REVIEW ARTICLE

# Review Article: Recommended reading list of early publications on atomic layer deposition—Outcome of the "Virtual Project on the History of ALD"

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Atomic layer deposition (ALD), a gas-phase thin film deposition technique based on repeated, self-terminating gas–solid reactions, has become the method of choice in semiconductor manufacturing and many other technological areas for depositing thin conformal inorganic material layers for various applications. ALD has been discovered and developed independently, at least twice, under different names: atomic layer epitaxy (ALE) and molecular layering. ALE, dating back to 1974 in Finland, has been commonly known as the origin of ALD, while work done since the 1960s in the Soviet Union under the name "molecular layering" (and sometimes other names) has remained much less known. The virtual project on the history of ALD (VPHA) is a volunteer-based effort with open participation, set up to make the early days of ALD more transparent. In VPHA, started in July 2013, the target is to list, read and comment on all early ALD academic and patent literature up to 1986. VPHA has resulted in two essays and several presentations at international conferences. This paper, based on a poster presentation at the 16th International Conference on Atomic Layer Deposition in Dublin, Ireland, 2016, presents a recommended reading list of early ALD publications, created collectively by the VPHA participants through voting. The list contains 22 publications from Finland, Japan, Soviet Union, United Kingdom, and United States. Up to now, a balanced overview regarding the early history of ALD has been missing; the current list is an attempt to remedy this deficiency. 
[http://dx.doi.org/10.1116/1.4971389]

## I. INTRODUCTION

Atomic layer deposition (ALD), a gas-phase thin film deposition technique based on repeated, self-terminating gas–solid reactions, has become the method of choice in semiconductor manufacturing and many other technological areas for depositing thin conformal inorganic material layers for various applications.[1–8] ALD has been discovered and developed independently at least twice under different names: molecular layering (ML) since the 1960s in the Soviet Union and atomic layer epitaxy (ALE) since 1974 in Finland. ALE is commonly known as the origin of ALD,[1–4,6,8] while the work made under the name ML has remained relatively poorly known and cited.[2,4,6]

A volunteer-based effort called virtual project on the history of ALD (VPHA) was launched in 2013 to make the early days of ALD more transparent. The invitation to participate in VPHA has been openly available since July 25, 2013, and is appended as supplementary material to this article.[9] Some previous knowledge of ALD and the ability to work in an atmosphere of openness, respect, and trust have been the requirements for participation in VPHA as a volunteer.[9] At the time of writing this manuscript, 73 persons from 21 countries in four continents have volunteered in VPHA. The main activity of VPHA has been to collect, read, and publicly share personal "comments" on early ALD works.[9] To define the time limit of "early," we chose to end it in year 1986, when a review article on ALE was written by authors other than the first pioneers of ALD themselves.[10] The ALD history activities leading to VPHA were triggered by discussions in professional social media in May 2013.[11] VPHA, in essence, continues the earlier ALD history activities of one of the current authors, whose results were published in a review article in 2005.[2] The earlier ALD history activities, in turn, had been motivated by the notion in a book chapter from 2002 that ML was an alternative name to ALD that "dates back to old Russian literature";[1] and a communication from 2002 entitled "Early work on atomic layer deposition cited."[12]

To-date, VPHA has resulted in four general conference presentations (Baltic ALD 2014; two presentations at ALD 2014; ALD 2016),[13–16] an exhibition on the 40 years of ALD in Finland (FinALD40),[17] two essays in the Chemical Vapor Deposition journal on ALE (Ref. 18) and ML,[19] and updates regarding the historical description in ALD-related pages in Wikipedia.[20–23] Several organizational presentations have also been made at various conferences (ALD Russia 2015, Baltic ALD 2015, HERALD COST network Helsinki 2014 workshop, Baltic ALD 2016).[24–27] An ALD history tutorial has been given at ALD 2014 (Ref. 28) and an invited plenary talk delivered at ALD 2016.[29] A website vph-ald.com has been set up as a central information hub of VPHA,[30] accompanied by a separate blog to facilitate efficient communication.[31]

This article continues from the VPHA poster presentation at the 16th International Conference on Atomic Layer Deposition, Dublin, Ireland, July 24–27, 2016,[16] which presented a "recommended reading list of early ALD publications." The recommended reading list has been created collectively through open voting among the VPHA volunteers; 30 out of the then-70 VPHA contributors participating in the voting. In addition to reporting the VPHA voting result in a condensed table format, the recommended reading list is presented chronologically in this article along with a dedicated description of the significance of each of the listed publications.

## II. METHODS

### A. VPHA's ALD-history-evolving-file

An openly accessible, cloud-based document called ALD-history-evolving-file has functioned as the core of the cocreation in VPHA.[32] This file contains the following parts:

Introduction and invitation to participate in VPHA, Instructions on how to participate in VPHA, List of early literature on ALD, with comments on the significance of the works by individual contributors and List of contributors. ALD-history-evolving-file has evolved continuously with time since the start of VPHA in July 2013. At the time of writing this communication on September 27, 2016, ALD-history-evolving-file contained references to 366 early ALD publications and 888 individual comments made on them by 73 volunteer contributors. "Early" has been defined to refer to publications up to the year 1986, as explained in the Introduction.

