Overview of early publications on Atomic Layer Deposition

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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

This poster at 14th International Conference on Atomic Layer Deposition, organized by AVS in Kyoto, June 15-18, 2014, is the second outcome of the project. The work continues.

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Disclaimer: The comments expressed herein are done so as private individuals. Any opinions are the person's own and do not represent the views of the companies/institutes the individual is employed by/affiliated with.

List of abbreviations

ALD	**Atomic Layer Deposition**
ALE	**Atomic Layer Epitaxy**
ALE	**Atomic Layer Evaporation**
DET	**Destruction-Epitaxial Transformations**
MD	**Molecular Deposition**
ML	**Molecular Layering**
MLD	**Molecular Layer Deposition**
MLE	**Molecular Layer Epitaxy**

1950s

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]**
Алесковский В. Б.. Остовная гипотеза и опыт приготовления некоторых активных твердых тел. Диссертацию на соискание ученой степени доктора химических наук, Ордена Трудового красного знамени Технологический институт имени Ленсовета, Ленинград, 1952.
{Aleskovskii1952} ru
Riikka Puurunen: In my opinion, clarifying the role of the doctoral thesis by V.B. Aleskovskii is one of the major tasks to be accomplished in the VPHA. Many sources cite that the ALD principles ("or ALD concept") were described there. However, I have not seen anyone describe in detail, what was actually said. If the principles of ALD were described there, the full details should be found and translated. On the basis of reading the title page, the contents list, the introduction, and a few pages of the dissertation, catalysis is the general area of the thesis. "Active" in the title refers to catalytic activity, as I understand.
Jonas Sundqvist: I think it is important to understand Aleskovskii´s Matrix/Framework hypothesis with the work of mainly german scientists (V. Kohlschütter, H.W. Kohlschütter, H-P. Boehm, and others) that studied functional groups (including hydroxyl groups) on silica in this time period.
Yury Koshtyal: After reading some parts (pages 1–12, 59–66, 98–104, 365–367) of Aleskovskii thesis I think that the influence of "framework" hypothesis on ML or ALD process can be explained in following way. There are two particularities of ML:
1. Reactions occur on the surface of solid and they involve functional groups and low-weight molecules.
2. Sequence of reactions allowing formation of atomic layer after each cycle of synthesis. According to Aleskovskii hypothesis a solid can be regarded as a stable framework covered by functional groups. Thus two types of reactions with solid substances can be identified:
a. Reactions with functional groups.
b. Reactions affecting framework.
Since reactions taking place during ML process are reactions involving functional groups (hydroxyls in case of silica) Molecular layering has appeared thanks to "framework" hypothesis. Did Koltsov and Aleskovskii use "framework" hypothesis for development of the ML process? The answer is obvious – yes. But the reactions with functional groups were well-known before introduction of "framework" hypothesis. For instance, Aleskovskii in his book «Стехиометрия и синтез твёрдых соединений» (page 28-29) mention the works of A.V. Kiselev:
«А. В. Киселев развил представление о глобулярном строении силикагеля и показал [51,52], что его специфические сорбционные свойства определяются гидроксильным покровом поверхности. По своей химической природе силикагель и активный кремнезём, согласно работам [30, 41, 42], - это поликремневые кислоты, то есть высокомолекулярные соединения, имеющие тот или иной кремнекислородный остов, функциональными группами которого служат гидроксильные группы.»
"A. V. Kiselev has developed the conception of silica's globular structure. He has shown [one of the papers dates 1936], that specific sorption properties of silica are determined by hydroxyl cover of the surface. According to [works of Aleskovskii] silicagel and active silica are polysilicium acids, e. g. polymers having one or another silicium-oxygen framework, functional groups are hydroxyl groups."
Jaan Aarik: The comments are based on pages 1–12, 59–66, 98–104 and 365–367 of the dissertation.
Describing the research background in his doctoral dissertation V.B. Aleskovskii has concluded that „compounds that have been formed in surface reactions should be considered as real bulk high-molecular ones rather than surface complexes" (page 63). Basing on this conclusion as well as some other parts of the dissertation text available one could suppose that Aleskovskii believed to be possible to synthezise solid materials in successive surface reactions. No information about experimental proof of the hypothesis could be found, probably also because Part 3 of the dissertation contains classified information as mentioned in Introduction.
A. A. Malygin: A few words follow about the "skeleton hypothesis" proposed by V.B. Aleskovskii in 1952 in his doctoral dissertation and about its connection with Molecular Layering.
1. V.B. Aleskovskii did not elaborate the Molecular Layering (ML) method as such. He developed new concepts of solids and ways of their physicochemical transformations. The basis of those new approaches to chemistry of solids was the skeleton hypothesis, which he formulated in his doctoral thesis. It is sometimes called a chemical model of a solid. Its essence is that any solid, regardless of its structure (crystalline or amorphous, porous or compact) and chemical nature (organic or inorganic), can be represented as a skeleton (matrix) that consists of atoms or other structural units connected by covalent or other chemical bonds and carries functional groups on its surface. For example, the skeleton of silica consists of [SiO_4] tetrahedra linked by covalent bonds, whereas the functional groups on the surface are OH-groups. He suggested that solids are classified according to the skeleton hypothesis as those with zero-, one-, two- and three-dimensional skeleton. The skeleton hypothesis enables two basic ways of transforming one solid to another: (1) substituting atoms in the skeleton and (2) reactions of functional groups; simultaneous occurrence of both processes is also possible.
2. In his doctoral thesis V.B. Aleskovskii provided only partial experimental proof for his hypothesis. Namely, ML-like sequential treatment with two reactants had not been introduced expressly. BUT!!! If even a single new atom appears on the surface of a solid, then that solid becomes a new material with new properties and a new functional group capable of taking part in new reactions. In other words, the possibility of further transformations on the surface of that new solid with new functional groups is assumed a priori. The most comprehensive experimental substantiation of the two aforementioned ways of transformation of solids was given later in doctoral dissertations by A.P. Dushina (the DET method, i.e. reactions of atoms of the skeleton) and S.I. Koltsov (the ML method, i.e. reactions of surface atoms, including repeated sequential treatment with the reactants). By 1971, when S.I. Koltsov defended his doctoral dissertation, a number of candidate dissertations on ML were defended under his and V.B. Aleskvskii's supervision (those by A.N. Volkova, R.R. Rachkovskii, G.V. Sveshnikova and G.N. Kuznetsova).
Summary. V.B. Aleskvskii's skeleton hypothesis has initiated the development of two new methods of synthesis. While the DET method (by A.P. Dushina) involves transformations of the skeleton, the ML method (by S.I. Koltsov) illustrates the processes caused by reactions of functional groups. V.B. Aleskovskii was a scientific ideologist, and indeed a co-author, of these new methods of synthesis of solids.
For Russian scientists from the group of V.B. Aleskovskii and S.I. Koltsov, the idea of ML is based on the skeleton hypothesis.

1960s, part 1 of 2

H.-P. Boehm, M. Schneider, F. Arendt,
Der Wassergehalt „getrockneter" Siliciumdioxyd-Oberflächen,
***Z. Anorgan und Allgem. Chem. B.* 320, 43-53, 1963 [in German]**
{Boehm1963}
Jonas Sundqvist: "The number of surface silanol groups on "Aerosil", an amorphous fine particle size silica, was determined by reaction with $SOCl_2$. Their number decreases sharply between 250° and 350°C. After reaction with anhydrous $AlCl_3$ and BCl_3. the "Aerosil" was analyzed for Al or B and Cl. The results show, that free, strongly adsorbed water is bound to the surface even after high vacuum heat treatment. From 100° to 350°C, there is one water molecule bound per two silanol groups. Above 350°C, the water content decreases to a greater extent than the number of silanol groups." Interesting for ALD research but no ALD was reported in this paper. This paper was in a special issue for H.W Kohlschütters 60th birthday (Professor H. W. Kohlschütter zum 60. Geburtstag gewidmet).
Riikka Puurunen: Koltsov refers to this in "Koltsov1969a", where the Boehm et al. paper is Reference 1. In Koltsov's words: "It was shown earlier [1-3] that when chlorides of certain elements (designated E) interact with hydroxyl groups of silica gel the reaction m(triple bond-Si-OH) + ECl_n --> m(triple bond-Si-O)_mECl_(n-m) + m HCl leads to formation of new functional groups <…> on the silica gel surface.

Kol'tsov, S. I., Aleskovskii, V. B.
Silica gel, its structure and chemical properties
***Goskhimizdat, Leningrad,* p.96 1963 [In Russian]**
Кольцов, С. И. & Алесковский, В. Б.. Силикагель, его строение и химические свойства. Госхимиздат, Ленинград, 1963, 96 страниц.
{Koltsov1963} ru
Riikka Puurunen. In this 96-page publication (in Russian), detailed analysis is presented of 1) the properties of silica gel, 2) the modification of silica with CCl4, and 3) the hydrolysis of the CCl4-treated silica surface with water, to regenerate the silanol groups and release COCl2 + HCl, where COCl2 further hydrolyzes to CO2 and HCl. I see for example analysis of the effect of surface OH group concentration to the CCl4 reaction, analysis of the effect of temperature and pressure on the CCl4 reaction, and nicely grafted saturation curves. About the significance of this work in the ALD literature. In my opinion, the experimental results don't count yet as a demonstration of the ALD growth principle, as although there are two successive gas--solid reaction steps, no layer gets grown. The characteristics of the separate chemisorption reactions are, of course, similar to the single chemisorption steps during ALD growth. Interestingly, in 1973, Malygin et al. refer to this work, saying that in the 1973 work, the same apparatus was used as described in this work from 1963.
Jonas Sundqvist: From my side I for now my opinion is that ALD has to be demonstrated by film growth in addition to investigations of half and/or complete ALD-cycles.
Nikolai Chekurov: Same (kind) of apparatus is used in a paper by Kol'tsov, S., Uhova, Volkoval from 1974.

Kol'tsov, S. I.
Synthesis of multilayered inorganic polymers
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1963, p. 27. [In Russian]**
Кольцов, С. И.. Синтез «многослойных» неорганических полимеров. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1963, стр. 27.
{Koltsov1963a} ru
Riikka Puurunen: This is a short abstract text in Russian. I have tried to translate the full text for this. Here's how it reads, in my words (note that my Russian is not fluent):
"1) Shown is the possibility of in principle getting inorganic polymers, conditionally (tentatively?) named multilayers. Proposed is the nomenclature for such compounds.
2) Synthesized are R-polysiloxide and R-polytitanoxide and their derivatives (hydrates, chlorides, hydrides). Several of their properties are studied."
For me personally, it is impossible to know on the basis of this description, what actually was made. Were the ALD principles described? There may have been a theoretical example of building layers, but one cannot know for sure, whether it would be for one cycle or for many cycles to grow a film (mentioning of multilayers points to the likelyhood of having several layers). Synthesis is mentioned but results not included. Term "molecular layering" is not yet used. This work has likely been an important step towards ALD by this research group. Was this also the first demonstration of the principles of ALD? I cannot know for sure, there is not enough information to confirm that. Interestingly, Aleskovskii did NOT refer back to this abstract in his 1974 paper (chemistry and technology of solids). Also Koltsov himself did NOT refer back to this for example in his 1969 paper on TiO2 growth {Koltsov1969a}.
Yury Koshtyal: I think that in first works Koltsov has tried to extend some reactions known in the field of organic chemistry to inorganic. It can be seen from terminology. The second proof is the references to works of Merrifield who suggested a synthesis of some organic molecules on the matrix. I think he likely used the same principles which were described in his Doctoral thesis. To my opinion the aim of this work and Doctoral thesis was to show that silica surface can be modified as any large organic molecule and different individual solid-state products can be obtained. The products with different extension of replacement of Chloride groups are different. Thus, even if Koltsov didn't use terms like Molecular Layering this work served to the development of ALD.
Jonas Sundqvist: I agree, there is not enough information to confirm ALD on the basis of this abstract text.

S. I Koltsov, G. N. Kuznetsova
Reaction of trichlorosilane with silica.
***Abstract of Scientific and Technical Conference (Leningr. technol. in-ta im. Lensoveta) Publisher - "Khimiya" L., 1964. P. 62.* [In Russian].**
С.И. Кольцов. Г. Н. Кузнецова. Взаимодействие трихлорсилана с силикагелем. Тезисы докл. научно-техн. конференции Ленингр. технол. ин-та им. Ленсовета, изд-во "Химия", Л., 1964, стр. 62
{Koltsov1964} ru
Translation of the abstract (Chekurov):
1. Stoichiometric ratios of "multilayer" product of poly(Cl, H)siloxane by hydrolysis of trichlorosilane by hydroxyl groups of silicagel have been studied. Layering practically stops after 5th layer because of exhaustion of the reactive functional groups.
2.Stability of obtained products to oxidation by air decreases when the number of "layers" is increased.
3.It is shown that kinetics of hydrolysis of poly(Cl, H)siloxane by water vapor changes with the increase of the number of layers. Maximal initial rate of hydrolysis is achieved at third "layer".
Kestutis Grigoras: Multilayered structure of poly(Cl, H)siloxane was prepared by reaction of trichlorosilane with water vapor. "Layering" process practically stops after reaching five layers, due to completed consumption of all active functional groups available.
Looks like ALD process, but strange that only five layers can be performed. Maybe this is related to s ome peculiar conditions of the process (temperature, pressure, ...)? By the way, it is still not completely clear what means "fifth layer" - is it fifth cycle after which one monolayer is fully completed? or layer thickness corresponding to five monolayers?
Riikka Puurunen: This is a very short abstract in Russian. I understand that a repeated process has been carried out of, treating silica gel with trichlorosilane and thereby hydrolyzing the trichlorosilane with the hydroxyl groups on silica gel. It is mentioned that "layering" (nasloenie, Наслоение) stops after the fifth "layer" due to exhaustion of the reactive functional groups (исчерпывания реакционноспособных функциональных групп). The word "multilayer" («многослойного» продукта) is mentioned. On the basis of the first paragraph, it remains unclear to me, whether there has been a repeated treatment of silica gel just with trichlorosilane, or has there been a cycle of hydrolysis (=water reaction) to complete a cycle. (The second paragraph discusses the stability of the products to oxidation by air.) The third paragraph discusses the kinetics of the hydrolysis of the poly (Cl, H) siloxane with water vapor. This indirectly may indicate that water vapor has been used as a second reactant, but one cannot be sure. Nothing is mentioned of the apparatus, temperature or pressure. [Later, in {Koltsov1967a}, Koltsov et al. refer back to this abstract (Ref. 2), saying that treatment with water vapour permits the addition of more =SiClH onto the surface → it is very likely that ALD/ML cycles indeed have been made.]
Henrik Pedersen: From the translation it seems to me that in 1. they exposed the silica gel to multiple exposures of trichlorosilane, but in 3. they alternated between trichlorosilane and water exposure. For me this is ALD cycles, but the complete lack of apparatus description makes it hard to fully judge if one should call the experiment ALD.
Jonas Sundqvist: To me this resembles repetition of an self terminating ALD process since it seems that it terminates after 5 cycles : "Layering practically stops after 5th layer because of exhaustion of the reactive functional groups". Meaning they would need to run a second pulse of a precursor realizing a chemisorbed layer of functional groups to refresh the surface and make it reactive again. To me there is not enough information to determine either that is or is not ALD. I am aware of other such self terminating ALD processes e.g. SiCl4/NH3 on TiN is selfterminating below 600°C, SiCl4/H2O on HfO2 is self terminating at 300°C, 4DMASi/O3 is also selftermination in many High-k ALD processes. These are all examples of dopants (Si) used to have ALD control of dopant distributin in 3D structures. Reading this, I come to think that most probably trichlorosilane/H2O can also be employed as a Si dopant in 3D High-k applications.

Aleskovskii, V. B. & Kol'tsov, S. I.
Some characteristics of molecular layering reactions
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1965, p. 67. [In Russian].**
Алесковский, В. Б. & Кольцов, С. И.. Некоторые закономерности реакций молекулярного наслаивания. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1965, стр. 67.
{Aleskovskii1965} ru
Riikka Puurunen: This is a short abstract in Russian. As I translate it to myself (with limited skills and a wordbook), the work discusses the regularities of the mechanisms of reactions of reactants with three ligands (e.g. SiHCl3, AlCl3), four ligands (tetrahalogenides of Group IV elements) or five ligands (pentahalogenides of Sb or P) with hydroxylated silica. Regarding the RX4-type compounds (I would write this as ML4, metal with four ligands), it is mentioned that the reaction product depends on the quality and structure of the pre-existing "layer" ("layer" is in parenthesis in the original publication also). **The term "molecular layering" (molekulyarnoye naslaivanie) is introduced.** There are no indications of ALD cycles in the work, but the reference to a pre-existing layer suggests that several reactions may have been made. Could this refer to successive treatments with two different chemicals from the list mentioned? Cannot be sure. This abstract is often referred to in later literature by the group.
Yury Koshtyal: This abstract summarizes the results of investigations of most probable (average) number of bonds formed between RX_3 ($SiHCl_3$, RX_4 (halides of fourth groups elements according to the text, maybe author used $SiCl_4$, $TiCl_4$ and $GeCl_4$), RX_5 ($SbCl_5$, PCl_5) and hydrated silica during their reaction (each RX_y and silica, y is equal to 3 or 4 or 5). The method of determination of the number of bonds (functionality of RX_y) is not communicated. It can be supposed that authors made their conclusions on the base of concentrations of hydroxyl groups on the surface of solid supports (silica and modified silica);elements forming part of modifying layers;chlorine in solid products of reaction.
The chlorine concentration was likely deduced from chemical analysis of solutions obtained after hydrolysis of solid products of reaction between support (silica, modified silica) and RX_y. Therefore it can be concluded that at least one layer of R-oxygen containing structures was synthesized. In the paragraph describing interaction of RX_4 and silica the authors mention a collocation – structure of previous layer . Thus at least two layers were synthesized with use of RX_4. The word layer is situated between quotation marks, this can mean that is unknown whether the structure of this layer is continuous or not.
During reaction with the support RX_3 formed two bonds, RX_4 formed two or three bonds. The functionality (number of bonds formed during reaction with silica) of RX_5 was not communicated in abstract. Authors just communicated that they investigated it.
Number of bonds, formed between RX4 and a support depended on the structure of previous layer. I suppose that "the structure of previous layer" can be read as a concentration of hydroxyl groups.
Jaan Aarik: "Some principles of reactions in molecular layering" by V.B. Aleskovskii and S.I. Kol'tsov reports about studies on adsorption of halides (SiHCl3, AlCl3 etc) on silica. Nothing about further reactions steps has been written.
Kestutis Grigoras: "Several trends of molecular epitaxy reactions"
1. On a bases of reaction of hydrated silicon oxide with trichloresilane (HSiCl3) and aluminum chloride (AlCl3) it is shown that RX3 type groups act in reactions of molecular epitaxy as bifunctional groups.
2. Chemical groups of RX4 type are interacting with hydroxile groups of hydrated silicon oxide by means of 2 or 3 atoms of halogene, depending on the content and structure of the previous "layer".
3. Pentahalogenides of antimony and phosphorus were used to evaluate the functionality of structures RX5.
From those few statements it is possible to guess that cyclic type of reactions was used (statement 2: "previous layer). also, expression like "Molecular epitaxy" is mentioned (in statement 1).
On the other hand, there is no data about number of cycles, and the term "cycle" was not mentioned here.

Aleskovskii, V. B.; Kol'tsov, S. I.; Kuznetsova, G. N. & Shevjakov, A. M.
Reaction of germanium tetrachloride with silica gel
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1965, p. 67. [In Russian]**
Алесковский, В. Б.; Кольцов, С. И.; Кузнецова, Г. Н. & Шевяков А. М.. Взаимодействие четыреххлористого германия с силикагелем. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1965, стр. 67.
{Aleskovskii1965a} ru
Riikka Puurunen: this is a very short abstract in Russian. The first paragraph states that the reaction of GeCl4 has been studied with hydroxylated silica gel. The second paragraph states that GeO2 was grown on silica by molecular layering, and the mechanism of that process was investigated. From the very short text, it is difficult to know what the significance of the work is. That one paragraph concentrates on the reaction of GeCl4 and another in the making of GeO2 suggests that probably the H2O reaction has been made---just once, or many times?

Aleskovskii, V. B.; Kol'tsov, S. I. & Petrov N. P.
Reaction of antimony pentachloride with silica gel
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1965, p. 68. [In Russian]**
Алесковский, В. Б.; Кольцов, С. И. & Петров Н. П.. Взаимодействие пятихлористой сурьмы с силикагелем. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1965, стр. 68
{Aleskovskii1965b} ru
Riikka Puurunen: This is a very short abstract in Russian. In the first paragraph, it is stated that the effect of temperature and of pre-calcination of silica and coal on the interaction with SbCl5 was studied. The second paragraph says that molecular layering of antimony oxide was exercised on silica gel and carbon. (Note use of carbon support! Was this the first time?) This has a similar structure as the abstract of the previous page: one paragraph about the reaction investigation, and one paragraph about the molecular layering. I wonder, what the "molecular layering" means here. Does it mean that cycles have been repeated? Or does it just mean one cycle of (presumably) SbCl5 and H2O reactions? I cannot know on the basis of the given information.
Jonas Sundqvist: Yes this is really the key here, as well as in the previous asbtract (GeCl4) - what did Molecular Layering mean exactly then. We need to figure that out - how I do not know.

Kol'tsov, S. I.
Interaction of trichlorosilane with silica gel.
***Zh. Prikl. Khim.*, 38, 1384, 1965 [In Russian]**
Кольцов, С. И.. Изучение взаимодействия трихлорсилана с силикагелем. Журн. прикл. химии., 1965, 38(6), 1384-1384.(Original article submitted March 28, 1964)
{Koltsov1965} en ru
Riikka Puurunen: This one-page paper reports the reaction of SiHCl3 with hydroxylated silica. With current-day terminology, we could call this the "first half-cycle" of an ALD process. There are no discussions or indications of a "second half-cycle", or thoughts of what would be a suitable second reactant. This paper does not pass yet my criterion of demonstrating the ALD principe, although I fully realize that the author may have been thinking and proceeding in that direction.
Henrik Pedersen: I agree with Riikka on this; half an ALD cycle is presented and no indication of plans to go further with a second half cycle is given.
Jonas Sundqvist: Yes half cycles of ALD or one complete cycle is really interesting but if there is no repetion it is not ALD and should fall in the same category as the Kohlschütter *et al* work.

G.N. Kuznetsova
Examination of a number of typical products of interaction of hydrated silica with ions of metals by the method of IR-spectroscopy.
***Diss. ... Cand. chem. Sciences* LTI - L – 236 pp 1965**
A. A. Malygin: In this work has not studied synthesis, and work is referenced by ML 1963 In this dissertation presents data on the use of the method of IR spectroscopy for studying the products obtained by the methods of DET and ML (DET = destruction-epitaxial transformations method).
Anatolii Malkov (on the DET abbreviation): This abbreviation is meaning - destructive epitaxial-conversion of solid materials. This method was based on the chemical reactions of solid core according to the chemical model of solids proposed by Prof. V.B. Aleskovskii. During these transformations the extraction of ions from the solid core to the solution was occurs. Then another ions (with different chemical nature) are incorporating into the structure of the solid's core.

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]
Translated from: Шевяков, А. М.; Кузнецова, Г. Н. & Алесковский, В. Б.. Взаимодействие тетрахлоридов титана и германия с гидратированным кремнеземом. - В кн.: Химия высокотемпературных материалов. Труды 2-го Всес. совещ. по химии окислов при высоких температурах. Л., "Наука", 1967, с. 149-155.
{Shevjakov1967} en ru
Riikka Puurunen: When I was digging through through the early ALD papers for my 2005 review [J. Appl. Phys. 97 (2005) 121301], this was the first one where I personally witnessed that ALD cycles have been carried out. (There is earlier work, where single chemisorption reactions are studied.) All the basic practical requirements of ALD can be identified in this work: separate, saturating chemisorption reactions of TiCl4 and H2O or GeCl4 and H2O, absence of physical adsorption, purging of the reaction by-products, and repeated reaction cycles (up to ten for TiCl4--H2O to make TiO2). Cycles denoted as "exposure--purging--hydrolysis--drying", and this sequence is repeated. All experiments are carried out at 180°C. The reproducibility of the depositions was studied also, and repeating the growth experiment gave consistently similar results, as should for chemistry-controlled ALD. Recently, I learned that also a complete English translation exists of the whole paper; earlier, I tried to make sense out of the original paper Russian, in Cyrillic letters. --- The question is, will this remain the first paper, where the ALD principle---with repeated cycles to grow a layer---has been demonstrated experimentally for the first time? --- I have also another question. Why did the Soviet researchers refer to this work very little later? In Kol'tsovs later mechanism paper [Zh. Prikl. Khim., 1969, Vol. 42, pp. 1023-1028] I don't see a reference to this work. To me it would be logical that there would be the reference, as it is clearly related.
Jonas Sundqvist. I am refering to the english version. Indeed this is ALD how most of us have learned to understand it. Classical -OH Group reaction chemistry above the point of physisorption ("..., without physical adsorption of water on the SiO2 surface"). Purge is realized with dry air, which is important here since the purge should in most case be inert. Repetition of ALD cycles is also taking place "Exposure-purging-hydrolysis-drying cycle was again repeated". Also, if you plot what we today know as growth (mass) you can see that there is a close to linear trend for the two Processes TiO2 rsp. GeO2 (Table 1.). In the case of TiO2, you could even think of two growth regimes one faster initial growth and then a steady state growth rate that is slightly slower.
Henrik Pedersen: (English version) To me this is ALD - they describe how they expose a silica surface to TiCl4 or GeCl4 in dry air, then they flush with dry air to remove byproducts and unreacted TiCl4/GeCl4 and then they expose the surface to water vapor to react away chlorides on the surface. This cycle was then repeated several times. Interesting to note that they refer to the formed GeO2/TiO2 as coating
Oili Ylivaara: Reactions between silica gel and TiCl4 or GeCl4 were studied. Precursors were delivered via dry air and temperature was 180C. Reaction sequence was exposure-purging-hydrolysis-drying. In the study, the silica gel was covered by a single layer of OxMeCl4-x groups (reactions called monomolecular overlap). Up to ten cycles tested for the TiCl4. Anatase was detected after fourth cycle and TiO2 after the first cycle by x-ray method. The GeO2 was detected in x-ray after 6th cycle.

Kol'tsov, S. I.; Kuznetsova, G. N. & Aleskovskii, V. B.
Properties of dioxochlorosilane groups on the surface of silica.
***Izv. Akad. Nauk SSSR, Neorg. Mater,* 3, 800-801 1967 [In English]**
Кольцов, С. И.; Кузнецова, Г. Н. & Алесковский, В. Б.. Свойства диоксохлоросиллановых групп на поверхности кремнезема. Изв. АН СССР. Неорган.материалы. 3(5), 1967, стр. 894-895.(Original article submitted on January 25, 1966)
{Koltsov1967a} ru en
Riikka Puurunen: Four cycles of trichlorosilane (in a stream of dry nitrogen) and water vapor at 180°C, to make "a layer of polyhydrisiloxane, chemically bonded to the surface". After the completion of the SiHCl3 reaction, "the hydrogen chloride and unreacted trichlorosilane were removed" --- thus, the normal ALD characteristics are there: (i) completion/saturation of the reaction, (ii) removal of unreacted precursor, (iii) removal of gaseous reaction product. The Cl and H contents are analyzed for four repeated cycles. Given as mg/g, H content goes up with cycles while Cl decreases with cycles (Cl groups are removed during the reactions). Hydrophobicity of the layer increases with cycles. The stability of the product to oxidation by atmospheric oxygen is studied.
Jonas Sundqvist: I have not read the paper, but I think that 4 cycles is not enough to say that it is an ALD process. If you could actually grow something resembling SiO2, in this case polyhydrisiloxane, with SiHCl3 and H2O without using any catalytic precursor like NH3 or pyridine at 180 °C that would actually have a number of industrial applications (e.g. double patterning for CMOS scaling). Has this process been studied later in time by others?

