

# On the Early History of ALD: Molecular Layering

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## Introduction: Virtual Project on the History of ALD

Virtual Project on the History of ALD (VPHA) is a worldwide open collaborative initiative, started in summer 2013. The goal is to explore the early history of ALD in an atmosphere of openness, respect and trust. For the invitation to participate, see <http://www.aldpulse.com/node/189>.

The core activity of the VPHA is to:

1. Create a complete list of early ALD publications until 1986
2. Have volunteers read the publications and comment on the work
3. Collect the comments of different people together

The full literature list created in the VPHA can be viewed and commented upon in the ALD-history-evolving-file in Google docs ([link](#)).

This poster at the 14<sup>th</sup> International Conference on Atomic Layer Deposition, organized by AVS in Kyoto, June 15-18, 2014, describes ALD research made under the name “Молекулярное Наслаивание” (MH), which has remained poorly known outside the USSR/Russia. MH is typically translated into English as “Molecular Layering” (ML), although occasionally, other names are also seen. In a way, this work continues the exploration of ML works started a decade ago, the initial results of which were published in J. Appl. Phys. 97 (2005) 121301.

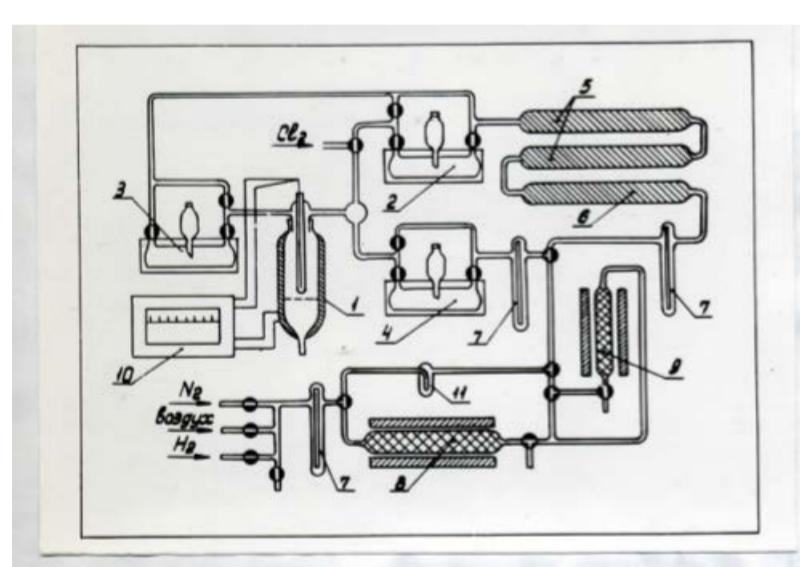
## The beginning of Molecular Layering (ML)