### B. VPHA voting

The voting rules as of May 8, 2016, were as follows (some typographical errors have been corrected):

(1) Each VPHA coauthor may vote
   - If you want to vote but are not yet a VPHA coauthor, please first become a coauthor by leaving at least one comment in ALD-history-evolving-file.
(2) Each VPHA coauthor can distribute up to 20 points to early ALD publications. One can also use less than 20 points.
(3) One can give up to three points to each publication. Thus, one can also give two or one point to each publication.
(4) To decide the result, the publications will be ordered on the basis of points received.
(5) The top ranked publications will form the "conclusive recommended reading list" for the VPHA poster at ALD 2016 Ireland.
(6) Voting is made under one's own name.
(7) Voting is open until June 15, 2016. Until then, one can update and modify one's own vote.

## III. RESULTS

### A. VPHA voting outcome

In total, 507 votes were counted in the VPHA voting by 30 volunteers. The spread in votes was large: 131 individual publications received at least one vote. In order to create a short list of 20–30 significant publications, the cut-off criterion for including an individual publication in the final list was that at least four people had recommended this publication in their voting by giving one or more points to it.

The voting resulted in a list of 22 publications, which all received at least four votes. The 22 publications[10,33–53] are listed in Table I, ordered according to the number of votes they received.

### B. Recommended reading list of early ALD publications

For a researcher interested in the origins of ALD, the outcome of the voting can serve as a good starting point: this collection of publications can with justification be regarded as a recommended reading list. We have in this subsection organized the recommended reading list chronologically and provided a brief description of each publication. The descriptions have been formulated on the basis of the comments in the VPHA's ALD-history-evolving-file[32] at the time of writing this manuscript. The main difference between these descriptions and the comments in the ALD-history-evolving-file is that the current descriptions are not only a single person's opinions as they have been collectively reviewed by the coauthors of this article.

In the descriptions, we have used the authors' notation of their techniques: ALE as used by the research emanating from the invention of Suntola[18] and ML from the invention of Aleskovskii and Koltsov.[19]

#### *1. Some characteristics of molecular layering reactions, Aleskovskii and Koltsov, 1965*

This is a half-page abstract by Russian authors of a local meeting in Leningrad, USSR (currently St. Petersburg, Russia), written in Russian.[51] The abstract discusses the regularities of the mechanisms of reactions of reactants with three ligands (e.g., $SiHCl_3$, $AlCl_3$), four ligands (tetrahalogenides of Group 14 elements), or five ligands (pentahalogenides of Sb or P) with hydroxylated silica. During reaction with the support, the reactant with three ligands $RX_3$ forms two bonds, while the reactant with four ligands $RX_4$ forms two or three bonds. The functionality (number of bonds formed during reaction with silica) of the reactant with five ligands $RX_5$ was not communicated in the abstract; the authors just state that they investigated it. Regarding the $RX_4$-type compounds (commonly written today as $ML_4$, i.e., metal with four ligands), it is mentioned that the reaction product depends on the quality and structure of the pre-existing "layer" (layer within quotation marks in the original publication as well). The term "molecular layering" (Молекулярное наслаивание, transliterated as molekulyarnoye naslaivanie) is introduced. There are no indications of ALD cycles in the work, but the reference to a pre-existing layer suggests that multiple cycles may have been made.

#### *2. Interaction of titanium and germanium tetrachlorides with hydrated silica, Shevjakov et al., 1967*

This is a conference proceedings paper by Russian authors, dating from a conference in 1965, originally published in Russian (1967), and thereafter translated and published in English.[38] All the basic practical requirements of ALD can be identified: separate, saturating chemisorption reactions of $TiCl_4$ and $H_2O$ or $GeCl_4$ and $H_2O$, absence of physical adsorption, purging of the reaction by-products by inert gas (in their case, $O_2$), and repeated reaction cycles (up to ten for $TiCl_4$-$H_2O$ to make $TiO_2$). Cycles are denoted as "exposure-purging-hydrolysis-drying," and this sequence is repeated. Silica gel was treated with $TiCl_4$ and $GeCl_4$ at 180 °C in air (pressure was not mentioned) and after the treatment the surface was treated with water vapor as long as HCl was released. This treatment (cycling) was repeated ALD-wise up to ten times. The products were characterized by elemental analysis, XRD, and IR spectroscopy. The amount of Ti and Ge increased with the number of ALD cycles, while the mass-percent increment decreased with the cycles (this is as expected for the coating of porous materials[2]). XRD showed

TABLE I. Outcome of the voting: 22 significant early publications on ALD. Please see the list of references for full bibliometric details.

