The reaction was reported to follow a self-limiting binary reaction scheme similar to ALD. However, because the precursors were organic and the molecular fragments from the precursors were intended to stay in the film, the process was referred to as MLD. Since then other groups have produced several other organic materials. The process is generally limited to species with sufficient vapor pressure at temperatures low enough to avoid thermal decomposition.

The range of materials that can be made by MLD expands greatly when the process uses a metal-organic precursor in combination with a functional organic co-reactant.33 This reaction sequence produces "hybrid organic–inorganic" thin films that contain metal centers covalently connected by organic linkages. A schematic of an example organic–inorganic MLD reaction using diethylzinc (DEZ) and ethylene glycol is shown in Fig. 9.34,35 This reaction is analogous to the well-known process for ZnO ALD from DEZ and water.

A wide range of metal precursors and organic linkers can be used to create a family of organic–inorganic materials referred to as “metalcones.”36 Combining ALD and MLD can also produce organic–inorganic alloys or nanolaminates, where the properties are tunable between pure inorganic and organic–inorganic.37,38 The number of materials is nearly endless considering the metals and types of organic linkages available.

Applications for MLD organic–inorganic solids are beginning to appear. Initial applications are in barrier and encapsulation layers, where the mechanical resiliency of the organic component gives the MLD films and their alloys with ALD films some desired flexibility.39 The organic–inorganic layers can also be calcined after deposition to form porous inorganic layers,34,40 for example, to produce membranes for separation applications.41 Organic–inorganic films produced to date appear to be primarily disordered. The capacity to grow ordered rectilinear organic–inorganic solids, such as metal organic frameworks, though an MLD approach would open many new application opportunities.

of polymer available is relatively small. This leads to new
mer bulk can saturate with the ALD precursor if the amount
occur quickly enough that the reactive sites within the poly-
reaction step. For some reactive polymers, the diffusion can
on polymers. However, on many polymers, precursors can
diffuse subsurface and either react directly with the poly-
ton polymers. This reaction scheme is appropriate for some ALD processes
additional ALD scheme involves the saturation of a reaction on
molecular layer deposition using diethylzinc and ethylene glycol as the
reactants.

The Helsinki group has reported efforts in this area at the
ALD2008 Conference in Bruges, Belgium.

C. ALD and vapor infusion into polymers

Another rapidly developing area is the coupling of inor-
organic ALD reaction schemes with organic polymers. The tra-
tional ALD scheme involves the saturation of a reaction on
a solid surface containing a limited number of reactive sites.
This reaction scheme is appropriate for some ALD processes
on polymers. However, on many polymers, precursors can
diffuse subsurface and either react directly with the poly-
mer and/or react with the co-reactant during the second half-
reaction step. For some reactive polymers, the diffusion can
occur quickly enough that the reactive sites within the poly-
mer bulk can saturate with the ALD precursor if the amount
of polymer available is relatively small. This leads to new
opportunities to go beyond two dimensions as is the norm in
typical ALD on solid surfaces. Diffusion of the ALD reac-
tant into the third dimension allows for the formation of new
material compositions. This approach has been used to create
nanopatterned metal oxide lines by infiltrating ALD precursors
into layered bulk co-polymer films.

D. Spatial ALD

Beyond microelectronics, there is growing need for ALD
materials to be produced rapidly under relatively mild pro-
cessing conditions. For example, encapsulation films and pas-
vivation layers are being explored for semiconductors,
displays, flexible electronics, and photovoltaics. Some of
these applications may be close to industrial implementa-
tion. A common problem with batch ALD processing is
the overall low deposition rates. Many of these new applica-
tions would benefit from lower cost and higher throughput
ALD processes.

One approach being studied to increase ALD throughput
is spatial ALD. In spatial ALD, the substrate is sequen-
tially exposed to the individual precursors. However, unlike
conventional ALD where precursor steps are separated in
time, the precursors are delivered spatially in separate pre-
cursor zones. This process is shown in Fig. 10. The zones are
often confined by vacuum, a gas shield, or a gas bearing.
One ALD cycle is completed by moving the substrate from
one zone to the other. This process is repeated until the
desired thickness is achieved. With the surface reaction
kinetics generally being very fast, and with much shorter
purge times than for a large reaction chamber, the net depo-
sition rate can reach the nm/s range. Consequently, spatial
ALD can achieve high throughput processing and the deposi-
tion of relatively thick films.