- In 1952, Aleskovskii finalized his Doktor Nauk (habilitation degree), “Matrix hypothesis and way of synthesis of some active solid compounds”, at Leningrad Lensoviet Institute of Technology. The matrix hypothesis (or skeleton hypothesis) enabled two basic ways of transforming a solid to another: (1) substituting atoms in the skeleton and (2) reactions of functional groups. Later, further work on (1) led to Destruction-Epitaxial Transformations method (A.P. Dushina) and on (2) to Molecular Layering (S. I. Koltsov).
- In 1963, Koltsov, who worked with Prof. Aleskovskii, published an abstract “Synthesis of multilayered inorganic polymers”. Some consider this the first ML/ALD publication, although no results are shared in the abstract from which ALD could be confirmed.
- In 1965, Aleskovskii and Koltsov published an abstract “Some characteristics of molecular layering reactions”. In this work, the term “Molecular Layering” was used for the first time. No experimental results were given in the abstract where the practice of ALD could be confirmed.
- In 1965 (Nov 26-29), a conference was held in Leningrad, with proceedings published in 1967. In these proceedings, Shevjakov, Kuznetsova and Aleskovskii reported ML cycles of TiCl<sub>4</sub>-H<sub>2</sub>O on silica particles with experimental data and repetition experiments. All ALD characteristics were included: separate, saturating chemisorption reactions of TiCl<sub>4</sub> and H<sub>2</sub>O, absence of physical adsorption, purging of the reaction by-products, and repeated reaction cycles (up to 10). Later, in 1969, Koltsov published as a sole author a journal article [Zh. Prikl. Khim. 42 (1969) 1023] with detailed analysis of similar results as in this proceedings paper. There have been many abstracts on molecular layering before this proceedings (not mentioned in this poster). The fact that this proceedings article contains such extensive experimental information on ALD cycles points to that several of the earlier abstracts who state that “molecular layering” was made, may also have contained information on ALD cycles. Unfortunately, detailed information is not available for us to confirm this.
- In 1970, Sveshnikova, Koltsov and Aleskovskii published a journal article [Zh. Prikl. Khim. 43 (1970) 430] “Interaction of titanium tetrachloride with hydroxylated silicon surfaces”. This is the first journal article of ML(ALD) on planar substrates, with 12 cycles of TiCl<sub>4</sub>-H<sub>2</sub>O on silicon (111) cleaned in two different ways.
- In 1971, Koltsov finished his habilitation degree thesis (doktor nauk) “Synthesis of solids by the Molecular Layering method”. The thesis was marked secret; the secrecy requirements were relaxed only in year 2013.

In 1967, Professor Aleskovskii founded the Chemistry of Solids chair in Lensoviet Leningrad Technological Institute. Professor Aleskovskii served as the rector of Lensoviet Leningrad Technological Institute from 1965 to 1975.

In 1978, Professor Aleskovskii founded the Solid State Chemistry chair in Leningrad State University. Professor Aleskovskii served as the rector of Leningrad State University from 1975 to 1985.