| Title | Authors | Year published | Reference | Points in the voting | Number of votes |
|---|---|---|---|---|---|
| Method and apparatus for the growth of compound thin films | Suntola and Antson | 1976[a] | 33 | 34 | 16 |
| Atomic layer epitaxy | Suntola and Hyvärinen | 1985 | 34 | 27 | 14 |
| Chemistry and technology of solids | Aleskovskii | 1974 | 35 | 26 | 14 |
| Method and equipment for deposition of compound thin films | Suntola *et al.* | 1980[b] | 36 | 22 | 13 |
| Atomic layer epitaxy | Goodman and Pessa | 1986 | 10 | 22 | 12 |
| Synthesis of solids by the molecular layering method | Koltsov | 1971 | 37 | 18 | 9 |
| Interaction of titanium and germanium tetrachlorides with hydrated silica | Shevjakov *et al.* | 1967 | 38 | 14 | 10 |
| Atomic layer epitaxy of III–V binary compounds | Bedair *et al.* | 1985 | 39 | 11 | 9 |
| Atomic layer epitaxy for producing EL thin films | Suntola *et al.* | 1980 | 40 | 11 | 7 |
| Preparation and investigation of the products of interaction between titanium tetrachloride and silica gel | Koltsov | 1969 | 41 | 10 | 6 |
| Chemical assembly of materials | Aleskovskii | 1975 | 42 | 9 | 5 |
| Synthesis and study of oxide coatings obtained by molecular layering on semiconductor surfaces | Drozd | 1978 | 43 | 9 | 5 |
| Formation of a silica layer of predetermined thickness on silicon by the molecular-layering method | Sveshnikova *et al.* | 1970 | 44 | 9 | 4 |
| Atomic layer epitaxy | Suntola | 1981 | 45 | 8 | 4 |
| Possibility of the use of a gravimetric method for studying the process of molecular layering in disperse silica samples | Tolmachev | 1982 | 46 | 7 | 6 |
| Interaction of titanium tetrachloride with hydroxylated silicon surfaces | Sveshnikova *et al.* | 1970 | 47 | 7 | 5 |
| Molecular layer epitaxy | Nishizawa *et al.* | 1985 | 48 | 7 | 5 |
| Preparation and investigation of the chemical composition of the products formed by successive chemisorption of titanium and phosphorus chlorides on the surface of silica gel | Koltsov *et al.* | 1969 | 49 | 6 | 5 |
| Quantum chemical studies of the formation of zinc sulfide surface by the ALE technique | Pakkanen *et al.* | 1984 | 50 | 5 | 5 |
| Some characteristics of molecular layering reactions | Aleskovskii and Koltsov | 1965 | 51 | 5 | 4 |
| A study of ZnTe films grown on glass substrates using an atomic layer evaporation method | Ahonen *et al.* | 1980 | 52 | 5 | 4 |
| Measuring thicknesses of ultrathin silicon oxide films deposited by molecular layering on the surface of single crystal silicon using polarization method | Sveshnikova *et al.* | 1969 | 53 | 4 | 4 |

[a]Patent priority date November 29, 1974.
[b]Patent priority date February 28, 1979.

anatase reflections after four cycles and $GeO_2$ reflections after six cycles. In IR, vibrations belonging to $TiO_2$ and $GeO_2$ can be seen in samples with the thickest films.

### 3. Preparation and investigation of the products of interaction between titanium tetrachloride and silica gel, Koltsov, 1969

This journal article by a Russian author was originally published in Russian in 1969, and thereafter translated and published in English.[41] In the Introduction, Koltsov describes the then-current knowledge on the molecular layering chemistry from metal chlorides and hydroxylated silica gel. He describes the formation of metal–oxygen bonds, the formation of HCl byproducts and the possibility of rehydroxylating the surface by water vapor. Also, the inaccessibility of OH groups in narrow pores is discussed. In the article, experimental results for ten cycles of $TiCl_4$-$H_2O$ made at 180 °C are shown. An expression was derived to calculate the $SiO_2$ content in a sample after a predetermined number of cycles, for the correct evaluation of the stoichiometry of reaction products. Calculated values were found to be in good agreement with the experimental data. The mechanism of reactions occurring during repeated exposures to $TiCl_4$ and $H_2O$ was investigated by chemical analysis of the reaction products. It was found that during the formation of the second layer, $TiCl_4$ molecules reacted both with either one or two hydroxyl groups; starting from the third layer $TiCl_4$ molecules reacted predominantly with two hydroxyl groups. HCl was identified as the only reaction by-product. The O/Ti ratio was found to increase from 1.5 to 2 with the increasing number of cycles, which corresponds to the formation of stoichiometric $TiO_2$. The

presence of anatase in the reaction products was confirmed using IR spectroscopy and XRD, where data obtained from the samples were compared to those obtained from commercial and/or synthesized anatase phase $TiO_2$. The author also pointed out that four Ti atoms were needed for the formation of the $TiO_2$ unit cell; therefore, XRD lines corresponding to the anatase phase appear only after four ML cycles.