Although the spatial ALD concept was already described
in an early ALD patent by Suntola and Antson, the concept
was more or less independently reinvented and developed by
several groups in the past several years. Eastman Kodak
presented their work on spatial ALD at the AVS ALD con-
fERENCE in 2008 in Bruges, Belgium. A first industrial
application for spatial ALD is surface passivation of c-Si so-
lar cells, where 5–10 nm of alumina is applied on solar cell
wafers at throughput rates exceeding 1 wafer/s. Production
tools are now commercially available. At present, a growing
number of groups and companies are developing spatial
ALD technology, processes, and applications, including roll-
to-roll spatial ALD for flexible electronics. Spatial ALD has
the potential to become a disruptive manufacturing tech-
nique for a wide number of applications, leaving open many
exciting prospects for future research and product invention.

E. ALD for energy applications

A growing segment within the ALD community is
researching and developing layer-by-layer technology for
energy applications such as energy conversion (photovol-
taics, fuel cells, photoelectrochemical cells), energy storage
(lithium batteries, ultracapacitors), and energy conservation
(improved catalysts). Evidence for the expanding interest in
these subjects is that the last two AVS ALD meetings have
each hosted four sessions devoted to the various topics
within ALD for energy. In contrast, earlier ALD meetings
typically lumped these subjects into a single session called
“Alternative Applications.”

Motivating this recent interest in ALD for energy is the
growing recognition that nanostructured materials are likely
to play a key role in fostering a green energy economy based
on renewable energy sources and reduced carbon emissions.
Atomic layer deposition is a powerful technology for synthe-
sizing nanomaterials by functionalizing porous scaffolds to
impacts the desired chemical, physical, or electronic properties. For instance, the wide-scale application of lithium batteries for transportation will require substantial improvements in their lifetime. George recently demonstrated that ultrathin ALD Al₂O₃ films applied to porous LiCoO₂ cathode powders dramatically improves the charge/discharge cyclability of lithium batteries.⁴⁸

In the area of photovoltaics, dye sensitized solar cells (DSCs) offer the potential for low-cost solar power using earth-abundant materials, but to date, the relatively low conversion efficiencies of DSCs have limited their adoption. ALD has yielded promising results by allowing the introduction of ultrathin transparent conducting films,⁴⁹ dye adhesion layers,⁵⁰ and barrier films⁵¹ into the DSC structure that could be combined with improved electrolytes and sensitizers to make a highly efficient DSC suitable for low cost mass production. Finally, one of the early applications for ALD technology, heterogeneous catalyst synthesis, has lately gained renewed interest with the advent of ALD methods to fabricate and stabilize metal catalysts with exquisite control over the nanoparticle size, composition, and structure.⁵²

V. CONCLUSIONS

Atomic layer deposition science and technology involves the basic understanding of self-limiting reaction sequences as they apply to formation of functional thin film materials. A technique that started in the 1960s and 1970s has grown to maturity for some applications but continues to evolve into a diverse range of fresh areas for fertile exploration. The flexibility and unique structure of the AVS and the AVS Division system allowed AVS to move quickly to become the primary home to share and communicate advances in ALD science and technology. The AVS continues to provide a critical and unique service to the ALD scientific community. Ultimately, the public also benefits from new products and services that emerge from new discoveries.

The AVS ALD Conference exemplifies how the AVS community brings together highly talented staff and experienced leaders to allow a small group of researchers to work on a shoestring budget to stimulate growth of a highly successful field. Through these collaborative efforts, the AVS ALD conference has created an important venue for science advancement, technology evolution, and professional growth for a large set of students, academics, researchers, and industry practitioners.

ACKNOWLEDGMENTS

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²²D. S. Kil et al., Dig. Tech. Pap. - Symp. VLSI Technol. 2006, 73.

JVST A - Vacuum, Surfaces, and Films
Gregory N. Parsons is Alcoa Professor of Chemical and Biomedical Engineering at North Carolina State University. He received a Ph.D. in Physics from NC State University in 1990 and did postdoctoral work at IBM TJ Watson Research Center in the area of thin film transistor materials for flat panel displays. In 1991, he earned an IBM Invention Achievement Award for his work in “Pulsed Gas Plasma Enhanced Deposition of Silicon.” He joined NC State Chemical Engineering as Assistant Professor in 1992 and became Alcoa Professor in 2009. In 2006, he launched NC State University’s Nanotechnology Initiative to address fundamental understanding of nanomaterials and nanoscale processing. Professor Parsons’ research focuses on surface chemistry and chemical processing of thin film materials by atomic and molecular layer deposition, including investigations of nanoscale surface chemistry on polymers and fibrous media. He explores applications in renewable energy, electronic device processing, protective materials for DoD systems and advanced reactors and processes for future nonmanufacturing. Professor Parsons has been a member of AVS since he started in graduate school in 1984. He was elected Fellow of the American Vacuum Society in 2005, and in 2010, he was elected for a 3-year term (2011–2013) as a member of the AVS Board of Directors. In 2009, he received an NC State University Alumni Outstanding Teacher Award and was named NC State’s Academy of Outstanding Teachers.