## Miscellaneous images

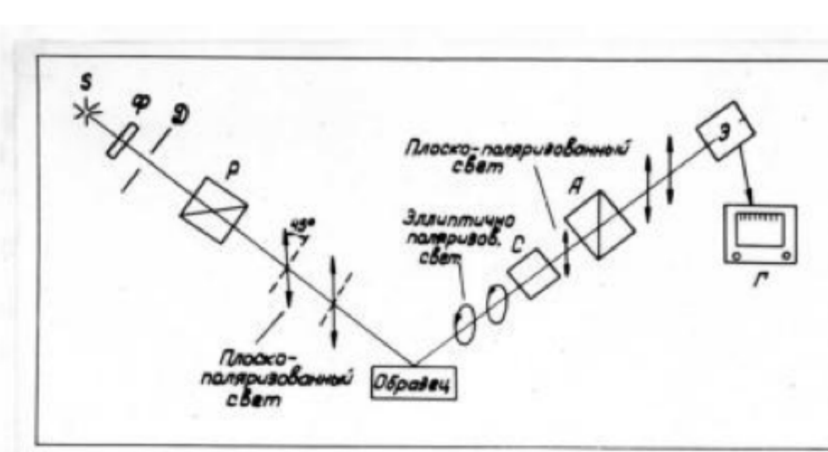


Reactor scheme from the thesis of Koltsov, 1971

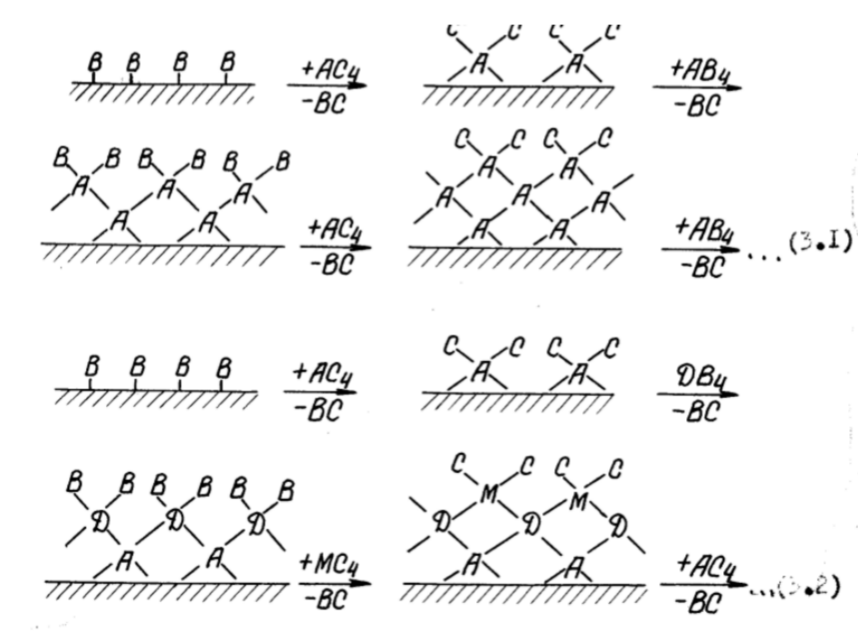
TABLE 14  
Investigation of the degree of functionalization of silicon surface by chlorine at different temperatures.

Temp. (°C)	Cl/Si	Si/Si	Cl/Si	Si/Si
100	1.00	-	0.21	0.18
120	1.00	-	0.18	0.17
140	0.18	1.18	0.16	0.16
160	0.10	0.99	0.16	0.16
180	0.10	0.99	0.16	0.16
200	1.00	-	0.17	0.17
220	0.96	0.96	0.17	0.17
240	1.00	-	0.17	0.17
260	0.96	0.96	0.15	0.15
280	1.00	-	0.15	0.15

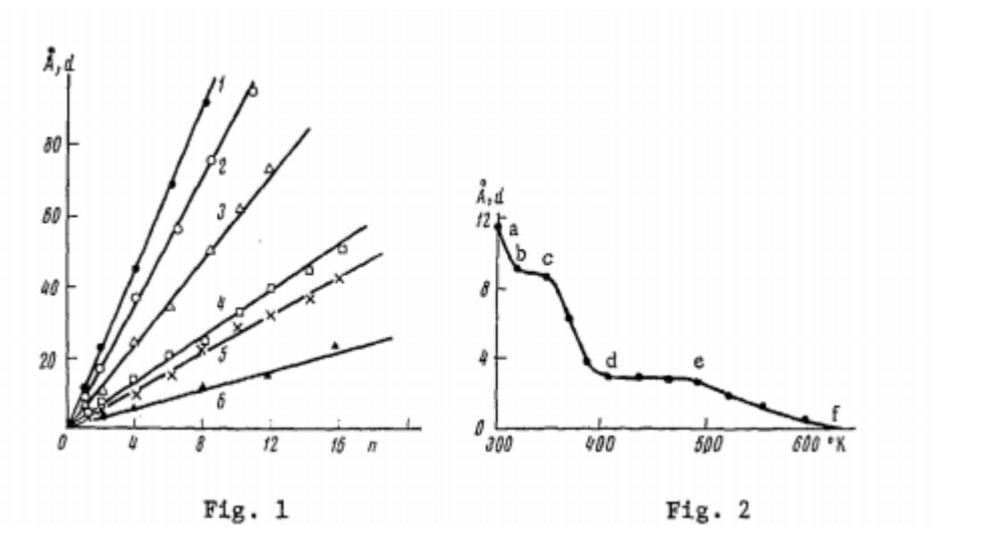
Chemical composition of functional groups from reaction of silica gel with chlorides at 180C, from the thesis of Koltsov, 1971