### 4. Preparation and investigation of the chemical composition of the products formed by successive chemisorption of titanium and phosphorus chlorides on the surface of silica gel, Koltsov et al., 1969

This journal article by Russian authors, originally published in Russian in 1969 and thereafter translated and published in English, describes the use of molecular layering of oxide multilayers deposited in a predetermined sequence.[49] Using $TiCl_4$, $PCl_3$, and water on silica gel, the authors made $TiO_2/P_2O_5$ multilayers at 180 °C. After each stage of synthesis, the Ti, P, and OH content were determined. The authors present several reaction schemes and suggest mechanisms based on the chemical composition of the films. The paper shows that the Aleskovskii group had a good understanding of the types of films that could be deposited by ML and the level of precision that could be achieved.

### 5. Measuring thicknesses of ultrathin silicon oxide films deposited by molecular layering on the surface of single crystal silicon using polarization method, Sveshnikova et al., 1969

This is a one-page abstract by Russian authors of a local meeting in Leningrad, USSR, written in Russian.[53] This paper discusses thickness evaluation by an optical polarization technique of ultrathin $SiO_2$ films prepared by molecular layering on silicon. Deposition cycles of 10–70 exhibit a linear dependence of film thickness versus cycle number. Layers with a thickness between 5 and 100 Å were measured.

### 6. Formation of a silica layer of predetermined thickness on silicon by the molecular-layering method, Sveshnikova et al., 1970

This is a journal article by Russian authors, first published in Russian in 1970 and translated and published in English in 1970.[44] It reports the growth of $SiO_2$ on electrochemically polished single-crystal Si (111) from $SiCl_4$ and $H_2O$ at 500 and 180 °C. The number of cycles was varied from 10 to 60 in steps of ten for both temperatures, with several repetitions to check the reproducibility of the growth. The growth cycles are explained as follows: "Each layering cycle comprised four successive stages: (1) interaction of the hydroxylated surface with silicon tetrachloride; (2) removal of the hydrogen chloride formed and of unconverted $SiCl_4$; (3) hydrolysis of chlorinated surface groups by water vapor at 180 °C; (4) drying of the specimen at the same temperature." Curves of measured thickness versus cycles (i.e., growth curves) were plotted; the growth was linear. The $SiO_2$ thickness was determined by "*an optical polarization method with the aid of a polarization goniometer*."

### 7. Interaction of titanium tetrachloride with hydroxylated silicon surfaces, Sveshnikova et al., 1970

This is a brief journal article by Russian authors, first published in Russian in 1970 and translated and published in English in 1970.[47] It reports the growth of $TiO_2$ on single-crystal Si (111) surface from $TiCl_4$ and $H_2O$ reactants at 180 °C. Two different predeposition cleanings were made for the surface: specimens A, for which "SR-4 etchant" had been used (the etchant is not specified in this article, but it is concluded that OH groups were present on the surface, and Si was etched) and specimens B, which were cleaned by HCl, treated in a current of hydrogen, and hydrated for 30 min at 180 °C and dried for 1 h at 180 °C before the deposition. Electron diffraction patterns were used to follow the deposition, and polycrystalline $TiO_2$ was detected. It is mentioned that 12 cycles were carried out, and thickness was estimated to be 2–2.5 nm. The authors note that "*the structure of the titanium dioxide films formed depends on the preliminary treatment of the silicon single crystal surfaces*." Thus, the importance and effect of the surface preparation for ALD has been recognized in this work.

### 8. Synthesis of solids by the molecular layering method, Koltsov, 1971

This is a Doctor of Sciences (habilitation degree) dissertation by a Russian author S. I. Koltsov from the Leningrad Technological Institute by Lensovet, written in Russian.[37] This dissertation describes Koltsov's works during the very early days of molecular layering. The dissertation is based on the "framework" hypothesis proposed by V. B. Aleskovskii in 1952.[19] The doctoral dissertation of S. I. Koltsov consists of three parts: The first one is devoted to the peculiarities of the structure and reactivity of solids from the standpoint of the framework hypothesis. The second part deals with the polymer-analogous conversion of the xerogel of polysilicic acid with chlorides of different elements. The third part is devoted to the targeted synthesis of solids by ML. In the thesis, Koltsov formulated the principles of the ML method, proposed a classification of ML reactions and the types of surface structures, which can be produced using ML. Koltsov's thesis has for decades served as a core reference for the Russian ML scientists.

