

Virtual Project on the History of ALD in perspective: past, present, and final steps

R.L. Puurunen,^a Yu. Koshtyal,^b J. Sundqvist,^c
J.R. van Ommen,^d O. Yurkeviche^e

^aAalto University, Finland, ^bIoffe Institute, Russian Federation, ^cLinköping University, Sweden, ^dTU Delft, The Netherlands, ^eCIC nanoGUNE BRTA, Spain

ALD Russia 2021
<http://technolog.edu.ru/aldrussia/>
Saint Petersburg, Russia
27–30 September 2021, with online participation

Atomic
Layer
Deposition
Russia 2021

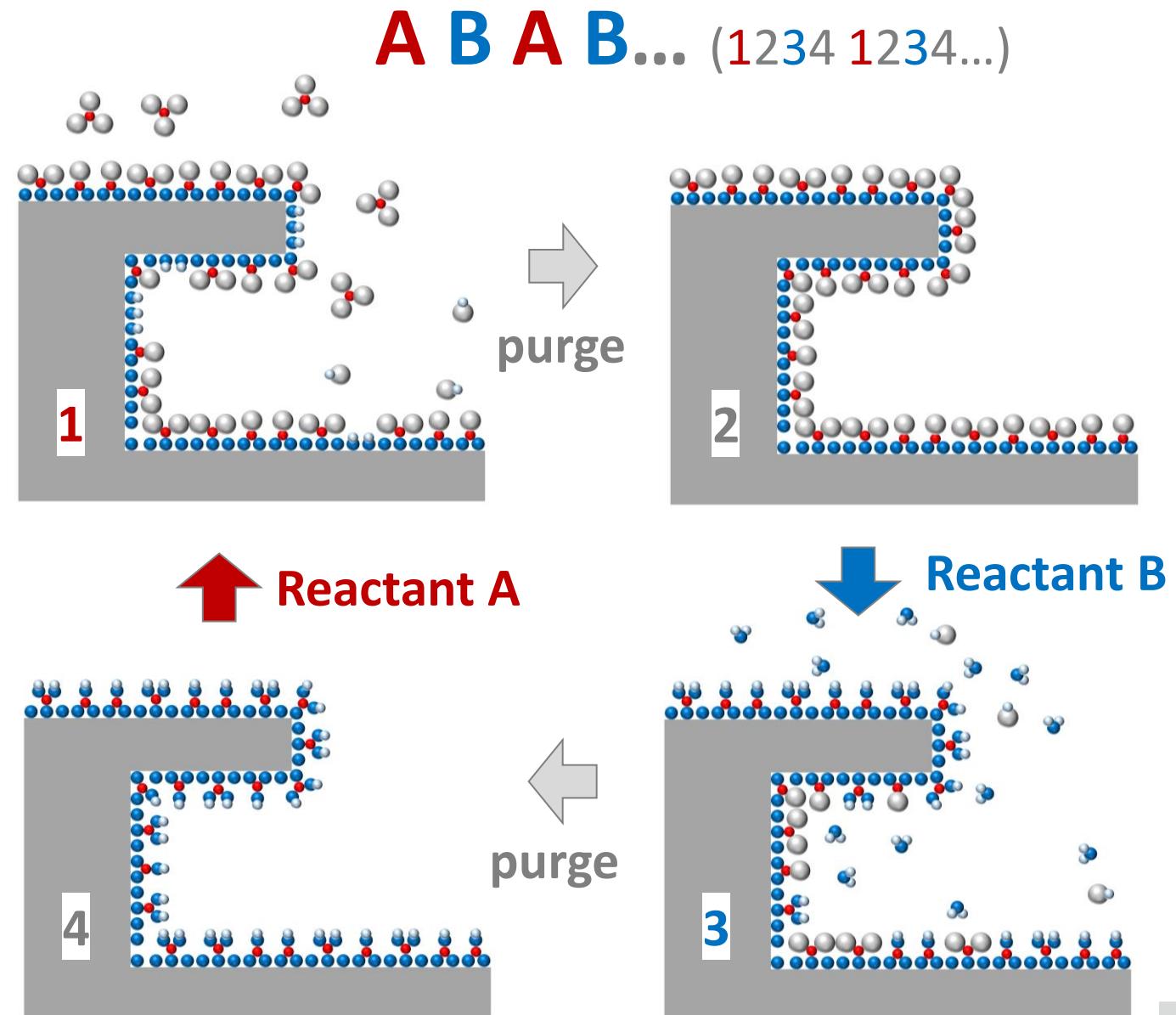
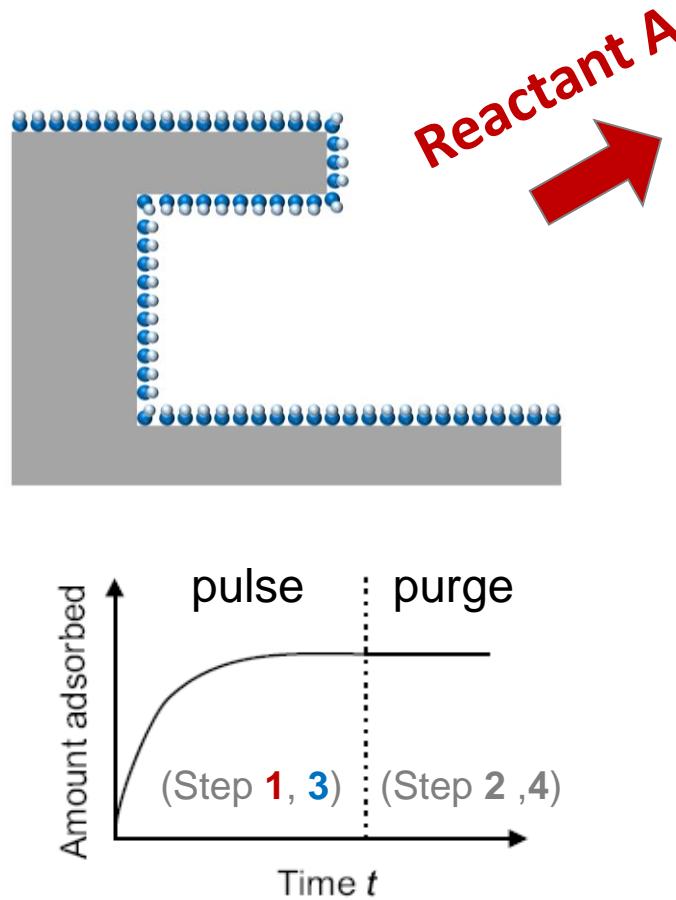


Workshop honoring
the 90th anniversary of the birth of
Stanislav Ivanovich Koltsov

VPHA, <http://vph-ald.com>: Worldwide collaborative effort, in atmosphere of openness, respect, and trust