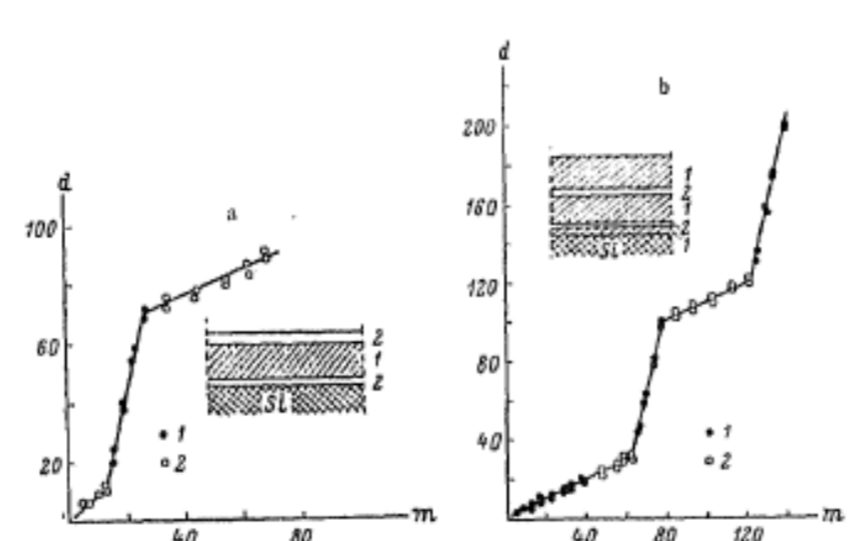
Scheme of a self-built ellipsometer from the thesis of Koltsov, 1971



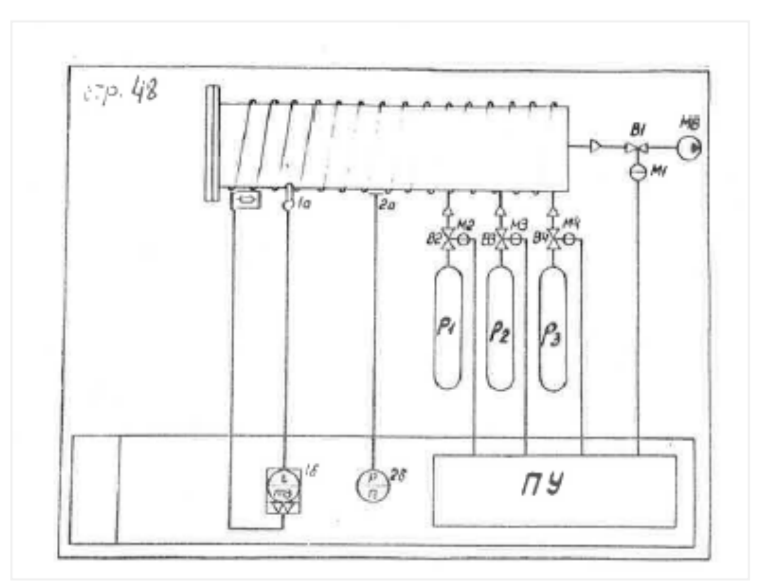
Schemes of Molecular Layering, from the thesis of Koltsov, 1971



From Koltsov, S. I., Drozd, V. E. & Aleskovskii, V. B. Investigation of degree of monocrySTALLINE silicon surface hydration at different temperatures. Dokl. Akad. Nauk SSSR, 1976, 229(5), 1145-1147.



From Aleskovskii, V. B. Chemistry and technology of solids. J. Appl. Chem. USSR., 47, 2207-2217, 1974