### 9. Chemistry and technology of solids, Aleskovskii, 1974

This is a review article written by a Russian author, published originally in Russian in 1974 and translated and republished in English in 1975.[35] The review reports sequential $SiO_2$ film saturating reactions and demonstrated nanolaminates ($SiO_2/TiO_2$) and outlined the strategy for applications to nanoscale devices; it has a broader scope than just molecular layering. The review reflects the vision of the Aleskovskii group(s), reviewing advances made by 1974 and predicting what could be achieved by molecular layering. Aleskovskii presents an early suggestion of surface-selective deposition: "*if necessary, part of its <i.e., support's> surface is shielded by flat (monolayer) or relief coating in the form of specified pattern*." He also notices the

possibility of using templates for growth "*at the end of the synthesis, the support is removed, if necessary, by chemical or mechanical methods*." He notices the possibility of fine regulation of pore size in sorbents and concludes that ML works in a similar manner on single crystals (e.g., silicon, germanium), porous materials (e.g., silica gel, carbon), and fine powders (e.g., talc, kaolin, aerosil). He notices, using several examples, that four to six "monolayers" (the name he used for ML cycles) are needed for the material to reach the properties that the solid material would have. He describes the deposition of ternary materials ($TiO_2$ and $PO_x$ combined as a mixed oxide) where the sequence of depositions in total of four ALD cycles (14 possible combinations of cycles, all synthesized) influences the catalytic activity of the system. Striking is Aleskovskii's comment on the potential applications of ML in the down-scaling of semiconductor technology: "*The route to further miniaturization of microelectronic devices and to molecular electronics is evident*."

### 10. Method and apparatus for the growth of compound thin films, Suntola and Antson, 1976

This is a patent publication by Finnish researchers from Instrumentarium Oy, originally published in Finnish and Swedish and at a later stage in many other languages, including English, German, Russian, and Japanese.[33] This patent is the first ALE patent by Suntola, priority date November 29, 1974, published in 1976, and it has been granted in over 20 countries.[18] The patent describes the principle of ALE using elements as source materials to deposit highly oriented, stoichiometric compound thin films. In the deposition, the substrate is alternatively exposed to the vaporized elements (e.g., Zn and S) and the growth proceeds atomic layer by atomic layer. The temperature is set so that only one atomic layer is reacting on the surface and no condensation of the elements occurs. Further, the patent presents an apparatus for carrying out the method of the invention. In the basic concept, the vacuum reactor is based on a rotating disk on which the substrates are mounted and above or below which the vapor sources of the elements are placed. A few alternative designs are also presented: stationary substrates and moving vapor sources, different reaction chambers for the two half-reactions, and vapor sources placed outside of the reactor. In examples, the growth of ZnS, $SnO_2$, and GaP from the respective elements is described. Interestingly, the $H_2S$ molecule is presented as an alternative source chemical to elemental sulfur. Description of further details of the work leading up to this patent can be found in Ref. 18.

### 11. Chemical assembly of materials, Aleskovskii, 1975

In this review article published in Russian, the author starts with describing the nature of chemical assembly and gives examples of chemical reaction with silica gel surfaces and $TiCl_4$.[42] He mentions that such a modified surface is easily hydrated with water vapor, which completes the ML cycle. He describes the alternating of the cycles to achieve monolayer by monolayer growth. He writes that a number of different chlorides have been already used for growth: titanium, germanium, tin, phosphorus, aluminum, iron, vanadium, and chromium chlorides. Also, other reactions can be used for ML growth: reactions that release hydrides, polymerization reactions, and reactions of molecular sorption of halides. The accuracy of the method is discussed: one monolayer of the material per cycle and linear character of the growth. The possibility of density modification of films by varying the growth temperature is described. Deposition of multilayer structures is mentioned, for example, alternating layers of phosphorus oxide and titanium dioxide.

### 12. Synthesis and study of oxide coatings obtained by molecular layering on semiconductor surfaces, Drozd, 1978

This is a Ph.D.-equivalent "candidate of sciences" thesis by a Russian author V. E. Drozd from Leningrad Technological Institute by Lensovet, written in Russian.[43] The work has been made under the guidance of Professor Aleskovskii and Dr. Koltsov on the research area of semiconductor and dielectric physics. The thesis describes the main aspects of the ML method and the tools used for the growth of dielectric oxides by ML on planar substrates, as well as growth and electrical characterization results. Earlier work on ML had been made for porous substrates at atmospheric pressures using long purge times of $>2$ h for one cycle. A hot-wall vacuum reactor built by Drozd increased the rate of the process by 100 times on planar substrates, at the same time enhancing the quality of the film. Drozd's reactor was equipped with "a programmable unit;" the reactant delivery valving was automated. The thesis presents growth of many oxides from the respective chlorides and water by ML: titanium, vanadium, chromium, zirconium, niobium, molybdenum, hafnium, tantalum, and tungsten, as well as multilayers of titanium and chromium oxides. Germanium and silicon were used as substrates; thicknesses of the coatings ranged from 0.6 to 5 nm. Current–voltage characteristics were evaluated for Schottky diodes made on Si with ML-made oxide dielectrics and Al contacts.