Jeff Elam is a Principal Chemist and Group Leader at Argonne National Laboratory where he directs a program in atomic layer deposition (ALD) technology with the goal of developing new applications for ALD in fields such as photovoltaics, catalysis, batteries, and large-area detectors. Jeff earned his B.A. in Chemistry from Cornell University and his Ph.D. in Physical Chemistry from the University of Chicago. As a Postdoctoral Researcher at the University of Colorado, Jeff developed ALD thin film growth methods. Dr. Elam has authored over 160 papers and is an inventor of over 35 patents and inventions related to ALD. Jeff has won three R&D100 Awards and is heavily involved in chairing and organizing the ALD sessions at ECS and AVS.

Steven M. George is Professor in the Department of Chemistry and Biochemistry and Department of Mechanical Engineering at the University of Colorado at Boulder. Dr. George received his B.S. in Chemistry from Yale University (1977) and his Ph.D. in Chemistry from the University of California at Berkeley (1983). Prof. George has more than 300 peer-reviewed publications in the areas of surface science, thin film growth, and physical chemistry. He also has 13 issued U.S. Patents and 10 U.S. patent applications. Dr. George is a Fellow of the American Vacuum Society (2000) and a Fellow of the American Physical Society (1997). He has also received a number of awards including the R&D 100 Award for Particle-ALD™ (2004) and an NSF Presidential Young Investigator Award (1988–1993). Prof. George’s research interests are in the areas of surface chemistry, thin film growth, and nanostructure engineering. He is currently directing a research effort focusing on ALD and MLD. This research is examining new surface chemistry, measuring thin film growth rates, characterizing the properties of films, and developing new applications for ALD and MLD.

Hyeongtae Jeon is a professor in the Division of Materials Science and Engineering at Hanyang University. He received his B.S. and M.S. degrees from Hanyang University (1982, 1984) and Ph.D. degree from North Carolina State University (1991). He worked for Hyundai Electronics (former SK Hynix) as a senior researcher in the diffusion team and moved to Hanyang University in 1992 as a full time instructor (faculty position). His Ph.D. thesis was about thin film reaction of Ti-silicide and its characterization and he examined some retardation of phase transition of metal silicide depending on the film thickness. Since that time he has been working on various fields of thin film research such as high-k gate oxide, metal silicide, and metal nitride. Especially he was interested in the surface reaction of thin film deposition and he concentrated in the field of atomic scale deposition which is atomic layer deposition (ALD). He started his ALD research in Korea in the mid of 1990 and he hosted AVS ALD 2002 meeting in Korea, and currently he is a chair of Korean ALD workshop started at 2005. He holds more than 40 Korean and international patents and has published more than 170 journal papers in the fields of semiconductor materials, solar cell buffer layers, flexible display passivation, remote plasma ALD, and CVD. He is Editor-in-Chief of Korean Journal of Materials Research, Vice president of MRS-Korea, committee member of AVS ALD, member of MRS, AVS, ECS, and many more.

Dr. Suvi Haukka is currently employed as an Executive Scientist for ALD applications by ASM Microchemistry Ltd. in Helsinki, Finland. ASM Microchemistry is a research company owned by ASM International, a global company that together with its subsidiaries designs and manufactures equipment and materials used to produce semiconductor devices. For more than 20 years, she has worked at ASM Microchemistry in various capacities, including Research Scientist, Catalyst Technology Manager, Process Development Manager, and R&D Manager, which have all been related to atomic layer deposition (ALD). In particular, her work has focused on ALD chemistry and applications of ALD for semiconductor processes, and devices as well as the development of ALD apparatus. Over the course of her career, she has been an author on over 60 scientific papers, primarily concerning ALD. In addition, Suvi Haukka is an inventor of more than 100 patents and patent applications in the field of atomic layer deposition technology. In 1994, she earned a Doctor of Philosophy degree from the Laboratory of Analytical Chemistry, University of Helsinki, Finland.