ALD
history

ALD principle discovered twice



van Ommen, Goulas, Puurunen, Kirk-Othmer Encyclopedia of Chemical Technology, 2021. <https://doi.org/10.1002/0471238961.koe00059>
Also in: Wikimedia Commons, [link](#), CC BY 4.0; [ALD-cartoons-evolving-file](#)

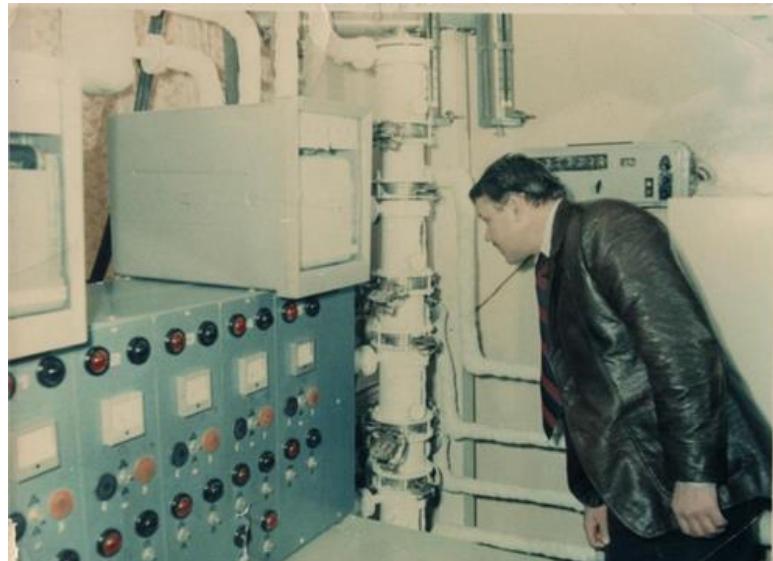
1960s St. Petersburg, Soviet Union

Molecular Layering

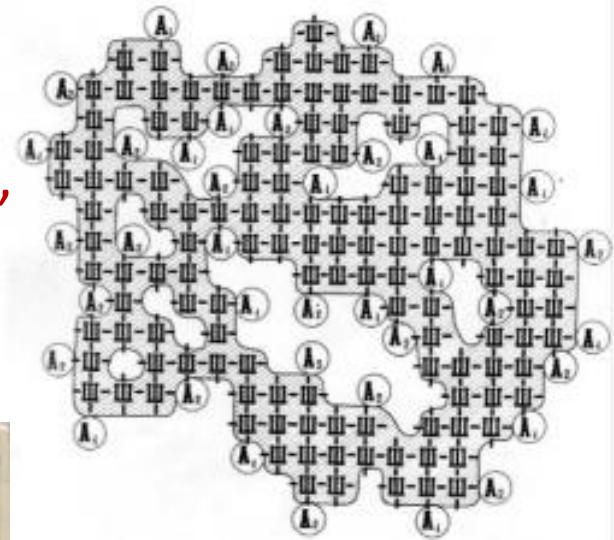
Aleskovskii “framework hypothesis”



Prof. Valentin Borisovich Aleskovskii
Prof. Stanislav Ivanovich Koltsov
St. Petersburg, USSR / Russia



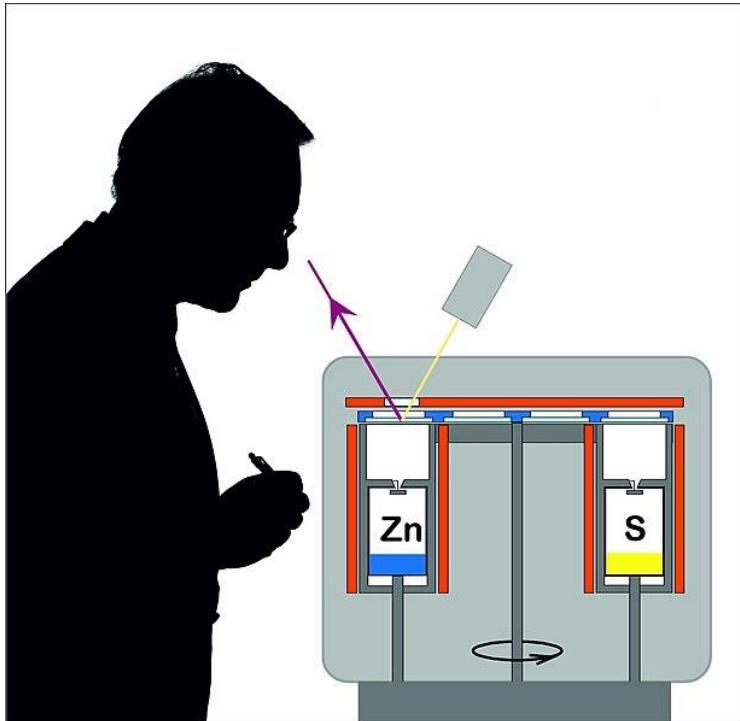
Prof. Malygin & particle ML-ALD reactor 1982



Essay on ML: Malygin et al., Chem. Vap. Deposition 21 (2015) 216-240, DOI: [10.1002/cvde.201502013](https://doi.org/10.1002/cvde.201502013)
https://en.wikipedia.org/wiki/Valentin_Aleskovsky

1974, Espoo, Finland

Atomic Layer Epitaxy



https://commons.wikimedia.org/wiki/File:Reconstruction_of_the_first_atomic_layer_epitaxy_experiment_by_Tuomo_Suntola.jpg

Helsinki-Vantaa (HEL) airport, 1983



Dr. Tuomo Suntola
2018 Millennium
Technology Prize

Essay on ALE: Puurunen, Chem. Vap. Deposition 20 (2014) 332-344, DOI: [10.1002/cvde.201402012](https://doi.org/10.1002/cvde.201402012)
https://en.wikipedia.org/wiki/Tuomo_Suntola, <https://finland.fi/business-innovation/finnish-physicist-tuomo-suntola-wins-millennium-technology-prize/>

Virtual Project on the History of ALD (VPHA)



VPHA launched in 2013 at ALD conference

- (from vph-ald.com): “VPHA is an open collaborative effort, whose goal is to clarify open questions related to the early history of the ALD thin film deposition technique. VPHA is based on voluntary efforts, and anyone interested in the history of ALD is welcome to join. All VPHA activities are made in an atmosphere of openness, respect and trust.”
- The core activity of VPHA is to collect together, and collectively read, and write short comments (in English) on early ALD works, which are then openly shared. Such work forms the factual basis to form a common understanding on the early works of ALD.