### 13. Method and equipment for deposition of compound thin films, Suntola et al., 1980

This patent application (priority date February 28, 1979) by Oy Lohja Ab and Finnish researchers was originally published in Finnish and later translated to several other languages, including English and Russian.[36] The patent has been granted in many countries, and is the basic patent for flow-type ALE reactors which later have been used both in industry and academia in large and small scale reactors. The patent presents a method and an apparatus for performing growth of compound thin films by alternately repeating separate surface reactions of the substances comprising the compound. A carrier gas acts as a barrier between the surface reaction steps to separate them from each other, and also to separate the precursor vapors from each other in the delivery lines ("inert gas valving"). The figures in the patent present cross-sections from different reactor designs, details for the source chemical tube, principle of spatial ALE, electrical characteristics of $Al_2O_3$ thin film, cross-section of an

electroluminescent device, and EL characteristics of the device. Examples presented in the patent show $Ta_2O_5$, ZnS, $Ta_2O_5$/ZnS(Mn), and $Al_2O_3$ growth by ALE from the respective metal chlorides and $H_2O$ or $H_2S$.

### 14. Atomic layer epitaxy for producing EL thin films, Suntola et al., 1980

This is a Society for Information Display international symposium digest paper by Finnish authors published in English.[40] The paper is related to the first public demonstration of the thin-film electroluminescent displays made with ALE. The paper is a two-page extended abstract. It briefly introduces and explains the principle of ALE and the ALE growth of ZnS from $ZnCl_2$ and $H_2S$, and shows voltage–luminance data for an ALE-EL device (36 $mm^2$ area). Key properties of ALE are mentioned such as: self-saturation, layer-by-layer deposition, temperature dependency, and uniformity on three-dimensional structures. The demonstration was a sensation and 3000–4000 product requests came after the conference, according to Suntola.[18]

### 15. A study of ZnTe films grown on glass substrates using an atomic layer evaporation method, Ahonen et al., 1980

This is a journal article by Finnish authors published in English.[52] This publication is the first peer-reviewed scientific article on ALE. Instead of epitaxy, the term "atomic layer evaporation" is used in this work. In the experimental section, the authors describe the growth of ZnTe films using zinc and tellurium bars as sources for growth on an amorphous glass substrate, in a growth chamber that is "*essentially the same as used in the MBE apparatus*" [molecular beam epitaxy (MBE)]. Layers up to 1500 nm thickness were grown at 593–673 K. Films were crystalline and compared to MBE, less dependent on the growth conditions. The authors suggest an island growth mechanism.

### 16. Atomic layer epitaxy, Suntola, 1981

In this two-page conference abstract in English, Suntola describes the basic principles of ALE. He distinguishes ALE from other thin film deposition techniques saying that it is surface-controlled while conventional techniques are controlled by the rate of the source.[45] Suntola mentions that instead of using element vapors, more volatile compounds of these atoms can be used to obtain more favorable conditions for ALE. At the end of the paper, Suntola explains where the name atomic layer epitaxy comes from—the use of word "epitaxy" had created a lot of discussion and even criticism.

### 17. Possibility of the use of a gravimetric method for studying the process of molecular layering in disperse silica samples, Tolmachev, 1982

This one-and-half page journal article by a Russian author was originally published in Russian (1982) and translated and published in English (1982).[46] In this paper, the mass evolution during ML was followed *in situ* on porous high-surface-area substrates. The author used a vacuum microbalance with quartz springs and deposited $TiO_2$ at 180 °C. A linear dependence of the increase in the weight of the layer synthesized on the number of cycles was observed. The author noted that the gravimetric method permits the quantitative monitoring of the course of the reaction with steam in each cycle, i.e., the decrease in weight of the sample as a consequence of the replacement of chlorine atoms by hydroxyl groups. A deviation from linearity (saturation behavior) was noted when the substrate contains pores, where the growing film eventually seals the pore resulting in a saturation effect in the plot of mass uptake versus number of cycles.

### 18. Quantum chemical studies of the formation of zinc sulfide surface by the ALE technique, Pakkanen et al., 1984

This is a conference proceedings paper by Finnish authors written in English, from a conference in 1984 in Espoo, Finland.[50] This publication reports of theoretical *ab initio* Hartree–Fock modeling of ZnS by ALE using $ZnCl_2$ and $H_2S$ chemicals. "*A maximum growth rate of one layer with three $ZnCl_2$-$H_2S$ cycles*" is concluded on the basis of the modeling.

### 19. Atomic layer epitaxy, Suntola and Hyvärinen, 1985

This is a review article by Finnish researchers, published in English.[34] It gives an interesting view on the development of ALD from the ALE perspective and a snapshot of ALE research in 1985. Early ALE reactor types are schematically shown and explained: first, the rotary reactor with which the ALE concept was demonstrated; then, the flow-type reactor used with compound reactants; and third the modified ultra-high vacuum MBE reactor, with which the first scientific ALE growth studies were carried out in Tampere, Finland. The term "growth rate" is used for the amount of material deposited per cycle ["growth per cycle"[2] (GPC) is not used]. It is noted that in ALE, only two-dimensional nucleation takes place. The on-going modeling of the ZnS process by Pakkanen and coworkers[50] is mentioned together with plans for *in situ* mass spectrometry measurements, to confirm the modeling results. An interesting statement is that "the temperature range between $T_A$ and $T_D$ is the actual ALE growth range because between these temperatures the molecules can adsorb, but will not desorb from the surface." By ALE, mainly hexagonal ZnS is obtained at 500 °C, although typically, the hexagonal phase transition temperature is around 1000 °C. The thickness of the "poor crystallinity region" in ZnS-Mn is reported as 35–50 nm. This is one third of the value reported for conventional deposition methods, which is an important factor for EL efficiency. Several oxide ALE processes are mentioned: $Al_2O_3$ process from $AlCl_3$/$H_2O$ (works at 200–600 °C) used to grow ion barriers, dielectrics and passivation films; $Ta_2O_5$ reaction mechanism investigation; $Al_2O_3$–$TiO_2$ mixture as a dielectric; $Ta_xTi_yO_z$ mixed dielectric; and $In_2O_3$-$SnO_2$ (ITO) as a transparent conductor. The growth of II–IV compounds, e.g., CdTe and $Cd_{(1-x)}Mn_xTe$, in Tampere on single crystal substrates is reviewed. The operation principle and structure of the ALE EL devices are explained. Also the GaAs works started by