Erwin Kessels is a full professor at the Department of Applied Physics of the Eindhoven University of Technology TU/e (the Netherlands). He is also the scientific director of the NanoLab@TU/e facilities which provides full-service and open-access clean room infrastructure for R&D in nanotechnology. Erwin received his M.Sc. and Ph.D. degree (cum laude) in Applied Physics from the TU/e in 1996 and 2000, respectively. His doctoral thesis work was partly...
carried out at the University of California Santa Barbara, and as a postdoc, he was affiliated to the Colorado State University and Philips University in Marburg (Germany). In 2007, the American Vacuum Society awarded him the Peter Mark Memorial Award for "pioneering work in the application and development of in situ plasma and surface diagnostics to achieve a molecular understanding of film growth." In recognition of his research, he received a NWO Vici grant in 2010 to set up a large research program on "nanomanufacturing" in order to bridge the gap between nanoscience/nanotechnology and industrial application. His research interests cover the field of synthesis of ultra-thin films and nanostructures using methods such as (plasma-enhanced) chemical vapor deposition (CVD) and atomic layer deposition (ALD) for a wide variety of applications, mostly within nanoelectronics and photovoltaics. Within the field of ALD, he has contributed to the field most prominently by his work on plasma-assisted ALD and his research related to ALD for photovoltaics. Erwin was one of the two chairs of the International Conference on Atomic Layer Deposition in 2008. Erwin has published over 170 papers with over 80 papers in the field of ALD.

Markku Leskelä has been a professor of inorganic chemistry at University of Helsinki since August 1990. He received his M.Sc. and Ph.D. degrees from Helsinki University of Technology. From 1979 to 1986, he worked as associate professor in University of Oulu and from 1986 to 1990 as professor in University of Turku. He has worked as visiting scientist/professor at University of Utrecht 1983, University of Florida 1987–88, and R&M Curie University 1999. During 2004–2009, he acted as Academy Professor funded by Academy of Finland. His research activities covers several topics including chemical fabrication of films and other nanostructured materials with emphasis in Atomic Layer Deposition and catalysis focused on activation of small molecules by metal complexes. He has co-authored more than 600 publications in peer-reviewed journals and holds several patents.

Paul Poodt is the senior scientist and program manager Spatial ALD at Holst Centre and TNO in Eindhoven, the Netherlands. He received his M.Sc. degree in chemistry in 2003 and his Ph.D. degree in physics in 2008 from the Radboud University Nijmegen. In 2008, he joined the Netherlands Organization for Applied Scientific Research (TNO) in Eindhoven, working on thin film deposition for solar cell applications. In 2009, he started in TNO’s spatial ALD group as lead process scientist, and in 2013, he became program manager Spatial ALD at Holst Centre.

Mikko Ritala is a professor of inorganic materials chemistry at University of Helsinki. He received his M.Sc. degree in 1991 from University of Turku and Ph.D. degree in 1994 from University of Helsinki, both in inorganic chemistry. During 1995–2003, he worked at University of Helsinki, first as a postdoctoral researcher and then as an academy research fellow, both posts granted by Academy of Finland. In 2003, he was nominated as a professor of inorganic materials chemistry at University of Helsinki. His main research activity is in Atomic Layer Deposition (ALD) of thin films for microelectronics and other applications. Another research area is preparation of nanostructured materials by, for example, templating with ALD and electrodeposition, and electrospinning of nanofibres. Mikko Ritala has published over 380 papers and holds several patents. In 2007, he was nominated as ISI Highly Cited Author in the field of materials science. He received Alfred Kordelin Foundation award in 2010.

Stephen M. Rossnagel has been a Research Staff Member at the IBM Thomas J. Watson Research Center in Yorktown Heights, New York since 1983. His most recent work has been with nanopores (in Si devices) for DNA sequencing and a new area known as piezotronics. Prior work centered on materials and process technology for interconnect and packaging applications, based mostly on PVD and ALD. He has been instrumental in various innovations in sputtering, including inventing hollow cathode-enhanced magnetrons and collimated sputtering, understanding gas rarefaction, the development of ionized magnetron sputtering, or I-PVD (1990s), and more recently, plasma-enhanced ALD (2000–). Steve was awarded the AVS Peter Mark Memorial Award in 1990, was made an AVS Fellow in 1994, and was awarded the Bunshah Award at the ICMCTF in 2008. Prior to IBM, Steve was at Penn State University (B.S. and M.S.) followed by work at Princeton with plasma-surface interactions. He returned to graduate school at Colorado State University, receiving his Ph.D. in 1982. Steve has published more than 185 papers and chapters, been awarded nearly 50 patents, and edited 7 books. Steve is editor-emeritus of the Noyes Materials Science Series and of the Physics of Thin Films Series (Academic). He has served as an Associate Editor and Head of the Editorial Board for JVST. Steve was the Chair of the 1996 AVS Annual Symposium, Chair of the Publications Committee overseeing JVST from 1991–1995, in which time he instituted the switch to CD-ROM publishing, a full electronic page, and other various improvements. He has served as a member of the Board of Directors (1991–1992), the Long Range Planning Committee, and has also been active in various division committees, serving as PSTD Chair in 1990 and on the Executive Committee of the Thin Films Division for the past several years. Steve was the Program Chair of the 1990 ICMC and ICTF. He joined AVS as a student in the mid-1970s and served as AVS President in 1999 and Treasurer from 2007 to 2012.