Kol'tsov, S. I.; Aleskovskii, V. B.; Kuznetsova, G. N. & Roslyakova, N. G.
Reaction of germanium tetrachloride with silica gel.
***Izv. Akad. Nauk SSSR, Neorg. Mater,*p. 1318-1319 1967 [in English]**
Translated from: Кольцов, С. И.; Кузнецова, Г. Н. & Алесковский, В. Б.. Реакция терахлорида германия с силикагелем. Изв. АН СССР. Неорган.материалы. 3(8), 1967, стр. 1509-1510.(Original article submitted on June 25, 1966)
{Koltsov1967c} en ru
Riikka Puurunen: GeCl4 reaction with porous silica gel at 180°C. Amounts of Ge and Cl attached and OH before and after reaction are quantified, and five repetitions of the same reaction made to gain statistics. The chemisorbed species are mostly Ge with two Cl ligands and to lesser extent Ge with one Cl. Interestingly, it is noted that only 40% of the surface OH groups react with GeCl4 (60% remain unreacted), which differs from the behaviour of other reactants observed earlier under similar conditions, TiCl4 and SiHCl3.
Cagla Ozgit-Akgun: $GeCl_4$ and silica gel were reacted in flowing dry air at 180 °C. After the reaction has been completed, excess $GeCl_4$ and reaction by-product (HCl) were removed from the reaction chamber via purging with dry air. The experiment was repeated 5 times. Results indicated that $GeCl_4$ molecules react preferentially with two and sometimes three -OH groups, which results with the formation of $GeCl_2$ and GeCl surface groups, respectively. Authors further indicated that about 60% of the -OH groups at the surface of silica gel do not react with $GeCl_4$ under the given conditions. In my opinion, this work is not related to ALD since there is neither a second precursor nor repeated cycles.
Jonas Sundqvist: on basis on the information in the comments above, I also agree that this is not ALD.

S. I. Kol'tsov, V. B. Aleskovskii.
Influence of dehydratation of silica on the mechanism reaction (hydrolysis) with trichlorosilane
***Zh. Fiz. Khim.* 41, 665-666 1967 [in Russian]**
С. И. Кольцов, В. Б. Алесковский. Влияние степени дегидратации силикагеля на механизм гидролиза на нем трихлорсилана. Журнал физической химии. 1967 Т. 41, вып. 3, С. 665-666.
{Koltsov1967e} ru

Kol'tsov, S. I. & Aleskovskii, V. B.
Classification of chemical transformations of macromolecular inorganic compounds. *Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1967, p.13-15 [in Russian]
Кольцов, С. И. & Алесковский, В. Б.. Классификация химических превращений неорганических высокомолекулярных соединений. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1967, стр. 13-15
{Koltsov1967d} ru
Andrew Akbashev: This abstract does not contain any information regarding ALD.

Volkova A. N; Kol'tsov, S. I. & Aleskovskii, V. B.
Study of phosphorus trichloride reaction with silica gel.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1967, p.19. [In Russian]**
Волкова А. Н.; Кольцов, С. И. & Алесковский, В. Б.. Изучение условий взаимодействия треххлористого фосфора с силикагелем. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1967, р. 19
{Volkova1967} ru
Andrew Akbashev: (**translation**) 1. When PCl3 interacts with OH (hydroxo) groups of silicagel, new functional groups of phosphorus(III) appear on the latter. The kinetics of the reaction is studied. 2. Optimal conditions for this reaction are found. 3. The dependence of PCl3 chemisorption on the degree of hydroxylation of the silicagel surface was studied.

1960s Part 2 of 2

Sveshnikova G. V.; Kol'tsov, S. I. & Aleskovskii, V. B.
Reaction of titanium tetrachloride with silicon.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1967, p.19. [In Russian]**
Свешникова Г. В.; Кольцов, С. И. & Алесковский В. Б.. Взаимодействие четыреххлористого титана с кремнием. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1967, стр.19
{Sveshnikova1967} ru
Andrew Akbashev: (**translation**) 1. The reaction and its conditions of TiCl4 with Si was studied. 2. Multiple treatment of Si with TiCl4 leads to a sequential increase in the number of chemisorbed TiCl4 from 0.0096 mg*atom/g to 0.0726 after the 4th treatment. 3. The dependence of the amount of chemisorbed TiCl4 on the surface area of Si particles was revealed.
My thoughts are: the authors showed (maybe not for the first time) the presence of the saturation of chemisorbed molecules after enough exposure to TiCl4 (or a larger number of "pulses"). After that they also indicate a very important fact that TiCl4 does cover all the particles (a kind of deposition on a high-aspect-ratio material) because they see the coverage (amount of adsorbed molecules) depends on the total surface.
Riikka Puurunen: From this abstract, I understand that the reaction of TiCl4, and cycles of TiCl4, have been investigated with silicon particles, with several surface areas. The reactant are not specified, apart from TiCl4, and also not the reaction temperature. Judging from other works from the same group, the cycles have been TiCl4/H2O (most likely at 180°C). Because the abstract is very short, I copy it below in the original form and as my translation.
Translation of the abstract:
1. Investigated was the reaction of titanium tetrachloride with silicon, an found some conditions (протекания?) this reaction.
2. Multiple treatment of silicon with titanium tetrachloride leads to a successive increase in the amount of chemisorbed titanium from 0.96 10-2. at-mg / g to 7.25 10-2. at-mg / g after the fourth treatment.
3. Noticed was the dependency of the content of titanium, chemisorbed on silicon, on the surface area of the particles of the silicon.
Original abstract:
1. Изучена реакция Четыреххлористого титана с кремнием, найдены некоторые условия протекания этой реакции.
2. Многократная обработка кремния четыреххлористым титаном приводит к последовательному увеличению количества хемосорбированного титана от 0,96 10-2 .мг ат/г до 7,25 10-2 .мг ат/г после четвертой обработки.
3. Выявлена зависимость содержания титана, хемосорбированного кремнием, от величины поверхности частиц последнего.

Kol'tsov, S. I. & Aleskovskii, V. B.
Interaction of titanium tetrachloride with silica gel
***J. Appl. Chem. USSR.* 40, 872, 1967 [in English]**
Translated from: Kol'tsov, S. I. & Aleskovskii, V. B. Interaction of titanium tetrachloride with silica gel. *Zh. Prikl. Khim.,* 1967, 40(4), 907. (Кольцов, С. И. & Алесковский В. Б.. Взаимодействие четыреххлористого титана с кремнеземом. Ж. Прикл. Химии, 1967, 40(4), 907) (Original article submitted on July 12, 1965)
{Koltsov1967} en ru
Riikka Puurunen: TiCl4 reaction with hydroxylated silica. The amounts of Ti and Cl adsorbed are determined, Ti by colorimetry and Cl by hydrolysis of the surface (!). No indication of repeated ALD cycles.
Oili Ylivaara: TiCl4 reacted with silica gel at 180C. Unreacted TiCl4 and reaction product (HCl) were removed by dry air at reaction temperature. Ti-Cl groups formed on silica surface. Not clear how many times cycles repeated.
Cagla Ozgit-Akgun: $TiCl_4$ and silica gel were reacted in a current of dry air at 180 °C. $TiCl_4$ hydrolyzed by the -OH groups in silica, and as the analysis of the product revealed, Ti-Cl groups were formed at the surface of silica. After the reaction, excess $TiCl_4$ and reaction by-product (HCl) were removed from the reactor via purging. In my opinion, this work is not related to ALD since there is neither a second precursor nor repeated cycles.
Ruud van Ommen: the paper describes half an ALD cyle: the reaction of silica gel with TiCL4. The second half cycle - the reaction with water - is used to analyse the sample (i.e., to determine the Cl content). The authors did check the self-limiting behaviour of the reaction. It is very short - just one page - and does not give the properties of the particles or the equipment.

Sergeeva, L. A. Kalinkin, I. P. & Aleskovskii, V. B.
Deposition, structure and some photoelectric properties of single and multi crystal chalcogenide films AIIBVI and AIVBVI. Cristallography reports. 12, P. 113-118, 1967 [in Russian]
Л. А Сергеева, И. П. Калинкин, В. Б. Алесковский. Получение, структура и некоторые фотоэлектрические свойства одно и многослойных монокристаллических халькогенидных пленок AII BVI и AIVBVI. Кристаллография 1967, Т. 12, вып. 1, С. 113-118.
Yury Koshtyal: not ALD.

Kol'tsov, S. I., Kuznetsova, G. N. & Aleskovskii, V. B.
Study of the stoichiometry of the products formed in the reaction of trichlorosilane with the functional groups of polysilisic acid,
***J. Appl. Chem. USSR.*, 40, 2644-2646, 1967 [in English]**
Translated from: Kol'tsov, S. I., Kuznetsova, G. N. & Aleskovskii, V. B., *Zh. Prikl. Khim.,* 1967, 40(12), 2774-2777. (Кольцов С. И., Кузнецова Г. Н., Алесковский В. Б., Изучение стехиометрии продуктов реакции трихлорсилана с функциональными группами поликремнекислоты., Ж. Прикл. Химии, 1967, 40(12), 2774-2777). Manuscript received in the journal editorial office 24.1.1966. (The English translation reads: original article submitted January 24, 1966).
{Koltsov1967b} en ru
Riikka Puurunen: In this paper, SiHCl3 + H2O ALD reaction cycles are carried out: up to four cycles at 180°C with dry air as carrier gas. Is this the first ALD paper with cycles demonstrated? Or is it the conference paper by Shevyakov? Both have been published in 1967, and for both, the experiments must have been made in 1965. Whichever was earlier, I think the Shevyakov et al. paper is more illustrative for the use of ALD, since in this paper by Kolt'sov et al., a Si-based layer was deposited on a silica support, so the build-up of material cannot be easily followed (the growth of TiO2 on silica was easy to follow in the Shevyakov work through the analysis of the Ti content).
Jonas Sundqvist: As I have stated previously, SiHCl3 / H2O ALD reaction is not to my knowledge possible at 180°C without further activation by catalytic (NH3, pyridene) or plasma species.

Kol'tsov S. I.
Chemisorption potential and linear decrease of differential chemisorption heat with increase of surface coverage degree
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1968, p.21. [In Russian]**
Кольцов С. И. Хемосорбционный потенциал и линейное падение дифференциальной теплоты хемосорбции с увеличением степени заполнения поверхности. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1968, стр. 21
{Koltsov1968a} ru

Kol'tsov, S. I. & Aleskovskii, V. B.
The change of silica porosity by molecular layering method.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1968, p.23. [In Russian]**
Кольцов, С. И. & Алесковский В. Б., Изменение пористости кремнезема методом реакций молекулярного наслаивания. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1968, стр. 23.
{Koltsov1968b} ru
Andrew Akbashev: In 1 the authors say that "during molecular layering of various oxides on silicagel surface the change of surface chemical composition is observed, and, most importantly, the structure of the surface changes, i.e., surface area, porosity and the radius distribution of pore volumes". In 2 they use molecular layering of TiO2 to observe the gradual decrease of the total volume of silicagel pores depending on the number of cycles of TiCl4 and H2O. So, importantly, the authors use cycling ML for the growth of conformal(?) TiO2 layer over the particles (high-aspect-ratio structure).

Volkova A. N; Kol'tsov, S. I. & Aleskovskii, V. B.
The study of stoichiometry of the products of multilayer chemisorption of PCl3 on silica gel.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1968, p.29. [In Russian]**
Волкова А.Н.; Кольцов, С. И. & Алесковский В. Б.. Изучение стехиометрии продукторв многослойной хемосорбции трехxлористого фосфора на силикагеле. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1968, стр. 29.
{Volkova1968} ru
Riikka Puurunen: This is an abstract in Russian - still quite short, but also more informative than the very early abstracts. From the text I understand that repeated reaction cycles were carried out of a three-step (! would this be the first three-step process?) ALD process on silica: PCl3 + Cl2 + H2O. The kinetics and the effect of temperature on the second step, the Cl2 reaction, were studied. It is not mentioned how many cycles were exactly carried out, but "all steps were repeated several times".

Volkova A. N; Kol'tsov, S. I. & Aleskovskii, V. B.
Influence of the degree of surface hydroxylation of silica gel on chemisorption of phosphorus trichloride.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1968, p.30. [In Russian]**
Волкова А. Н., Кольцов, С. И. & Алесковский В. Б.. Влияние степени гидроксилирования поверхности силикагеля на хемосорбцию трехxлористого фосфора. Науч.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 1968. стр. 30.
{Volkova1968a} ru
Andrew Akbashev: The reaction of PCl3 with dehydrated surface of silicagel was studied. It was shown that the decrease of the OH-group concentration on the surface of silicagel leads to the change of the interaction mechanism of PCl3 with hydroxyls. As a result, new functional groups =P-Cl appeared additionally to

1970s on

Rachkovskii, R. R.; Kol'tsov, S. I. & Aleskovskii, V. B..
Reaction of tin tetrachloride with silica gel
***Rus. J. Inor. Chem.*, 15, 1646-1647, 1970 [in English and Russian]**
Translated from: Rachkovskii, R. R.; Kol'tsov, S. I. & Aleskovskii, V. B.. *Zh. Neorg. Khim.,* 1970, 15(11), 3158-3158. Изучение взаимодействия четыреххлористого олова с силикагелем.
{Rachkovskii1970} en ru
Henrik Pedersen: This very short paper describes what could be regarded as an ALD half cycle where SnCl4 reacts with OH groups on a silica gel surface. Hydrogen gas is used to purge away unreacted SnCl4 and HCl byproducts. The method is referred to as "molecular lamination". It is suggested that SnCl4 reacts with two OH to form two HCl as byproducts. The intent seems to be functionalization of the silica gel surface rather than forming a film on the gel. No suggestions that a second pulse of water could be used to form a SnO2 film.
Riikka Puurunen: Indeed, there is a mistake in the English translation here of the carrier gas. The Russian text says: "в токе сухого воздуха", and this is translated as "in the current of dry air". "Molekulyarnoe naslaivanie" has been translated as "molecular lamination". I think that there has not been one correct English translation of the name available, but there are various translations found from the literature. The ones I encountered by the time of making the 2005 review, I summarized in a table in the review [J. Appl. Phys. **97**, 121301 (2005); http://dx.doi.org/10.1063/1.1940727].

Kol'tsov, S. I.
Changes in the structure of silica gel during formation of a layer of titanium dioxide on its surface.
***J. Appl. Chem. USSR.*, 43, 1976-1979, 1970 [In English]**
Translated from: Kol'tsov, S. I.. *Zh. Prikl. Khim.,* 1970, 43(9), 1956-1959.
С. И. Кольцов. Изменение структуры силикагеля при формировании на его поверхности слоя двуокиси титана. Журнал прикладной химии, 1970. Т. 43, вып. 9, С. 1956-1959.
{Koltsov1970} en ru
Henrik Pedersen: As the title indicates, this paper is totally focused on the change of pore size and volume of the silica gel when an ALD like process is used to deposit TiO2 onto the gel. All discussion on the actual ALD process is given in references. Could be regarded as a paper that uses ALD rather than reporting ALD.
Gloria Gottardi: The paper describes the theoretical modeling of the structural changes (variations of specific surface and specific pore volume) induced by repeated alternate treatments of silica gel with titanium tetrachloride and water vapors, which lead to the deposition of a titanium dioxide layer. Following the basic ALD (here described as molecular layering reactions) process principles an accurate calculation of the evolution of the treatments in terms of their effects on the porous structure was performed. In particular, on the base of the specific half-reactions the authors calculated the average particle diameter increase, per each layering cycle, and the corresponding specific surface and pore volumes decrease. The accordance between the calculated and the experimental data (measured on various specimen) demonstrated that regular changes in the porous structure of silica gel can be designed in advance and accurately produced by successive deposition of a specified number of oxide monolayers by an ALD like process. Even if the paper is not properly focused on the development of an ALD process, it surely helps to underline some ALD fundamental features, like the possibility to control the deposition effects at the atomic level and the possibility to treat porous structures.
Oili Ylivaara: Kol'tsov studied changes in the coarse-pored silica gel structure with molecular layering by repeating TiCl4 and water vapor cycles. Apparently the experimental setup was pretty much the same as presented already in Kol'tsov, S. I., Preparation and investigation of the products of interaction between titanium tetrachloride and silica gel. J. Appl. Chem. USSR., 1969, 42(5), 975-979

S. I. Koltsov, A. N. Volkova, V. B. Aleskovskii
Synthesis and investigation of products of reaction between PCl_3 and silica
***Neorganicheskiye materialy,* 6, 1370-1372, 1970**
С. И. Кольцов, А. Н. Волкова, В. Б. Алесковский. Получение и исследование химического состава продуктов взаимодействия трехxлористого фосфора с силикагелем. Неорганические материалы, 1970, Т. 6, вып. 7, С. 1370-1372.
{Koltsov1970i} ru

Sveshnikova, G. S., Kol'tsov, S. I. & Aleskovskii, V. B.
Interaction of titanium tetrachloride with hydroxylated silicon surfaces
***J. Appl. Chem. USSR.*, 43, 432-434, 1970 [in English]**
Translated from: Sveshnikova, G. V.; Kol'tsov, S. I. & Aleskovskii, V. B. *Zh. Prikl. Khim.,* 1970, 43(2), 430-431. (Original article submitted June 18, 1969).
{Sveshnikova1970b} en ru
Riikka Puurunen: In this paper, TiO2 growth is reported on single-crystal Si (111) surface from the TiCl4 and H2O reactants at 180°C. Two different cleans were made for the surface: Specimens A, for which "SR-4 etchant" had been used (not specified, what it is, but it 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 TiO2 is detected. It is mentioned that 12 cycles were carried out, and thickness was estimated at 2-2.5 nm. Very interestingly, 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. The authors also investigate the effect of carrying out the dehydration step at 115°C (I am not sure if the TiCl4 reaction was then at 180 or 115°C). It is noticed that a similar electron diffraction pattern is obtained in only 3 cycles as needed at 180°C in 10 cycles, and it is concluded that a layer of molecularly adsorbed water accounts for the increased growth. (Is it possible that they say that the TiO2 layer is crystalline one one type of surface and amorphous on the other? In the English translations, partly a bit weird words are used, so I am not sure.)
Henrik Pedersen: In addition to Riikka's description above, it is worth to note that the authors briefly describe that when the time for "removal of the reaction products and drying", what we would call purge time in today's ALD, is increased from 10 minutes to 4 hours, an amorphous layer is formed on specimen A. This might give a hint that the cycle times were very long.
Alexander Pyymäki Perros: This article studies the influence of surface treatment of silicon crystals on the growth of TiO2 by alternate treatment of TiCl4 and H2O vapor. One noteworthy finding is that surface treatment and temperature affect the nucleation TiO2 and whether the film is amorphous or polycrsytalline. The method of deposition of TiO2 fulfills all the characteristics of atomic layer deposition and should be considered as such. The authors also report that the deposited film uniformally coats etch pits. It is correctly noted that 'irregularities' can 'influence only the rate of diffusion of the reaction components and products' thus presaging ALD's ability to coat surfaces unreachable by other conventional deposition techniques

Tammenmaa, M.; Leskelä, M.; Koskinen, T. & Niinistö, L.
ZINC-SULFIDE THIN-FILMS DOPED WITH RARE-EARTH IONS
J. Less-Common Met., **1986**, *126*, 209-214
{Tammenmaa1986} en
Bechelany: The paper by Tammenmaa et al. describes the synthesis of zinc sulfides thin films doped with rare earth ions using atomic layer epitaxy. The authors show that the crystallinity of the thin film changed as the functions of the zinc source and the growth temperature. The films doping could be controlled within large limits by the pulsing technique. This paper does not give a lot of details about the synthesis process but it focus on the luminescence properties of these thin films.

Tischler, M. A.; Anderson, N. G. & Bedair, S. M.
Ultrathin InAs/GaAs single quantum well structures grown by atomic layer epitaxy
Appl. Phys. Lett., **1986**, *49*, 1199-1200
{Tischler1986c} en
Bechelany: This paper reports the synthesis of extremely thin InAs/GaAs single quantum well structures by ALE. The wells were 2 and 4 InAs monolayers thick. Again the same set up as in the "Journal of Crystal growth 77 (1986) 89-94" has been used to growth the III-V compound thin film. In this paper, the spatial thickness uniformity has been studied on large sample (1.5 cm on a side). The photoluminescence measurement shows that ALE has the capacity to grow uniform, high quality material with excellent control of layer thickness and interface abruptness on large substrates.

Tischler, M. A. & Bedair, S. M.
Growth and characterization of compound semiconductors by atomic layer epitaxy
J. Cryst. Growth, **1986**, *77*, 89-94
{Tischler1986} en
Bechelany: This paper by Tischler et al. describes the synthesis of III-V compound thin films using atomic Layer epitaxy. This paper gives a very nice introduction about Atomic layer epitaxy and the conditions needed to achieve a monolayer per cycle. The deposition set up is well described. The substrate sits in the rotating part of the susceptor. The susceptor has two openings windows in the fixed part through which the gases flow. The precursor gases impinge on the wafer when the substrate is rotated in the opening. So the wafer is alternatively exposed to precursor gases for the accurate control of the thickness of the thin film. The exposed time to the stream is 0.3 s and the time per cycle is 2.6 s. This paper described as well the mechanism of the selflimiting growth of III-V compound.

Tischler, M. A. & Bedair, S. M.
Self-limiting mechanism in the atomic layer epitaxy of GaAs
Appl. Phys. Lett., **1986**, *48*, 1681-1683
{Tischler1986b} en
Bechelany: The paper described the self-limiting mechanism observed for the growth of GaAs deposited by ALE. The thickness of the deposited films was found to be independent of the mole fractions of the precursors in the gas phase. The same system of deposition as in the "Journal of Crystal growth 77 (1986) 89-94" has been used. The obtained GaAs is single crystal as showed by TEM. This paper is similar to the work reported by the same author in Journal of Crystal growth with a longer explanation of the self-limiting mechanism.

Tischler, M. A. & Bedair, S. M.
Improved uniformity of epitaxial indium-based compounds by atomic layer epitaxy
Appl. Phys. Lett., **1986**, *49*, 274-276
{Tischler1986d} en
Bechelany: At this paper, Tischler et al. synthesized another type of III-V based thin film: the indium based compounds by ALE. Again the same set up as in the "Journal of Crystal growth 77 (1986) 89-94" has been used to grow the thin films and a mechanism of self-limiting has been found which control the thickness deposited per cycle independent of the flux.

Usui, A. & Sunakawa, H.
GaAs atomic layer epitaxy by hydride VPE
Jpn. J. Appl. Phys., Part 2, **1986**, *25*, L212-L214
{Usui1986} en
Gloria Gottardi: The paper provide an interesting example of Atomic Layer Epitaxy of GaAs films accomplished by using a dual-growth chamber reactor. Differently from the standard ALE proposed by Suntola, the alternative adsorption of reactant gas molecules onto the growing surface is not obtained by the sequential introduction of the two precursors in the same reaction chamber (eventually separated by a purging step), but switching the position of the substrate between two separate chambers, each of which contains the specific precursor. The physical separation of the two chambers ensures the separation of the two half-reactions.

Yao, T.
Dynamic Reflection High-Energy Electron Diffraction Observations of the Atomic Layer Epitaxy Growth of Zn Chalcogenides
Jpn. J. Appl. Phys., Part 2, **1986**, *25*, L942-L944
{Yao1986b} en
Gloria Gottardi: The paper is fully focused on the use of the RHEED (reflection high energy electron diffraction) technique to investigate atomic layer epitaxy growth of Zn chalcogenides films. One period of the RHEED intensity oscillation corresponds to a monolayer growth of the crystal. The work demonstrates the power of this tool for an in situ investigation of the growth dynamics, by allowing the measurement of the adsorption times of the different beam fluxes and the calculation of some thermodynamic values relevant to surface kinetics.

Yao, T.
The Effect of Lattice Misfit on Lattice Parameters and Photoluminescence Properties of Atomic Layer Epitaxy Grown ZnSe on (100)GaAs Substrates
Jpn. J. Appl. Phys., Part 2, **1986**, *25*, L544-L547
{Yao1986c} en
Pia Sundberg: This is a XRD and photoluminescence study of ALE grown ZnSe using (100)GaAS as substrates. Of the growth process details only substrate temperature is given (280 °C); the thickness of the films varied between 60 to 350 nm. In conclusion, it was said that thinner than 170 nm films suffered complete tetragonal distortion, while thicker than 170 nm films showed relief from the misfit strain. In thin films the deep emission was said to be prominent while in the thicker films the deep emission became very weak.

Yao, T. & Takeda, T.
Growth process in atomic layer epitaxy of Zn chalcogenide single crystalline films on (100)GaAs
Appl. Phys. Lett., **1986**, *48*, 160-162
{Yao1986} en
Gloria Gottardi: The paper investigates the initial and successive stages of the Atomic Layer Epitaxy growth of Zn chalcogenides films (ZnSe and ZnTe) on a (001) GaAs substrate. The deposition is performed using a conventional molecular beam epitaxy system, where each constituent element was alternatively deposited onto the substrate as molecular beam pulses of Zn, Se and Te_2 from separated sources. In particular the authors' main purpose is to clarify the initial and successive stages of the growth process by in situ RHEED analyses. What comes out from such investigation is that three-dimensional growth mechanism dominates the initial stage of the epitaxy, while, after the deposition of at least 50 monolayers, the film becomes smooth due to the coalescence of islands on the surface and the establishing of a two-dimensional growth mechanism. This is mainly due to the chemical bond mismatch between the substrate (GaAs) and the overgrowth, which does not favor the two-dimensional growth.
Honestly, even if the authors claims that one atomic layer is grown during the open period of a constituent element, the three dimensional growth appears to me rather far from a real ALD growth mechanism. I'm doubtful about the paper conclusions.