Nishizawa of Tohoku University, Japan, are mentioned. "Nishizawa uses photo energy to overcome a reaction threshold that would otherwise require too high a temperature for the GaAs material itself." In addition, Suntola and Hyvärinen predict the coming of plasma ALD: "The use of extra energy in the form of light emission or plasma can make new reactant compounds possible at lower temperatures, and can widen the selection of materials that can be grown with ALE."

### *20. Atomic layer epitaxy of III–V binary compounds Bedair et al., 1985*

This is a journal paper by American authors, published in English, reporting on the ALE of III–V compounds.[39] For the deposition of GaAs, $AsH_3$ and $Ga(CH_3)_3$ were used as precursors and AlAs was deposited using $AsH_3$ and $Al(CH_3)_3$. The carrier gas was $H_2$. One hundred cycles of GaAs were grown at 560–600 °C, with 10 s cycle time. The ALE GaAs layer was sandwiched between metal-organic chemical vapor deposition (MOCVD) grown $GaAs_{1-x}P_x$ films for characterization. AlAs film was correspondingly sandwiched between MOCVD grown GaAs layers for characterization. The film quality was characterized by photoluminescence emission measurements and TEM studies, which proved the grown films to be single crystal GaAs and AlAs. A growth rate of 8 and 3 Å/cycle are reported for GaAs and AlAs, respectively. The reactor developed for this resembles Suntola's original rotating-disk spatial ALD reactor.[33] An inert gas (in this case hydrogen) tube was positioned between the precursor inlet tubes to prevent the mixing of the precursor gases. The authors interestingly call the deposition method MOCVD and state that ALE of GaAs and AlAs has now been first time demonstrated by MOCVD.

### *21. Molecular layer epitaxy, Nishizawa et al., 1985*

This is a journal paper by Japanese authors, published in English.[48] The authors grew homoepitaxial GaAs film using alternative injection of $AsH_3$ and $Ga(CH_3)_3$ onto the heated GaAs substrate under a moderate pressure of $10^{-3}$–$10^{-2}$ Pa, and refer to the technique as molecular layer epitaxy (MLE). The ALE technique of Suntola is mentioned in the Introduction where the difference between ALE and MLE is pointed out: the authors want to call the process ALE if the "specific atomic elements" are used as source material while it is called MLE if "gas molecules containing the elements" are used as a source material. Later, Nishizawa acknowledged that ALE and MLE are the same technique (see Ref. 18). The authors compared their results with Suntola's earlier works on the ALE of CdTe and ZnTe, and MLE of polycrystalline ZnS and $Ta_2O_5$. They clearly observed saturation of growth rate (thickness/cycle) to a value slightly lower than the monolayer thickness (0.283 nm) for both $AsH_3$ and $Ga(CH_3)_3$ doses at 500 °C, suggesting the surface saturation behavior of ALD. They also observed that the growth at higher temperature (600 °C) induced almost linearly increasing growth rate with the increasing $Ga(CH_3)_3$ dose, so thermal decomposition occurred at that temperature. However, the films were excessively p-type doped, which is an unwanted aspect of the process. Photoirradiation improved the film quality and decreased the undesirable carrier density.