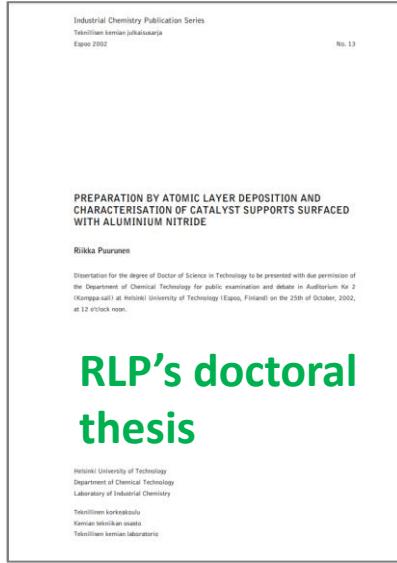
VPHA launched in 2013 at ALD conference

- (from vph-ald.com:) “VPHA is an **open collaborative effort**, whose goal is to **clarify open questions related to the early history of** the **ALD** thin film deposition technique. VPHA is **based on voluntary efforts**, and **anyone interested** in the history of ALD **is welcome to join**. All VPHA activities are made in an **atmosphere of openness, respect and trust**.”
- The core activity of VPHA is to **collect** together, and collectively **read**, and **write** short comments (in English) on early ALD works, which are then openly **shared**. Such work forms the factual basis to form a common understanding on the early works of ALD.

What were the pre-VPHA ALD
history activities,
paving way to VPHA?

RLP's (the speaker's) personal story





RLP's doctoral thesis

Helsinki University of
Technology, Espoo, 2002.

Chapter 2

ATOMIC LAYER DEPOSITION

Mikko Ritala, Markku Leskelä

Department of Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland

Handbook of Thin Film Materials, edited by H.S. Nalwa

Volume 1: Deposition and Processing of Thin Films

“Several terms are used in the literature to describe processes that are based on repeating separate, saturating gas–solid reactions. **In addition to ALD**, terms such as **atomic layer epitaxy (ALE)**, atomic layer chemical vapour deposition (ALCVDTM), **molecular layering**, atomic layer growth, atomic layer processing and chemical surface coating can be found. **Atomic layer epitaxy was the original term, used by Suntola and co-workers, who developed the technique in the 70’s for the preparation of ZnS thin films for electroluminescent devices.**”

Table I. Alternative Names to the ALD Method

Name	Acronym	Comments
Atomic layer deposition	ALD	General, covers all kinds of films In a close connection with the original name
Atomic layer epitaxy	ALE	The original name, but should be reserved for epitaxial films only
Atomic layer growth	ALG	Like ALD but less used
Atomic layer chemical vapor deposition	ALCVD	Emphasizes the relation to CVD
Molecular layer epitaxy	MLE	Emphasizes molecular compounds as precursors
Digital layer epitaxy	DLE	Emphasizes the digital thickness control
Molecular layering	ML	Dates back to old Russian literature
Successive layerwise chemisorption		
Sequential surface chemical reaction growth		
Pulsed beam chemical vapor deposition		

???

ALD
history

A. A. Malygin, V. M. Smirnov, "Early work on atomic layer deposition cited," Solid State Technol. 45 (2002) 14-14.

Early work on atomic layer deposition cited

We would like to comment on the article "Assault on ITRS road-blocks led by atomic layer deposition," Jan. 2001, pp. 70-72. Some comments on the article are also given in the article "Catalytic and inert ALD" (pp. 73-74).

The first implementors of the new method, then called "molecular layering," were V.B. Aleksovskii and S.I. Koltsov, as described in an article published in 1974 (V.B. Aleksovskii, "Chemistry and technology of solids," *Zhurnal Prikladnoi Khimii*, Vol. 47, No. 10, pp. 2145-2157, Oct. 1974. Original article submitted April 8, 1974.). The first publication on this new technology appeared in the USSR (in Russia) in 1965 (see Ref. 48 in the literature cited).

A.A. MALYGIN, professor and head, Chemical Technology of Materials for Electronic Instruments Department, and
V.M. SMIRNOV, professor, Chemistry of Solids Department, St. Petersburg State Technological Institute, St. Petersburg, Russia

[REDACTED] chooses not to respond formally at this time, but maintains the correctness of the statements made in the article.

- RLP with two questions:
- Is it really the same technique?
 - Is it older than ALE?

I needed to find out by myself!

Review article written as postdoc, published in 2005

APPLIED PHYSICS REVIEWS

JOURNAL OF APPLIED PHYSICS 97, 121301 (2005)

<https://doi.org/10.1063/1.1940727>

“The starting point of ALD is somewhat controversial: depending on the source, the credit of first realizing the principles of ALD is given to different groups.”

⁸³ S. I. Kol'tsov, V. B. Kopylov, V. M. Smirnov, and V. B. Aleskovskii, *Zh. Prikl. Khim.* (S.-Peterburg) **49**, 516 (1976) [J. Appl. Chem. USSR **49**, 525 (1976)].

⁸⁴ A. P. Nechiporenko, T. M. Sukhareva, A. A. Malygin, S. I. Kol'tsov, and V. B. Aleskovskii, *Zh. Prikl. Khim.* (S.-Peterburg) **51**, 2447 (1978) [J. Appl. Chem. USSR **51**, 2333 (1978)].

⁸⁵ S. I. Kol'tsov, T. V. Tuz, and A. N. Volkova, *Zh. Prikl. Khim.* (S.-Peterburg) **52**, 2196 (1979) [J. Appl. Chem. USSR **52**, 2074 (1979)].

⁸⁶ N. A. Stepanova, V. D. Kupriyanov, and A. A. Malygin, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **23**, 377 (1987) [Inorg. Mater. **23**, 331 (1987)].

⁸⁷ Even the American Vacuum Society topical conference on atomic layer deposition, ALD 2004 (Helsinki, Finland, 16–18 August 2004), was organized “celebrating 30 years of ALD.” ALD was then defined to have started from filing the first Finnish ALE patent (Ref. 75) in 1974, disregarding the work made in the Soviet Union already in the 1960s.

⁸⁸ V. V. Brei, V. A. Kasperskii, and N. E. Gulyanitskaya, *React. Kinet. Catal. Lett.* **50**, 415 (1993).

⁸⁹ V. M. Gun'ko, *Kinet. Katal.* **34**, 463 (1993) [Kinet. Catal. **34**, 406 (1993)].

⁹⁰ S. I. Kol'tsov, V. M. Smirnov, R. R. Rachkovskii, T. V. Malalaeva, and V. B. Aleskovskii, *Zh. Prikl. Khim.* (S.-Peterburg) **51**, 2596 (1978) [J. Appl. Chem. USSR **51**, 2475 (1978)].

⁹¹ Yu. K. Ezhovskii and A. I. Klusevich, *Neorg. Mater.* **39**, 1230 (2003) [Inorg. Mater. **39**, 1062 (2003)].

⁹² G. V. Anikeev, Yu. K. Ezhovskii, and S. I. Kol'tsov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **24**, 619 (1988) [Inorg. Mater. **24**, 514 (1988)].