Yao, T.; Takeda, T. & Watanuki, R.
Photoluminescence properties of ZnSe single crystalline films grown by atomic layer epitaxy
Appl. Phys. Lett., **1986**, *48*, 1615-1616
{Yao1986d} en

Jidkov AB Kinetics of heterogeneous synthesis of titanium carbide and nitride from a gas phase on the surface of carbon materials : Diss . ... Candidate . Chem. Science / TRL - L. , 1986 . – 202 Жидков А.Б. Кинетика гетерегенного синтеза карбида и нитрида титана из газовой фазы на поверхности углеродных материралов: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1986. - 202 с. (title translated by Riikka Puurunen)
(no code)

Jukka A. Lahtinen, Electro-optical studies of semiconductor compounds for electroluminescent and laser devices, Doctoral dissertation, Helsinki University of Technology, **1986**, 51 p + 6 publications. Acta Polytechnica Scandinavica, Ph, Applied Physics Series.
(no code)

Lviva TB Chemical modification of the coal from the gaseous phase compounds of vanadium (V), chromium (VI), phosphorus (III) and the study of properties of the obtained adsorbents : Diss . ... Candidate . Chem. Science / TRL - L. , 1986 . - 186 p. (EAF) Львова Т.Б. Химическое модифицирование углей из газовой фазы соединениями ванадия (V), хрома (VI), фосфора (III) и исследование свойств полученных адсорбентов: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1986. - 186 с. (ДСП)
(no code)

(1970s continues)
Massimo Tallarida: This paper discuss the growth of anatase TiO2 with TiCl4 and H2O on Si substrates (two substrates prepared differently). There is one figure representing a RHEED pattern of the bare Si sample and another RHEED of one sample after 12 TiCl4+H2O “treatments”. The process works at 180°C.
They cite a previous paper of Kol’tsov (Kol'tsov, S. I., Preparation and investigation of the products of interaction between titanium tetrachloride and silica gel. J. Appl. Chem. USSR., 1969, 42(5), 975-979) where it was shown that TiCl4 and H2O are able to produce anatase TiO2 thin films. I don’t have the paper for judging, but from the comments posted here it seems that Kol’tsov used the same temperature: is it not too low to have crystalline TiO2 thin films only by ALD? I don’t have a direct experience with TiCl4, but I think so.
Also in this manuscript, the RHEED pictures show the presence of (poly)-crystalline TiO2 films. Maybe the answer is at the end of the paper, where they discuss the drying between subsequent “treatments” (see below).
Massimo Tallarida (continues): The part with the description of RHEED measurements is difficult to understand probably because of the translation. I don't understand what they mean with points 2 and 3 in the discussion of how the RHEED patterns change with deposition. For point 1 it is clear, as they refer to figure 1b, which is lately explained to correspond to sample A after 12 treatments, but for the other points? Does somebody try to explain to me?
It seems that after 7 "treatments" the film on both substrates is the same, but it is different after 12 cycles. They also give a value of 20-25Å after 7 cycles, which corresponds to about 2.8Å per cycle. Isn’t it too much for pure ALD?
They prepared samples A and B differently (sample A etched with SR-4 and sample B with HCl+hydration at 180°C and drying). How is it possible that the different pre-deposition treatment influences the growth after 7 cycles and not in the first 7? Have I completely misunderstood something? Or is there something wrong in the translation?
The last part of the paper is in my opinion the most interesting. As far as I understood they want to say: if they dry the sample for 4h instead of 10min they obtain amorphous films instead of crystalline. They obtain crystalline films also if they leave a monolayer of water on the sample before the next TiCl4, showing that the drying for 10 minutes is probably not enough to remove water and that the growth discussed above is influenced by parasitic CVD. This is also confirmed by the island-like growth (the “cellular structure”, as they call it). So, I would call ALD only the method with the 4 hours delay between water exposure and the next TiCl4. I don’t know if the authors were aware of the combination of CVD and “Molecular layering” at this stage, the don’t comment it. It could be interesting to find out in the following publications if they decided to improve the drying to obtain amorphous films or if the crystalline films with 10 minutes drying were good enough for their scopes.
Luca Lamagna: The paper presents the formation of TiO2 on hydroxilated silicon surfaces and the authors directly claim to use the molecular layering method. They refer to the possibility to take advantage of the hydroxyls surface reactivity towards TiCl4 and then to further replace Cl by other OH groups brought by H2O vapor thus being able to repeat the reaction from the first step. The experimental structure presents a single deposition temperature (i.e. 180 °C), two different surface preparations of Si(111) obtained by means of a Si etchant (A) or etch, clean and hydration (B) and the main characterization of the layers is carried out by means of electron diffractions. The first intriguing finding is the dependence of the structural properties on the number of treatments (N-cycles), and thus on the TiO2 thickness. This aspect brings the authors to carry out a sort of investigation of ultra-thin layers revealing and amorphous or polycrystalline oxide on the two different surfaces. Moreover, a second part of the study is dedicated to the purge time dependence which is also integrated by a drying stage investigation. The authors seem well aware of several key ALD parameters such as the surface chemical termination while they carry out something more exploratory the effect of the cycles structure. This paper contains useful anticipations on the characterization of the early stages (from 1 to 10 cycles) of the ALD growth and clearly underline the role of the chemical surface groups in the ALD reactions.
Claudia Wiemer: This article presents two main aspects of modern ALD:
-purging by inert N2 after reaction (it is however not so clear when the purge was performed, if after a full cycle or after each precursor injection....)
-the fundamental role of surface preparation on the properties of the thin growing layer

Sveshnikova, G. V.; Kol'tsov, 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]**
Translated from: Sveshnikova, G. V.; Kol'tsov, S. I. & Aleskovskii, V. B.. *Zh. Prikl. Khim.,* 1970, 43(5), 1150-1152. Original article submitted October 15, 1969
{Sveshnikova1970} en ru
Riikka Puurunen: This paper reports the growth of SiO2 on electrochemically polished single-crystal Si (111) from SiCl4 and H2O at 500 and 180 degrees centigrade. Up to 60 cycles were made (10, 20, 30, 40, 50, 60) at 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 SiCl4; 3) hydrolysis of chlorinated surface groups by water vapor at 180ºC; 4) drying of the specimen at the same temperature.” Curves of measured thickness vs cycles (i.e., growth curves) were plotted; the growth was linear. The SiO2 thickness was determined by “an optical polarization method with the aid of a polarization goniometer”. At 500 degrees centigrade, the slope of the growth curve (i.e., the “growth per cycle”) was 0.11 nm, which the authors noticed to be significantly less than the monolayer thickness of SiO2. Speculation followed of the meaning of this, which led to probably erroneous calculations giving a very high density for the deposited SiO2 (the in my opinion in the hindsight erroneous assumption was that a “monolayer” of SiO2 would still have been deposited, even though the measured thickness was less, hence the SiO2 had to be very dense). At 180 degrees centigrade, the slope of the growth curve was 0.19 nm, which would be close to a monolayer and give a sensible density for SiO2.
When reading a second time, I actually don’t understand what is the difference between graphs 1 and 2 in Fig 1. Is it really just the heat-treatment temperature before ALD? Or was there a hydroxylation step at the given temperature always after SiCl4 reaction at 180C? I think the text does not explain this well.
In my opinion, this work is very interesting. That ALD was made, should be recognizable to anyone working with thin film deposition by ALD: careful surface treatment, identical growth principles, and a similar thickness range as could be in “modern” applications. The cycle times were not reported in the paper and they were probably much longer than in the commercial reactors today, but as we know, they should not matter in ALD anyway, once the ALD conditions are achieved (sufficiently high doses, sufficient purge steps). I also recognize that the same authors have presented an abstract of the same work in the seminar series “*Scientific and Technical Conference, Goskhimizdat, Leningrad*” in the same year (1969) as the submitted paper has been received at the editorial office.
Henrik Pedersen: Not much to add after Riikka’s detailed description above. As I understand it, the difference between plots 1 and 2 in Fig 1 is the temperature of the hydroxylation before ALD. I agree with Riikka that a major fault of the paper is that they assume that one monolayer is deposited per ALD cycle, this induces an error in their calculations. Personally, I like the note in the experimental section ‘The “Razdan-2” digital computer was used for calculation of film thickness.’
Massimo Tallarida: Indeed, here it seems to have a real ALD process. It is nice to see the linear increase of thickness with number of treatments. The density calculation is clearly wrong, because they assumed that they were depositing 1 monolayer after each treatment. Why they didn't consider the possibility of a less than 1 monolayer deposition per treatment? The did not develop the concept of steric hindrance, probably. Do they consider it later on?
Claudia Wiemer: A very interesting paper indeed. Although the density calculation is clearly wrong, as already noticed, I want to point out the importance of this work for what concerns the dependence of growth rate on the temperature of hydroxylization of the initial Silicon surface. Such considerations are of paramount importance for the future applications of modern ALD in microelectronics, where surface treatments of the semiconductor substrate can in influence the performances of MOS structures with ALD-grown dielectric.
Marcel Junige: In 1970 (original article submitted October 1969), Sveshnikova et al. have reported on the “Formation of a silica layer of predetermined thickness on Silicon by the Molecular-Layering method”. In their report, the authors have unequivocally described the molecular-layering (ML) method, which is nowadays commonly referred to as Atomic Layer Deposition (ALD), for the production of thin SiO2 films of pre-determined thickness on Silicon single crystals. They have included a specification of the self-saturating nature of two separated and alternately repeated surface reactions as well as the ALD-characteristic four-step pulsing sequence. Even one of the main benefits of ALD, a very precise film thickness control, has been pointed out and also demonstrated within a ± 3 Å range for SiO2 films up to 117 Å.
Interestingly, Sveshnikova et al. have utilized an “optical polarization method” for determining the SiO2 film thickness, which means that they presumably have applied a single-wavelength ellipsometer like the one reported by R. J. Archer in 1957.[1] During that time, driven by the needs of microelectronics, much progress has been made in the development of ellipsometry for investigating the oxidation of Si.[2] Hence, the development of a deposition process for SiO2 by ML (ALD) might have been motivated by similar demands of that time.
Regarding a critical review of the mentioned paper’s measurement technique, some issues need to be concerned:
1) Calculating the SiO2 film thickness, a formula from a paper that dates back to 1938 has been used. The formula itself seems to be correct; however, the exact values of the parameters within the formula have not been given. So, the constant A for the given support (presumably the initial Silicon single crystal) as well as the refractive index n1 of the SiO2 film remain unclear.
2) Later on, the authors have claimed a difference in the density of SiO2 depending on the hydroxylation temperature of the starting Silicon surface. This, in turn, would also mean that the refractive index of the SiO2 films changed and cannot be assumed constant in the aforementioned formula calculating the film thickness.
3) As far as I understood the experimental procedure correct, the starting Silicon surfaces have been hydrated in the reactor for 2 h in water vapor at 500 °C and 180 °C, respectively. First of all, I would expect an oxidation of the initial Silicon substrates at least under the elevated temperature conditions as this follows the principle of a wet oxidation process. Contrastingly, such an offset in the SiO2 thickness cannot be observed for no-applied ML (ALD) cycles (m = 0). Possibly, the Silicon single crystals already contained a specific native Silicon oxide layer, which then contradicts the author’s statement of coincidence between the goniometric (i. e. presumably the ellipsometric) characteristics of the original single crystals (with possible native oxide) compared to the Silicon after etching away the ML (ALD) as well as native SiO2 films in hydrofluoric acid.
[1] R. J. Archer, J. Electrochem. Soc., 104, 619 (1957).
[2] Eugene A. Irene, In: Handbook of Ellipsometry, pp. 569 (William Andrew, 2005).

Murray, J.; Sharp, M. J. & Hockey, J. A.
The polymerization of propylene by the SiO2/TiCl4/AlMe3 system.
***J. Catal.,* 18, 52-56 1970**
(get a copy)

S. I. Kol’tsov, V.M. Smirnov, V. B. Aleskovskii
Influence of the carrier on catalysts properties
Kinetics and Catalysis, 11, 835-841, 1970
С. И. Кольцов, В. М. Смирнов, В. Б. Алесковский. Изучение влияния носителя на свойства катализатора. 1 Кинетика и катализ. 1970. Т. 11, вып. 4, С. 1013-1021.
{Koltsov1970h} ru en
David Cameron: This paper demonstrates the growth of Ti and P oxide multilayers on silica gel by MLD using PCl3 or TiCL4 and H2O at 180C. The thickness of these layers is proportional to the number of cycles as measured by ellipsometry? (this is referenced to an earlier paper - Sveshnikova 1969). It shows how the coordination of the P or Ti changes from the initial layer to the upper layers. It also shows that the surface area of the silica gel decreases as film growth continues due to interconnection of the silica globules by the molecular layer. The TiO2 films of up to 4 layers were amporphous but for thicker films weak anatase peaks were seen. The catalytic activity of the films for the decomposition of CCl4 depended on thickness of the film. For the P oxides, it depended only on the surface area which decreased as the film grew. for the Ti oxides, it decreased additionally with the distance of the surface from the silica gel substrate.

Kol'tsov, S. I. & Aleskovskii, V. B.
Homology of three dimensional inorganic polymers with globular type structure.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.9. [In Russian]**
Кольцов, С. И., Алесковский В.Б. Гомология трехмерных неорганических полимеров глобулярного типа строения. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Koltsov1970b} ru
Yury Koshtyal: This abstract concerns modeling of solids and from my point of view it is not related to ALD or ML method.
Authors propose that a solid with a globular structure can be presented by formula (AnBs)m. n – number of atoms (A) forming a globule. s – number of functional groups (B) on the surface of globule. m – number of globules in the solid (m depends on the mass of a solid).
In most cases a solid with globular structure is fragmentized with breaking of bonds linking the globules thus this process can be described by following reaction:
(AnBs)m=>2(AnBs)m/2 =>…=>m(AnBs).
A coalescence of the globules can be modeled by following reactions:
m(AnBs)=>(m-2)(AnBs)2=>…=>(m-k)(AnBs)k=>…=>(AnBs)m.
Authors introduce some concepts (notions):
A row of globular homologues: (AnBs)1=>(AnBs)2=>…=>(AnBs)m {n is constant, a number of globules augments in the solid)
A row of normal homologues: (AnBs)m=>(An+sBs1)m=>…=>(A_MB_S)m {number of globules is constant (m) a radius (mass, number of atoms) of globule increases)
A row of isohomologues: (AnBs)m=>(An+sBs1)m-k=>…=>A_NB_S (number of globules decreasing a weight of globules augments).

Kol'tsov, S. I. & Aleskovskii, V. B..
Relation between structures of globular polymers and their chemical composition. *Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.11. [In Russian]
Кольцов, С. И., Алесковсий, В.Б. Взаимосвязь структуры глобулярных полимеров с их химическим составом. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Koltsov1970c} ru
Yury Koshtyal: A communication is concerns to a modeling of solids and it is not related to ALD. The authors introduced a derivation of the formula of relation (K) between specific surface area (S) and B/A (B – number of functional groups on the surface of the globule, A – number of atoms forming a volume of the globule).
Taking into account the following assumptions:
1. Globules have one size;
2. Each atom on the surface of globule connected to a functional group;
authors came to a conclusion that K has a following analytical view:
K≈(μ^(2/3))*N/M
Where μ – is an average globule diameter,
N – Avogadro’s number,
M – molecular weight of the substance forming a globular material.
The calculated K value for isohomological row of silicas was equal to 1265 m^2/g.

Kol'tsov, S. I. & Aleskovskii, V. B.
Polymeranalogous transformation of three dimensional inorganic polymers. *Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.13. [In Russian]
Кольцов, С. И., Алесковский, В.Б., Полимераналогичные превращения трехмерных полимеров Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Koltsov1970d} ru
Yury Koshtyal: Two (of 3) types of reactions with functional groups of solids are considered in communication:
1. Reactions of substitution
2. Reactions of dissociation and association
3. Oxidation-Reduction reactions (not considered)
Authors introduced several definitions
Polymeranalogous row is a row of the same solids different functional groups:
$A_{n-s}(AB)_s$=>$A_{n-s}(AC)_s$=>$A_{n-s}(AD)_s$
Properties of polymeranalogous row:
1. B/A=C/A=D/A
2. reactions in polymeranalogous row are completely reversible:
$A_{n-s}(AB)_s$=> $A_{n-s}(AC)_s$=> $A_{n-s}(AB)_s$
3. A member of polymeranalogous row can be synthesized from its neighbours in the row:
$A_{n-s}(AB)_s$=> $A_{n-s}(AC)_s$ <=$A_{n-s}(AD)_s$
4. It is possible to obtain another member of the row through reactions with different low-weight molecular substances:
$A_{n-s}(AB)_s$+CD=> $A_{n-s}(AC)_s$
+CE=> $A_{n-s}(AC)_s$
The intermediate substances obtained during incomplete substitutions form **genetic row**
$A_{n-s}(AB)_s$=> $A_{n-s}(AB)_{s-1}AC$=>… =>$A_{n-s}(AB)_{s-k}(AC)_k$…=> $A_{n-s}(AC)_s$
Properties of genetic row:
1. The reactions within genetic row are reversible
2. Number of functional groups is constant (B+C)/A = constant
3. Every member of the row can be obtained from neighbours.
As a consequence – the multifunctional substances can be synthesized.
Isological row is a row of substances with different number of dissociated functional groups.
$A_{n-s}(AB)_s$=> $A_{n-s}(AB)_{s-1}A$=>… =>$A_{n-s}(AB)_{s-k}A_k$…=> $A_{n-s}(A)_s$
Dissociation can undergo through two mechanisms homolytic (radicals are formed) and heterolytic (ions are formed).

Kol'tsov, S. I. & Aleskovskii, V. B.
Interrelation between products of polymeranalogous reactions of three dimensional inorganic polymers.
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.15. [In Russian]**
Кольцов, С. И., Алесковский В.Б., Взаимосвязь продуктов полимераналогичных реакций трехмерных полимеров. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Koltsov1970e} ru
Yury Koshtyal: Authors describe in general chemical equations leading to the synthesis of homological row of macromolecules, i. e. a row of macromolecules with various numbers of atoms in the frame. For materials with globular structure this means a possibility to regulate (increase or decrease) a radius of globules.
Reactions leading to an increase of the frame:
$A_{n-s}(AB)_s$+sDAC=>$A_{n-s}(AAC)_s$+sBD (1)
By substitution of “C” atoms by “B” atoms:
$A_{n-s}(AAC)_s$+sBE=>$A_{n-s}(AAB)_s$+sBE (2)
a substance $A_{n-s}(AAB)_s$ or $A_n(AB)_s$ can be obtained.
Reactions 1 and 2 are particular case of Molecular Layering method or ALD.
If the chemical bond between functional group and atoms of the frame (A-D) is stronger than the chemical bond between atoms of the frame it is possible to break A-A bond with formation of macroradical:
$A_{n-s}(A^*)_s$+sD*=>$A_{n-s}(AD)_s$;
$A_{n-s}(AD)_s$=>$A_{n-2s}(A^*)_s$+sAD (3)
By saturation of macroradical with B atoms:
$A_{n-2s}(A^*)_s$+sB*=>$A_{n-2s}(AB)_s$ (4)
The reactions 3, 4 are named by authors as Molecular Destruction Method.
Thus by using reactions 1-4 a homological row:
$A_{n-2s}(AB)_s$ => $A_{n-s}(AB)_s$ => $A_n(AB)_s$
can be synthesized.

Kol'tsov, S. I.
Change in supermolecular structure of globular inorganic polymers during the process of polymeranalogous transformations
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.16. [In Russian]**
Кольцов, С. И., Изменение надмолекулярной структуры глобулярных полимеров в процессе их полимераналогичных превращений. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Koltsov1970f} ru
Yury Koshtyal: Author proposes a model describing the changes in specific surface and specific pore volume of the substance with a globular structure during ALD process.
According to the presented model the specific surface of the modified substance is a function of:
1. Diameter of initial globules;
2. Number of contacts between globules;
3. Thickness of adsorbed gas layer used for the specific surface determination
4. Thickness of grown layer
5. Number of layers
6. Weight of initial substance in 1 g of modified one.
According to proposed model the specific pore volume is function of above mentioned 6 parameters + Volume of initial substance.

Kol'tsov, S. I.
The interrelation between the heat of chemisorption and the location of functional groups on the surface of three dimensional inorganic polymers
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.17. [In Russian]**
Кольцов, С. И., Взаимосвязь между теплотой хемосорбции и расположением функциональных групп на поверхности трехмерных полимеров. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Koltsov1970g} ru
Yury Koshtyal: Solid is represented as a macromolecule and its properties change during chemisorption. New functional groups formed on the surface of this macromolecule influence on subsequently conducted chemisorption reactions.
According to a previous works a differential heat of chemisorption (q) diminishes linearly with increase of surface filling degree (Θ=k/s)
An-s(AB)s => … An-s(AB)s-k(AC)k => … An-s(AC)s
q=α0•β0•q0•(1-Θ)
where α0•β0 – activities of surface atoms and chemosorbing particles,
q0 – initial heat of chemisorption.
Taking into account that new functional groups can inductively decrease (-γ) of increase (+γ) activity of initial functional groups during chemisorption reaction author deduced and a dependence q form Θ (q=f(Θ)). The sequence of mathematical deduction is presented.
Basing on deducted dependence the author concluded that in case of negative induction effect (-γ) new functional groups are single and distributed evenly until the surface filling degree reaches 0,34. A subsequent chemisorption accompanied by formation of groupings consisted of two or three (Θ≈0,45) functional groups. These groupings merge and form (Θ>0,55) “islands” and “stripes”.
If the positive inductive effect is observed (+γ) the islands of functional groups formed at low degree of surface fillings (Θ) continue to grow until Θ=0,68.
Subsequent chemisorption reactions lead to merging of these “islands” to the “stripes”.

Rachkovskii, R. R.; Kol'tsov, S. I. & Aleskovskii, V. B.
Study of the reaction of tin tetrachloride with silica gel
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.21. [In Russian]**
Рачковский, Р.Р., Кольцов, С. И., Изучение взаимодействия галогенидов олова (IV) с силикагелем. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Rachkovskii1970a} ru
Yury Koshtyal: The interaction of $SiCll_4$ and SnI_4 with silica hydroxyl groups undergoes according to equation:
m(≡Si-OH) + $SnHal_4$ <=> (≡Si-O-)$_m$$SnHal_{4-m}$ + m HCl (1),
m varies from 3 to 1
Reaction is reversible therefore the mechanism of $SnHal_4$ interaction with silica surface changes during reaction. The initially formed (≡Si-O-)$_3$SnCl reacts with HCl:
(≡Si-O-)$_3$SnCl + HCl => (≡Si-O-)$_2$$SnCl_2$ + ≡Si-OH (2)
The complete elimination of tin oxychloride from silica surface can be achieved by HCl gas treatment.
The reaction between SnI_4 and silica surface (reaction – 1) is less reversible due to decomposition of formed HI.
Treatment of solid product formed during reaction 1 by water vapours leads to formation tin hydroxide bonded chemically to the silica surface:
(≡Si-O-)$_m$$SnHal_{4-m}$ + (4-m) H_2O => (≡Si-O-)$_m$$Sn(OH)_{4-m}$ + (4-m) HCl (3)
HCl produced during reaction 3 cause partial destruction of ≡Sn-O-Sn≡ bonds.

Malygin A. A.; Kol'tsov, S. I.; Volkova A. N. & Aleskovskii, V. B.
Interaction between phosphorous containing silica gel and ammonia
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.21. [In Russian]**
Малыгин, А.А., Кольцов, С. И., Волкова, А.Н., Алесковский, В.Б. Взаимодействие фосфорсодержащего силикагеля с парами аммиака. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Malygin1970} ru
Yury Koshtyal: In present study the reaction of phosphor-containing silica synthesized through 1-3 ML cycles with NH_3 was studied. Phosphor content in products was 1.07, 1.87, 2.49 mg·at/g SiO_2 for silicas modified after 1, 2, 3 cycles, correspondingly.
The effect of temperature, time of reaction and water content in NH_3 vapours were determined. It was stated that the quantity of chemisorbed NH_3 diminishes with increase of temperature. The maximum of ammonia nitrogen content was found in products treated at 22°C. The increase of water content in ammonia led to a bigger content of nitrogen in products of reaction.
With increase of phosphorus content in initial samples the quantity of nitrogen in products of reaction of phosphor containing silica and NH_3 augmented from 0.85 to 3.91 mg·at/gSiO_2 (reaction with humid NH_3) and from 0.76 to 2.79 mg·at/gSiO_2 (reaction with dry NH_3)

Malygin A. A.; Kol'tsov, S. I.; Volkova A. N. & Aleskovskii, V. B.
Study of the properties of reaction products between phosphorous containing silica gel and ammonia
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.22. [In Russian]**
Малыгин, А.А., Волкова, А.Н., Кольцов, С. И., Алесковский, В.Б. Изучение некоторых свойств продуктов реакции фосфорсодержащего кремнезема с парами аммиака. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Malygin1970a} ru
Yury Koshtyal: The thermal stability of products obtained by reaction of phosphor containing silica with ammonia vapours was studied in temperature interval – 22-180°C.
The quantity of ammonia nitrogen in products heated above 22°C diminished to a value typical for corresponding temperature. The product heated at 100°C and 140°C contained 35% and 17% of initial nitrogen quantity.
The humidity of atmosphere doesn't influence on thermal stability of the samples.

Sveshnikova, G. V.; Kol'tsov, S. I. & Aleskovskii, V. B.
Synthesis of a titanium oxide layer of predetermined thickness on monocrystalline silicon by the molecular layering method
***Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad,* 1970, p.27. [In Russian]**
Свешникова, Г.В., Кольцов, С. И., Алесковский, В.Б. Синтез слоя двуокиси титана заданной толщины на поверхности монокристалла кремния. Наун.-техн. конф. Ленингр. техн. ин-та им. Ленсовета, Тез. Докл., Л., 19
{Sveshnikova1970a} ru
Yury Koshtyal: Ultrathin films of TiO_2 were deposited by ML on the surface monocrystal silicium. Before deposition the surface monocrystal silicium was electrochemically polished or treated by hydrofluoric acid (HF). The thickness of deposited TiO_2 layers was determined by ellipsometry. The difference between the thickness measured in different point of support and average one did not exceed ±2Å.
By varying the number (up to 60) of cycles (chemisorption of $TiCl_4$ – hydrolysis of oxychloride) the samples of silicium with determined thickness (2-30) of layers were obtained. The difference of film thickness for parallel samples and average one did not exceed ±2Å.
The linear dependence between number of cycles and film thickness was observed.

S. I. Kol'tsov, A. N. Volkova, V. B. Aleskovskii
Effect of the extent of silica dehydratation on the chemisorption mechanism of PCl3
***Zh. Fiz. Khim.* 44, 2246-2250 1970 [In Russian]**
С. И. Кольцов, А. Н. Волкова, В. Б. Алексковский. Влияние степени дегидратации силикагеля на механизм хемосорбции треххлористого фосфора. Журнал физической химии. 1970. Т. 44, вып. 9. С. 2246-2250.
{Koltsov1970a} ru
Yury Koshtyal: The effect of the extent of dehydroxilation on the mechanism of PCl_3 chemisorption was studied for the large pore silica. Large pore silica was purified from impurities and it was dried at 180°C. Every time before chemisorption silica (purified and dried) was dried for 2 hours at corresponding temperature (180, 300, 400, 500, 600, 700, 800°C). Hydroxyl concentration was measured for heated silicas. PCl_3 chemisorption was conducted in the flow of dry nitrogen. After desorption of PCl_3 excess and formed gaseous products (HCl) a concentration of P^{+3}, P^{+5}, Cl, OH-groups were determined in solid-state products. On the base of measured concentrations and using possible schemes (1-3) of chemisorption authors introduced a method of calculation of ratio of phosphor atoms chemisorbed to the silica surface with formation of 1, 2 and 3 bonds.

3(≡Si-OH) + PCl_3 <=> (≡Si-O-)$_3$P + 3 HCl (1)
2(≡Si-OH) + PCl_3 <=> (≡Si-O-)$_2$P-Cl + 2 HCl (2)
(≡Si-OH) + PCl_3 <=> (≡Si-O-)P-Cl_2 + HCl (3)

According to presented results the decrease of the extent of hydroxylation causes a change of mechanism of reaction between PCl_3 and silica OH groups. On the fully hydroxylated surface (3.46 mg·eq/g) PCl_3 molecule interacts with three OH-groups. When the concentration of silica OH-groups lies in the range – 2.85-2.04 mg·eq/g (preliminary heated at 300-500°C) three or two OH-groups involved in the reaction with one PCl_3 molecule. If concentration of silica OH-groups varies from 1.64 to 1.18 mg eq/g (preliminary heated at 600-700°C) two or one OH-groups involved in the reaction with one PCl_3 molecule. The subsequent decrease of OH-groups concentration to 0.85 mg eq/g (preliminary heated at 800°C) resulted in the reaction of PCl_3 only with one OH-group.

Kol'tsov, S. I.
Synthesis of solids by the Molecular Layering Method
Doktor nauk thesis, 1971, 383 p. [In Russian]
Кольцов, С. И. Синтез твёрдых веществ методом молекулярного наслаивания : дис. … д-ра хим. наук / Кольцов Станислав Иванович. – Л., 1971. – 383 с.
{Koltsov1971} ru
Victor E. Drozd: Doctoral dissertation of S.I.Koltsov played an important role in my life. Me, as a physicist, was surprised very original point of view on solid state. His ideas concerned in a main part silicagel. Only one of his students (R. Rachkovsky) worked with silicon. For me it was basic material in microelectronics that time. Dissertation of S.I.Koltsov opened my eyes on new way of technology in microelectronics. Principles of growth in layer-by-layer was very attractive but very slow. Theoretical model of films growth on the example of TiCl4 + H2O reaction is very easy understandable for reader. Of course, in 3D it is not easy. I remember very amusing moment when our colleague in preparing his doctoral dissertation tried to build-up anatase octahedron from tetrahedron of TiCl4. Of course, it is impossible but that time he did not know that. I think that the most important results of his dissertation are two principles and three consequences of ML method. I've seen a lot of dissertations and the S.I.Koltsov's one is the best for my point. Interesting moment is that "Soviet Committee of discovery and invention" did not gave V.B.Aleskovsky and S.I.Koltsov diploma on discovery as they asked but only certificate on invention. Now some people discuss ALD as a subject of Nobel Prize. Unfortunately too late.

Sveshnikova G.V.
Synthesis and study of thin oxide layers on the silicon surface
Diss . ... Candidate . Chem. Science / LTI - L. , 1971, 184 pages.
Свешникова Г.В. Синтез и исследование тонких окисных слоев на поверхности кремния: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1971.
{Sveshnikova1971} ru
A. A. Malygin: Synthesis and study of thin oxide layers (Ti-, Si-oxide and two components Ti-Si-oxide) on silicon surfaces.

Kunawicz J.; Jones P. & Hockey J.A.
Reactions of silica surfaces with hydrogen sequestering agents.
***Trans. Far. Soc.* 67, 846-853, 1971 [In English]**
{Kunawicz1971} en
Henrik Pedersen: This paper looks at an ALD half cycle where TMA, TiCl4 and Si(CH3)3Cl is reacted onto the surface of silica. The focus is to show which site, Si-OH or Si-O-Si, is more reactive towards the molecules. This is studied by infrared spectroscopy by comparing the intensity of the peaks related to each site after pulses of the reacting molecules. There seems to be no intention to make a second half cycle to complete the ALD cycle. I would say that this is a pure surface chemistry paper that has very little to do with the history of ALD, it could be used to understand ALD but I don't think that it contributed to the development of the technique.
Riikka Puurunen: This paper investigates the reaction of several "hydrogen sequestering agents" with silica, namely Me3Al, TiCl4 and Me3SiCl. The paper comes from Great Britain and is a surface chemistry investigation, not linked to and not referencing the Soviet ALD (molecular layering) works existing at that time. This paper has been significant for the understanding of the Me3Al/H2O process chemistry developed much later, as it is shown that Me3Al reacts with the siloxane bridges, and is more effective in this reaction than many other chemicals are.

K. Unger, K. Berg, E. Gallei, G. Erdel
Chemische Modifizierung der Oberfläche fester Gerüstsubstanzen
***Fortschrittsberichte über Kolloide und Polymere*, 55, 34-36, 1971 [in German]**
{Unger1971} ger

Chien J. C. W.
A study of surface structures of submicron metal oxide by vanadium tetrachlorlde as a paramagnetic probe.
***J. Amer. Chem. Soc.* 93, 4675-4681, 1971 [In English]**
{Chien1971} en
Henrik Pedersen: In this paper, VCl4 is allowed to chemisorb onto silica and alumina, the chemisorbed V atoms are then used as paramagnetic probes in electron paramagnetic spectroscopy (EPR). By using the EPR signal, the author deduces the amount of V on the surface and by studying the amount of formed HCl the adsorption mode of VCl4 is determined. The focus of the paper is not to study the surface chemistry of VCl4 but to determine the surface structure of the hydroxylgroups on alumina and silica. It can be regarded as a complementary study to some of the studies from Aleskovsii's group in that this study is based on EPR rather than FTIR.