### *22. Atomic layer epitaxy, Goodman and Pessa, 1986*

This is a review article in English by a British and a Finnish author.[10] In this review, two ALE modes are distinguished; the MBE-type growth based on heated elemental source materials, and the chemical vapor deposition-type growth, relying on sequential surface exchange reactions between compound reactants. The authors state that ALE should not be considered as a new method but as a special mode of these well-established growth techniques. The term GPC may have been introduced for the first time in this work, as the authors write: "The formation of 'layer per cycle' is the specific feature that conceptually distinguishes the ALE mode from other modes of vapor phase deposition; the latter all give a growth rate, ALE gives growth per cycle." A list is given of the materials grown by ALE by that time: CdTe, $Cd_{(1-x)}Mn_xTe$, GaAs, ZnS, ZnTe, and oxides: ZnO from $Zn(CH_3COO)_2 + H_2O$; $Ta_2O_5$ from $TaCl_5/H_2O$; $Al_2O_3$ from $AlCl_3/H_2O$ (at ca. 450 °C), mixture of $Al_2O_3$-$TiO_2$, and $SnO_2$ from $SnCl_4/H_2O$; and ITO. The materials developed under the name ML were not included in the list, as the authors were not aware of them. Perhaps the most interesting part of this review is the outlook for future extensions of ALE to other materials. The authors proposed that following the general schemes metal halide + $H_2O$ or $O_2$ → oxide; metal halide + $H_2S$ or sulfur vapor → metal sulfide; metal halide + $H_2Se$ or selenium vapor → metal selenide, one can preview a long list of new compounds, as many chlorides will most likely work in ALE similarly to the chlorides already used: $CdCl_2$, $HgCl_2$, $CaCl_3$, $InCl_3$, $SiCl_4$, $GeCl_4$, $ZrCl_4$, $NbCl_5$, and also other transition metal halides, e.g., $FeCl_3$. Thus, the processes for the future high-k materials were largely foreseen. Metalorganics (TMGa, TEGa, TMAl) were commented upon as new development, but a note of caution was given related to the thermal stability. $NH_3$, $PH_3$, and $AsH_3$ were also pointed out as pathways to nitrides, phosphides, and arsenides. Finally, more complex materials were envisioned, such as ferrites with special magnetic properties, multilayers with ferrites combined with nonmagnetic films giving "two-dimensionality" on magnetic properties. Also, the growth of elements such as silicon was foreseen.

## IV. DISCUSSION

The outcome of the voting, performed in the framework of the VPHA, has yielded a collection of 22 documents out of >350 candidates on the early history of ALD. We have called this collection the recommended reading list of early ALD publications. It gives a brief chronological overview of the development of ML in the 1960s in the Soviet Union, of ALE in Finland in the 1970s, and the start of ALD spreading around the world. In addition to the listed publications, for those wanting a quick overview of the initiation of the field, we recommend the two essays resulting from VPHA: one on ML (Ref. 19) and one on ALE.[18]

The recommended reading list of early ALD publications comprises abstracts, full original research articles, review papers, patents, and academic theses. Two academic theses,[37,43] one journal article,[42] and two meeting abstracts[51,53] are only available in Russian; all other listed publications are available in English. The earliest item in the recommended reading list is the conference abstract from 1965, where the name molecular layering was proposed.[51] The first publication on "atomic layer epitaxy" in the patent from 1974, which gained the most points during the generation of the recommended reading list by voting, appears roughly in the middle of the chronological list.[33] The latest item in the recommended reading list is the review article published on ALE in 1986 by scientists other than the technique's first pioneers[10]—coincidentally, the review article which has been chosen to define the end year of VPHA. It is remarkable how already decades ago several authors recognized the potential impact of ALD.

The recommended reading list of early ALD publications is concise. While the brevity is advantageous for grasping a quick overview of the subject, many significant ALD publications did not make it to the recommended reading list created in the VPHA voting. In addition to those mentioned in the list, other noteworthy publications from the time period considered in VPHA, where a specific topic has been reported/proposed presumably for the first time, are at least the following: catalysts by ALD from 1972,[54] geometrical modeling of surface site filling during ALD from 1975,[55] particle coating in a fluidized bed from 1979,[56] ALD with an electric field to guide the growth from 1981,[57] quantum chemical modeling from 1983,[58] amine-catalyzed $SiO_2$ ALD from 1984,[59] ALD on polymers from 1984,[60] and the proposal of photo ALD from 1984.[61]

Some words of caution are necessary regarding the usage of the list published in this work. The methodology of voting used to compose the list is to a certain degree arbitrary; the results depend on who participated on the voting. Also, the voting was made with a deadline at a time when the core work of VPHA—the listing, reading and commenting of early ALD publications—was not completed. Despite these limitations, we believe that with 30 voters who have read through many historical ALD papers before voting, we have compiled a meaningful list that reflects the main developments in the first decades of ALD.

## V. SUMMARY AND CONCLUSIONS

In this work, we have described the creation and contents of a recommended reading list of early ALD publications, an outcome of VPHA, the virtual project on the history of ALD. This work expands the contents of the poster presented at the 16th International Conference on Atomic Layer Deposition, Dublin, Ireland, July 24–27, 2016.

The earliest publication in the list dates from 1965 and the last from 1986, which is the last year considered in VPHA. The list contains publications from Finland, Japan, Soviet Union, United Kingdom, and United States. The most frequent names appearing in the list are the core pioneers of ALD: Aleskovskii, Koltsov, and Suntola. The listed publications are available in English, except that two abstracts, one article, and two theses are in Russian.

The recommended reading list of early ALD publications, created through voting and published in this article, is a step forward in understanding the early history of ALD and describing both early development routes (ALE, ML) simultaneously. We hope that this list provides a starting point for people new to the field of ALD, as well as for researchers with more experience in ALD who want to increase their knowledge about the early days of the technique.

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