

# On the early history of atomic layer deposition: most significant works and applications



VPHA, [vph-ald.com](http://vph-ald.com): *Worldwide collaborative effort, in an atmosphere of openness, respect and trust*

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## VPHA in a nutshell

- In VPHA, volunteer scientists from all around the world work together in an atmosphere of openness, respect and trust, to better understand the early days of ALD.
- VPHA was started in July 2013 and is open for anybody with an ALD background to participate. In a way, VPHA continues the earlier ALD history work started in [J. Appl. Phys. 97 \(2005\) 121301](#).
- In VPHA, we collect, read and comment upon early ALD literature up to 1986. [ALD-history-evolving-file](#) forms the core of VPHA: it contains the Invitation to participate, list of ALD literature up to 1986, and personal comments on their contents.
- Several conference presentations and two essays on the history of ALD [1,2] have been created earlier as VPHA outcomes.

## Creating the list of most significant publications

VPHA has for this poster created a "conclusive recommended reading list of the most significant early ALD publications". This has been made through open voting that ended June 15<sup>th</sup>, 2016.

- Each VPHA co-author had the right to vote.
- Each participant could give in total 20 points, 1-3 points per publication, to any publication listed in the ALD-history-evolving-file.
- 30 co-authors participated in the voting, giving in total 507 points.

The next table report the 22 most significant ALD publications, according to the voting. The results have been ordered on the basis of (1) number of points (pts), (2) number of people (#) giving points to the particular article (minimum: four) and (3) the year of publication.

## Early ALD applications

The most significant early industrial application of ALD has been thin-film electroluminescent (TFEL) displays, enabled by Mn-doped ZnS and other ALD layers. Production started in 1985 by Lohja Oy and still continues in Espoo by Beneq Oy [1].

Other noteworthy early applications are for example catalysts, sorbents, polymer fillers.



Flight display modules with ALD (ALE) TFEL character units at Helsinki-Vantaa airport, 1983. Photo courtesy of Beneq Oy.