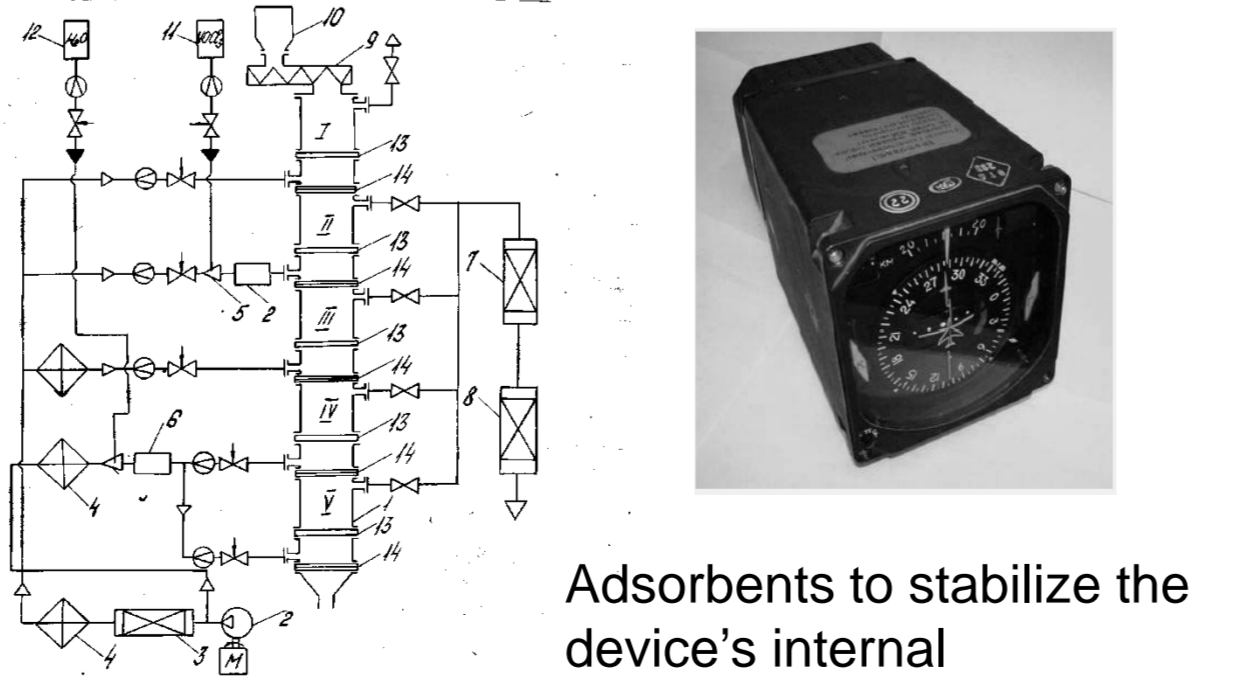


Scheme of a vacuum thin film ML reactor from the thesis of Drozd, 1978

Table 1. Barrier heights of Si-Al junctions containing oxide interlayers vs oxide interlayer composition.

Oxide interlayer composition	Interlayer thickness (nm)	Barrier height (eV)	Barrier slope (eV/nm)
SiO <sub>2</sub>	1.0	0.54	0.57 - 0.61
TiO <sub>2</sub>	1.0	0.57	0.60
Al <sub>2</sub> O <sub>3</sub>	1.0	0.47	0.45 - 0.51
SiO <sub>2</sub>	2.0	0.46	0.50
Al <sub>2</sub> O <sub>3</sub>	2.0	0.40	0.40
SiO <sub>2</sub>	2.0	0.40	0.40
Al <sub>2</sub> O <sub>3</sub>	2.0	0.40	0.40

From Aleskovskii and Drozd, Acta Polytech. Scand., Chem. Technol. Ser., 1990, 195, 155-161. Data originally from the thesis of Drozd, 1978, p. 114.



Column apparatus for ALD coating of particles, from the thesis of Malygin, 1991.