⁹³ V. E. Drozd, A. A. Tulub, V. B. Aleskovskii, and D. V. Korol'kov, *Appl. Surf. Sci.* **82/83**, 587 (1994).

⁹⁴ V. V. Brei, V. A. Kasperskii, and A. A. Chuiko, *Zh. Prikl. Khim.* (S.-Peterburg) **69**, 378 (1996) [Russ. J. Appl. Chem. **69**, 335 (1996)].

⁹⁵ M. A. Eremeeva, A. P. Nechiporenko, G. N. Kuznetsova, S. I. Kol'tsov, and V. B. Aleskovskii, *Zh. Prikl. Khim.* (S.-Peterburg) **47**, 2332 (1974) [J. Appl. Chem. USSR **47**, 2390 (1974)].

⁹⁶ I. V. Mischenko, A. A. Malygin, and S. I. Kol'tsov, *Chemomater.*

<https://twitter.com/rlpuu/status/1281470239356657664?s=20>

Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process

Riikka L. Puurunen^{a)}

Interuniversity Microelectronics Center (IMEC vzw), Kapeldreef 75, B-3001 Leuven, Belgium, University of Leuven (K.U.Leuven), Integrated Systems (INSYS), Kasteelpark Arenberg, B-3001 Leuven, Belgium, and VTT Technical Research Centre of Finland, Information Technology, Tietotie 3, FI-02044 Espoo, Finland

(Received 20 September 2004; accepted 8 April 2005; published online 30 June 2005)

121301-5 Riikka L. Puurunen					J. Appl. Phys. 97, 121301 (2005)
TABLE I. Some Soviet-Russian ALD investigations.					
Z ^a	Material	Reactant A	Reactant B	Substrate ^b	Refs.
5 Boron	B ₂ O ₃	BBBr ₃	H ₂ O	SiO ₂ gel	85
	B _x P _y O _z	B(OMe) ₃	POCl ₃	SiO ₂ gel	88 and 89
13 Aluminum	Al ₂ O ₃	AlCl ₃	H ₂ O	SiO ₂ gel	83, 90, and 91
		AlCl ₃	H ₂ O	Al ₂ O ₃ gel	90
		AlCl ₃	H ₂ O	Si, Al	91
		AlBr ₃	H ₂ O	Si	92
		AlMe ₃	NO ₂	Si	93
	Al _x Si _y O _z	AlCl ₃	Si(OEt) ₄	SiO ₂ gel	94
	Al _x Cr _y O _z	AlMe ₃	CrO ₂ Cl ₂	Si	93
	SiO ₂	SiCl ₄			
		SiCl ₄			
14 Silicon		SiCl ₄			
		SiCl ₄			
		SiCl ₄			
		SiCl ₄			
		SiCl ₃ H			
	Si _x Al _y O _z	Si(OEt) ₄			
	Si _x Ti _y O _z	Si(OEt) ₄			
		TiCl ₄			
			SiO ₂ gel		88

**JAP 2005, Table I on history:
RLP's “public apology to the world”
(for having missed the ML origin in
own thesis)**



Riikka Puurunen @rlpuu · 10. heinäk. 2020

I notice it is 15 years ago that my review on #ALDep surface chemistry was published, J. Appl. Phys. 97, 121301 (2005); doi.org/10.1063/1.1940727. That was my first review in APR. Review has been impactful, but its path to publication was not easy. A thread. #ALDepChat #TMAwater

ALD history

RLP hoped that the high-visibility JAP 2005 review would make the ALD community change its view on the history, but – it didn't.

(only ALE, no ML)

(Another review, five years later)

Atomic Layer Deposition: An Overview

Steven M. George*

[View Author Information](#) ▾

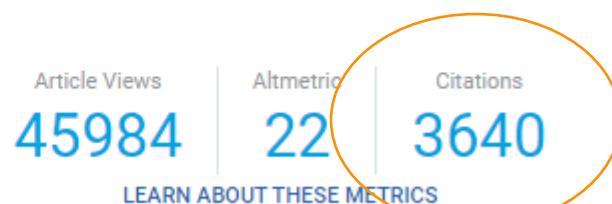
Cite this: *Chem. Rev.* 2010, 110, 1, 111–131

Publication Date: November 30, 2009 ▾

<https://doi.org/10.1021/cr900056b>

Copyright © 2009 American Chemical Society

[RIGHTS & PERMISSIONS](#) ✓ Subscribed



~~etc., and how compares with the processes in the field.~~

The history of ALE and ALD dates back to the 1970s in Finland. The original pioneer of ALE was Tuomo Suntola, who demonstrated some of the first ALE processes as early as August/September 1974.¹⁶ The first ALE system developed was ZnS.¹⁶ The first ALE patent emerged in 1977.¹⁷ The first literature paper on ALE appeared in 1980 in *Thin Solid Films*.¹⁸ The first application of ALE was electroluminescent displays. The first public display of an ALE device was an electroluminescent display that operated in the Helsinki airport from 1983 to 1998. The first commercial ALE reactor was the F-120 sold by Microchemistry in 1988. The first of a series of ALE meetings was held in 1990 and continued through 1996. The first of a series of yearly ALD meetings was held in 2001 and has continued through the present date.

Many earlier reviews have addressed the basics of ALE

When the view finally started getting updated in 2010s, misleading (and even erroneous) excuses started to appear and they are still spreading in the literature: “published (only) in Russian”, etc.



- It became clear that work is still needed to clarify the early history of ALD
- The work is too much to do for one person (and not a single person's responsibility!)
- A group of interested scientists soon gathered – via Sundqvist-managed LinkedIn group ALD – Atomic Layer Deposition

Riikka Puurunen posted in ALD - Atomic Layer Deposition ...

 ALD - Atomic Layer Deposition

 **Riikka Puurunen**
Associate Professor at Aalto University
9yr 

May 6, 2013

What are the "Molecular layering" papers by Koltsov from "early 1960's"?

I noticed that the "hall of fame" of [aldpulse.com](#) has been updated with a few faces, among them Aleskovskii and Koltsov.

Of Koltsov, the text reads: "ALD principle was first published under name "Molecular Layering" in the early 1960s by Prof. S.I. Kol'tsov from Leningrad (Lensovet) Technological Institute (LTI)." I assume that [aldpulse.com](#) has copied this text from somewhere else (where?), as think I recall to have read this earlier, probably word to word.

The question is: what are these papers published "early in 1960's" by Koltsov?

So, if anyone has info on this, please share, for the common benefit. --- The references should preferably be detailed enough so that a skilfull librarian gets a copy orderd with that info.