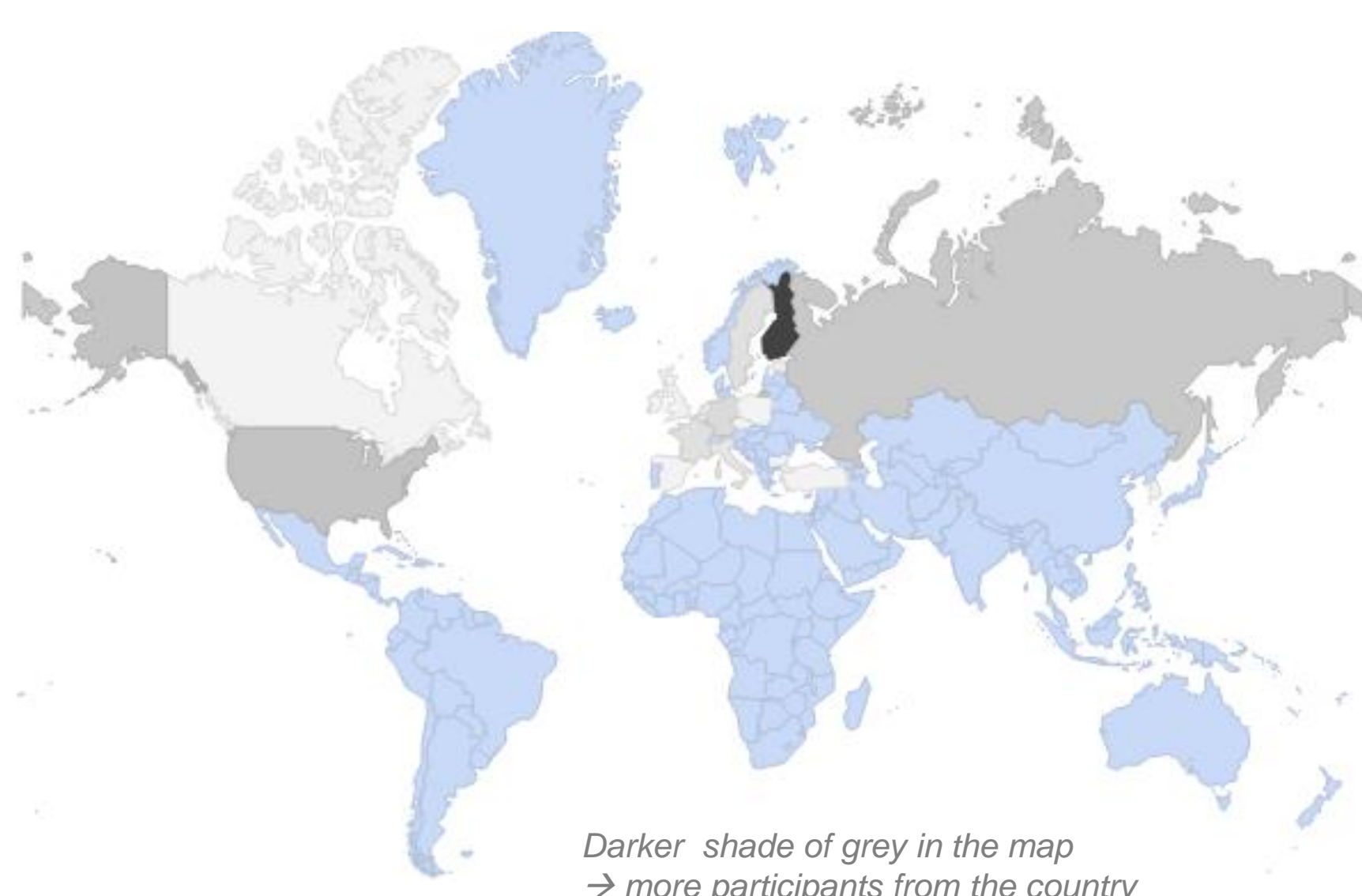
## VPHA in numbers

as of July 19, 2016

- 70 co-authors from
- 19 countries and
- 3 continents

There are:

- 365 articles listed
- 779 comments given



Darker shade of grey in the map → more participants from the country

## Recommended reading list of early ALD publications:

Author(s), title, publication details, unique VPHA code	pts	#
T. Suntola, J. Antson, Menetelmä ja laite yhdisteohutkalvojen kasvattamiseksi. (–Method and apparatus for the growth of compound thin films). Patent FIN 52359 - filed 29 November 1974, published 30 May 1976, granted 10 September 1977. US Patent 4 058 430 (Suntola1976) fi swe en ru ...	34	16
T. Suntola, J. Hyvärinen, Atomic layer epitaxy, Annu. Rev. Mater. Sci., 1985, 15, 177-195 (Suntola1985) en	27	14
V. B. Aleskovskii, Chemistry and technology of solids. J. Appl. Chem. USSR., 47, 2207-2217, 1974; Translated from: Zh. Prikl. Khim. 47, 2145-2157, 1974. (Aleskovskii1974) en ru	26	14
T. Suntola, A. Pakkala, S. G. Lindfors, Menetelmä ja laite yhdisteohutkalvojen kasvatuksessa (–Method and equipment for deposition of compound thin films) [in Finnish], SF patent 57975, Feb 28, 1979. US Patent 4389973 and 4413022 A (Suntola1980a) fi swe en ru ...	22	13
C. H. L. Goodman, M. V. Pessa, Atomic layer epitaxy, J. Appl. Phys., 1986, 60, R65-R81 (Goodman1986) en	22	12
S. I. Kol'tsov, Synthesis of solids by the Molecular Layering Method, Doktor Nauk thesis ("professor's thesis"), 1971, 383 p. [In Russian] (Kol'tsov1971) ru	18	9
A. M. Shevjakov, G. N. Kuznetsova, V. B. Aleskovskii, Interaction of titanium and germanium tetrachlorides with hydrated silica, Chemistry of high temperature materials. Proceedings of 2nd USSR conference on high temperature chemistry of oxides, November 26-29, 1965, Leningrad, USSR, Nauka, Leningrad, USSR, p. 162-168 1967. (Shevjakov1967) en ru	14	10
S. M. Bedair, M. A. Tischler, T. Katsuyama, N. A. El-Masry, Atomic layer epitaxy of III–V binary compounds, Appl. Phys. Lett., 1985, 47, 51-53 (Bedair1985) en	11	9
T. Suntola, J. Antson, A. Pakkala, S. Lindfors, Atomic layer epitaxy for producing EL thin films, SID International Symposium in San Diego, California, 29 April-1 May 1980, Digest of Technical Papers, SID, 1980, 108-109. (Suntola1980) en	11	7
S. I. Kol'tsov, Preparation and investigation of the products of interaction between titanium tetrachloride and silica gel, J. Appl. Chem. USSR. 42, 975-979 1969; Translated from: Zh. Prikl. Khim., 1969, 42(5), 1023-1028. (Kol'tsov1969a) en ru	10	6
V. B. Aleskovskii, Chemical assembly of materials, Vestn. Akad. Nauk SSSR, 1975, 48-52. [In Russian] (Aleskovskii1975) ru	9	5
V. E. Drozd, Synthesis and study of oxide coatings obtained by molecular layering on semiconductor surfaces, Dissertation for Kandidat Nauk (PhD), Leningrad Technological Institute by Lensovet, 1978. 131 pages. [in Russian] (Drozd1978-PhD)	9	5
G. V. Sveshnikova, S. I. Kol'tsov, V. B. Aleskovskii, Formation of a silica layer of predetermined thickness on silicon by the molecular-layering method, J. Appl. Chem. USSR, 43, 1155-1157, 1970; Translated from: Zh. Prikl. Khim., 1970, 43(5), 1150-1152. (Sveshnikova1970) en ru	9	4
T. Suntola, Atomic Layer Epitaxy, Tech. Digest of ICVGE-5, San Diego, 1981, 125a-125b. (Suntola1981) en	8	4
V. A. Tolmachev, Possibility of the use of a gravimetric method for studying the process of molecular layering in disperse silica samples. J. Appl. Chem. USSR., 1982, 55(6), 1298-1299; Translated from: Zh. Prikl. Khim., 1982, 55(6), 1410-1412. (Tolmachev1982) en ru	7	6
G. S. Sveshnikova, S. I. Kol'tsov, V. B. Aleskovskii, Interaction of titanium tetrachloride with hydroxylated silicon surfaces, J. Appl. Chem. USSR, 43, 432-434, 1970; Translated from: Zh. Prikl. Khim., 1970, 43(2), 430-431. (Sveshnikova1970b) en ru	7	5
J. Nishizawa, H. Abe, T. Kurabayashi, Molecular Layer Epitaxy, J. Electrochem. Soc., 1985, 132, 1197-1200 (Nishizawa1985) en	7	5
S. I. Kol'tsov, A. N. Volkova, V. B. Aleskovskii, 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, J. Appl. Chem. USSR. 42, 980-984 1969; Translated from: Zh. Prikl. Khim., 1969, 42(5), 1028-1034. (Kol'tsov1969b) en ru	6	5
T. Pakkanen, M. Lindblad, V. Nevalainen, Quantum chemical studies of the formation of zinc sulfide surface by the ALE technique, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 14-17. (Pakkanen1984) en	5	5
V. B. Aleskovskii, S. I. Kol'tsov, Some characteristics of molecular layering reactions, Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad, 1965, p. 67. [In Russian]. (Aleskovskii1965) ru	5	4
G. V. Sveshnikova, S. I. Kol'tsov, V. B. Aleskovskii, Measuring thicknesses of ultra-thin silicon oxide films deposited by molecular layering on the surface of single crystal silicon using polarization method, Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad, 1969, p.18. [In Russian] (Sveshnikova1969a) ru	4	4
M. Ahonen, M. Pessa, T. Suntola, A study of ZnTe films grown on glass substrates using an atomic layer evaporation method, Thin Solid Films, 1980, 65, 301-307. (Ahonen1980) en	5	4

## Conclusion

This poster presents a recommended reading list of early ALD publications from all over the world. The list has been created collectively in collaboration of tens of scientists from around the world. Although the currently presented list should be the most balanced list currently available, it is also evident that many significant early ALD publications remain outside of this short list.

## References

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- A. A. Malygin, V. E. Drozd, A. A. Malkov, V. M. Smirnov, "From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition". Chemical Vapor Deposition 21 (2015) 216–240. DOI: [10.1002/cvde.201502013](https://doi.org/10.1002/cvde.201502013)

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