Hertl W. & Hair M. L.
Reaction of hexamethyldisilazans with silica
***J. Phys. Chem.* 75, 2161-2165, 1971 [In English]**
(no code)
Henrik Pedersen: The reaction kinetics between hexamethyldisiazane (HMDS) and -OH groups on the surface of silica were studied. The motivation for this is to deactivate gas chromatographic support materials, as mentioned in the introduction. The chemistry was mainly studied at 800 C and low pressure (5-15 Torr) using IR spectroscopy. Although the paper discuss reactions with HMDS and other amines with -OH on silica, there are no discussions in the direction of using this chemistry to build up a thin film.

Sharygin L. M., Tret'yakov S. Ya., Gonchar V. F. & Shtin A. P.
Chemisorption of tin tetrachloride on silica gel
***Russ. J. Phys. Chem.*, 45, 1524-1525, 1971 [in English]**
Original: ***Zh. Fiz. Khim.*, 45, 2684-2685, 1971 [in Russian]**
Л. М. Шарыгин, С. Я. Третьяков, В. Ф. Гончар, А. П. Штин. Хемосорбция четыреххлористого олова на силикагеле. Журнал физической химии. 1971, Т. 45, вып. 10, С. 2684-2685.
Full text: Статья полностью депонирована в ВИНИТИ за № 3127-71 Деп. от 23 июля.
{Sharygin1971} ru en
A.A.Malkov: In this paper , in contrast to earlier publications by Raczkowski RR (Rachkovskii1970-cyr.pdf, Rachkovskii1970a.pdf, Rachkovskii1970.pdf), chemisorption of SnCl4 was carried out in static conditions under vacuum. Under these conditions, the reaction product, HCl, is accumulating in the reaction space. This could lead to the formation of -SnCl3 groups. Treating -SnCl3 groups with water vapour is accompanied by replacement of chloride groups in the adsorption complex by OH groups . However, the authors do not continue the process further , as well as in their later publications (1973 and 1976) in the reaction with TiCl4 on various silicas.

A. N. Volkova, S. I. Kol'tsov, V. B. Aleskovskii
Reaction of phosphorus-containing silica with AgNO3
***Izv. Vysshikh Uchebn. Zavedenenii, Khim. i Khim. Tekhnol.* 14, 26-27, 1971**
А. Н. Волкова, С. И. Кольцов, В. Б. Алесковский. Взаимодействие фосфорсодержащего кремнезема с азотнокислым серебром. Изв. Высших учебных заведений СССР. Химия и химическая технология. 1971, Т. 14, вып. 1, С. 26-27.
{Volkova1971} ru

Kol'tsov, S. I.; Volkova, A. N. & Aleskovskii, V. B.
Effect of surface coverage of silica gel with phosphorus on subsequent chemisorption of titanium tetrachloride
***Rus. J. Phys. Chem.*, 46, 742-745, 1972 [in English]**
(Translated from: ***Zh. Fiz. Khim.*, 46, 1292-1296, 1972 [in Russian]).**
{Koltsov1972} en ru
Henrik Pedersen: This paper shows the blocking effect of P to chemisorption of TiCl4 on hydroxylated silica. When more and more P in the form of PCl3 is adsorbed onto the silica, the adsorption mode of TiCl4 is changed from chemisorption where HCl is formed, to physisorption where no byproducts are formed. Received November 1968
David Cameron: This paper looks at the mechanisms of TiCl4 reaction with surface OH groups to form chemisorbed Ti-O-Cl on the surface and how this, and the Cl group density, is affected by OH surface density. The number of T-Cl It also shows how physisorption of TiCl4 occurs with no available surface OH.

T. V. Poltavtseva, S. I. Kol'tsov, A. N. Volkova, V. B. Aleskovskii.
Study of stability of titanium-containing silica in acid solutions
***Izv. Vysshikh Uchebn. Zavedenenii, Khim. i Khim. Tekhnol.* 15, 1140-1142, 1972**
Т. В. Полтавцева, С. И. Кольцов, А. Н. Волкова, В. Б. Алесковский. Исследование устойчивости титансодержащего кремнезема в кислых растворах. Известия ВУЗов СССР, Химия и химическая технология, 1972, Т. 15, вып. 4, С. 1140-1142.
{Poltavtseva1972} ru
(get english copy)

Volkova, A. N., Malygin, A. A., Smirnov, V. M., Koltsov, S. I. & Aleskovskii, V. B.
Interaction between chromyl chloride and silica gel
***Zh. Obshsc. Khim.* 42, 1422-1424, 1972**
Translated from: Волкова, А.Н., Малыгин, А.А., Смирнов, В. М., Кольцов, С. И., Алесковский, В.Б.. О взаимодействии хлористого хромила с силикагелем. Ж. Общ. Хим. 42(7), 1972, 1431-1434.
{Volkova1972} en ru
Henrik Pedersen: In this paper, the surface chemistry between Si-OH groups on silica gel and cromyl chloride, CrO2Cl2, is studied. The experimental procedure very much resembles an ALD half cycle in that it is done under dry nitrogen atmosphere at 180 C and that unreacted cromyl chlorde and formed HCl were flushed away with dry N2. It is shown that CrO2Cl2 reacts with two Si-OH groups forming a -Si-O-Cr-O-Si- bridge on the surface where the Cr atom also forms double bonds to two additional oxygen atoms. It was further shown that the adsorption reaction was reversible; the adsorbed CrOx groups could be removed by a flow of HCl ay 180 C. This reaction scheme indicates that a second ALD cycle, to continue to deposit CrOx, can not be done directly after the first since the surface lacks OH-groups for the preceding surface chemistry. The thermal stability of the adsorbed CrOx-groups was investigated; annealing (the term roasting is used in the paper) at 330 c in dry nitrogen reduces the Cr (IV) to Cr (III) upon removal of O2 and leads to Cr-O-Cr cross linking between the Cr atoms on the surface which could form the starting point for subsequent ALD cycles. However, no comments on any subsequent surface reactions are made in the paper.

Malygin, A. A.; Volkova, A. N.; Kol'tsov, S. I. & Aleskovskii, V. B.
Reaction of chromium-containing silica gel with hydrogen chloride
***Rus. J. Gen. Chem.*, 42, 2373-2375, 1972**
(Translated from: ***Zh. Obshch. Khim.*, 42, 2368-2370, 1972).**
{Malygin1972} en ru
Riikka Puurunen: In this paper, the reaction of chromyl chloride, CrO2Cl2 modified silica is studied with HCl at 180 C. The motivation is to separately study the reverse reaction that may occur during the modification of silica with chromyl chloride; hints that the reverse reaction could be important have been obtained earlier due to the observation that a significant amount of OH groups are present after the chromyl chloride reaction with silica. It is observed that through the HCl reaction, all Cr(VI) is either removed from the surface as CrO2Cl2 or reduced to Cr(III), which remains on the surface. The generation of OH groups In the reaction is observed, but their amount is less than it would be if all broken O--Cr bonds would have been replaced with OH groups, which is taken as evidence that neighbouring OH groups most likely have condensed to give siloxane bridges and release water. The kinetics of the reaction are studied by using two different feed concentrations of HCl and quantifying the reaction products as function of reaction time. Interestingly, with the higher HCl concentration, the reaction is concluded to be completed in one minute.
Henrik Pedersen: This is essentially an etching study in which a surface with CrOx groups adsorbed onto silica (as described in Volkova 1972) is etched with HCl. The authors conclude that even though HCl is a byproduct in the adsorption reaction of cromyl chloride, CrO2Cl2, onto silica, simply adding HCl to a surface where CrOx is adsorbed to silica does not restore the silica surface with -OH groups. Etching with HCl removes the adsorbed CrOx groups but also leads to the formation of siloxanes, Si-O-Si on the silica surface, water is eliminated in this process. This is an etching study that can be viewed as a study of the effect of insufficient purging of an ALD process, although no such comments are made in the paper.
Jaana Kanervo: A clear and concise ALD-related work that describes the effect of resolving the molecular chromium oxide layer on silica gel by treating with gaseous hydrogen chloride. It is shown that with certain HCl concentrations and treatment times almost all silica-bound hexavalent chromium can be removed by the reverse reaction of the original deposition reaction. During the HCl treatment some of hexavalent chromium is converted to trivalent. General significance is the demonstration that ALD reactions may be partly reversible which could be one factor why complete monolayers are not achieved without carefully optimized conditions.

V.B. Kopylov, A. N. Volkova, S. I. Kol'tsov, V. M. Smirnov, V. B. Aleskovskii,
Interaction of aluminium chloride with silica
***Izv. Vssh. Ucheb. Zaved. Ser. Khim. i Khim Tekhnol,* 15, 957-959, 1972**
В. Б. Копылов, А. Н. Волкова, С. И. Кольцов, В. М. Смирнов, В. Б. Алесковский. Взаимодействие хлористого алюминия с силикагелем. Известия высших учебных заведений, Химия и химическая технология. Т. 15, вып. 6, С. 957-959.
{Kopylov1972} ru
Maria Berdova: The main conclusion of the work: After the reaction of aluminium chloride with OH-groups of hydroxylated silica, each molecule of aluminium chloride reacts with two hydroxyls forming groups >Al. In their experimental work, aluminium reacted with silica at 200oC in the air for 2 hours. The references are mainly to Koltsov's works.

Rachkovski R.R.
Synthesis and study of thin oxide layers on the surface of single-crystal silicon
Diss . ... Candidate . Chem. Science / LTI - L. , 1972, 133 pages.
Рачковский Р.Р. Синтез и исследование тонких окисных слоев на поверхности монокристаллического кремния: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1972.
{Rachkovskii1972} ru
A. A. Malygin: Synthesis and study of thin oxide layers (monolayers of Si-, Ti-, P-, Cr-, V-, Ge-, Sn-oxide; polylayers of Si-, Ti-, Ge-, Sn-oxide and two components Ti-Sn-oxide) on silicon surfaces

M. I. Yatsevskaya, N. F. Yermolenko, L. A. Pavlyukevich
Effect of temperature treatment on sorption and catalytic properties of titanium-containing silicas
***Izvestia AN BSSR, seriya - khimicheskiye nauki (Vesti Akademii Navuk Belaruskay SSR (Seryya khimichnykh navuk))*, 5, 17-23, 1972**
М. И. Яцевская, Н. Ф. Ермоленко, Л. А. Павлюкевич. Влияние термообработки на сорбционные и каталитические свойства титаносиликагелей. Вести АН БССР, серия - химические науки (Весці Акадэміі Навук Беларускай ССР (Серыя хімічных навук)), 1972, № 5, С. 17-23.
{Yatsevskaya1972} ru

Malygin, A. A.; Volkova, A. N.; Kol'tsov, S. I. & Aleskovskii, V.B.
Reaction of vanadyl trichloride with silica
***Rus. J. Gen. Chem.*, 43, 1426-1429, 1973**
(Translated from: ***Zh. Obshch. Khim.*, 43, 1436-1440, 1973)**
А. А. Малыгин, А. Н. Волкова, С. И. Кольцов, В. Б. Алесковский. О взаимодействии оксихлорида ванадия (V) с кремнеземом. Журнал общей химии, 1973, Т. 43, вып. 11, 1436-1440.
{Malygin1973} en ru
Riikka Puurunen: In this article, the reaction of vanadyl trichloride VOCl3 is investigated with silica dried at 180C, and the reaction of HCl with VOCl3-modified silica to study the reversibility of the reaction. Dry nitrogen is used as carrier gas and reactions are mostly carried out at 180C. After the reactions, the vanadium, Cl and OH concentrations are determined. It is found that the amount of vanadium chemisorbed after completion of the VOCl3 reaction is not affected by the flow rate of the carrier gas (5-50 ml/min, with VOCl3 of 1.3x10^-2 to 5x10^-2 mmol/min), weight of silica (0.5-2 g) or the reaction temperature (20-180C). The saturation curve of the reaction is measured, and it is observed that VOCl3 reacts with three OH groups all through the saturation curve, also at the very early parts of it.The HCl reaction with VOCl3-modified silica removed practically all V from the surface, indicating that the reaction is reversible in nature. In early stages of the reaction, one OH group was created for each broken O-V bond as expected, but for higher conversion levels, the number or OH was less, indicative of condensation of OH groups to siloxane bridges. Also some reduction of V(V) to V(IV) by HCl was observed, accompanied by release of Cl2. In practice, due to the excess of VOCl3 and the removal of HCl, the reaction of VOCl3 with silica can be carried out irreversibly, and almost 100% of the OH groups are reacted.

A. A. Malygin, A. N. Volkova, S. I. Kol'tsov, V. B. Aleskovskii.
Reaction of VOCl3 with hydroxilated surface of silica
***Ivestiya vysshikh uchebnykh zavedeny. Khimiya i khimicheskaya tekhnologiya,* 16, 1471-1474, 1973**
А. А. Малыгин, А. Н. Волкова, С. И. Кольцов, В. Б. Алесковский. Исследование взаимодействия треххлористого ванадила с гидроксилированной поверхностью силикагеля. Ивестия высших учебных заведений. Химия и химическая технология. 1973, Т. 16, вып. 10, С. 1471-1474.
{Malygin1973b} ru

Kol'tsov, S. I.; Uhova T.V.; Volkova, A. N. & Aleskovskii, V.B..
Study of the stability of thin titanium oxide films of various thicknesses on the surface of silica gel
***Bulletin of Higher Educational Institutions. Chemistry and Chemical Technology,* 16, 517-519, 1973 [in Russian]**
С.И. Кольцов, Т.В. Ухова, А.Н. Волкова, В.Б. Алесковский. Изучение устойчивости титанкислородных слоев различной толщины на поверхности силикагеля. Известия высших учебных заведений. Серия: Химия и химическая технология. 1973, Т. 16, 517-519.
{Koltsov1973a} ru
Yury Koshtyal: An interaction between thin titanium-oxide layers (1-5, $T_{synthesis}$? = 180°C) and sulphuric acid was studied. Conditions: Temperature 20-22°C, time of interaction – 24 hours, volume of H_2SO_4 solution was 300 higher than mass of the samples.
The dissolution of titanium oxide layers was observed in solutions of H_2SO_4 with pH ≤2. The quantity of titanium extracted to the solution augmented with decrease of pH in the interval (2<pH<0). The subsequent increase of H_2SO_4 concentration didn't influence on titanium extraction. The dependences of each sample are shown.
Second dissolution (with new H_2SO_4 solution) didn't lead to additive extraction of titanium from the samples.
Dissolution in H_2SO_4 solution (pH=0).
One titanium oxide layer was completely dissolved after first dissolution. When the samples with 3 and 5 deposited titanium-oxide layers reacted with sulphuric acid solution the quantity of titanium atoms passed into solution exceed the quantity of atoms deposited during last synthesis cycle (3^{rd} and 5^{th} correspondingly). When the samples with 2 and 4 deposited titanium oxide layers reacted with sulphuric acid solution the quantity of extracted atoms sought to the
When the solution of sulphuric acid (pH<2) was used the quantity of atoms deposited during last synthesis cycle (2^{nd} and 4^{th} correspondingly).
Authors concluded that for the samples with even number of layers only external Titanium-oxide layer is dissolved, while for the samples with odd number of layers the underlying layer is also partly dissolved by H_2SO_4 solution.
According to authors opinion a higher stability of inner layers related to possibility of increment of coordination (quantity of oxygen atoms surrounding titanium) of inner titanium atoms (increment of density) on the account of oxygen atoms situated in higher layers.

S. I. Kol'tsov, V. B. Kopylov, A. N. Volkova, V. B. Aleskovskii
The effect of hydratation of silica on the mechanism of reaction between silica and aluminum chloride
***Ivestiya vysshikh uchebnykh zavedeny. Khimiya i khimicheskaya tekhnologiya*, 16, 1475-1477, 1973**
С. И. Кольцов, В. Б. Копылов, А. Н. Волкова, В. Б. Алесковский. Влияние степени дегидратации силикагеля на механизм его взаимодействия с хлористым алюминием. Ивестия высших учебных заведений. Химия и химическая технология. 1973, Т. 16, вып. 10, С. 1475-1477.
{Koltsov1973b} ru

S. I. Kol'tsov, V. M. Smirnov, V. B. Aleskovskii
Influence of carrier on the properties of catalyst. II
***Kinet Katal.*, 14, 1300-1303, 1973**
С. И. Кольцов, В. М. Смирнов, В. Б. Алесковский. Изучение влияния носителя на свойства катализатора. II. Кинетика и катализ, 1973, Т. 14, вып. 5, С. 1300-1303.
{Koltsov1973c} ru

Kol'tsov, S. I.; Malygin, A. A.; Volkova, A. N. & Aleskovskii, V. B.
Effect of Degree of Hydroxylation of Silica Chemisorption of Vanadyl Trichloride
***Zh. Fiz. Khim.*, 47, 988-991, 1973**
(*Rus. J. Phys. Chem.*, 47, 558-560, 1973)
С. И. Кольцов, А. А. Малыгин, А. Н. Волкова, В. Б. Алесковский, Влияние степени гидроксилирования поверхности кремнезема на хемосорбацию хлорокиси ванадия, Журнал физической химии, Т. 47, вып. 4, 1973, С. 988-991.
{Koltsov1973} ru en
Yury Koshtyal: The structure of the investigation presented in this article resembles one presented in S. I. Kol'tsov, A. N. Volkova, V. B. Aleskovskii. Effect of the extent of silica dehydratation on the chemisorption mechanism of PCl3. Zh. Fiz. Khim. V. 44, I. 9, P. 2246-2250 (1970). {Koltsov1970a} ru
The effect of the extent of dehydroxilation on the mechanism of $VOCl_3$ chemisorption was studied for the large pore silica. Large pore silica was purified from impurities and it was dried at 180°C. Every time before chemisorption silica (purified and dried) was dried for 2 hours at corresponding temperature (180, 300, 400, 500, 600, 700°C). Hydroxyl concentration was measured for heated silicas. $VOCl_3$ chemisorption was conducted in the flow of dry nitrogen. After desorption of $VOCl_3$ excess and formed gaseous products (HCl) a concentration of V, Cl, OH-groups were determined in solid-state products. On the base of measured concentrations and using possible schemes (1-3) of chemisorption authors introduced a method of calculation of ratio of phosphor atoms chemisorbed to the silica surface with formation of 1, 2 and 3 bonds.

3(≡Si-OH) + $VOCl_3$ <=> (≡Si-O-)$_3$V=O + 3 HCl (1)
2(≡Si-OH) + $VOCl_3$ <=> (≡Si-O-)$_2$VO-Cl + 2 HCl (2)
(≡Si-OH) + $VOCl_3$ <=> (≡Si-O-)VO-Cl_2 + HCl (3)

According to presented results the decrease of the extent of hydroxylation causes a change of mechanism of reaction between VOCl3 and silica OH groups. On the fully hydroxylated surface (3.23 mg·eq/g) VOCl3 molecule interacts with three OH-groups. 0,12 mg·eq/g of hydroxyl group didn't react. When the concentration of silica OH-groups lies in the range – 2.66-2.23 mg·eq/g (preliminary heated at 300-400°C) three or two OH-groups involved in the reaction with one VOCl3 molecule. When the surface concentration decreased to 1.93 (500 °C) every molecule of VOCl3 (99,6%) reacted with two OH-groups. Subsequent decrease of silica OH-groups from 1.57 to 1.17 mg eq/g (preliminary heated at 600-700°C) lead to an increment of number of molecules VOCl3 chemisorbed by reaction 3 (11 and 16%, correspondingly). The observed effect of hydroxyl concentration on the mechanism of chemisorption coincided with effect of hydroxyl group concentration reported for chemisorption of TiCl4 and PCl3 molecules.
Nikolai Chekurov: Youry summarizer it all. In my opinion the paper is not ALD-related.

V. N. Pak, S. I. Kol'tsov, V. B. Aleskovskii
Diffuse reflectance spectrum from the surface of SiO2 containing titanium
***Teoreticheskaya i eksperimental'naya khimiya*, 9,451-452, 1973**
В. Н. Пак, С. И. Кольцов, В. Б. Алексковский. Спектр диффузного отражения поверхности титансодержащего кремнезема. Теоретическая и экспериментальная химия 1973. Т. 9, вып. 4, С. 567-569.
{Pak1973} ru en
Yury Koshtyal: Silica with one layer of titanium oxide structures ($T_{Synthesis}$=180°C) was studied by UV-Vis Diffuse Reflectance Spectroscopy. Initial silica was used as a reference sample. The intensive absorption band was observed in the 200-750 nm interval. A maximum of the band situated at 355 nm (3,49 eV). The appearance of the maximum was related to electronic transition from molecular orbital of oxygen to the t_{2g} – level of Ti^{4+}. The authors supposed that observed maximum may point on octahedral coordination of titanium atom caused by adsorption of water molecules.

Robin Ras: This study involved UV-VIS diffuse reflection spectroscopy of silica gel (I assume it means a powder of silica nanoparticles) of very high surface area (214 m^2/g), coated with a single deposition cycle of $TiCl_4$ followed by reaction with water. A high concentration of Ti atoms was observed (1,09 mg-at/g). The spectrum showed a clear peak at 355 mμ or 3,49 eV (the unit mμ is unknown to me, most likely it is nm). Their model is that a layer of TiO_6 is formed on the surface of the silica. The authors write that the close proximity of the peak to the peak of rutile at 3,67 eV confirms their hypothesis.

L. M. Sharygin, S. Ya. Tretyakov
Chemosorption of $TiCl_4$ on the silica
Kinet. Katal. 14, 1600, 1973
Л. М. Шарыгин, С. Я. Третьяков. Хемосорбция четыреххлористого титана на силикагеле. Кинетика и катализ. 1973, Т. 14, вып. 6, С. 1600.
{Sharygin1973} ru

Volkova, A. N. Malygin, A. A. Kol'stov, S. I. & Aleskovskii, V. B.
Reaction of Phosphoryl chloride with hydrated silica
***J. Gen. Chem. USSR.*, 43, 723-726, 1973**
Translated from: Volkova, A. N. Malygin, A. A. Kol'stov, S. I. & Aleskovskii, V. B. *Zh. Obshch. Khim.* 1973, 43(4), 724-728
{Volkova1973} en ru
Henrik Pedersen: In this paper, the surface chemistry between Si-OH groups on silica gel and phosphoryl chloride, POCl3, is studied. The experimental procedure very much resembles an ALD half cycle in that it is done under dry nitrogen atmosphere at 180 C and that unreacted phosphoryl chlorde and formed HCl were flushed away with dry N2. It is shown that POCl3 primarily reacts with three Si-OH groups forming three Si-O-P bonds. The P=O bond in POCl3 is unaffected by the reaction. By increasing the concentration of POCl3 in the gas mixture above the silica, another reaction path opened up where only two of the three Cl on POCl3 reacted leaving on P-Cl bond. There is no discussion on any subsequent reaction cycles in the paper.

Malygin A.A.
The interaction of vanadium , phosphorus, chromium oxychlorides with silica - reactions of the molecular layering
Diss . ... Candidate . Chem. Science / LTI - L. , 1973 . - 163 p.
Малыгин А.А. Взаимодействие оксихлоридов ванадия, хрома и фосфора с силикагелем - реакции молекулярного наслаивания:/ Дисс. ... канд. хим. наук/ ЛТИ - Л., 1973. - 163 с.
{Malygin1973a} ru
A. A. Malygin: First used in the reactions of ML oxochlorides of phosphorus (5), vanadium (5) and chromium (6) on the surface of silica gel. Studied oxidation-reduction reactions in the processes of molecular layering. First synthesized chrome (3)oxide layer using CrO2Cl2, hydrogen and water. Using redox reactions synthesized two-component oxide layers P(5)-V(3) Cr(3)-P(5) and other.

Smirnov V.M.
Synthesis and investigation of the activity of thin oxide layers on the surface of silica, Disc . ... Candidate . Chem. Science / LTI - L. , 1973 . - 128 p.
Смирнов В. М. Синтез и исследование активности тонких оксидных слоев на поверхности кремнезема: Дисс. …канд. хим. наук/ ЛТИ - Л., 1973. - 128 с.
(no code)
A. A. Malygin: First studied the catalytic properties of titanium-oxide ultrathin layers and found the effect of monolayer drastic change in the material properties when applied on the surface of 1-3 titanium-oxide monolayers.

Patent # 422446 (USSR)
Date of submission: **31.03.1972** (dd/mm/yyyy)
Date of publication: **05.04.1974** (dd/mm/yyyy)
Authors of invention: A.N. Volkova, A.A. Malygin, S.I. Kol'tsov, V.B. Aleskovskii
From: Leningrad Technological Institute (Ленинградский технологический институт имени Ленсовета)
Title: The method of synthesis of Cr(III) and P(V) oxide layers on the silicagel surface
(Способ получения оксидного Cr(III) и P(V) слоя на поверхности кремнезема)
Body (*important parts – not a full translation yet*):
The invention is related to the method of synthesis of two-component layers of Cr(III) and P(V) oxides, which can be applied for the reactions of catalytic dehydrogenation, dehydrocyclization, etc. One way of the Cr(III)-P(V) layer formation on silicagel is the treatment of its surface with inorganic Cr- and P-containing compounds. The drawback of this method is the non-uniformity of the layer, insufficient bonding of the layer with the surface and the complexity of the synthesis technology.
The treatment can be performed more effectively via the sequential adsorption of CrO2Cl2 and PCl3 vapors in the flow of inert gas at temperatures no more than 200 C, with a removal of the residual (=not chemically reacted) volatile components from the surface at the same temperature using the flow of the inert gas, and with a subsequent treatment with H2O vapor and annealing (*not specified at what temp.!*). The proposed method allows the production of a uniform ultrathin layer of P2O5 and Cr2O3, well-bounded to the surface of silicagel, with the pre-defined thickness and a specified molar ratio between the components, using a more effective technology. f
{Volkova1974} ru
Andrew Akbashev: The original document can be found here:
http://patentdb.su/2-422446-sposob-polucheniya-okisnogo-crill-i-pv-sloya-na-poverkhnosti-kremnezela.html
It is a two-page document. You can click (enlarge) the images and download them.
Riikka Puurunen: In this SSSR author's certificate/"patent", the synthesis of dual-component oxides of Cr(III) and P(V) for the purpose of catalytic dehydrogenation, dehydrocyclization and other reactions are developed. The patent follows a similar structure as the "Western" patents, with the examples and the description of the coverage of the patent. Gaseous CrO2Cl2 and PCl3 are used as reactants, and they are transported to silica in a stream of inert gas at temperatures no higher than 200°C (examples are given for 100°C and 200°C). Water vapour is used at the same temperature as a second reactant. Results for repetitions of cycles are shown up to four, giving a product with 68 weight-% SiO2 and 32 weight-% of CrO3-Cr2O3-P2O5. Interestingly, the fraction of Cr(VI) can be controlled by exact choice of cycles made.
Repeated ALD cycles are used for controlling the amount of adsorbed material, so here the material growth feature of ALD is shown and applied.

G. M. Bliznakov, K. Petrov.
Some morphological peculiarities of coatings deposited by molecular layering – single dimension model
***Doklady Bolgarskoy akademii nauk.* 27, 365-368, 1974**
Г. М. Близнаков, К. Петров. О некоторых морфологических особенностях покрытий, полученных реакцией молекулярного наслоения – одномерная модель. Доклады Болгарской Академии Наук. 1974, Т. 27, № 3, С. 365-368.
{Bliznakov1974} ru

Smirnov, V. M.; Kol'tsov, S. I. & Aleskovskii, V. B.
Regarding the chemical activity of titanium containing silica.
***Bulletin of Higher Educational Institutions. Chemistry and Chemical Technology*, 17, 1759-1761, 1974 [in Russian]**
В.М. Смирнов, С.И. Кольцов, В.Б. Алесковский. О химической активности титансодержащего кремнезема. Известия высших учебных заведений. Серия: Химия и химическая технология. 1974, Т. 17, Вып. 12, С. 1759-1761.
{Smirnov1974a} ru
Anatolii Malkov: The activity of silica samples with different numbers of titanium-oxide monolayers deposited at the silica surface was investigated in the reaction of catalytic hydrolysis of CCl4. The calculation of changes of the porous structure, that occurs when building titanium-oxide layer, should not cause an additional diffusion inhibition of the catalytic reaction. Based on this conclusion was suggested that the titanium-containing specimens activity decreasing is due to the chemical composition of the surface layer of the catalyst.