 3 • 22 comments

VPHA opened July 25, 2013 + ALD 2013 San Diego

"Virtual project on the history of ALD"

- Goal: generate a common view on the early evolution of ALD in a collaborative project by the whole ALD community
 - "Unknowns" especially in the Molecular Layering work (Soviet Union)
- Invitation to participate published July 25, 2013, [aldpulse.com](#) (Riikka Puurunen, Aziz Abdulagatov, Jonas Sundqvist and Annina Titoff)
 - Everyone welcome to join, different backgrounds beneficial
- List of early ALD publications will be created
- Participation: read & comment on the significance of at least one historical publication that interests you (not much work!)
- Result to be published, names of all contributors announced
- Plan: project will be open until the end of 2013

More info: invitation at [aldpulse.com](#); LinkedIn "ALD History" subgroup; or Riikka Puurunen at the ALD 2013 conference (Tue: poster 369)

<https://www.slideshare.net/RiikkaPuurunen/ald2013-ald-historyoneslidepuurunenfinal>

Now
2021,
still
active...

VPHA's scope and achievements

“ How was the concept developed? What were the first ALD experiments? When, where and by whom were they made? Why were they made?

...

1. First, we should generate a complete list of early ALD publications.
2. Second, interested individuals should pick up some of the early publications, read them, and comment on the work. For example: was ALD made (i.e., do you recognize the work as ALD), and if yes, which process it was; and other noteworthy things.
3. Third, the individual should share their comments with others, and the comments of different people should be collected together.”

Current status:**

- Number of publications listed: 366
- Contributors: 79, from > 20 countries
- Comments given: 938
- Comments needed: 281

ALD-history-evolving-file

- Goal: Collect at least three (3) personal comments per article
- Limitation to scope: up to 1986 *

* Basis of limitation to scope: year when review on ALD (then ALE) by others than original inventors was published:

Goodman & Pessa, J. Appl. Phys. 60 (1986) R65; <https://doi.org/10.1063/1.337344>

** VPHA-reading-overview-file, accessed 27.9.2021

Related to VPRA: Four (4) scientific journal articles

Chemical Vapor Deposition
DOI: 10.1002/cvde.201402012
Essay
A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy**
By Rükka L. Puurunen*

Atomic layer deposition (ALD) is a thin film growth technique based on the repeated use of separate, saturating gas-solid reactions. The principle of ALD has been discovered twice: in the 1960s under the name "molecular layering" in the Soviet Union, and in the 1970s under the name "atomic layer epitaxy" (ALE) in Finland. In 2011, a worldwide patent on ALE as a method for the growth of compound thin films. This essay briefly tells the story of ALE as shared by its Finnish inventor, Dr. Tuomo Suntola, the growth of high-quality polycrystalline ZnS thin films for electroluminescent (EL) diodes, the selection of ALE increased, and the application areas were extended to photovoltaics beyond. Fast, production-worthy ALD reactors were imperative for industrial success: technologies and products with ALE, initiated by Dr. Tuomo Suntola and led by him until his industrial history, the fruits of which are seen today in numerous applications.

Keywords: ALD, ALE, EL displays, History, ZnS

1. Introduction

ALD is a thin film growth method which belongs to the general class of CVD techniques, and which has become more commonly acknowledged origin of ALD dates back to the "atomic layer epitaxy" technique originally developed for electroluminescent (EL) flat panel displays in Finland, during the 1970s.^[1,2] The other article in this special issue



<https://doi.org/10.1002/cvde.201402012>

Chemical Vapor Deposition
DOI: 10.1002/cvde.201502013
Essay
From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition**
By Anatoli A. Malygin*, Victor E. Drozd, Anatoli A. Malkov, and Vladimir M. Smirnov

This essay is dedicated to the history of creation and development of the molecular layering technique (ML) which, in the modern community of non-Russian scientists, is commonly referred to as atomic layering of solid surfaces using the ML method in the light of V. B. Aleskovskii in 1952 is discussed. A number of questions raised by internal members of the Virtual Project on the History of ALD (VPRA, 2013), and scientists from Kyoto (Japan, June 2014), and personal communications amongst peers are addressed. The paper provides information about V. B. Aleskovskii and S. I. Kol'tsov who are closest to the original idea of the ML technique in the Soviet Union. This paper also informs the scientific community about the ML research in Russia and introduces the scientific school of "Chemistry of thin films" supervised by V. B. Aleskovskii.

Keywords: ALD, molecular layering, history, "framework" hypothesis

1. Introduction

There are three main names for what is considered to be the same technology of gas-phase layer by layer deposition. Russians commonly refer to the technology as molecular layering (ML) or atomic layering (ALD). The term "atomic layer epitaxy" (ALE) is used in the West, especially in the United States. The term "molecular layering" is used in Japan. The term "atomic layer deposition" (ALD) is used in the United Kingdom and Germany. The term "atomic layer epitaxy" (ALE) is used in the United States. The term "molecular layering" is used in Japan. The term "atomic layer deposition" (ALD) is used in the United Kingdom and Germany.



<https://doi.org/10.1002/cvde.201502013>

ECS Transactions, 86 (6) & 17 (2018)
10.1149/08606.0003ecst ©The Electrochemical Society

Learnings from an Open Science Effort: Virtual Project on the History of ALD
R. L. Puurunen
Aalto University, School of Chemical Engineering,
Department of Chemical and Metallurgical Engineering, Finland

This work summarizes learnings from an Open Science effort "Virtual project on the History of ALD" (VPRA), started in 2013 to clarify the early history of atomic layer deposition (ALD). ALD is a multi-tool of nanotechnology and has been e.g. enabler of the continuation of Moore's law of transistor scaling. ALD has been developed historically through two independent routes: atomic layer epitaxy (ALE) and molecular layering (ML). Early details on ML have remained little known to a broader scientific community. In this contribution, learnings in VPRA are seen from the viewpoint of its voluntary coordinator (the author self). Historical details of ALD as well as from an original viewpoint and some other viewpoints. Selected details of ALD's history not fully accurately described in three earlier articles are pointed out. The work made in VPRA has provided the foundation for granting the 2018 Millennium Technology Prize to Dr. Tuomo Suntola. At the time of this contribution, in July 2018, VPRA is still on-going and volunteers are welcome to join the effort.



<https://doi.org/10.1149/08606.0003ecst>

<https://vph-ald.com/Publication%20Plan.html>
<https://vph-ald.com/ALD-history-publications.html>

Presentations (10): Baltic ALD 2014, ALD 2014 Kyoto (3x), ALD 2015, ALD 2016, Baltic ALD 2016, Baltic ALD 2019, ALD 2019, ALD Russia 2021.