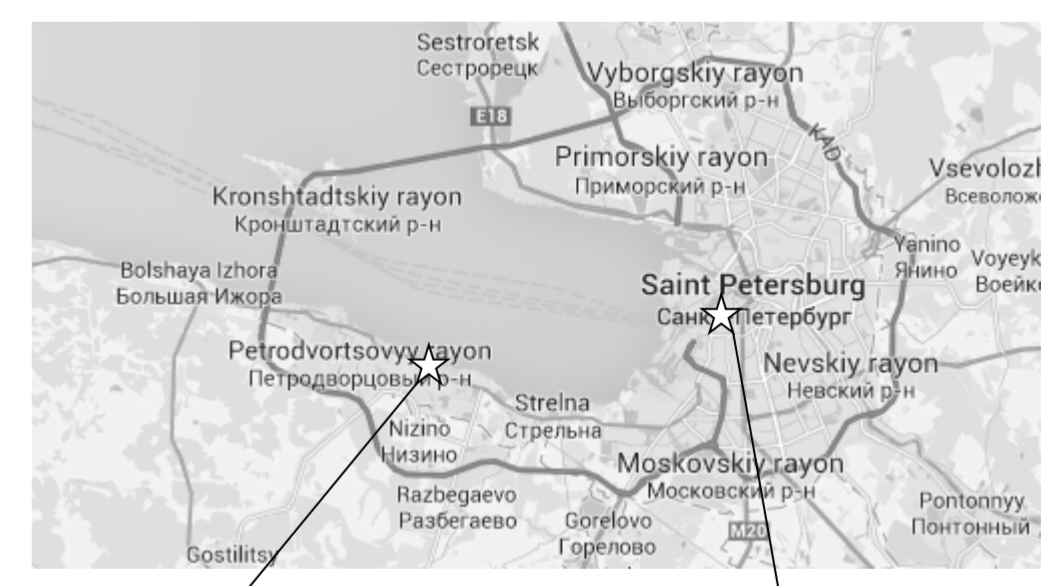
## Some key references of ML published by year 1986