Smirnov, E. P.; Kol'tsov, S. I. & Aleskovskii, V. B.
Interaction of water vapor with chlorine-containing microcrystalline carbon
***Journal of general chemistry of the U.S.S.R.* 44, 923-925, 1974**
Е. П. Смирнов, С. И. Кольцов, В.Б. Алесковский. Изучение взаимодействия паров воды с хлорсодержащим микрокристаллическим углеродом. Журнал общей химии, Т. 44, вып. 5, С. 961-964.
{Smirnov1974} en ru
Henrik Pedersen: This paper describes the replacement of Cl adsorbed onto carbon by OH via reaction with an argon/water gas mixture. Two sets of experminets were done; chlorination and hydoxylation at the same temperature (20-600 C) and chlorination at 500 C followed by hydroxylation at 20-600 C. The higher reaction temperatures the more complete reactions, at least 100 C is needed for any reaction to happen. At the highest temperatures is the carbon substrate partly combusted. No comments are made on the possibility to use this chemistry to form an oxide layer in an ALD like process.
David Cameron: Paper describes ways of enhancing the OH group density on carbon by first a chlorination step and then a hydroxylation step with 500C being the most effective temperature for this. The information would certainly be useful in getting ALD on carbon but the paper makes no linkage between the results and the possibility of subsequent deposition so I do not think it is really an "ALD paper".

Aleskovskii, V. B.
Chemistry and technology of solids.
***J. Appl. Chem. USSR.*, 47, 2207-2217, 1974 [in English]**
(Translated from: ***Zh. Prikl. Khim.* 47, 2145-2157, 1974**)
В. Б. алесковский, О химии и технологии твердых веществ. Журнал прикладной химии, 1974, Т. 47, вып. 10, С. 2145-2157.
{Aleskovskii1974} en ru
Thomas E. Seidel: "What I found amazing in Aliskovskii's work: Chemistry and Technology of Solids, Translated from Zhurnal Prikladnoi Khimii, Vol. 47, No.10, p 2145, Oct 1974 - is that it not only first published sequential SiO2 film saturating reactions but demonstrated nanolaminates (SiO2/TiO2) and outlined the strategy for applications to nanoscale devices. He and his group pesented a rather complete prescient vision. Unfortunatley, he has passed away and Nobel awards are only for the living." (Comment copied from a LinkedIn discussion in the group "ALD - Atomic Layer Deposition" by Riikka Puurunen, with permission given by Tom Seidel. The discussion thread full title reads: "Do you think the invention of the ALD process is significant enough to deserve the Nobel prize?")
Riikka Puurunen: This is an amazing article indeed. It reviews advances obtained by the time of writing the work and looks into the future, what all can be achieved by molecular layering (ALD). I understand that Aleskovskii presents an early suggestion of surface-selective ALD ("if necessary, part of its <i.e., support's> surface is shielded by flat (monolayer) or relief coating in the form of specified pattern"). Also he notices the possibility of using templates for ALD growth ("at the end of the synthesis, the support is removed, if necessary, by chemical or mechanical methods"). The general advances of ALD for material synthesis at "comparatively low temperatures and pressures". He notices the possibility of fine regulation of pore size in sorbents. He discusses "multizone structures", which we nowadays know as nanolaminates, and gives examples of nanolaminates of SiO2 and TiO2. He concludes that ML (ALD) works in a similar manner on single crystals <silicon, germanium>, porous materials (silica gel, carbon), and fine powders (talc, kaolin, Aerosil). He notices, using several examples, that four to six "monolayers" (the name used for ML cycles, that is, ALD cycles) are needed for the material to reach the properties that the solid material would have---this I understand as an early evidence of the closure of the film after four to six cycles. He describes the deposition of ternary materials (TiO2 and POx combined as a mixed oxide) where the sequence of deposition in total of four ALD cycles (14 possible combinations of cycles, all synthesized) influences the catalytic activity of the system. Aleskovskii also describes how materials (example is SiO2) of different densities can be made---but here I think the logics go wrong, as densities are calculated just from the thickness deposited per cycle (called "monolayer"); the mistake in my opinion is that it is not realized that less than a monolayer of SiO2 is actually deposited per cycle. Aleskovskii ends: "Evidently this method <molecular layering> can be used for synthesizing materials and physical devices, and eventually biological tissues and organs. Thus, in our view chemistry of the solid state is becoming an important new branch not only of general chemistry but also of technology." It is from this already clear that the method was not viewed as "just scientific", but the early researchers were powerfully thinking of applications, too. And one paragraph, in p. 2214, impressively summarizes the vision that Prof. Aleskovskii had on the impact of ALD: "In illustration, we may cite certain practical problems now being solved by the molecular-layering method. They include buildup of material, increase of its mass, including the above-mentioned build-up of carbon mass on carbon and of silicon on silicon; production of protective layers on microparticles of pigments, e.g., aluminum-oxygen layers in pigment-grade titanium dioxide, or of silicon-oxygen layers on molybdate chromes. The route to further miniaturization of microelectronic devices and to molecular electronics is also evident."
Massimo Tallarida: Indeed it is impressive the treatment of ALD in this review. I would add that in the initial part of the paper, Aleskovskii discusses how difficult is to produce materials (expecially compounds) with same physical-chemical properties. He ends the paper saying that molecular layering is the best way to solve the problem. This is probably still true! I see a problem regarding the wrong calculation of density. Already in the paper of Sveshnikova (1970b) they showed a wrong calculation of the density. The mistake was induced by the assumption that one ML step corresponds to the deposition of one layer. It seems that after 4 years the idea was still the same: 1ML step=1layer. There still no consideration of the steric hindrance effect in ALD.
Jyrki Molarius: Aleskovskii review, which first discusses the Nature of Solid Substances, then discusses molecular layering (ML/ALD) in theoretical as well as with practical examples eg. TiO2/SiO2. He investigates "buffer"/seed layers, too. Striking is his comment of the applications of ML: "The route to further miniaturization of microelectronic devices and to molecular electronics is evident."

Pak, V. N.; Kostikov, Yu. P.; Kol'tsov, S. I. & Aleskovskii, V. B.
Determination of coordination number of titanium atoms on a titanium-containing silica surface by measuring shifts in K(alfa1) X-ray lines
***Kinet. Catal.*, 15, 1205-1206, 1974 [In English]**
(Translated from: ***Kinet. Katal.*, 15, 1358-1359, 1974)**
В. Н. Пак, Ю. П. Костиков, С. И Кольцов, В. Б. Алесковский. Определение координационного числа атомов титана на поверхности титансодержащего кремнезема методом измерения сдвигов рентгеновских K(alfa1) линий. Кинетика и катализ. 1974, Т. 15, вып. 5, С. 1358-1359.
{Pak1974} en ru
Massimo Tallarida: here the authors discuss the coordination of Ti after 1 ALD cycle (or to be more precise, after 1 TiCl4 and H2O treatment). They say that for a cycle at 180°C, the Ti-O coordination is octahedral, while after exposure to 350°C it becomes tetragonal and dehydroxilation takes place.
David Cameron: In this paper the authors continue their study of the chemisorption of Ti to Si-OH surfaces. They show by measuring x-ray peak shifts that after a TiCl4 and H2O treatment at 180C produced a Ti atom chemically bonded to three surface O atoms and an OH group. Additionally H2O groups were attached to the Ti by hydrogen bonding in an octahedral configuration. The hydrogen bonded water can be removed by hearting to 350C and the process is reversible.

Pak, V. N.; Ventov N. G. & Kol'tsov, S. I.
The electronic spectrum of ultra thin titanium oxide films on the surface of quartz.
***Theor. Exp. Chem.*, 10, 711-713, 1974**
Пак, В. Н.; Вентов, Н. Г. & Кольцов, С. И. Электронные спектры сверхтонких титанокислородных пленок на поверхности кварца. ТЭХ, 1974, 10(5), 711-713.
{Pak1974a} ru
Original article submitted on April 11th of 1973
Maria Berdova: the paper is related to the growth of TiO2 on quartz using TiCl4&H2O. Even one layer of TiO2 was enough to absorb UV-light. Annealing at 500oC did not change the stability of films.

V. N. Pak.
Surface dehydration of titanium-containing silica investigated by thermal desorption *Russian Journal of Physical Chemistry* 48, 1383-1384, 1974
Исследование дегидратации поверхности титансодержащего кремнезёма методом термодесорбции / В. Н. Пак // Журнал физической химии. – 1974. – Т. 48, № 9. – С. 2339-2341.
{Pak1974b} ru en
Maria Berdova: The work reports the dehydration by thermal desorption of silica gel, titania gel and titanium-silica obtained by molecular layering. In case of titanium-silica, there were observed highly active centers of water sorption. The correlation between thermal desorption and catalytic activity of the specimens is observed and investigated.
David Cameron: A strudy of the Ti bonding on a TiOx monolayer on silica gel by TiCl4 and H2O at 180C. The Ti is octahedrally bonded with additional H2O molecules sorbed to the Ti-OH surface group. These H2O groups are desorbed at 350C but can be restored by steam treatment at 180C. No indication of any effects on multilayer growth - only a monolayer is considered.

Kol'tsov, S. I.; Aleskovskii, V. B.; Volkova, A. N. & Smirnov, V. M.
Change in the structure of silica gel in the process of the formation of a layer of phosphorus pentoxide on its surface
***J. Appl. Chem. USSR.*, 47, 1292-1295, 1974**
(Translated from: *Zh. Prikl. Khim.*, 47, 1254-1258, 1974)
С. И. Кольцов, В. Б. Алексковский, А. Н. Волкова, В. М. Смирнов. Изменение структуры силикагеля в процессе образования на его поверхности слоя пятиокиси фосфора. Журнал прикладной химии, 1974, Т. 47, вып. 6, С. 1254-1258.
{Koltsov1974} en ru
Cagla Ozgit-Akgun: In this study, P_2O_5 was formed on the silica gel surface via the multiple repetition of two successive reactions: (1) chemisorption of PCl_3, and (2) the oxidation of the tervalent phosphorus by chlorine in the presence of water vapor. During this process, chemisorption of a PCl_3 molecule consumes three hydroxyl (-OH) groups, whereas in the following step, the oxidative hydrolysis at each newly added P atom results in the formation of only two new -OH groups on the surface. Therefore, the number of surface -OH groups gradually decrease with each cycle, which in turn results with the formation of strained phosphorus-oxygen bonds and the change in the coordination of chemisorbed phosphorus on its oxidation and subsequent hydrolysis. These cause changes in the structure of silica gel, such as the specific surface, total pore volume, mean pore diameter, etc. The article focuses on the changes occurring in the structure of the silica gel upon the formation of P_2O_5, rather than the ALD process itself. The P_2O_5 ALD process might have been first reported in Ref. 3 (S. I. Kol'tsov et al., Neorganicheskie Materialy, 6, No. 7, 1370 (1970).).

Eremeeva, M. A.; Nechiporenko, A. P.; Kuznetsova, G. N.; Kol'tsov, S. I. & Aleskovskii, V. B.
Investigation of ultrathin SiO2 films on the surface of single-crystal germanium
***J. Appl. Chem. USSR.*, 47, 2332-2333, 1974 [In English]**
(Translated from**: *Zh. Prikl. Khim.*, 47, 2332-2333, 1974)**
М. А. Еремеева, А. П. Нечипоренко, Г. Н. Кузнецова, С. И. Кольцов, В. Б. Алесковский. Исследование сверхтонких окисных пленок SiO2 на поверхности монокристаллического германия. Журнал прикладной химии, 1974, Т. 47, вып. 10, С. 2332-2333.
{Eremeeva1974} en ru
Riikka Puurunen: In this paper, SiO2 is grown on single-crystal germanium. The authors state the purpose of the work as follows: "The purpose of the work was to compare the results of chemical and spectral analyses of molecular layers of silicon dioxide on single-crystal silicon." The authors talk of "four to 20 monolayers" of SiO2. Thicknesses are reported as 8 to 30 ångströms, 0.8-3 nm. With the current background knowledge, I interpret that the authors have carried out four to 20 ALD cycles. (In some earlier works from the same group, one ML cycle was "defined" to deposit "a monolayer" of material.) In this work, they do not define what the reactants were and what the ALD temperature was. However, the same group of authors has worked with SiO2 deposition earlier by ALD (ML), so one can assume that for this short work, the same reactants SiCl4 and H2O have been used (it was probably too trivial to mention these).

Kol'tsov, S. I.; Uhova T. V. & Volkova, A. N.
Study of the products of successive interaction of boron tribromide and titanium tetrachloride with silica gel
***Journal of Applied Chemistry of the USSR.* 47, 18-20, 1974**
С. И. Кольцов, Т. В. Ухова, А. Н. Волкова. Изучение продуктов последовательного взаимодействия трехбромистого бора и четыреххлористого титана с силикагелем. Журнал прикладной химии 1974, Т. 47, вып. 1, С. 20-22.
{Koltsov1974a} ru en
Nikolai Chekurov: BBr3 - TiCL4 - H2O @ T = 180 deg celsius reaction was investigated.
The composition of resulting (bi-oxide) material was analyzed and a likely formulation of the oxide stack was proposed.
No repetition of the cycles is mentioned.
An apparatus from 1963 was used.
David Cameron: describes the deposition of a double molecular layer of B and Ti oxides by using BBr3/H2O/TiCl4/H2O at 180C. Purging in dry hydrogen (nitrogen) for the BBr3 (TiCl4). No continuation of process.

Smirnov E.P.
Synthesis of titania and carbon layers on the carbon surface by molecular layering
Dis .... kand.him.nauk . - L. , 1974 . - 184 p.
Смирнов Е.П. Синтез титаноксидных и углеродных слоев на поверхности углерода методом молекулярного наслаивания: Дис.... канд.хим.наук. - Л., 1974. - 184 с.
(no code)

Tooz .T.V
Synthesis and investigation of the stability of thin oxide layers on the surface of silica Diss . ... Candidate . Chem. Science / LTI - L. , 1974 . - 113.
Туз Т.В. Синтез и исследование устойчивости тонких оксидных слоев на поверхности кремнезема: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1974. - 113 с.
(no code)

Petrov, K. P.; Genchev, G. M. & Bliznakov, G. M.
Density of multilayer coatings formed as a result of reactions of molecular stratification - two-dimensional models
***Dokladi na Bulgarskata akademiia na naukite (Proceedings of the Bulgarian Academy of Sciences),* 28, 939-941, 1975**
К. П. Петров, Г. М. Генчев, Г. М. Близнаков. О плотности монослойных покрытий, образованных в результате реакций молекулярного наслоения - двумерные модели. Доклады Болгарской академии наук. 1975, Т. 28, вып. 7, 939-941.
{Petrov1975} ru
Riikka Puurunen: It seems that there is no English translation. Judging from Figure 1, they analyse for crystalline plane, how dense the adsorbate layer can be, if reaction takes place with two OH groups simultaneously.

Pak, V. N.; Kol'tsov, S. I. & Aleskovskii, V. B.
Formation of positive benzene ions on surface of titanium-containing and aluminum-containing silicas prepared by the molecular-coating method
***Russ. J. Gen. Chem.* 45, 218, 1975**
(Translated from: ***Zh. Obshch. Khim.,* 45, 234, 1975**)
В. Н. Пак, С. И. Кольцов, В. Б. Алесковский. Образование положительных ионов бензола на поверхности титан- и алюминийсодержащих кремнеземов, полученных по методу молекулярного наслаивания. Журнал общей химии, 1975, Т. 45, вып. 1. С. 234.
{Pak1975} en ru
Riikka Puurunen: This is a one-page letter to the editor. It is concluded that on the samples created with molecular layering (ALD), more active proton-donor and electron-acceptor centres are formed than in aluminosilicate catalysts prepared by reference methods. It is not indicated, how many ALD cycles were carried out, and also not the reactants; for those, references 2 and 3 are pointed.

Pak, V. N.
Optical spectra of silicas [and silica gel] in the range 200--400 nm
***Russ. J. Phys. Chem.,* 49, 1734-1745, 1975 [In English]**
(Translated from: ***Zh. Fiz. Khim.,* 49, 2938-2939, 1975)**
В. Н. Пак, Оптические спектры кремнеземов в области 200-400 ммк. Журнал физической химии, 1975, Т. 49, вып. 11, С. 2939-2939.
{Pak1975b} en ru
Riikka Puurunen: This paper does not contain ALD, but I add the reference in the list anyway, because this reference comes up in the old ALD (ML) publications and the author has also done ALD work. Not ALD

Pak, V. N. & Ventov N. G.
Electronic spectra of titanium (VI) containing compounds
***Zh. Fiz. Khim.,* 49, 2535-2537, 1975 [In Russian]**
В.Н. Пак, Н.Г. Вентов. Электронные спектры окисных соединений четырёхвалентного титана. Журнал физической химии. Т. 49, вып. 10, С. 2535-2537
{Pak1975a} ru
Anatolii Malkov: This work devoted to the development of quantum chemistry concepts (ligand field theory) and spectroscopy of coordination compounds in relation to the consideration of the spectra of solids. From the work's data was concluded that the increase in the coordination number of titanium atoms and lowering of the symmetry type of the coordination polyhedra in solid oxides may lead to a shift of absorption band edge to longer wavelengths region.
Riikka Puurunen: This paper does not report on ALD but is listed because it is written by an author with ALD-ML publications and it is referred to in the early ML literature.

Hanke, W.; Bienert, R.; Jerschkewitz, H. G.
Unter-Suchungen an Katalytisch aktive Oberflachenverbindungen, I. Herstellung und Untersuchung von Vanadium-Oxide-Phasen auf SiO. (Studies on catalytically active surface compounds 1. Preparation and investigation of vanadium oxide phases on silica)
***Z. Anorg.Allg.Chem.* 414, 109-129, 1975 [In German]**
{Hanke1975} ger

Aleskovskii, V. B.
Chemical assembly of materials
***Vestn. Akad. Nauk SSSR,* 1975, 48-52.** [In Russian]
В. Б. Алесковский. Химическая сборка материалов. Вестник Академии наук СССР, 1975, С. 48-52.
{Aleskovskii1975} ru

Volkova, A. N.; Malygin, A. A.; Kol'tsov, S. I. & Aleskovskii, V. B.
Interaction of chromium-containing silica gel with phosphorus trichloride
***Zh. Obshch. Khim.,* 44, 3-7, 1975**
А. Н. Волкова, А. А. Малыгин, С. И. Кольцов, В. Б. Алесковский. Изучение взаимодействия хромсодержащего силикагеля с треххлористым фосфором. Журнал общей химии, 1975, Т. 44, вып. 1, С. 3-7
{Volkova1975b} ru

A.N. Volkova, A.A. Malygin, S.I.Kol'tsov, V.B. Aleskovskii.
Chemical composition of reaction products of silicon-containing phosphorus (III) and silicon-containing phosphorus (V) with vanadium oxychloride.
***Zhyrnal neorganicheskoi khimii.* 20, 2695-2698, 1975**
А.Н. Волкова, А.А. Малыгин, С.И. Кольцов, В.Б. Алесковский. О химическом составе продуктов взаимодействия фосфор (III) и фосфор (V) содержащих кремнеземов с оксихлоридом ванадия. Журнал неорганической химии. 1975. Т. 20, вып. 10, С. 2695-2698.
{Volkova1975a} ru

D. Damyanov, D. Mehandjiev, Ts. Obretenov
Preparation of Chromium oxides on the surface of silica gel by the method of molecular deposition. IV. Catalytic properties
***Proc. III Inter. Symp. Heterogeneous Catalysis-Varna,* 1975, p. 191-195**
(no code)
(a copy?)

Aleskovskii, V. B.
Stoichiometry and synthesis of solid compounds.
***Journal of Applied Chemistry of the USSR,* 49, 268-272, 1976**
В.Б. Алесковский. Стехиометрия и синтез твердых соединений. Журнал прикладной химии. 1976, Т. 49, вып. 2, 265-270.
{Aleskovskii1976} en ru
David Cameron: This paper discusses the formation using molecular layering of non-stoichiometric materials by using different compound layers in a sequence, that is by producing nanolaminates. The individual layers are stoichiometric but considered over the sum of the deposited material, the stoichiometry need not be exact. The materials described are chalcogenides where Cd, Pb or Zn combine with S, Se or Te. It clearly indicates the flexibility of molecular layering in producing synthetic materials via nanolaminates.
Henrik Pedersen: This is an overview paper by Aleskovskii from a conference where he discuss stoichiometry of solid compounds, using some of his own research results to highlight general concepts. As David writes above, Aleskovskii describes the synthesis of nanolaminates of different chalcogenides. In the conclusions, Aleskovskii refers to the synthesis technique as chemical buildup and seems to have a good idea of the level of control that can be achieved with this technique.

V. B. Aleskovskii
Stoichiometry and synthesis of solid compounds
Ed. Nauka, Leningrad, 1976, 142 p.
В. Б. Алесковский. Стехиометрия и синтез твердых соединений. 1976, Изд-во: Наука, Ленинград, 142 с.
{Aleskovskii1976a} ru

D. Damyanov, D. Mehandjiev
Preparation of metal oxide layers deposited on a support by a surface reaction. I. Chromium oxides on silica gel.
***Bulgarian Academy of Science Communications of the Department of chemistry.* 9, 294-303,1976**
Д.Дамянов,Д.Механджиев, Изв. По химии БАН 9, 2 (1976) 294-303. "Получение окисных слоев металлов на носителе методом молекулярного наслоения. I. Нанесение окислов хрома на силикагель".
{Damyanov1976} ru
Riikka Puurunen: I am copying here the summary: “The possibility of producing chromium oxides deposited on silica gel by the interaction of chromium dioxichoride and surface situated OH groups has been investigated. Several molecular layers were deposited by consecutively repeating the process of halogenation and hydrolysis. A series of samples heat-treated under vacuum were also exposed to the action of chromium dioxichloride vapours in the temperature range of 200-900°C. The experiments were made in a vacuum apparatus especially designed for the purpose. It has been established that chromium dioxichloride reacts with the maximum hydrolised surface. After the repeated treatment of the silica-gel samples (preliminarily treated at 200°C) with chromium dioxichloride, multilayer films of chromium oxides are obtained.” Thus, reactions of CrO2Cl2 and H2O, up to six cycles.

D. Damyanov, D. Mehandjiev
Preparing metal oxide layers by a molecular surface deposition reaction. II. Porous structure of silica gel with deposited chromium oxides .
Bulgarian Academy of Science Communications of Department of the chemistry. 9, 385-393, 1976
Д.Дамянов,Д.Механджиев, Изв. По химии Болгарской АН 9, 3 (1976) 385-393. "Получение окисных слоев металлов на носителе методом молекулярного наслаивания. II. Влияние наслаивания окислов хрома на пористую структуру силикагеля".
{Damyanov1976b} ru

D. Damyanov, D. Panayotov, D. Mehandjiev. Ts. Dbretenov
Preparing metal oxide layers by a molecular deposition reaction. III IR spectra of modified with chromyl chloride silica gels
***Bulgarian Academy of Science Communications of Department of the chemistry.* 9, 394-403, 1976**
Д.Дамянов, Д.Панайотов, Д.Механджиев, Цв.Дбретенов Изв. По химии БАН 9, 3 (1976) 394-403. "Получение окисных слоев металлов на носителе методом молекулярного нослаивания. III. Инфракрасные спектры силикагелей, модифицированных хлористым хромилом".
{Damyanov1976c} ru

D. Damyanov
Reaction of $TiCl_4$ with silica and possibility of synthesis of active catalysts
***1a Nauch. konf. na issled. nauchen. raboty i spets. Neft. i khimiya. Burgas.* 1976/77 P. 117-124.**
Д. Дамянов. О взаимодействии титанового четыреххлорида с силикагелем и возможности получения активных катализаторов. 1а Науч. конф. на исслед. научен. работы и спец. Нефт. и химия. Бургас. 1976/77 С. 117-124. (РЖХимия 1980 № 15Б1304)
{Damyanov1976a} bul
Yury Koshtyal: from A. A. Malkov

V. N. Pak.
Structure of surface complexes obtained by reaction of VOCl3 with silica and aerosil *Zhurnal fizicheskoy khimii.* 50, 1404-1407, 1976
В. Н. Пак. Строение поверхностных комплексов, полученных в результате взаимодействия VOCl3 с силикагелем и аэросилом. Журнал физической химии. 1976, Т. 50, вып. 6, С. 1404-1407.
{Pak1976a} ru

Pakkala A
Electroluminescence in zinc sulfide
Master's thesis, Helsinki University of Technology, 1976 [in Finnish] pages?
(no code)

V. M. Smirnov, S. I. Kol'tsov, V. B. Aleskovskii
Effect of the chemical composition of surface layer on the activity of oxide catalyst *Zhurnal fizicheskoy khimii,* 50, 1592-1594, 1976
В. М. Смирнов, С. И. Кольцов, В. Б. Алесковский. Изучение активности окисного катализатора в зависимости от химического состава поверхностного слоя атомов. Журнал физической химии, 1976, Т. 50, вып. 6. С. 1592- 1594.
{Smirnov1976} ru

Suntola T. and Antson J.
Menetelmä ja laite yhdisteohutkalvojen kasvattamiseksi - Förfarande och anordning för uppbyggande av tunna föreningshinnor (~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,
Instrumentarium Oy [In Finnish and Swedish]
US Patent 4 058 430, 15 November 1977 fetch the name
SSSR patent SU 810085 - 29 ноября 1974, опубликовано 28 февраля 1981. Ой Лохья АБ. Способ получения составных плёнок неорганических плёнок.
{Suntola1976} ru
Riikka Puurunen: This patent is the first public document of Atomic Layer Epitaxy and as such historically very valuable. Growth of ZnS from Zn and S is described, using a rotating substrate system (nowadays known as “Spatial ALD”). This patent has been applied and granted in many (26?) countries, including the Soviet Union. According to Dr. Tuomo Suntola (private communication), the patent office in Moscow made a thorough investigation for this, including a public hearing, where Dr. Suntola also travelled to. The patent was granted as applied. Public hearings were organized also in USA, Japan, and Germany.
Andrew Akbashev: Here are the patents issued in the USSR in Russian accessible online:

http://www.findpatent.ru/patent/81/810085.html
http://www.findpatent.ru/patent/108/1085510.html
Both are the “machine-recognized” versions, so if you need to see an actual patient, right-click on images (even if you don’t see them) and do “save as”.
A.A. Malygin on the first Finnish patent. My opinion: I think that this patent is very useful from the point of view of the entrance ALD in the world scientific community. Suggested approaches are somewhat different from the classical version of molecular layering. The authors offer the example of obtaining the sulphide of zinc, of tin oxide and calcium phosphide use solid sources elements Zn, Sn, Ca, S, P and in obtaining oxide oxygen plasma. In the method MN use functional groups on the surface of solid and more complex reagents. For example, a pair of chlorides and water (in the synthesis of oxide structures), sulfur (in the synthesis of sulfide structures) etc.
Publications of Russian (Soviet) scientists and some scientists from other countries of the socialist camp were not known, as published only in their countries. Author's certificates of the USSR, too, were only in the USSR. Perhaps someone from foreign colleagues read articlesof Russian scholars (scientific) about of the molecular layering method. But, apparently, was not supposed to refer to these publications. So thank our Finnish colleagues for the first international patent about of ALD.

Kol'tsov, S. I., Drozd, V. E. & Aleskovskii, V. B.
Investigation of the degree of hydration of the surface of single-crystal silicon at different temperatures
***Proceedings of the USSR Academy of Sciences*, 229, 718-720, 1976**
Кольцов С. И., Дрозд В. Е., Алесковский В. Б. Исследование степени гидратации поверхности монокристаллического кремния при различных температурах. Доклады Академии Наук СССР, Т. 229, Вып. 5, 1145-1147.
{Koltsov1976a} ru en
David Cameron: This paper studies ALD of TiO2 using TiCl4 and water on Si substrates. The "ALD window" is defined which is limited at high temperature (500K) by removal of OH groups from the surface and at low temperature (400K) by excess water molecules adsorbed on the surface. In this window the growth rate is approx. 3Å/cycle. It also shows that on OH terminated Si, there is no non-linear growth region in the initial stages. the growth per cycle is the same even after 2 cycles.

Kol'tsov, S. I.; Kopylov, V. B.; Smirnov, V. M. & Aleskovskii, V. B.
Synthesis and investigation of aluminum--oxygen layers on the surface of silica
***Journal of Applied Chemistry of the USSR,* 49, 525-528, 1976**
С. И. Кольцов, В. Б. Копылов, В. М. Смирнов, В. Б. Алесковский. Синтез и исследование алюминийкислородных слоев на поверхности кремнезема. Журнал прикладной химии. 1976, Т. 49, вып. 3, С. 516-519.
{Koltsov1976b} en ru
Cagla Ozgit-Akgun: In this paper, authors investigated the mechanism of molecular-layering reactions occurring during the synthesis of Al-O layers on hydroxylated silica gel, using $AlCl_3$ and H_2O (at 200 °C?, "the product was treated with water vapor at 200 °C"). After each half-cycle, excess precursor molecules and reaction by-product were purged away from the equipment. And several cycles were performed. As they investigated the reaction mechanism for Al_2O_3, they found out that the reaction coefficient K is 1/2 for the first two monolayers. However, starting with the first half-cycle of 3rd monolayer, the character of $AlCl_3$ chemisorption changes, and K becomes 2. For the following monolayers, it varies as 1/2, 2, 1/2, 2,... Therefore starting from the 2nd monolayer, regular alteration of K occurs, which results with the uniform deposition of aluminum-oxygen layers. Authors confirmed the presence of Al_2O_3 in the reaction products by IR spectroscopy. X-ray diffraction (XRD) studies showed an amorphous layer. For the samples (4-6 Al-O monolayers on silica gel) annealed at 450 °C, XRD patterns revealed weak peaks corresponding to crystalline Al_2O_3 phase.