- Website vph-ald.com (not forever!)
- Blog aldhistory.blogspot.fi (RLP)
- Wikipedia updates (#WikiALD)

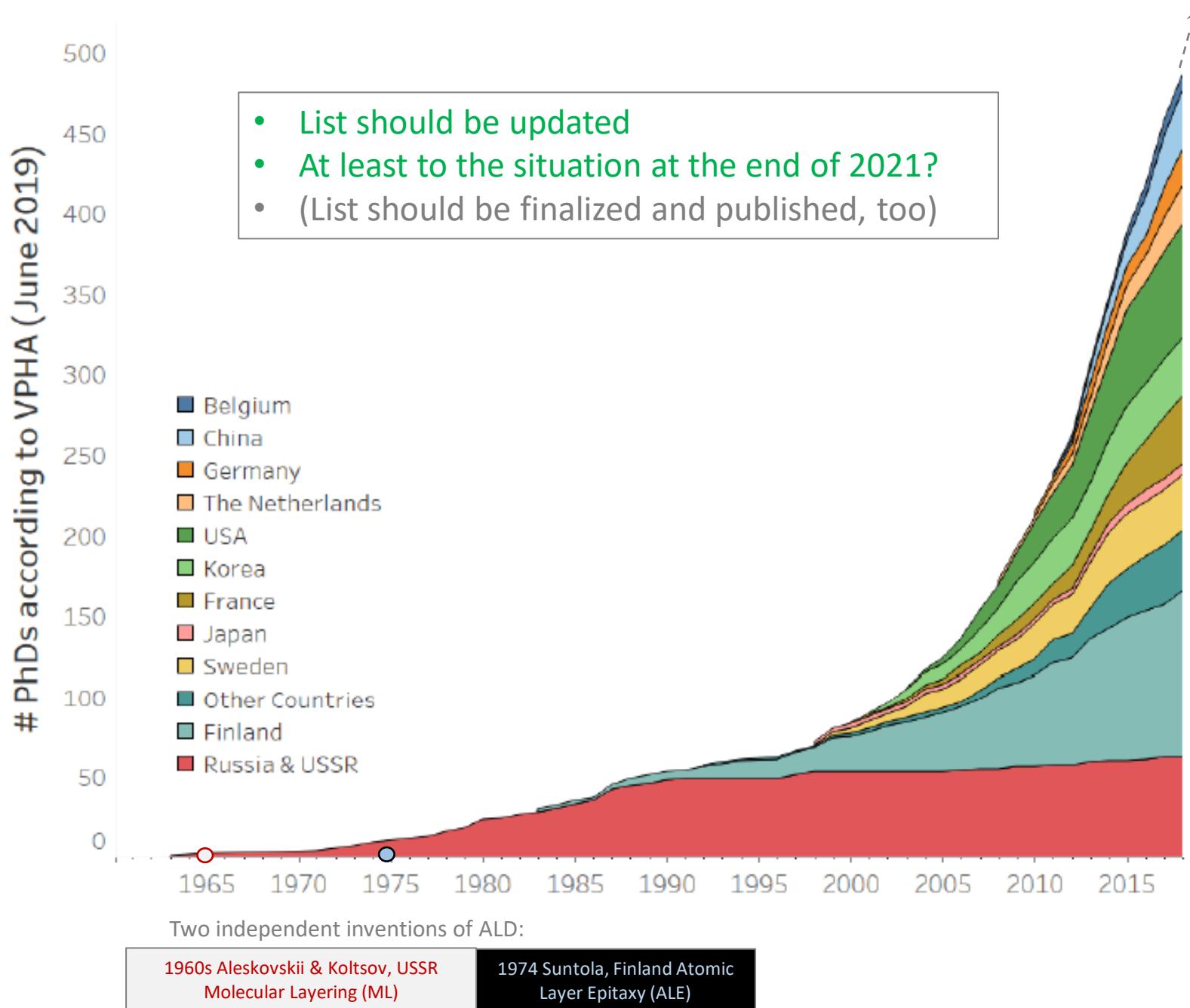
VPRA's evolving files, e.g.

- [ALD-history-evolving-file](#)
- [VPRA-ALD-thesis-list](#)
- [VPRA-ALD-reviews](#)

Indirectly linked to VPRA

- Exhibition: 40 Years of ALD in Finland – Photos, Stories
- 2018 Millennium Technology Prize to Suntola
- openlearning.aalto.fi → ALD

ALD
history



EuroCVD 22 -
Baltic ALD 16, in
Luxembourg,
June 24-28,
2019. Virtual
Project on the
History of ALD
(VPHA).
Abstract Poster



<http://vph-ald.com>
aldhistory.blogspot.fi



Final steps for VPHA

- Although VPHA has already booked significant progress, the work is not completed yet.
- **Target: each early ALD publication should receive comments from at least three persons to be shared in the collective “ALD-history-evolving-file” document.**
- **Of the ~170 articles still missing one or two comments, ~140 are available only in Russian.**
- To complete the reading effort, it is essential to have a significant number of researchers from the Russian ALD community, too, to actively participate in the reading effort.
- **With this presentation, the final stage of VPHA is launched.** Third (and last) coordinated reading and commenting activity tentatively to start in November 2021.

- Goal: **finalize the reading and commenting work**, and **optionally write a review article** on the history of ALD on the basis of the information collected.
- **We invite all researchers worldwide, interested in ALD and especially in its early roots, to volunteer to work together in VPHA, to build together fact-based understanding of the early ALD works.**
- **Especially we invite Russian-speaking ALD researchers to volunteer:** thorough understanding of both the technique and the technical language used to describe ALD both in Russian and English will give the best result when writing brief comments on Russian-only articles in English.

→ *To let us know that you are interested,
please contact us via info@vph-ald.com*

Thank you for your attention, questions? Спасибо за внимание, есть вопросы?



Fig. 23. Conference in Linz
V. Drozd, L. Niinisto, M. Leskis
is Professor S. M. George Parsons
with permission of Victor Dr

From: Essay on ML: Malygin et al.,
DOI: [10.1002/cvde.201502013](https://doi.org/10.1002/cvde.201502013)

BALD Engineering AB @jv3sund · 25. heinäk. 2016
Prof Malygin From Saint Petersburg State Inst of Tech Plenary on Molecular Layering @ALD2016_Ireland #ALD2016

ALD 2016
Dublin, Ireland

<https://twitter.com/jv3sund/status/757495966891122689?s=20>

#BalticALD
#FinALD40



Riikka Puurinen @rlpuu · 27. toukoku. 2014
Poster at #BalticALD, with @jv3sund and @rlpuu. First outcome of #ALDep history project aldpulse.com/node/248 #VPHA

Sundqvist, Puurinen, VPFA, BalticALD

<https://twitter.com/rlpuu/status/471248727471325185?s=20>
Photo: Madeleine Sundqvist 2014

#ALDRussia

Riikka Puurinen @rlpuu · 21. syysk. 2015
At #ALDRussia #ALDep workshop Moscow, from left: Puurinen, Malygin, Parsons. Photographer: Abdulagatov. @AVS_Members

<https://twitter.com/rlpuu/status/645967531442876416?s=20>

VPFA, <http://vph-ald.com>: Worldwide collaborative effort, in atmosphere of openness, respect, and trust

ALD
history

Virtual Project on the History of ALD in perspective: past, present, and final steps

R. L. Puurunen,^a Yu. Koshtyay,^b J. Sundqvist,^c J. R. van Ommen,^d O. Yurkevich,^e
^a Aalto University School of Chemical Engineering, Kemistintie 1, Espoo, Finland

^b Ioffe Institute, 26 Politekhnicheskaya, St Petersburg 194021, Russian Federation

^c Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden

^d TU Delft, Chemical Engineering, Van der Maasweg 9, Delft, The Netherlands

^e CIC nanoGUNE BRTA, Tolosa Hiribidea 76, Donostia-San Sebastián E-20018, Spain
riikka.puurunen@aalto.fi

Atomic layer deposition (ALD), a materials growth technique based on repeated separate self-terminating reactions, has become an enabler for semiconductor technology and is currently being investigated for a growing range of other applications.