Year published	Reference	Notes
1952	Aleskovskii, V. B., Matrix hypothesis and way of synthesis of some active solid compounds. Thesis for Doctor of Sciences (Habilitation) degree. Leningrad Lensoviet Institute of Technology, Leningrad, 1952. [In Russian]	Matrix hypothesis paved the way for ML investigations
1965	Aleskovskii, V. B. & Koltsov, S. I. Some characteristics of molecular layering reactions. Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad, 1965, p. 67. [In Russian].	Name "molecular layering" introduced
1967	Shevjakov, A. M.; Kuznetsova, G. N. and Aleskovskii, V. B. 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 [in English and in Russian]	TiO <sub>2</sub> by TiCl <sub>4</sub> -H <sub>2</sub> O on particles (repeated cycles)
1970	Sveshnikova, G. S., Koltsov, S. I. & Aleskovskii, V. B. Interaction of titanium tetrachloride with hydroxylated silicon surfaces J. Appl. Chem. USSR., 43, 432-434, 1970 [in English and in Russian]	TiO <sub>2</sub> by TiCl <sub>4</sub> -H <sub>2</sub> O on Si
1970	Sveshnikova, G. V.; Koltsov, S. I. & Aleskovskii, V. B. Formation of a silica layer of predetermined thickness on silicon by the molecular-layering method. J. Appl. Chem. USSR, 43, 1155-1157, 1970 [in English and Russian]	SiO <sub>2</sub> by SiCl <sub>4</sub> -H <sub>2</sub> O on Si
1971	Koltsov, S. I. Synthesis of solids by the Molecular Layering Method, Doktor nauk thesis, Lensoviet Leningrad Technological Institute, 1971, 383 p. [In Russian]	"The ML thesis"
1974	A.N. Volkova, A.A. Malygin, S.I. Koltsov, V.B. Aleskovskii, The method of synthesis of Cr(III) and P(V) oxide layers on the silicagel surface, Patent # 422446 (USSR) Date of submission: 31.03.1972, Date of publication: 05.04.1974	Author's certificate with catalysts made in four ALD cycles
1974	Aleskovskii, V. B., Chemistry and technology of solids. J. Appl. Chem. USSR., 47, 2207-2217, 1974 [in English and in Russian]	Review of ML/ALD and other things, with future prospectives indicated
1976	A. A. Malkov, S. I. Koltsov, V. D. Ivin, E. P. Smirnov, V. B. Aleskovskii, Effect of surface modification of carbon fibers with titanium oxide groups on their reactivity, J. Appl. Chem. USSR, 49, 1650-1652, 1976. [In English and in Russian]	One TiCl <sub>4</sub> -H <sub>2</sub> O cycle by ML on pre-functionalized carbon
1978	Drozd V.E., Synthesis and study of oxide coatings obtained by molecular layering on semiconductor surfaces, Kandidat nauk thesis, Leningrad Technological Institute named on Lensoviet, 1978, 131 p. [in Russian]	ALD for semiconductors, thin film reactors, e.g., HfO <sub>2</sub> , ZrO <sub>2</sub> .
1979	V. N. Krilov, M. M. Mironova, V. E. Drozd, V. B. Aleskovskii, Influence of oxides interlayers on the properties of contact metal-semiconductor, Fizika i Technika Poluprovodnikov, 13, 2272-2274, 1979.	MOS diodes on Si: Cr <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> , TiO <sub>2</sub>
1979	Yakovlev, S. V.; Malygin, A. A.; Koltsov, S. I.; Aleskovskii, V. B.; Chesnokov, Yu. G. & Protodyakonov, I. O. Mathematical model of molecular layering with the aid of a fluidized bed, J. Appl. Chem. USSR, 52, 959-963, 1979. [in English and in Russian]	Modelling of fluidized bed for ALD on particles
1981	Koltsov, S. I.; Kopylov, N. N.; Drozd, V. E. & Aleskovskii, V. B. Investigation of the electric-field influence on the synthesis of titanium-oxide layers on the surface of silicon of the method of molecular layer coating. Dokl. Akad. Nauk SSSR, 1981, 256(6), 1415-1418. [in Russian]	ALD in electric field
1982	Tolmachev, V. A. Possibility of the use of a gravimetric method for studying the process of molecular layering in disperse silica samples. J. Appl. Chem. USSR., 55(6), 1298-1299, 1982. [in English and in Russian]	In-situ gravimetry
1982	Egorov A. L. Ezhovskii Yu. K.. Preparation of ultra thin silicon dioxide films on the tantalum surface by the chemical buildup method. J. Appl. Chem. USSR, 57(4), 685-688, 1984. [in English and in Russian]	Amine-catalyzed SiO <sub>2</sub> deposition
1984	B. Z. Motsenyat, Yu. K. Ezhovskii, L. M. Levan'kova, N. V. Mikhailova. Formation and reactions of hydroxyl groups on polyimide surface with titanium tetrachloride. J. Appl. Chem. USSR, 1984, V. 57, I. 1, P. 153-155. [in English and in Russian]	TiCl <sub>4</sub> on modified polymer
1985	A. A. Abakumov, Yu. K. Ezhovskii, S.I. Koltsov. Chemical assembly of a silicon-nitrogen layer on silicon. J. Appl. Chem. USSR, 1985, V. 58, I. 8. P. 1718-1721. [in English and in Russian]	SiCl <sub>4</sub> -NH <sub>3</sub> to silicon nitride
1985	V. D. Ivin, R. M. Levit, A. A. Malkov, E. P. Smirnov. Interaction of methane with the chlorinated surface of carbon fibers. J. Appl. Chem. USSR, 1985, V. 58, № 3, P. 592-595. [in English and in Russian]	CCl <sub>4</sub> -CH <sub>4</sub> to carbon

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## Conclusion and Outlook

The amount of ALD investigations made under the name Molecular Layering is large and this poster can give only a short, incomplete overview of those works. Although this information is based on publicly available sources, much of it is “new” in the way that it cannot be found in the existing ALD reviews. The information presented will help today’s growing global ALD community to see their research in perspective. The VPHA continues and more people are warmly welcome to join.

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