Kol'tsov, S. I.; Malkov, A. A.; Smirnov, V. M. & Aleskovskii, V. B.
Chemical homogenization of carbon surfaces
***Journal of Applied Chemistry of the USSR.,* 49, 1277-1280, 1976**
С. И. Кольцов, А. А. Малков, В. М. Смирнов, В. Б. Алесковский. Химическая гомогенизация поверхности углерода. Журнал прикладной химии, 1976, Т. 49, вып. 6, С. 1242-1246.
{Koltsov1976c} en ru
Tanja Kallio: Investigation of functionalization of carbon surface with Cl2 (20-700oC, 1.5-2 h) and after that with water (100-500oC) resulting in reaction bonds C–Cl > C–OH + HCl. The idea of successive reactions is here.
David Cameron: This paper reports the removal of impurities, including oxygen and water, from the surface of various types of carbon, by heating it to 1000-1100C (in Argon?) for several hours. Some H remains on the surface. It can then be 'standardised' by chorination with HCl followed by hydroxylation with H2O leaving an OH terminated surface. Not really an ALD paper - just deals with chlorination of a carbon surface.

Koval'kov, V. I.; Smirnov, E. P.; Kolt'sov, S. I. & Aleskovskii, V. B.
Synthesis of proton-donor OH groups on the surface of highly dispersed carbon
***Journal of Applied Chemistry of the USSR.,* 46, 2069-2070, 1976**
В. И. Ковальков, Е. П. Смирнов, С. И. Кольцов, В. Б. Алесковский. Синтез протонодонорных ОН групп на поверхности высокодисперсного углерода. Журнал общей химии, Т. 46, вып. 9, 2151-2152.
{Kovalkov1976} en ru
Tanja Kallio: Carbon is first purified in He (1000-1100oC) so that surface heteroatoms (O, S) are removed. This is followed by functionalization with Cl2 (20-500oC) resulting in functionalized carbon C–Cl which finally reacts with water vapor (100-500oC) as follows C–Cl > C–OH + HCl. No purge times are given. completely new?
David Cameron: Essentially the same as Koltsov 1976c

A. A. Malkov, S. I. Kol'tsov, V. D. Ivin, E. P. Smirnov, V. B. Aleskovskii
Effect of surface modification of carbon fibers with titanium oxide groups on their reactivity
***Journal of Applied Chemistry of the USSR*, 49, 1650-1652, 1976**
А. А. Малков, С. И. Кольцов, В. Д. Ивин, Е. П. Смирнов, В. Б. Алесковский. Влияние модифицирования поверхности углеродных волокон титаноксидными группами на их реакционную способность. Журнал прикладной химии, 1976, Т. 49, вып. 7, С. 1624-1626.
{Malkov1976} ru en
David Cameron: This paper is a follow-on from Kol'tsov 1976c where the chlorinated C materials has a TiO layer using TiCl4 and water. Concerned with the rate of oxidationn of the carbon when heated subsequently - it is greater with the TiO layer. Not really an ALD paper.

Malygin, A. A.; Volkova, A. N.; Kol'tsov, S. I. & Aleskovskii, V. B.
Oxidation--reduction reactions of phosphorus trichloride and vanadyl(V) chloride with vanadium(V)- and phosphorus(III)- containing silica gels
***Journal of general chemistry of the U.S.S.R.,* 46, 2085-2088, 1976**
А. А. Малыгин, А. Н. Волкова, С. И. Кольцов, В. Б. Алесковский. Изучение окислительно-восстановительных реакций терхлористого фосфора и оксихлорида вандаия (V) с ванадий (V)- и фосфор (III)-содержащими силикагелями. Журнал общей химии, 1976, Т. 46, вып. 10, 2166-2169
{Malygin1976} en ru
David Cameron: This paper shows the results of sequential exposure of the surface of silica gel to P and V compounds and then hydrolysing with steam. This gave either a PV-OH or VP-OH structure depending on the sequence. It deals only with the single layer, with no suggestion of more than one alternating sequences of exposure. It is therefore more of basic understanding of how groups bond to the surface rather than any ALD-like process.

Pak, V. N.
Structural effects of silica surfaces on molecularly superposed titanium-oxygen layers
***Zh. Fiz. Khim.,* 50, 1266-1268, 1976**
В. Н. Пак. Структурно-химическая природа поверхности кремнеземов и ее влияние на строение титанкислородных слоев, синтезированных по методу молекулярного наслаивания. Журнал физической химии. 1976, Т. 50, вып. 5, С. 1266-1268.
{Pak1976} en ru
Henrik Pedersen: This short paper focuses on the chemical structure of the silica and titania surfaces after ALD of titania on silica. To me, this is definitely ALD, it is described as irreversible chemisorption of TiCl4 followed by hydrolysis of unchanged chlorine atoms by water. The ALD process is done at 300 C in hydrogen, there is nothing written about the pressure in the process or on the number of ALD cycles. The author discuss on the possible structure of the titania formed on the silica; tetrahedral TiO4 or octahedral TiO6 are the possible structures. If I understand the authors correctly, the author seem to suggest that the structure of the film replicates the structure of the substrate and that the author thus suggests some sort of epitaxial growth.
David Cameron: This paper deals with the structure of Ti oxide monomayers on different types of silica by exposure first the TiCl4 then H2O. On silical gel surfaces the Ti is octahedrally bonded to O because the underlying surface has octahedrally coordinated Si-O whereas on Aerosil, like quartz the Ti is tetrahedrally bonded to O.

S. Ya Tretyakov, L. M. Sharygin
Chemisorption of $TiCl_4$ on the dehydroxylated samples of silica
***Zhurnal fizicheskoy khimii.* 50, 2445-2445 1976**
С. Я Третьяков, Л. М. Шарыгин. Хемосорбция четыреххлористого титана на дегидроксилированных образцах силикагеля. Журнал физической химии. Т. 50, вып. 9, С. 2445-2445.
{Tretyakov1976} ru

V. N. Pak, Yu. P. Kostikov
Structure of the surface, dehydratation and reduction of titanium-containing silicas *Kinetika i kataliz.* 18, 475-479, 1977
Строение поверхности, дегидратация и восстановление титансодержащих кремнезёмов / В. Н. Пак, Ю. П. Костиков // Кинетика и катализ. – 1977. – Т. 18, № 2. – С. 475-479.
{Pak1977} ru

Hair, M. L.
Effect of surface structure on the reaction of silica surface with hydrogen-sequestering agents
***J. Colloid Interface Sci.,* 60, 154-161, 1977**
{Hair1977} en
David Cameron: This paper measured the kinetics of Si chlorosilanes and Ge and B chlorides on OH terminated Si surfaces. This was done using FTIR absorption measurements of the OH vibrations and how they changed as a reaction progressed. The focus is on detailed analysis of the reaction kinetics for one single layer with no suggestion of its implications for multiulayer growth. In my opinion this is not really an ALD paper although it contains information of importance to ALD.
Henrik Pedersen: This paper is, to me, a pure surface chemistry paper where BCl3, GeCl3, SiClnMe4-n and (Me3Si)2NH is adsorbed onto silica and their reaction kinetics with surface -OH groups are studied with FT-IR. There is to me no signs of any indication that this could be used for film deposition by any ALD-like process.

Khalif, V. A.; Aptekar', E. L.; Krylov, O. V. & Öhlmann, G.
Heats of adsorption of oxygen on vanadium oxide applied to Aerosil by molecular stratification
***Kinet. Katal.,* 18, 1055-1059, 1977**
В. А. Халиф, Е. Л. Аптекарь, О. В. Крылов, Г. Ольман. Теплоты адсорбции кислорода на окиси ванадия, нанесенной на аэросил методом молекулярного наслаивания. Кинетика и Катализ, 1977, Т. 18, вып. 4, 1055-1059.
{Khalif1977} en ru
David Cameron: This paper studies monolayer vanadium catalysts on silica surfaces. It reacts VOCl3 on SiOH and then a further hydrolysis in water vapour, all at 200C. The heats of adsorption of oxygen at various temperatures was measured. The aim was monolayer catalyst development, not multilayers so it is stretching things to call it an ALD paper although it does use the term "molecular stratification" to describe the process.
Simon Elliott: This paper describes treatment with gaseous VOCl3 followed by gaseous H2O, yielding a 2D film of V2O5, rather than the 3D product of the solution phase. A self-limiting chemistry is thus implicit, but the consequences are not discussed explicitly.
Jaana Kanervo: This relates to ALD indirectly by concerning characterization of silica supported ALD prepared vanadium oxide catalyst. The heats of adsorption of oxygen have been determined calorimetrically at different temperatures for 0.8% V/SiO2. This work demonstrates that oxygen is adsorbed predominantly in form O2-, which is not responsible for low temperature (< 200 ^{0}C) oxidations. However there exist two types of oxygen uptake processes: unactivated and activated one. Difference between the surface structure of impregnated and ALD prepared vanadium oxide catalyst is indirectly brought out.

Kol'tsov, S. I.; Drozd, V. E.; Redrova, T. A. & Aleskovskii, V. B.
Investigation of the structure of titanium oxide layers synthesized by molecular stratification on the surface of single-crystal backings
***Dokl. Akad. Nauk SSSR,* 235, 1090-1092, 1977**
Кольцов С. И., Дрозд В. Е., Редрова Т. А. Алесковский В. Б. Исследование структуры титаноксидных слоёв, синтезированных методом молекулярного наслаивания на поверхности монокристаллических подложек. Доклады Академии Наук СССР, 1977, Т. 235, Вып. 5. С. 1090-1092.
{Koltsov1977} en ru
Henrik Pedersen: The introduction of this paper shows that the Koltsov-Aleskovskii group had really started to understand molecular stratification and its applications in 1977 (original article submitted May 10 1977). They describe the ability to synthesise oxide films by alternating pulses of metal chlorides and water to synthesize films with angstrom precision. In this paper, the authors study the crystallinity of titania films deposited on single crystal substrates. Ge, Si, SiC with natural oxides and STA mica was used as substrates. ALD, or molecular stratification, was done in the 300-800 K range. No mention on the pressure is given so I suspect that it was done at atmospheric pressure. By electron diffraction, crystalline titania of the anatase polymorph was found to be deposited at 420 K. At 570 K, the films are of the rutile polymorph. The authors speculate that the presence of oxide on the Si, Ge and SiC substrates hinders any epitaxial effects to affect the deposition. Films deposited below 420 K are mixtures of titania and titanium hydroxide, no chlorine was found in the films.
David Cameron: This paper shows that multilayer film by molecular layering can be achieved and that the thickness is a linear function of the number of growth cycles. It reports that the growth per cycle depends on the OH concentration on the substrate. It deals with TiO2 growth from TiCl4 and H2O and shows that the anatase structure can be obtained at 420K on Si and at different temperatures on different substrates. At higher temperatures (570K), rutile is obtained. below 420K the films contain hydroxide because of the adsorption of excess water on the surface - an element of CVD growth.

Stepanova, N. A.; Smirnov, V. M.; Kol'tsov, S. I. & Aleskovskii, V. B.
Study of the reaction between zinc chloride and silica gel
***Journal of Applied Chemistry of the USSR* 50, 450, 1977**
Н. А. Степанова, В. М. Смирнов, С. И. Кольцов, В. Б. Алесковский. Изучение взаимодействия хлорида цинка силикагелем. Журнал прикладной химии, 1977, Т. 50, вып. 2, С. 465-465.
The full text of the paper is deposited in the **VINITI** (All-Union Institute of Scientific and
Technical Information of the Academy of Sciences of the USSR), No. 3210-76, August 30, 1976.
{Stepanova1977} en ru
David Cameron: This is the abstract of a paper in the All-Union Institute of Scientific and Technical Information of the Academy of Sciences of the USSR (1976) Where a monolayer of ZnO is deposited on silical gel be explosing to ZnCl2 vapour at 450-600C followed by hydrolysation at 180C.

Eremeeva M.A.
Synthesis and investigation by IR - spektoroskopii MNPVO and ellipsometry of ultrathin oxide films on the surface of single-crystal germanium and silicon
Diss . ... Candidate . Chem. Science / LTI - L. , 1977. - 184 p.
Еремеева М.А. Синтез и исследование методами ИК - спектороскопии МНПВО и эллипсометрии сверхтонких окисных пленок на поверхности монокристаллов германия и кремния: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1977. - 184 с.
(no code)

Kovalkov V.I.
Synthesis of highly dispersed solids with desired structural and chemical properties of the surface by molecular layering and investigation of their properties
Diss .... Candidate . Chem. Science / LTI - L. , 1977 . - 181 p. [in Russian]
Ковальков В.И. Синтез высокодисперсных твердых веществ с заданными структурно- химическими свойствами поверхности методом молекулярного наслаивания и исследование их свойств: Дисс.... канд. хим. наук/ ЛТИ - Л., 1977. - 181 с.
(no code)

Kopylov V.B.
Synthesis of carbon layers on the surface of silica by molecular layering and the study of their properties
Diss . ... Candidate . Chem. Science / LTI - L. , 1977 . - 147 p.
Копылов В.Б. Синтез углеродных слоев на поверхности кремнезема методом молекулярного наслаивания и исследования их свойств: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1977. - 147 с.
(no code)

AA Malkov
Synthesis by the of molecular layering method of E -O layers on the surface of carbon fibers and study of their properties
Diss . ... Candidate . Chem. Science / LTI - L. , 1977 . - 163 p. [in Russian]
Малков А.А. Синтез методом молекулярного наслаивания Э-О слоев на поверхности углеродных волокон и исследование их свойств: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1977. - 163 с.
{Malkov1977} ru

Kol'tsov, S. I.; Smirnov, V. M.; Rachkovskii, R. R.; Malalaeva, T. V. & Aleskovskii, V. B.
Study of aluminosilicate systems synthesized by the molecular-layering method
***Journal of Applied Chemistry of the USSR,* 51, 2475-2477, 1978**
С. И. Кольцов, В. М. Смирнов, Р. Р. Рачковский, Т. В. Малалаева, В. Б. Алесковский. Изучение алюмосиликатных систем, синтезированных методом молекулярного наслаивания. Журнал прикладной химии, 1978, Т. 51, вып.11, 2596-2598.
{Koltsov1978} en ru
David Cameron: This paper reports the structure of nanolaminate films containing Al and Si oxides. The sequence of layers is changed to change the Al/Si ratio. The activity is affected by the distance between the surface Si-O groups and the aluminosilicate surface.
This clearly shows the development of complex layer structures by MLD

Nechiporenko, A. P.; Sukhareva, T. M.; Malygin, A. A.; Kol'tsov, S. I. & Aleskovskii, V. B.
Ultramicrochemical investigation of chromium oxide layers synthesized by molecular layering on single-crystal germanium and silicon surfaces
***Journal of Applied Chemistry of the USSR,* 1978, *51 (11)*, 2333-2337**
А. П. Нечипоренко, Т. М. Сухарева, А. А. Малыгин, С. И. Кольцов, В. Б Алесковский. Ультрамикрохимическое исследование хромоксидных слоев, синтезированных методом молекулярного наслаивания на поверхности монокристаллических германия и кремния. Журнал прикладной химии, 1978, Т. 51, вып. 11, С. 2447-2151
{Nechiporenko1978} en ru
Henrik Pedersen: This paper describes the development of a spectroscopic technique for analysis of chromium oxide layers on single crystal Si and Ge. It is quite clear that the Aleskovskii group here has understood that ALD, or molecular layering as they call it here, can be used to make thin films with very high thickness precision. They discuss on the need to have a spectroscopic method to study the thickness of films from various number of ALD cycles. The authors use an ALD process with CrO2Cl2 and H2 to make cromia films. Nothing is written about either temperature or pressure. The authors describe a destructive technique where the films are removed from the substrates by boiling in water and the cromia dissolved and the resulting solution is analyzed. The authors conclude that the spectroscopic technique is well in agreement with elipsometric data. I am not sure if the authors seek to show that ellipsometry is a good technique or if they have doubts that ellipsometry is a good technique. To me, it seems better to use nondestructive ellipsometry.

Postnova, A. M. & Kol'tsov, S. I.
Influence of the number of phosphorus oxide monolayers on the catalytic activity of vanadium- and phosphorus-containing silica gels prepared by the molecular-stratification method
***Journal of general chemistry of the U.S.S.R.,* 48, 861, 1978**
А. М. Постнова, С. И. Кольцов. О влиянии количества фосфороксидных монослоев на каталитическую активность вандий-фосфорсодержащихся силикагелей, полученных методом молекулярного наслаивания. Журнал общей химии. 1978. Т. 48, вып. 4. С. 941-941.
{Postnova1978} ru en
David Cameron: Abstract of a paper describing how mixed composition multilayers of V and Ti oxides can be made by "molecular stratification" and how these affect catalytic behaviour. Clearly mentions the MLD technique.

Smirnov, E. P.; Gordeev, S. K.; Kol'tsov, S. I. & Aleskovskii, V. B.
Synthesis of halide functional groups on the surface of diamond
***Journal of Applied Chemistry of the USSR.,* 51, 2451-2455, 1978**
Е. П. Смирнов, С. К. Гордеев, С. И. Кольцов, В. Б. Алесковский. Синтез галоид-функциональных групп на поверхности алмаза. Журнал прикладной химии. 1978, Т. 51, вып. 11, С. 2572-2577.
{Smirnov1978} en ru
Tanja Kallio: Diamond micropowder purified by boiling in a HClO4 solution is subjected to He at temperatures up to 900oC and after that to halide (Cl2 or Br2) up to 700oC. Durations of the reactions are not given. During the first step (treatment in He) surface oxides (-COOH, -OH, -C=O etc. are removed at different temperatures). During the second step carbon surface is covered by halides.
David Cameron: This is an extension of Kol'tsov 1976c where the chlorination of carbon fibre is extended to the chlorination and bromination of diamond powder. Not ALD

A. N. Volkova, L. V. Ivanova, S. I. Kol'tsov, V. I. Yakovlev
Reaction of vinyl-containing silica with phosphorus (III) chloride
***Zh. Prikl. Khim.* 51, 2654-2657, 1978**
А. Н. Волкова, Л. В. Иванова, С. И. Кольцов, В. И. Яковлев. Изучение взаимодействия винилсодержащего силикагеля с треххлористым фосфором. Журнал прикладной химии. 1978, Т. 51, вып. 12, С. 2654-2657.
{Volkova1978} ru
Yury Koshtyal: Maybe this article is not related to ALD, but authors refer to molecular layering in the introduction.

Drozd V.E.
Synthesis and study of oxide coatings obtained by molecular layering on semiconductor surfaces
Diss ... Candidate . nat . mat. Science / LTI. - L., 1978 . – 131 p. [in Russian]
Дрозд В.Е. Синтез и исследование оксидных покрытий, полученных методом молекулярного наслаивания на поверхности полупроводников: Дисс… канд. физ. мат. наук/ ЛТИ. – Л., 1978. – 131с. (ДСП)
{Drozd1978-PhD}
Fred Roozeboom: Chapter 3 of the PhD thesis of Victor Drozd (*Synthesis and Analysis of Oxide Coatings, created by Molecular Layering on Surfaces of Semiconductors*, Leningrad, 1978) starts with the precautions to be taken to eliminate the dominating role of water and water condensation on reactor walls, and on highly porous substrates. Then comes a section (incl. Fig. 5) that gives an introduction on what parts are needed to ***"dramatically increase the rate of coating synthesis (approximately by 100 times)"***. The author pointed to automation of hundreds of (automated) actuation steps to carry out hundreds of monolayers. The automated actuations needing the parts described in this section:
- quartz or metal reactor tubes
- parts for automated feed and removal of reactants and reaction product
- vacuum pump
- zeolite sorption pump, with specification of at least 500 liters / sec
- resistive heating of all the parts of the reactor.
Then follows a scheme of the set-up for the synthesis by the ML method, followed by the description of
- vacuum valves, etc., and valves for the actuation of the reactor lines, including the note, that the reaction valves should resist aggressive vapors such as metal chlorides and HCl
- DC motors for actuation
- valve manual control coupled with vacuummetric pressure gauge
When I interviewed V. Drozd right after the translation V. Drozd made the following remark here: '*Question is that before my vacuum reactor* ***only atmospheric pressure*** *flow type reactors were in use with very slow gas flow*'.
It is interesting to realize that atmospheric pressure ALD has never been far away even in those days!
Riikka Puurunen: It was when reading this work in fall 2013 that I for the first time ever saw a scheme of an ML-ALD reactor intended for processing thin films on flat substrates. It is a hot-wall system, equipped with reactant delivery and "a programmable unit". I understand that already in those years there has been thus a system for doing valving automatically and not by hand. The thesis contains electrical characterization of ALD films on silicon, where aluminium has been deposited as contact on top. There is also a table where the barrier heights are reported for films between Si and Al. There are many materials, including ZrO2, HfO2. It is mentioned that metal chlorides are used as reactants. The film thicknesses are on the 2 nm range. A table from this thesis was shown by Prof Victor Drozd in his invited talk at the Baltic ALD conference (May 12-13, 2014, Helsinki, Finland), translated into English.

Stepanova N.A.
The synthesis of the iron- and zinc-containing layers on the surface of silica
Diss . ... Candidate . Chem. Science / LTI - L. , 1978 . - 176 p.
Степанова Н.А. Синтез железо- и цинксодержащих слоев на поверхности кремнезема: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1978. - - 176 с.
(no code)

Postnova A.M.
Investigation of the structure and reactivity of vanadium-containing silica, obtained by molecular layering
Dis . ... Candidate . Chem. Science / LTI - L. , 1978 . – 166 p.
Постнова А.М. Исследование строения и реакционной способности ванадийсодержащих кремнеземов, полученных методом молекулярного наслаивания: Дис. ... канд. хим. наук/ ЛТИ - Л., 1978. - - 166 с.
(no code)

V.N. Krylov, M. M. Mironova, V. E. Drozd, V. B. Aleskovskii
Effect of oxide interlayers on the properties of Metal-Semiconductor contact
***Fizika i Technika Poluprovodnikov*. 13, 2272-2274, 1979**
В. Н. Крылов, М. М. Миронова, В. Е. Дрозд, В. Б. Алесковский. Влияние оксидных прослоек на свойства контакта металл-полупроводник. Физика и техника полупроводников. 1979, Т. 13, вып. 11, С. 2272-2274.
{Krylov1979} ru
Yury Koshtyal: This paper is devoted to determination of current-voltage characteristic of structure consisted of three film layers Si-Me_xO_y-Al.
Before deposition of Me_xO_y the surface of silicon (n-type) was plasmochemically etched with use of CF_4. The subsequent metal oxide deposition was carried out at 500 K (reactor temperature) according to procedure described in (Kol'tsov, S. I. et al. Proceedings of the USSR Academy of Sciences, 229, 718-720, 1976, Koltsov1976a). Authors varied type of metal oxide (Cr_2O_3, V_2O_5, TiO_2) and its thickness in the range of 10-63 Angstrom. The final layer of Al was deposited by vacuum deposition. The effect of the time of heating at 770K of obtained structures on the current-voltage characteristic was studied.
When Cr_2O_3 or V_2O_5 was used as interlayer of the system Si-Me_xO_y-Al the following regularities were found. With increase of interlayer thickness (for Cr_2O_3 42A=>55A=>63A) the direct drop of voltage augmented. The angle of the slope of dependence lg(I) from U elevated with increase of the heating time.
For the stacked layers Si-TiO_2-Al the drop of voltage was lower than for the Si-Al. After heating for less than 10 minutes the drop of voltage diminished. The longer duration of heating favored the increase of drop of voltage. Structure Si-TiO_2-Al after heating at 770K during 40 minutes had the same drop of voltage as Si-Al. According to suggested hypothesis the continuous heating leads to the dissolution of TiO_2 layer in silicon or aluminum.
The height of energetic barrier was determined from linear area of current-voltage dependence. The height of energetic barrier seemed to be independent from the film thickness (from 10A to 40A). For the structures with metal oxide interlayers (40A thickness) the energetic barriers diminished in the row Cr_2O_3 (0,64V), V_2O_5 (0,56V), TiO_2 (0,46V). The height of energetic barriers of Si-Me_xO_y-Al and Si-Al was different. The maximal difference (0,2V) was observed for Si-TiO_2-Al structure. The height of energetic barriers for the structures Si-Me_xO_y-Al and Si-Me (where Me is Cr, V, Ti) were almost the same.
Kestutis Grigoras: Current-voltage characteristics of contact between aluminum and n-Si were investigated with presence of thin oxide layers between them. As such intermediate layer the oxide of titanium, chromium and vanadium were used, as prepared by method of molecular layering (ML = molekuliarnoje naslaivanije), performed at 500 K, as described in more details in [1: Koltcov et al, in Reports of Academy of Sciences of USSR, 1976].
This is the first and the only sentence in article where method of ML was mentioned. The whole text describes the differences of IV characteristics depending on the thickness of oxides (10-60 Å) and duration of a subsequent annealing at 770 K temperature, and the differences of evaluated metal-semiconductor barrier. In the conclusions, authors also mention that ML technique allows the modelling of thin intermediate oxide layers of different chemical content, what is usually within a metal-semiconductor contact.
This article does not give any detail of ML process, only reference to another work [1].

Aleskovskii, V. B.; Drozd, V. E.; Kiselev, V. F.; Kozlov, S. N.; Kol'tsov, S. I.; Petrov, A. S. & Plotnikov, G. S.
Electrical properties of the surface of germanium in contact with transition-metal oxides formed by the molecular deposition method
***Fiz. Tekh. Poluprovodn.,* 13, 1397-1401, 1979**
В. Б. Алесковский, В. Е. Дрозд, В. Ф. Киселев, С. Н. Козлов, С. И. Кольцов, А. С. Петров, Г. С. Плотников. Об электрофизических параметрах поверхности германия, контактирующей с окислами переходных металлов, полученных молекулярным наслаиванием. Физика и техника полупроводников, 1979. Т. 13, вып. 7, 1397-1401
{Aleskovskii1979} en ru
Claudia Wiemer: This paper presents the electrical characterisation of Ge/transition metal oxide heterostructures, where the oxides, Cr2O3, TiO2 and V2O5 have been deposited by "molecular deposition". Details of the growth process are not reported except from the growth temperature (500 K) and metal precursors (Titanium tetrachloride, chronium oxychloride, vanadium oxychloride). It is not possible to understand if the growth process is in someway related to ALD. Details should be reported in ref 1 and 2 of the present paper, which correspond to: Aleskovskii1976 and Koltsov1976a of our list.
I'm not an expert of the electrical characterization performed here, but it is interesting to notice how this characterization can provide information on electrical defects at the semiconductor/oxide interface.
The Authors performed systematic studies as a function of the type of oxide, of oxide thickness and of annealing in vacuum. They also provided evidence on the effect of exposure to dry and moist oxygen on the electrical characteristics.
Stracks formed by two different oxides were also analysed, although the study presented here is not systematic.
From the point of view of an optimized growth to reduce defects at the semiconductor/oxide interface, a subget of paramount relevance for modern microelectronics, this article is pioneering the investigation of the effect of thickness on interface properties. It is interesting to notice how thickness does not play a major role when the grown oxide is amorphous, whereas lower thickness implies less defects when the grown oxide is crystalline.
The results presented in this work necessitate more experimental investigation in order to confirm the observed trends. In particular, correlation with structural and morphological propertiMaybe some answers can be found in ref 1 and 2, as stated above.
I want however to underline how the problematics faced here are the same encountered during the development of oxides on high mobility substrates including not only Ge but also III-Vs, in the years 2000s.
Luca Lamagna: The paper presents a structured study of the electrical properties of Ge/transition metal oxides interface. TiO2, Cr2O3 and V2O5 were deposited by molecular deposition method at 500 K in a quartz reactor. Only few experimental details about the growth are reported by the authors; titanium tetrachloride, chromium oxychloride and vanadium oxychloride were used as Ti, Cr and V source respectively. Structural and chemical analysis are mentioned but in this respect only some information on structure and thickness are reported in the text. The variation of the traps density is investigated as a function of film thickness, post-deposition heating and exposure to oxygen and moisture. Moreover, charge accumulation and charge lakage measurements are reported addressing the application of storage of optical data. From the ALD/growth point of view the paper is poor of experimental details; however, it addresses two interesting items such as the oxide/Ge and oxide/GeO2 interface characterization and the fabrication composite coatings (nanolaminates) alternating the growth of different materials aiming at the realization of nanostructured stacks.