ALD has two historical roots. The international community is in general aware of the invention of ALD under the name atomic layer epitaxy (ALE) in Finland in 1974 [1,2]. The community is significantly less aware of developments under the name molecular layering in USSR/Russia since the 1960s [3,4]. For example, the world's most cited review on ALD only cites the early Finnish developments [5]. Another review article (written by several leading authors in the field) to describe the history of ALD (and its relation to AVS) [6] recently had to be corrected with respect to its description of the USSR-Russian developments [7,8].

Why the molecular layering works have remained poorly known and cited, is not known. An explanation has repeatedly been offered in the literature that the works were published in Russian [9,10]. This statement is not quite correct. While there have been many publications in Russian only, there have also been plenty of publications in English, typically published in journals published in Russian, which automatically receive an English translation. Two such references are given here as examples [11,12]. Also, the first international symposium on ALE (i.e., ALD) in Espoo, Finland in 1990 received participants from the USSR/Russian ALD community [13,14].

The seeds for the Virtual Project on the History of ALD (VPHA, <http://vph-ald.com>) were sown already almost twenty years ago, when the article in Solid State Technology called “Early work on atomic layer deposition cited” by Malygin et al. was published in 2002 [15]. This article (response to an earlier article in the same journal) triggered the interest of R.L.P. while a postdoc at IMEC, Belgium. R.L.P. contacted the lead author (Malygin) with a request to get copies of some of the early works. Copies were soon provided, and the work to find facts about early ALD developments under the name molecular layering (and sometimes, other names) started. The results of the research were published in a review article (Table 1 of it) in 2005 [16]. To our knowledge, this review was the first review in English (after the contribution of Aarik in 1990 [17]), to clearly acknowledge the independent invention of ALD in the USSR/Russia. The author hoped that this article would change the way the scientific community sees the history of ALD, and would trigger others to find out about the history, too. While some advances were booked, leading mainstream works continued to acknowledge only the atomic layer epitaxy origin of ALD.

VPHA was launched in July 2013 with the following statement [18] “VPHA is an open collaborative effort, whose goal is to clarify open questions related to the early history of the ALD thin film deposition technique. VPHA is based on voluntary efforts, and anyone interested in the history of ALD is welcome to join. All VPHA activities are made in an atmosphere of openness, respect and trust.”

The core activity of VPHA is to collect together, and collectively read, and write short comments (in English) on early ALD works, which are then openly shared. Such work forms the factual basis to form a common understanding on the early works of ALD; common understanding of the facts related to early ALD developments has been clearly missing. Outcomes presenting the progress of VPHA have been presented at various conferences [19], and VPHA has directly or indirectly resulted in four scientific journal articles [1,3,20,21]. The authors understand that the VPHA has also contributed to awarding the Millennium Technology Prize 2018 to the Finnish inventor of ALD, Tuomo Suntola [22].

Although VPHA has already booked significant progress, the work is not completed yet. Setting as the target that each early ALD publication should receive comments from at least three persons to be shared in the collective “ALD-history-evolving-

file” document, the reading work is about half completed. Of the ~170 articles still missing one to two comments, ~140 are available only in Russian. So far, 79 contributors from over 20 countries have participated in the reading activity. To complete the reading effort, it is essential to have a significant number of researchers from the Russian ALD community, too, to actively participate in the reading effort.

With this abstract at the ALD Russia 2021 conference — chaired by the first author of the “Early work on atomic layer deposition cited” letter [15] — the final stage of VPHA is launched. The purpose is to finalize the reading and commenting work, and optionally to write a review article on the history of ALD on the basis of the information collected and findings made. **We invite all researchers worldwide, interested in ALD and ALD's early roots, to volunteer to work together in VPHA, to build together fact-based understanding of the early ALD works.** Especially we invite Russian-speaking ALD researchers to volunteer: thorough understanding of both the technique and the technical language used to describe ALD both in Russian and English will give the best result when writing brief comments on Russian-only articles in English. To join, please contact us via info@vph-ald.com.