D. P. Damyanov
Changes in the porous spectrum of titanium-containing silica gels obtained by the molecular deposition method
***Doklady Bolgarskoy akademii nauk.* 32, 51-54, 1979**
{Damyanov1979} en
David Cameron: MLD process shows the change in silica gel pore structure depending on the number of molecular layers (TiCl4 + H2O, 150C). Pore absorption measured by BET method. Plugging of smaller pores occurs as number of layers increases.

Kol'tsov, S. I.; Tuz, T. V. & Volkova, A. N.
Molecular layering of boron oxide on the surface of silica
***Journal of Applied Chemistry of the USSR,* 52, 2074-2077, 1979**
С. И. Кольцов, Т. В. Туз, А. Н. Волкова. Молекулярное наслаивание бороксида на поверхности кремнезема. Журнал прикладной химии, 1979, Т. 52, вып. 10, С. 2196-2199.
{Koltsov1979} en ru
Claudia Wiemer: This paper presents the molecular layering process of boron oxide by the use of alternating treatments of a silica gel surface with boron bromide vapor and water vapor. In this work, the chemical reactions are described and commented. Excess reagent were eliminated, but the Authors don't mention how this happen. The amount of B, OH and SiO2 were measured after each cycle. It is interesting to notice how the concept of cycle is introduced and used here to discuss the completeness of each reaction. The formation of boron oxide layers is described as an equilibrium reaction, and compare dto the reaction giving TiO2 from TiCl4 and H2O.
The amount of oxigen incorporated in the layers has been also calculated and found to result in a O/Br ratio equal to 1.5.This is a nice work on a relatively simple reaction. It is interesting to notice how the concept of equilibrium reaction is here associated with the concept of uniform reaction on a surface, which is the basis of modern ALD.
Hele Savin: This is basically the continuation of their previous work (Ukhova 1974, also listed in this Google document) . The main difference is that in 1974 paper it is probably not ALD growth while here they describe in more detail the cycles and emphasize other characteristics of ALD growth.
The main goal in this study was i) to demonstrate uniform nature of boron oxide layers by ALD ii) to study the formation mechanism (and chemical structure) of the boron oxide layers

A. A. Malkov, S. I. Kol'tsov, V. D. Ivin, E. P. Smirnov, V. B. Aleskovskii
Catalytic oxidation of carbon fibers containing titanium oxide groups
***Mezhvuzovskii sbornik trudov. Geterogennye kataliticheskiye sistemy. LTI im. Lensoveta, Leningrad*, 1979, P. 28-33.**
А. А. Малков, С. И. Кольцов, В. Д. Ивин, Е. П. Смирнов, В. Б. Алесковский. Каталитическое окисление углеродных волокон, содержащих поверхностные титаноксидные группы. Межвузовский сборник трудов. Гетерогенные каталитические системы. ЛТИ им. Ленсовета, Ленинград, 1979, С. 28-33.
{Malkov1979} ru

Malygin, A. A.; Yakovlev, S. V. & Kol'tsov, S. I.
Study of the properties of vanadium-containing silica gel
***Journal of Applied Chemistry of the USSR,* 52, 1976-1978, 1979**
А. А. Малыгин, С. В. Яковлев, С. И. Кольцов. Исследование свойств ванадийсодержащего силикагеля. Журнал прикладной химии, 1979 Т. 52, вып. 9, 2094-2096.
{Malygin1979} en ru
Ruud van Ommen: This paper described the use of molecular layering on silica gel to make a humidity indicator. The authors first apply half an ALD cycle (silica gel + VOCl3). Since the color of the obtained material depends on the extent to which the second half reaction (reaction with water) runs, it can indeed be used to quantify humidity levels. When the temperature is increased to 180-400°C the second half reaction is reversed. This short paper mostly focuses on the application of indicating humidity, and gives little information about the actual ALD process.

Malygin, A. A.; Kol'tsov, S. I.; Aleskovskii, V. B.

Chemical composition and structure of a chromium oxide layer synthesized on the surface of silica gel surface by the molecular-stratification method
***Journal of Applied Chemistry of the USSR*, 49, 1703-1708, 1979**
А. А. Малыгин, С. И. Кольцов, В. Б. Алесковский. О химическом составе и строении хромоксидного слоя, синтезированного на поверхности силикагеля методом молекулярного наслаивания. Журнал общей химии, 1979, Т. 49, вып. 9, С. 1936-1941.
{Malygin1979a} ru en

Morrow, B. A. & Hardin, A. H.
Raman spectra of some hydrogen sequestering agents chemisorbed on silica
***J. Phys. Chem.,* 83, 3135-3141, 1979**
{Morrow1979} en
Pia Sundberg: Raman spectroscopy study of chemisorbed species of various hydrogen sequestering agents MC14-nMe, [n = C-3, M = Si or Ge, Me = CH3], TiCl4, AlMe3, and Me3Si(NH)SiMe3 on silica. The used hydrogen sequestering agents were dosed in gas phase, but no further treatment was reported: not ALD.

Smirnov, E. P.; Gordeev, S. K.; Kol'tsov, S. I. & Aleskovskii, V. B.
Synthesis of hydride functional groups on the surface of diamond
***Journal of Applied Chemistry of the USSR,* 52, 176-178, 1979**
Е. П. Смирнов, С. К. Гордеев, С. И. Кольцов, В. Б. Алесковский. Синтез гидридфункциональных групп на поверхности алмаза. Журнал прилкладной химии, 1979, Т. 52, вып. 1, С. 199-201.
{Smirnov1979} en ru
Tanja Kallio: Not quite ALD as I think of it. Reaction of chlorine functionalized diamond with either H2 (200-500oC) or CH4 (300-500oC, up to 4 h) gas resulting in diamond with hydride or methyl functionalized surface, respectively.

Smirnov, E. P.; Kol'tsov, S. I.; Aleskovskii, V. B.

Study of chemical and absorption-structural changes on the surface of carbon during molecular stratification of titanium hydroxy groups
***Zhurnal Fizicheskoi Khimii*, 53, 258, 1979**
Е. П. Смирнов, С. И. Кольцов, В. Б. Алесковский. Исследование химических и адсорбционно-структурных изменений на поверхности углерода в процессе молекулярного наслаивания титаноксидных групп. Журнал физической химии, 1979, Т. 53, вып. 1, С. 258.
Full-text - VINITI № 1105-78 Dep 30.03.1978
{Smirnov1979a} ru

M. Velikova, D. Damyanov, D. Mehandjiev,
The TiCl4 with amorphous SiO2 interaction in the process of catalysts preparation by the molecular deposition method
***Bulgarian Academy of Science, Communications of the department of chemistry* 12, 647-651, 1979**
М. Великова, Д. Дамянов, Д Механджиев. Взаимодействие TiCl4 с аморфным SiO2 в процессе приготовления катализаторов методом молекулярного наслаивания. Болгарская Академия Наук. Сообщения по отделу химии. 1979, Т. 12, № 4, С. 647-651.
{Velikova1979} ru en
David Cameron: A single layer is deposited usinbg TiCl4 + H2O at 150C on silica gel after pretreatment from 200 - 800C. The amount of OH on the silical gel reduces with temperature which then affects the density of the Ti on the surface layer. Shows that the molecular coverage is dependent on the availability of surface OH groups.

Yakovlev, S. V.; Malygin, A. A.; Kol'tsov, S. I.; Aleskovskii, V. B.; Chesnokov, Yu. G. & Protod'yakonov, I. O.
Mathematical model of molecular layering with the aid of a fluidizided bed
***Journal of Applied Chemistry of the USSR,* 52, 959-963, 1979**
С. В. Яковлев, А. А. Малыгин, С. И. Кольцов, В. Б. Алесковский, Ю. Г. Чесноков, И. О. Протодьяконов. Математическая модель процесса молекулярного наслаивания с использованием псевдоожиженного слоя. Журнал прикладной химии. Т. 52, вып, 5, С. 1007-1011.
{Yakovlev1979} en ru
Ruud van Ommen: This paper briefly described both the experimental deposition of vanadium on silica gel particles using molecular layering in a fluidized bed, as well as the modelling of this process (while the title may suggest that it is just about modelling). The authors carry out one ALD half-cycle (reaction of VOCl3 with hydroxyl-group of silica gel at 180 degr C); the second half-cycle is not even mentioned. It is very interesting to discover that they already used fluidized beds to perform ALD on particles; to my best knowledge, it is the first time this has been described (in English, at least). Since 2000, fluidized bed ALD has been reported much more frequently in journal papers (>50 papers), but – as far as I am aware – nobody has referred to this first paper. The authors work with 2 and 4 g of coarse-pored silica particles of 0.5-1 mm diameter, and fluidized these particles with dry air. They coat these particles during 1 – 15 min, and obtain up to 1 mg vanadium per 1 g silica. In their modelling approach, they assume plug flow of the gas and complete mixing of the solids, which seems reasonable for a simple fluidized-bed model. Their model predicts this loading with about 10% error, which is quite good for the relatively simple model they use. Due to the brevity of their paper, unfortunately some questions remain unanswered: the lay-out of their set-up and the operation pressure (rough vacuum or atmospheric) are not given.
Jaana Kanervo: This concise article is directly on the title's topic and starts with expressing the assumptions made in the modeling. Next, continuum equations are written for gas and solid phases along with the boundary conditions. The experimental system here concerns vanadium oxide layering (ALD) on silica gel. Under certain simplifying assumptions the model of vanadium content as a function of time has been fitted to experimental observations and the values for 'overall mass-transfer coefficients' have been determined. Agreement between the modelled and measured vanadium content is satisfactory. This belongs probably pioneering works in modeling of ALD processes. The determined parameters ('overall mass-transfer coefficients') probably lump together effects of processes of physical and chemical nature. Main characteristics and driving forces appear to be anyhow sound.

D. Damyanov, M. Velikova, S. Angelov, D. Mehandjiev,
Activity, with respect to ethylene polymerization, of titanium-containing catalysts obtained by the method of molecular deposition
Proc. IV Inter. Symp. Heterogeneous Catalysis - Varna, 2, 139-144, 1979
(no code)

M. Velikova, D. Damyanov, D. Mehandjiev
The TiCl4 with amorpous SiO2 interaction in the process of catalysts preparation by the molecular deposition method
Comm. Dep. Chem., 12, 647-651, 1979
(no code)

Gromov V.K.
Synthesis titanium- oxygen layers on the surface of quartz, silicon , copper by molecular layering and ellipsometric study boundary interface substrate - a synthesized layer
Disc .... Candidate . Chem. Science / LTI - L. , 1979 . - 179 p. [in Russian]
Громов В.К. Синтез методом молекулярного наслаивания титан-кислородных слоев на поверхности кварца, кремния, меди и эллипсометрическое исследование границы сопряжения подложка - - синтез
(no code)

Postnov VN
Synthesis of inorganic matrices using the molecular layering method and the study of their reactivity in the process of adsorption of amino acids
Dis . ... Candidate . Chem. Science / TRL - L. , 1979 . - 166 .
(EAF) Постнов В.Н. Синтез неорганических матриц методом молекулярного наслаивания и исследование их реакционной способности в процессе сорбции аминокислот: Дис. ... канд. хим. наук/ЛТИ - Л., 1979. - 166 с.
(ДСП)ированный слой: Дисс.... канд. хим. наук/ ЛТИ - Л., 1979. - - 179 с.
(no code)

Markku Ylilammi,
Tinadioksidi- ja alumiinioksidikalvojen kasvatus vuorottaisten pintareaktioiden avulla (Growth of thin oxide and aluminium oxide films through alternating surface reactions), M. Sc. thesis, Helsinki University of Technology, Department of electrical engineering, 1979, 67 pages.
{Ylilammi1979} fi

T. Suntola, A. Pakkala, S. Lindfors,
Method and equipment for deposition of compound thin films [in Finnish], SF patent 57975, Feb 28, 1979**.**
Method for performing growth of compound thin films. Priority date: Feb 28, 1979; applied: Jun 21, 1979; publication date: Nov 1, 1983. US 4413022 A
Т. Сунтола, А Паккала, С. Линдфорс. Способ получения составной плёнки и устройства для его осуществления. Патент СССР SU 1085510 A
{Suntola1980a} ru
Riikka Puurunen: This is the second international ALE patent. It describes e.g. a batch-type flow reactor and a spatial ALD reactor.

Ahonen, M.; Pessa, M. & Suntola, T.
A study of ZnTe films grown on glass substrates using an atomic layer evaporation method
Thin Solid Films, **1980***, 65*, 301-307
{Ahonen1980} en
Riikka Puurunen: This seems to be the first scientific publication on "ALE". ALE is not called "atomic layer epitaxy" here though, but "atomic layer evaporation".
Hele Savin: I though "evaporation" was sort of misprint here since they refer to Suntola patent 1977 where ALE acronym is presented and clearly stated that it is "epitaxy".
In the experimental section they describe in very detailed manner the growth of the films (i.e. ALD process), maybe because this is their first article on ALE. They use Zinc and tellurium bars as sources for the film. Very thick layers were also grown (1500 nm!)
Main conclusion: Special characteristics/benefits for ALD growth: crystal properties (e.g. film texture, elemental composition) do not depend on growth conditions

V. E. Drozd, S. I. Kol'tsov, T. A. Redrova. Investigation of reactions of condensation on the surface of semiconductors (reactions of molecular layering) with use of ellipsometry. Modern problems of ellipsometry / ed by A. V. Rjhanov, 1980, Novosibirsk, Nauka, P. 134-141.
В. Е. Дрозд, С. И. Кольцов, Т. А. Редрова. Изучение реакций конденсации на поверхности полупроводников (реакций молекулярного наслаивания) с помощью эллипсометрии. Современные проблемы эллипсометрии / отв. ред. А. В. Ржанов, 1980, Новосибирск, Наука, С. 134-141.
{Drozd1980a} ru

G. V. Sveshnikova, S. I. Kol'tsov, V. B. Aleskovskii. Investigation by ellipsometry of multi-layered systems deposited on the surface of silicon. Modern problems of ellipsometry / ed by A. V. Rjhanov, 1980, Novosibirsk, Nauka, P. 141-145.
Г. В. Свешникова, С. И. Кольцов, В. Б. Алесковский. Исследование многослойных систем на поверхности кремния методом эллипсометрии. Современные проблемы эллипсометрии / отв. ред. А. В. Ржанов, 1980, Новосибирск, Наука, С. 141-145.
{Sveshnikova1980} ru

A. P. Garshin, G. V. Sveshnikova, V. B. Aleskovskii. Ellipsometry and investigation of process of chemical modifying of SiC. Modern problems of ellipsometry / ed by A. V. Rjhanov, 1980, Novosibirsk, Nauka, P. 162-165.
А. П. Гаршин, Г. В. Свешникова, В. Б. Алесковский. Эллипсометрия и исследование процесса химического модифицирования карбида кремния. Современные проблемы эллипсометрии / отв. ред. А. В. Ржанов, 1980, Новосибирск, Наука, С. 162-165.
{Garshin1980} ru

Gordeev, S. K.; Smirnov, E. P.; Kol'tsov, S. I. & Aleskovskii, V. B.
Synthesis of hydroxyl functional groups on the surface of diamond
Journal of Applied Chemistry of the USSR,* 1980, 53 (1)*, 81-84**
С. К. Гордеев, Е. П. Смирнов, С. И. Кольцов, В. Б. Алесковский. Синтез гидроксилфункциональных групп на поверхности алмаза. Журнал прикладной химии. 1980, Т. 53, вып. 1, С. 94-97.

{Gordeev1980} en ru
Tanja Kallio: In my opinion this not an ALD reaction. Chlorine functional groups on the surface of diamond are replaced with hydroxyl functional groups in a gas phase reaction (H2O vapor in He) and full replacement takes place at 430oC, no pulse times are given. However, this information is later used for ALD reactions.

Drozd, V. E.; Kozlov, S. N.; Plotnikov, G. S.

Effect of molecular stratification of thin oxide layers on electrophysical properties of a semiconductor-oxide system
Deposited Doc., Issue: VINITI 2661-80, 15 pp., Report, **1980**
В. И. Дрозд, С. Н. Козлов, Г. С. Плотников Влияние молекулярного наслаивания тонких окисных слоев на электрофизические свойства системы полупроводник-окисел. Деп. Рукопись. 1980 ВИНИТИ 2551-80, 15 С.

{Drozd1980} ru
Riikka Puurunen: Very quick view shows that this paper discusses transition metals Cr2O3, ZrO2, HfO2, TiO2, Ta2O5, Nb2O5. "Synthesis of the oxide layers with thickness of 40-70 Å occurred in a quartz reactor at temperature of 500 K with a method described earlier (a reference given)."

Kol'tsov, S. I.; Malygin, A. A. & Aleskovskii, V. B.
Structural characteristics of chromium-containing silica gel prepared by molecular coating
Russian Journal of Physical Chemistry* , 1980, 54(9)*, 1326-1327**
С. И. Кольцов, А. А. Малыгин, В. Б. Алесковский. Физико-химические исследования структурных характеристик хромсодержащего силикагеля, синтезированного методом молекулярного наслаивания. 1980, Т. 54, вып. 9, С. 2331-2334.
{Koltsov1980} en ru
Henrik Pedersen: This paper describes synthesis of Cr2O3 films by **what is today called ALD, but is referred to as molecular coating**. Cr2O3 is deposited on porous silica gel by alternating pulses of CrO2Cl2 and H2. No purging steps between the precursor pulses are described. There are no discussions on specific surface chemistry, but the redox chemistry from Cr(VI) to Cr (III) is discussed briefly. Special attention is given to the effect of the cromia film in the pores and the authors conclude that the molecular coating method (now known as ALD) can be used for fine control of pore size and surface properties of pores given the monolayer precision. To me it is clear that they have started to understand the potential of what we now call ALD.

Gromov, V. K.; Rachkovskii, R. R.; Kol'tsov, S. I.

Optical properties of superthin layers of titanium oxide synthesized by the molecular stratification method on a single-crystal silicon surface
Zhurnal Prikladnoi Khimii, Volume: 53, Issue: 9, Pages: 2151, 1980
В. К. Громов, Р. Р. Рачковский, С. И. Кольцов. Оптические свойства сверхтонких слоев оксида титана, синтезированных по методу молекулярного наслаивания на поверхности монокристаллического кремнеия. 1980 Т. 53, вып. 9, С. 2151.
Full text: VINITI AN SSSR, № 3947-79 Dep 21.11.1979
{Gromov1980} ru

V. D. Ivin, E. P. Smirnov, R. M. Levit, S. I. Koltsov, A. A. Malkov. Interaction of chlorine with the surface of carbon fibers. Journal of Applied Chemistry of the USSR. 1980, V. 53, №. 1., P. 93-97.
В. Д. Ивин, Е. П. Смирнов, Р. М. Левит, С. И. Кольцов, А. А. Малков. Взаимодействие хлора с поверхностью углеродных волокон. Журнал прикладной химии. 1980, Т. 53, вып. 1., С. 109-114.
{Ivin1980} ru en
Yury Koshtyal: ?not ALD
David Cameron: Extension of earlier work by Kol'tsov on chlorination of carbon. Not ALD.

E. V. Kukharskaya, V. M. Makarskaya, M. N. Tsvetkova, S. I. Koltsov, M. G. Voronkov. Protection of glass and quartz fibers by titanium oxide coatings. Zhurnal prikladnoy khimii, 1980 V. 53, №. 9, P. 2086-2088.
Э. В. Кухарская, В. М. Макарская, М. Н. Цветкова, С. И. Кольцов, М. Г. Воронков. Защита стеклянных и кварцевых волокон титаноксидными покрытиями. Журнал прикладной химии, 1980, Т. 53, вып. 9, С. 2086-2088.
{Kukharskaya1980} ru

Malygin, A. A.; Kol'tsov, S. I. & Aleskovskii, V. B.
Chemical composition of silica containing chromium and phosphorus synthesized by the molecular-stratification method
Journal of general chemistry of the U.S.S.R.,* 1980, 50 (12)*, 2121-2123**
А. А. Малыгин, С. И. Кольцов, В. Б. Алесковский. О химическом составе хром-фосфорсодержащего кремнезема синтезированного методом молекулярного наслаивания. Журнал общей химии, 1980, Т. 50, вып. 12, С. 2633-2636.
{Malygin1980} en ru
Ruud van Ommen: This papers describes the application of molecular layering (or ALD) to silica gel. The authors start with a phosphorous-oxygen layer on a Cr(VI)-containing silica gel, and apply successively vapours of CrO2Cl, H2O and PCl. The chemical composition after each half cycle is determined, up to two-and-a-half cycle. They show that the reactions indeed stoichiometrically with respect to the available surface groups.

Suntola, T.; Antson, J.; Pakkala, A. & Lindfors, S.
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
Riikka Puurunen: This was the first public presentation of the electroluminescent displays as a demo during a conference talk. The presentation was a sensation and 3000-4000 contact requests came after the conference, as told by Suntola.
Henrik Pedersen: Interesting to see how much Suntola and co-workers understood about the ALD process 1980, or ALE as it was called then. The self limiting deposition mode is there, so is the surface chemistry when using molecular precursors, ZnCl2 and H2S for ZnS as described here. News to me was that they also used atoms from evaporation of Zn or S as an alternative ALE route.
Jonas Sundqvist: this is to my opinion a must read for all ALD researchers out there. We should ask Suntola if he could give the presentation again at BALD 2014 in Helsinki.

Suntola, T., Antson, J., Pakkala, A., Lindfors, S., Sähkö, 1980, 53(12), 368.
(no code)
Riikka Puurunen: Ref. 5 in the 1983 paper by Aidla and Tammik.

V.-P. Tanninen, T. Tuomi, M. C. Typpi, R. O. Törnqvist, T. Suntola, J. Antson, A. Pakkala, S. Lindfors, Luminescence and X-ray diffraction studies of AC-electroluminescent ZnS:Mn thin film structures, Proc. 8th international Vacuum congress, Cannes, 1980, 01-4.
(no code)
Riikka Puurunen: Aidla and Tammik (1983) refer to this as: Proc. 8th Int. Vac. Congr. Trienn. Meet. Int. Union Vac. Sci., Techn. and Appl., Cannes, 22-26 Sept., 1980, Vol. 1. Paris, 1980, 401. (Temporary comment, to be removed when we have the paper.)

Gordeev , SK Synthesis of diamond on the surface of carbon , titanium oxide and chromium, and the study of their physico- chemical properties : Diss . ... Candidate . Chem. Science / TRL - L. , 1980 . - 210 p. (EAF) Гордеев С.К. Синтез на поверхности алмаза углерода, оксидов титана и хрома и исследование их физико-химических свойств: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1980. - 210 с.
(ДСП)
(no code)

J. Skarp, ALE-menetelmällä kasvatetun sinkkisulfidin seostaminen eri värien aikaansaamiseksi elektroluminesenssiohutkalvonäytöissä, Doping of ALE ZnS for producing different colours in electroluminescent thin films [in Finnish], Master's thesis, Helsinki University of Technology, 1980, 57 p.
(no code)

BD Sokolov. Influence of physico- chemical properties of carbon fiber reinforcement composite materials: Diss . ... Candidate . Chem. Science / TRL - L. , 1980 . - 219 p. (EAF) Соколов Б.Д. Влияние физико-химических свойств поверхности углеродных волокона упрочнение композиционных материалов: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1980. - 219 с. (ДСП)
(no code)

Tolstoy VP Synthesis and physico- chemical study of ultrathin oxide layers on metal surfaces : Dis . ... Candidate . Chem. Science / TRL - L. , 1980 . - 143 p. Толстой В.П. Синтез и физико-химическое исследование сверхтонких оксидных слоев на поверхности металлов: Дис. ... канд. хим. наук/ЛТИ - Л., 1980. - 143 с.
(no code)

Tsvetkova MN , The molecular layering of active structures on the surface of the glass microspheres and investigation of their physical and chemical properties : Diss . ... Candidate . Chem. Science / TRL - L. , 1980 . - 196 p . Цветкова М.Н, Молекулярное наслаивание активных структур на поверхности стеклянных микросфер и исследование их физико-химических свойств: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1980. - - 196 с.
(no code)

Yu. K. Ezhovskii, S. I. Kol'tsov, V. B. Aleskovskii, N. V. Krivosheev. A method of producing of an optical coating. Description of invention for the authorship certificate № 789452. Claimed: 04.12.78, Published 23.12.80
Ю. К. Ежовский, С. И. Кольцов, В. Б. Алесковский, Н. В. Кривошеев. Способ получения оптического покрытия. Описание изобретения к авторскому свидетельству 789452. Заявлено: 04.12.78, Опубликовано: 23.12.80.
{Ezhovskii1980} ru
http://patentdb.su/2-789452-sposob-polucheniya-opticheskogo-pokrytiya.html

M. N. Tsvetkova, A. A. Malygin, S. I. Koltsov. Synthesis and examination of titanium oxide coatings on glass microspheres. Journal of Applied Chemistry of the USSR., 1980, T. 53, №. 6, P. 952-954.
М. Н. Цветкова, А. А. Малыгин, С. И. Кольцов. Синтез и исследование титаноксидных покрытий на поверхности стеклянных микросфер. Журнал прикладной химии, 1980, Т. 53, вып. 6, С. 1226-1229.
{Tsvetkova1980} ru en
David Cameron: ALD of titanium oxide films on hollow glass microspheres diameter 10 - 200 um. Shows film thickness proportional to number of cycles. Process details refer to Kol'tsov 1969. Demonstrates ALD coating on powder particles.

T. Suntola, *"Atomic Layer Epitaxy"* Tech. Digest of ICVGE-5, San Diego, 1981, 125a-125b
{Suntola1981} en
David Cameron: Abstract of a paper which outlines Suntola's ALE process.

P. M. Vainshtein, Y. K. Ezhovskii, S. I. Koltsov. The Possibility of a Quantitative Estimate of the Reactivity of Silanol Groups on the Surface of Silica. Russian Journal of Physical Chemistry 1981, V. 55, I. 2, P. 217-219.
П. М. Вайнштейн, Ю. К. Ежовский, С. И. Кольцов. О возможности количественной оценки реакционной способности силанольных групп поверхности кремнезема. Журнал физической химии. 1981, Т. 55, Вып. 2. С. 394-399.
{Vainshtein1981} ru en
David Cameron: Silicon oxide monolayers on silica gel by exposing to dimethylsilane (DMS) at 150C for 4h, heating to 400C in vacuum to remove excess DMS, then exposing to water vapour at 100C for 4h then heating in vacuum at 400C. Discusses the nature of the Si bonding to the surface groups. Not an ALD paper.

E. A. Avrutina, A. V. Gusev, S. I. Koltsov, G. N. Kuznetsova, A. A. Malygin. Products of interaction of zinc oxide with titanium tetrachloride. Journal of Applied Chemistry of the USSR, 1981, V. 54, №. 9, P. 1861-1863.
Э. А. Аврутина, А. В. Гусев, С. И. Кольцов, Г. Н. Кузнецова, А. А. Малыгин. Исследование продуктов взаимодействия окиси цинка с четыреххлористым титаном. Журнал прикладной химии, 1981 Т. 54, вып. 9, С. 2125-2127.
{Avrutina1981} ru en
Yury Koshtyal: Surface reaction.
David Cameron: Surface studies of the reaction of TiCl4 with ZnO showing the complexity of the surface layer which contains mixed ZnTiOCl formations.Not ALD

Dergachev, V. F.; Malygin, A. A. & Kol'tsov, S. I.
Macrokinetics of the reaction of vanadium oxychloride with silica gel
***Journal of Applied Chemistry of the USSR,* 1981*, 54 (9)*, 1722-1725**
В, Ф. Дергачев, А. А. Малыгин, С. И. Кольцов. Исследование макрокинетики реакции оксихлорида ванадия с силикагелем. Журнал прикладной химии. 1981, Т. 54, вып. 9, С. 1972-1975.
{Dergachev1981} en ru
Jaana Kanervo: A sound work that addresses the operation regimes in molecular layering (ALD) processes in fluidized bed for this specific reaction system. It was demonstrated that with overly low reactant flow rates (<0.045 m/s) external diffusion limited the rate of overall process whereas with higher flow rates the intraparticle diffusion in silica gel limited the rate of deposition. Highly relevant considerations in scale-up.
Ruud van Ommen: The authors first state that using fluidized beds molecular layering (ALD) on particles can be carried out faster than in a packed bed. They study in this paper kinetics and mass transfer of the reaction of vanadium oxychloride reaction with silica gel. They conclude that for most of the relevant operating conditions (gas velocity > 0.045 m/s, particle size 0.2 – 3 mm) internal diffusion is the rate-limiting step.