- [1] R.L. Puurunen, Chem. Vapor Deposition, 2014, 20, 332-344. DOI:[10.1002/cvde.201402012](https://doi.org/10.1002/cvde.201402012)
- [2] T. Suntola, J. Antson, FIN 52359 (29.11.1974); U.S. patent 4 058 430 (25 November 1975).
- [3] A.A. Malygin, V.E. Drozd, A.A. Malkov, V.M. Smirnov, Chem. Vapor Deposition, 2015, 21, 216-240.
DOI:[10.1002/cvde.201502013](https://doi.org/10.1002/cvde.201502013)
- [4] V.B. Aleskovskii, S.I. Koltsov, Abstract of Scientific and Technical Conference of the Leningrad Technological Institute by Lensovet (Goskhimizdat, Leningrad, 1965), pp. 67–67.
- [5] S.M. George, Chem. Rev. 2010, 110, 111-131. DOI:[10.1021/cr900056b](https://doi.org/10.1021/cr900056b)
- [6] G.N. Parsons et al., J. Vac. Sci. Technol. A, 2013, 31, art. 050818. DOI:[10.1116/1.4816548](https://doi.org/10.1116/1.4816548)
- [7] G.N. Parsons et al., J. Vac. Sci. Technol. A, 2020, 38, art. 037001. DOI:[10.1116/6.0000143](https://doi.org/10.1116/6.0000143)
- [8] ALD History Blog, Riikka Puurunen 9.6.2020, <http://aldhistory.blogspot.com/2020/06/analysis-of-erratum-jvsta-history-of-ALD-and-relationship-AVS.html>, accessed 14.6.2021
- [9] G.N. Parsons, S.M. George, M. Knez, MRS Bulletin, 2011, 36, 865-871. DOI:[10.1557/mrs.2011.238](https://doi.org/10.1557/mrs.2011.238)
- [10] B.J. O'Neill et al., ACS Catal., 2015, 5, 1804-1825. DOI:[10.1021/cs501862h](https://doi.org/10.1021/cs501862h)
- [11] S.I. Koltsov, Zh. Prikl. Khim., 1969, 42, 1023-1028 [J. Appl. Chem. USSR, 1969, 42, 975-979]
- [12] V.B. Aleskovskii, Zh. Prikl. Khim., 1974, 47, 2145 [J. Appl. Chem. USSR, 1974, 47, 2207].
- [13] V.B. Aleskovskii, V.E. Drozd, Acta Polytechnica Scandinavica – Chemical Technology series, 1990, issue 195, pages 155-161.
- [14] ALD History Blog, Riikka Puurunen 12.2.2017, <http://aldhistory.blogspot.com/2017/02/ald-history-and-prof-em-markus-pessa.html>, accessed 14.6.2021
- [15] A. A. Malygin, V. M. Smirnov, Solid State Technol., 2002, 45, 14-14.
- [16] R.L. Puurunen, J. Appl. Phys., 2005, 97, art. 121301. DOI:[10.1063/1.1940727](https://doi.org/10.1063/1.1940727)
- [17] J. Aarik, Atomic layer epitaxy, Proceedings on Electroluminescence XVIII. Tartu Ülikooli Toimetised 908, Tartu, Estonia 1990, pp. 5-33. <http://dspace.ut.ee/handle/10062/32165>
- [18] <http://vph-ald.com>, accessed 14.6.2021
- [19] See <https://vph-ald.com/Publication%20Plan.html>, accessed 18.6.2021.
- [20] Ahvenniemi et al., J. Vac. Sci. Technol. A, 2017, 35, 010801. DOI:[10.1116/1.4971389](https://doi.org/10.1116/1.4971389)
- [21] R.L. Puurunen, ECS Trans. 2018, 86 (3) 3-17. DOI:[10.1149/08606.0003ecst](https://doi.org/10.1149/08606.0003ecst)
- [22] D. Cord, May 2018, <https://finland.fi/business-innovation/finnish-physicist-tuomo-suntola-wins-millennium-technology-prize/>, accessed 14.6.2021



[From VPHA's ALD-history-evolving-file:]

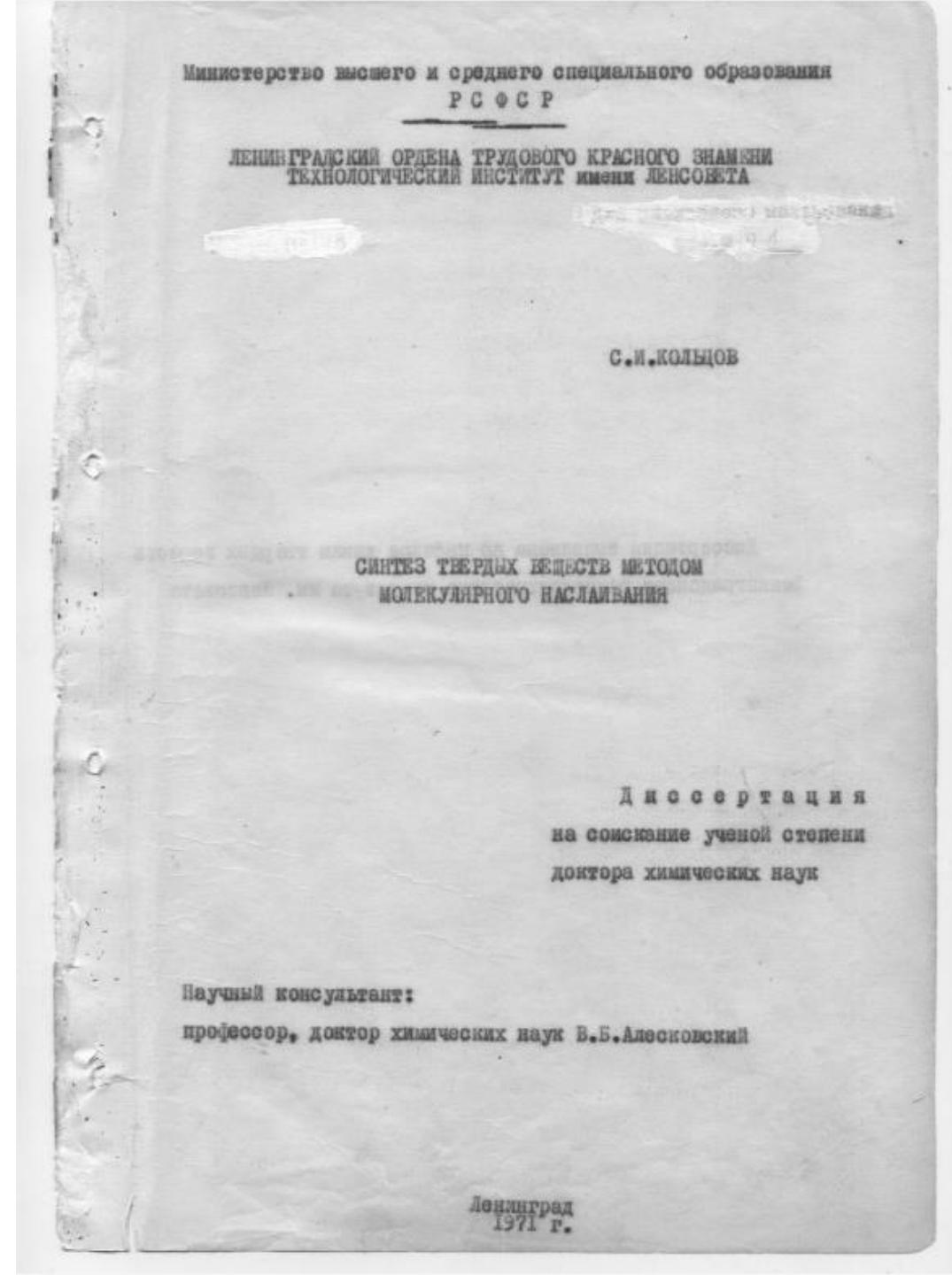
Kol'tsov, S. I. **Synthesis of solids by the Molecular Layering Method**
Doktor nauk thesis, Leningrad Technological Institute by Lensovet,
1971, 383 p. [In Russian]

Кольцов, С. И. Синтез твёрдых веществ методом молекулярного
наслаждания : дис. ... д-ра хим. наук / Кольцов Станислав Иванович.
— Л., 1971. — 383 с.



Workshop honoring
the 90th anniversary of the birth of
Stanislav Ivanovich Kol'tsov

VPHA, <http://vph-ald.com>: Worldwide collaborative
effort, in atmosphere of openness, respect, and trust



Atomic
Layer
Deposition
Russia 2021



<http://aldhistory.blogspot.com/>

ALD
history
blog

<http://www.blog.balengineering.com/>

 **BALD** Engineering

ALD
history