Kopylov, V. B.; Tsvetkova, M. N.; Pak, V. N.; Malygin, A. A. & Kol'tsov, S. I.
Spectroscopic study of the interaction of an epoxy resin with the surface of glass fillers modified by molecular lamination
***Journal of Applied Chemistry of the USSR,* 1981*, 54 (2)*, 186-189**
В. Б. Копылов, М. Н. Цветкова, В. Н. Пак, А. А. Малыгин, С. И. Кольцов. Спектроскопическое исследование взаимодействия эпоксидныой смолы с поверхностью стеклянных наполнителей, модифицированных методом молекулярного наслаивания. Журнал прикладной химии, Т.54, вып. 2, С. 293-296.
{Kopylov1981} en ru
Title in SciFinder: Spectroscopic study of the interaction of an epoxy resin with the surface of glass fillers modified by the method of molecular stratification
Pia Sundberg: This work's main focus is not ALD (or molecular lamination, like called in the paper), but like the title indicates on the interaction of an epoxy resin (ED-20) and sodium borosilicate. The investigations were done by diffuse reflection electronic spectroscopy from untreated sodium borosilicate powder, as well as from powder coated by titanium and chromium oxide. The ALD process used for coating the powder is not discussed, only references are given. The authors concluded that π-complexes of the epoxy molecules with the metal atoms from the oxides were detected. They also claimed to be able to determine the strength of the surface compound by the changes in characteristic absorption band maximum position and in the energy state of investigated element.

A. V. Krasnobryzhii, E. P. Smirnov, S. I. Koltsov. Adsorption of titanium tetrachloride on the surface of technical carbon. Journal of Applied Chemistry of the USSR. 1981. V. 54, №. 7, P. 1375-1377.
А. В. Краснобрыжий, Е. П. Смирнов, С. И. Кольцов. Адсорбция тетрахлорида титана на поверхности технического углерода. Журнал прикладной химии. 1981. Т. 54, вып. 7, С. 1605-1607.
{Krasnobryzhii1981} ru en
Yury Koshtyal: half cycle.
David Cameron: Studies the reaction of TiCl4 on carbon surfaces. Not ALD

Low, M. J. D.; Severdia, A. G. & Chan, J.
Reactive silica. XV. Some properties of solids prepared by the reaction of trimethylaluminum with silica
J. Catal., **1981***, 69*, 384-391
(no code)
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S. I. Kol'tsov, S. A. Trifonov, A. A. Malygin, V. V. Barsova. The influence of phosphorus-containing additives on the properties of foam stamps PEN-I. Plasticheskie massy. 1981, №7, P. 59.
С. И. Кольцов, С. А. Трифонов, А. А. Малыгин, В. В. Барсова. Влияние фосфорсодержащих добавок на свойства пенопласта марки ПЭН-И. Пластические массы. 1981, №7, С. 59.
{Koltsov1981a} ru

Pessa, M.; Mäkelä, R. & Suntola, T.
Characterization of surface exchange-reactions used to grow compound films
Appl. Phys. Lett., **1981***, 38*, 131-132
{Pessa1981} en
Riikka Puurunen: Ta2O5 films from TaCl5/H2O and ZnS from ZnCl2/H2S, studied by Auger electron spectroscopy, SEM and X-ray diffraction. "The growth mechanism has been explained."
Jonas Sundqvist: is this the first Ta2O5 ALD process? If so that is a major milestone in growth of high-k materials.

Postnova, A. M.; Pak, V. N. & Kol'tsov, S. I.
The protic acidity of titanium-containing silica gels obtained by molecular deposition in layers
***Russian Journal of Physical Chemistry,* 1981*, 55 (8)*, 1215-1217**
А. М. Постнова, В. Н. Пак, С. И. Кольцов. Исследование протонной кислотности титансодержащих силикагелей, полученных методом молекулярного наслаивания. 1981, Т. 55, вып. 8, 2140-2142.
{Postnova1981} en ru
David Cameron: This paper discusses how the layer thickness and composition of metal oxide films are precisely determined by multiple ML cycles and this can be used to control the acidity of metal oxide.

E. P. Smirnov, A. V. Krasnobryzhy. Synthesis of proton-generating functional groups by oxidation of carbon surface. Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i khimicheskaya tekhnologiya. 1981. – V. 24, № 8, P. 1029-1033.
Е. П. Смирнов, А. В. Краснобрыжий. Синтез протоногенных функциональных групп окислением поверхности технического углерода. Известия Высших Учебных Заведений, Химия и химическая технология. 1981. – Т. 24, вып. 8, С. 1029-1033.
{Smirnov1981a} ru
Yury Koshyal: Preparing of the surface before ALD.

Syrkov, A. G.; Smirnov, V. M.

Simple glass apparatus for carrying out reaction of solids with vapors of hard to vaporize halides
Deposited Doc., **1981**, (VINITI 4462-81), 6 pp
А. Г. Сырков, В. М. Смирнов. Простая стеклянная установка для осуществления взаимодействия твердых тел с парами труднолетучих галогенидов. 1981, Депонированная рукопись, ВИНИТИ 4462-81, 6 С.
{Syrkov1981} ru

Smirnov, E. P.; Krasnobryzhii, A. V.; Kol'tsov, S. I.
Synthesis by molecular stratification of titanium oxide layers on the surface of technical grade carbon
Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, Volume: 24, Issue: 10, Pages: 1288-90, 1981
Е.П. Смирнов, А. В. Краснобрыжий, С. И. Кольцов. Синтез методом молекулярного наслаивания титаноксидных слоев на поверхности технического углерода. Ивестия высших учебных заведений, Химия и химическая технология. 1981, Т. 24, вып. 10, С. 1288-1290.
{Smirnov1981} ru

Sokolov, B. D.; Smirnov, E. P.; Kol'tsov, S. I. & Aleskovskii, V. B.
Application of the molecular stratification method for the enhancement of polymer adhesion to metal
Dokl. Akad. Nauk SSSR, **1981***, 256*, 1443-1446
Б. Д. Соколов, Е. П. Смирнов, С. И. Кольцов, В. Б. алесковский. Применение метода молекулярного наслаивания для усиления адгезии полимеров к металлу. Доклады Академии Наук, 1981, Т. 256, С. 1443-1446.
{Sokolov1981} ru
Riikka Puurunen: Short, quick comment: "The goal of the work was to study the effect of a layer of chromium oxide, grown on a metal surface by the method of molecular layering, on the adhesion in metal-polymer systems." This thus reports on an adhesion layer by ALD.

Nechiporenko, A. P.; Shevchenko, G. K.; Sukhareva, T. M.; Kol'tsov, S. I.; Aleskovskii, V. B.
Microspectrophotometric study of titanium oxide layers synthesized by molecular stratification on solid surfaces
Zhurnal Prikladnoi Khimii, Volume: 54, Issue: 6, Pages: 1260-4, **1981**
А. П. Нечипоренко, Г. К. Шевченко, Т. М. Сухарева, С. И. Кольцов, В. Б. Алексковский. Микроспектрофотометрическое исследование титанкислородных слоев, синтезированных методом молекулярного наслаивания на поверхности твердых тел. Журнал прикладной химии. 1981, Т. 54, вып. 6, С. 1260-1264.
{Nechiporenko1981} ru
get a copy of the paper in English

Tanninen, V.-P.; Oikkonen, M. & Tuomi, T. O.
X-ray diffraction study of thin electroluminescent ZnS films grown by atomic layer epitaxy
Phys. Status Solidi A, **1981***, 67*, 573-583
{Tanninen1981} en
David Cameron: Describes the crystal structure of ALE-grown ZnS films on ALD grown SnO2, Ta2O5, Al2O3 and on multilayers of these oxides. The ZnS shows cubic growth when grown at 350C and Hexagonal structure at 500C. The strongest orientation was found with ta2O5 substrates and the weakest with Al2O3. Detailed assessment of crystal size effects.

Pak, V. N.; Tuz, T. V.; Kol'tsov, S. I.

Participation of adsorbed water in molecular stratification reactions Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya 1981, 24(8), 985-6.
В. Н. Пак, Т. В. Туз, С. И. Кольцов. Участие адсорбированной воды в реакциях молекулярного наслаивания. Известия высших учебных заведений. Химия и химическая технология. 1981, Т. 24, вып. 8, С 985-986.
{Pak1981} ru
Jaan Aarik: Pak et al. have investigated molecular layering (atomic layer deposition) of TiO_2 from $TiCl_4$ and H_2O at 25 and 200°C and demonstrated that, in addition to hydroxyl groups formed on the oxide surface during the H_2O pulse, molecular H_2O adsorbed on the surface markedly contributes to the deposition of TiO_2 at lower temperatures. Due to this contribution, 4 times higher growth rate was observed at 25°C than at 200°C.

Kol'tsov, 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.
С.И. Кольцов, Н.Н. Копылов, В. Е. Дрозд, В. Б. Алесковский. Исследование влияния электрического поля на синтез титаноксидных слоёв на поверхности кремния методом молекулярного наслаивания. Доклады Академии наук СССР, 1981, Т. 256, Вып. 6, 1415-1418.
{Koltsov1981} ru
Title in SciFinder: "Study of the effect of an electric field on the synthesis of titanium oxide layers on a silicon surface by a molecular stratification method"
Maria Berdova: The article describes the influence of applied electric field to the growth of a molecular layer. Due to applied electric field the thickness varies. If the near surface (Si substrate) has holes as the main carrier, the amount of adsorbed molecules is increasing. In case of electrons, the amount is reducing.

J. Hyvärinen, Vuorottaisella pintareaktiolla kasvatetun ZnS:Mn-ohutkalvon seostaminen ja sähköoptiset ominaisuudet - Doping and electrooptical characteristics of ZnS:Mn thin film deposited by alternating surface reactions [in Finnish], Master's thesis, Helsinki University of Technology, 1981.
(no code)

Krasnobryzhy AV The reaction of titanium chloride (IV) and iron (III) oxychloride, vanadium (V) , and chromium (VI) with carbon materials : Diss . ... Candidate . Chem. Science / TRL - L. , 1981 . - 183 p. (EAF) Краснобрыжий А.В. Взаимодействие хлоридов титана (IV) и железа (Ш), оксихлоридов ванадия (V) и хрома (VI) с углеграфитовыми материалами: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1981. - 183 с. (ДСП)
(no code)

Weinstein PM The structure and physico-chemical properties of the functional groups on the silica surface : Dis . ... Candidate . Chem. Science / TRL - L. , 1981 . - 151 p. (EAF) Вайнштейн П.М. Строение и физико-химические свойства функциональных групп на поверхности кремнезема: Дис. ... канд. хим. наук/ЛТИ - Л., 1981. - 151 с. (ДСП)
(no code)

Yu. K Ezhovskii, A L. Egorov, S. I. Kol'tsov, M. N. D'yakonov, V. M. Muzhdaba, I. V. Neputskii, S. D. Khanin. A method of manufacturing of capacitors with oxide dielectric. Description of invention for the author certificate № 890463. Claimed: 24.04.80. Published 15.12.81.
Ю. К. Ежовский, А. Л. Егоров, С. И. Кольцов, М. Н. Дьяконов В. М. Муждаба, И. В. Нетупский и С. Д. Ханин. Способ изготовления кондесаторов с оксидным диэлектриком. Описание изобретения к авторскому свидетельству 890463. Заявлено: 24.04.80, Опубликовано: 15.12.81
{Ezhovskii1981} ru

Kol'tsov, S. I.; Kopylov, N. N.; Drozd, V. E.; Trofimov O.A. & Aleskovskii, V. B. Influence of an electric-field on the structure of titanium-oxide layers. *Dokl. Akad. Nauk SSSR,* 1982*, 262(2)*, 375-377.
С. И. Кольцов, Н. Н. Копылов, В. Е. Дрозд, О. А. Трофимов, В. Б. Алесковский. Влияние электрического поля на структуру титаноксидных слоёв. Доклады Академии Наук СССР, Т. 262, Вып. 2, 375-377.
{Koltsov1982} ru
Maria Berdova: The influence of electric field to the structure of titanium oxide (grown by molecular layering) on silicon surface is investigated. The discharge current was kept as 10^{-9} A, with electric field of 10^6 V/cm. All experiments were carried at room temperature. The layers were thicker when negative voltage was applied, in comparison with zero-voltage. Electron diffraction methods revealed that all layers remain amorphous independent on thickness. Instead, when positive voltage was applied films were polycrystalline (001 and 310) and the thickness was smaller in comparison with zero-voltage.

M. V. Silanova, Yu. K. Ezhovskii, A. V. Smirnov, S. I. Kol'tsov. Surface Reactions in the system Cu-Cu2O-CH3OH, Journal of Applied Chemistry of the USSR, 1982, V. 55, I. 7, P. 1342-1344
М. В. Силанова, Ю. К. Ежовский, А. В. Смирнов, С. И. Кольцов. Поверхностные реакции в системе Cu-Cu2O-CH3OH. Журнал прикладной химии, 1982, Т. 55, вып. 7, С. 1472-1475
{Silanova1982} ru en
Cagla Ozgit-Akgun: Authors investigated the role of lattice oxygen in an oxidized Cu surface in the surface conversions of lower aliphatic alcohols, particularly methanol (CH_3OH). Oxide layers, which were formed by thermal oxidation, were exposed to methanol vapor. Reaction products were analyzed using a mass spectrometer. In my opinion, this article is not related to ALD.

Aleskovskii, V. B.
The nature of solid chemical compounds
***Zh. Prikl. Khim.,* 1982*, 55 (4)*, 662-666.**
В. Б. Алесковский. О природе химических соединений. Журнал прикладной химии. 1982, Т. 55, вып. 4, С. 725-730.
{Aleskovskii1982} en ru
Massimo Tallarida: Here there is the ALD of carbon (diamond) using CH4 and CCl4 as precursors at T=300-600°C. The ligand-exchange reaction is proposed:
$[C]_C Cl + CH_4$ -> $[C]_C CH_3 + HCl$ and
$[C]_C CH_3 + CCl_4$ -> $[C]_C C\text{-}CCl + 3HCl$
note that $[C]_C C\text{-}CCl = [C]_{C+2} Cl$
A layer-by-layer growth is predicted. Well, considering that methane is used for the CVD of graphene, maybe this route could allow the ALD of graphene? Who tries first? Similarly, SiO2 is proposed with the use of SiCl4 and H2O as precursors. Aleskovskii says that the linear increase is verified. **self-assembly** is also cited here and a comparison with biological systems (viruses, DNA) is also proposed.
Riikka Puurunen: A quick, short comment. This article mentions the growth of carbon in alternating, repeated reactions of CCl4 and CH4. According to the author, CH4 reacts easily with a C-Cl -terminated surface at 300-600°C "under irreversibility conditions". CCl4 can be reacted with the surface again an cycles repeated to grow carbon.

Gordeev, S. K. & Smirnov, E. P.
Interaction of titanium tetrachloride with diamond preparations
***Journal of general chemistry of the U.S.S.R.,* 1982*, 52 (7)*, 1294-1297**
С. К. Гордеев, Е. П. Смирнов. Исследования взаимодействия тетрахлорида титана с препаратами алмаза. Журнал общей химии, 1982, Т. 52, вып. 7, С. 1464-1468.
{Gordeev1982b} en ru
Henrik Pedersen: This is a pure surface chemistry paper where the reaction mechanism and kinetics of the reaction between TiCl4 and -OH groups on diamond. There is no discussion on adding a second ALD half cycle with water to make an ALD process.
Massimo Tallarida: in this paper there is a tentative investigation of the surface reactions between TiCl4 and a functionalized diamond substrate (clorinated). They observe the formation of complex Cl-Ti-O-C compounds. It is not directly ALD, because there is no cycling and no O-source, but it is a study of the reaction of an ALD precursor onto a functionalized substrate. Nowadays it would have been a typical experiment of half-cycle ALD.

Gordeev, S. K.; Smirnov, E. P. & Kol'tsov, S. I.
Synthesis of hydroxyl--titanium--carbon solid compounds on diamond by the molecular-stratification method
***Journal of general chemistry of the U.S.S.R.,* 1982*, 52(7)*, 1298-1302**
С. К. Гордеев, Е. П. Смирнов, С. И. Кольцов. Синтез оксититануглеродных соединений на основе алмаза методом молекулярного наслаивания. Журнал общей химии, 1982, Т. 52, вып. 7, 1468-1470.
{Gordeev1982} en ru
Henrik Pedersen: ALD of TiO2 using TiCl4 and water on diamond substrates is described. The name molecular stratification is used for ALD, no pulse or purge times are reported. The authors note that a higher temperature, 670 K, is needed to replace -Cl with -OH during the water pulse in the initial layers, close to the diamond substrate. As the film grows thicker, this substrate effect is less pronounced and film deposition can be done at lower temp, 490 K.
Massimo Tallarida: It seems the authors show here ALD of TiC on diamond. They show a linear increase of Ti with molecular-stratification number of cycles. the hydroxyl group mentioned in the title should be the -OH termination of TiC. It seems that there is a strong contamination of Cl, explained with the weak reactivity of the precursor.
Riikka Puurunen: ALD of TiO2 on diamond. "The chemical reactions on the diamond preparations were conducted in a flow-type quartz reactor … the reactor was heated with a resistance furnace. The vapor pressures of the reagents in the gas mixture under the experimental conditions used were: water 40 kPa, TiCl4 1 kPa. ..." It is concluded that the carbon surface influences the character of the Ti-Cl bonds formed.

Gordeev, S. K.; Smirnov, E. P.; Kol'tsov, S. I. & Aleskovskii, V. B.
The reciprocal influence of functional-groups in substitution-reactions on the diamond surface
Dokl. Akad. Nauk SSSR, **1982***, 262*, 127-130
С. К. Гордеев, Е. П. Смирнов, С. И. Кольцов, В. Б. Алесковский. О влиянии функциональных групп в реакциях замещения на поверхности алмаза. Доклады Академии Наук, 1982, Т. 262, вып. 1, С. 127-130.
{Gordeev1982c} ru

Nechiporenko, A. P.; Shevchenko, G. K. & Kol'tsov, S. I.
Surface activity of metals (Ni, Ti) in molecular stratification reactions
***Journal of Applied Chemistry of the USSR,* 1982*, 55(6)*, 1133-1138.**
А. П. Нечипоренко, Г. К. Шевченко, С. И. Кольцов. Исследование активности поверхности металлов (Ni, Ti) в реакциях молекулярного наслаивания. Журнал прикладной химии, 1982, Т. 55, вып. 6, С. 1239-1245.
{Nechiporenko1982} en
Marja-Leena Kääriäinen: Surface activity of metals (Ni, Ti) in molecular stratification (MS)reactions. The word stratification could be replaced by layering or deposition. The investigators define the MS method as "a molecular probe method where the modifier element serves as a 'probe molecule'". They further explain "it (MS) can be used as "instrument" to study and control surface state and surface phenomena". In this study nickel and titanium were used as substrates. Chromium content was determined after a one-time treatment by CrO2Cl2 vapor as a function of an etch time (etching with sulfur acid). Water vapor or air were used in surface treatment after etching. The investigators write: "steam and chromyl chloride were introduced in a flow type apparatus in a dry oxygen free carrier gas (argon)." The results show that in the case of titanium, the steam treatment is undesirable because it intensifies the oxidation. In the case if nickel it is required since preliminary hydroxylation is needed for chromium chemisorption. This paper is more of a study of chemisorption reactions than actual deposition. Although the process can be understood as one cycle of (molecular layer) deposition, it is not mentioned by the investigators.

V. D. Ivin, E. P. Smirnov, A. A. Malkov, R. M. Levit, I. M. Stark, S. I. Koltsov. Influence of heat treatment on structure-chemical transformation of carbon fibers made by the carbonization process. Journal of Applied Chemistry of the USSR. 1982, V. 55, № 11. P. 2390-2392.
В. Д. Ивин, Е. П. Смирнов, А. А. Малков, Р. М. Левит, И. М. Старк, С. И. Кольцов. Влияние термической обработки на структурно-химическую реорганизацию карбонизированных углеродных волокон. Журнал прикладной химии. 1982, Т. 55, Вып. 11. С. 2632-2634.
{Ivin1982} ru en
Yury Koshtyal: ?not ALD

A. A. Malkov, V. D. Ivin, R. M. Levit, E. P. Smirnov, T. A. Shcherbakova, S. I. Koltsov. Influence of chlorine chemisorption on the thermooxidative destruction of carbon fibers. Zhurnal prikladnoy khimii. 1982. V. 52, № 3, P. 1027-1032.
А. А. Малков, В. Д. Ивин, Р. М. Левит, Е. П. Смирнов, Т. А. Щербакова, С. И. Кольцов. Влияние хемосорбции хлора на термоокислительную деструкцию углеродных волокон. Журнал прикладной химии. 1982. Т. 52, вып. 3, С. 1027-1032.
{Malkov1982} ru
Yury Koshtyal: ?not ALD.

Nechiporenko, A. P.; Malygin, A. A.; Kol'tsov, S. I.; Aleskovskii, V. B.

Microspectrophotometric study of chromium oxide layers synthesized by molecular stratification on the surface of metals
Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, Volume: 25, Issue: 3, Pages: 323-7, 1982
А. П. Нечипоренко, А. А. Малыгин, С. И. Кольцов, В. Б. Алесковский. Микроспектрофотометрическое исследование хромоксидных слоев, синтезированных методом молекулярного наслаивания на поверхности металлов. Известия высших учебных заведений. Химия и химическая технология. 1982 Т. 25, вып. 3, С. 323-327.
{Nechiporenko1982a} ru

Törnqvist, R. & Korpela, S.
ON THE AGING OF ZnS-Mn ELECTROLUMINESCENT THIN-FILMS GROWN BY THE ATOMIC LAYER EPITAXY TECHNIQUE
J. Cryst. Growth, **1982***, 59*, 395-398
{Tornqvist1982} en
Gloria Gottardi: The paper does not contain information on the ALE process at all. It is focused on the study of the aging mechanisms in electroluminescent devices (AC ZnS:Mn) grown by ALE. It seems in fact that such devices suffer from changes in the brightness versus voltage characteristic which are related to the aging process of the material.
Tommi Kääriäinen: The paper reports aging phenomena and its effect on performance of AC ZnS:Mn TFEL devices grown by atomic layer epitaxy. Does not provide detailed information about the ALE process or properties of individual layers. However, very well known industrial application of ALD.

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.,* 1982, 55(6), 1298-1299. (Original article submitted in May 13, 1981). Translated from: Tolmachev, V. A. *Zh. Prikl. Khim.,* 1982*, 55(6)*, 1410-1412.
В. А. Толмачев. Исследование возможности применения гравиметрического метода для изучения процесса молекулярного наслаивания на дисперсных кремнеземных образцах. Журнал прикладной химии, Т. 55, вып. 6, С. 1410-1412.
{Tolmachev1982} en ru
Riikka Puurunen: In this work, the mass evolution during ALD has been followed in situ. (First time?) In this case it was for porous high-surface-area substrates. Tolmachev says nicely: *"Fundamental information on the process of molecular layering can be obtained by making a direct measurement of the weight of the substances synthesized during the actual course of the synthesis. In the present work, for such an investigation and also to determine sorption characteristics we used a vacuum microbalance with quartz springs (ref. 3). The synthesis of titanium oxide layers was carried out at T = 453 K (ref. 4)."* A bit later in the text: *"a linear dependence of the increase in the weight of the layer synthesized on the number of cycles being observed."* (I want to add, though, that the first cycle appears a bit different and points to "substrate-enhanced growth", as defined in J. Appl. Phys. **97**, 121301 (2005); http://dx.doi.org/10.1063/1.1940727.) Further: *"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 hydroxy groups (ref. 4)."* In some cases, the decrease of reactivity because of filling of micropores is observed.
Marja-Leena Kääriäinen: A gravimetric method is used for studying the process of molecular layering in disperse silica samples. The investigator defines molecular layering as a method where any number of monomolecular oxide layers with a thickness of fractions of a nanometer or more can be synthesized. The reference for molecular layering is "abstracts of lectures" by S.I. Kol'tsov from Lensovet Leningrad Technical Institute 1963. In the study a in situ weighing by vacuum microbalance with quartz springs is used during the synthesis of TiO2 at 180C. In addition sorption characteristics are studied. Powder of KU-1 quartz glass is used as a substrate. The growth of TiO2 is shown to be uniform and linear. During the monitoring of the reactions the decrease in the weight is realized when the chlorine atoms are replaced by hydroxyl groups during the water vapor exposure. In addition the deposition into pores is realized in a decrease of the growth rate. This is an ALD paper.

A. A. Malygin, V. F. Dergachev. Influence of technological parameters on the synthesis of vanadium-containing silicas. Fourth all-Union conference in Nizhny Tagil (15-18 of June) "Chemistry, technology and application of the vanadium compounds", Part II, Polygraphite, Sverdlovsk, 1982, P. 37
А. А. Малыгин, В. Ф. Дергачев. Исследование влияния технологических параметров на синтез ванадийсодержащего силикагеля. Четвёртое Всес. Совещ в г. Нижнем Тагиле (15-18 июня), Химия, технология и применение ванадиевых соед. Часть II. Полиграфит, Свердловск, 1982, С. 37.
{Malygin1982a} ru

A. A. Malygin, S. A. Trifonov, S. I. Koltsov The effect of vanadium-containing additives on thermal-oxidative stability and combustibility of polymeric materials. Fourth all-Union conference in Nizhny Tagil (15-18 of June) "Chemistry, technology and application of the vanadium compounds", Part II. Polygraphite, Sverdlovsk, 1982, P. 38
А.А. Малыгин, С.А.Трифонов, С.И.Кольцов. Влияние ванадийсодержащих добавок на
термоокислительную устойчивость и горючесть полимерных материалов. Четвёртое
Всес. Совещ в г. Нижнем Тагиле (15-18 июня), Химия, технология и применение
ванадиевых соед. Часть II. Полиграфит, Свердловск, 1982, С. 38.
{Malygin1982} ru

A. A. Malkov, V. D. Ivin, S.I. Koltsov. Influence of vanadium-oxychloride surface groups on the properties of carbon fibers. Fourth all-Union conference in Nizhny Tagil (15-18 of June) "Chemistry, technology and application of the vanadium compounds", Part II. Polygraphite, Sverdlovsk, 1982, P. 39
А. А. Малков, В. Д. Ивин, С. И.Кольцов. Влияние ванадийоксихлоридных поверхностных групп на свойства углеродных волокон. Четвёртое Всес. Совещ в г. Нижнем Тагиле (15-18 июня), Химия, технология и применение ванадиевых соед. Часть II. Полиграфит, Свердловск, 1982, С. 39.
{Malkov1982a} ru

M. N. Tsvetkova, A. A. Malygin, S. I. Koltsov. Synthesis with use of molecular layering method of vanadium-containing glass microspheres and investigation of their properties Fourth all-Union conference in Nizhny Tagil (15-18 of June) "Chemistry, technology and application of the vanadium compounds", Part II. Polygraphite, Sverdlovsk, 1982, P. 40
М. Н. Цветкова, А. А. Малыгин, С. И.Кольцов. Получение методом молекулярного
наслаивания ванадийсодержащих стеклянных микросфер и исследование их свойств.
Четвёртое Всес. Совещ в г. Нижнем Тагиле (15-18 июня), Химия, технология и применение ванадиевых соед. Часть II. Полиграфит, Свердловск, 1982, С. 40.
{Tsvetkova1982a} ru

S. K. Gordeev, S. G. Taushkova, E. P. Smirnov. Diamond – vanadium (V) oxychloride : chemistry of interaction. Fourth all-Union conference in Nizhny Tagil (15-18 of June) "Chemistry, technology and application of the vanadium compounds", Part II. Polygraphite, Sverdlovsk, 1982, P. 68
С. К. Гордеев, С. Г. Таушкова, Е. П. Смирнов. Алмаз – оксихлорид ванадия (V) : химия взаимодействия. Четвёртое Всес. Совещ в г. Нижнем Тагиле (15-18 июня), Химия, технология и применение ванадиевых соед. Часть II., Полиграфит, Свердловск, 1982, С. 68.
{Gordeev1982a} ru

A. P. Nechiporenko, T. A. Bourenina. Spectroscopic investigation of ultra-fine oxide layers deposited by molecular layering method on the surface of glass and single crystal silicium. Fourth all-Union conference in Nizhny Tagil (15-18 of June) "Chemistry, technology and application of the vanadium compounds", Part II. Polygraphite, Sverdlovsk, 1982, P. 108.
А. П. Нечипоренко, Т. А. Буренина. Спектроскопическое исследование ультратонких кислородных слоев, синтезированных методом молекулярного наслаивания на поверхности стекла и монокристаллического кремния. Четвёртое Всес. Совещ в г. Нижнем Тагиле (15-18июня), Химия, технология и применение ванадиевых соед. Часть II., Полиграфит, Свердловск, 1982, С. 68.
{Nechiporenko1982b} ru

M. N. Tsvetkova, A.A. Malygin, S.I. Koltsov, V. B. Aleskovskii. Preparing of spheroplastics with improved properties. Conference "New methods of obtaining and spheres of application of gas-filled polymers", 26-28 October 1982, NIITEKHIM, Cherkassy 1982, P. 81-81.
М. Н.Цветкова, А.А. Малыгин, С.И.Кольцов, В. Б. Алесковский. Получение сферопластиков с улучшенными свойствами. Конференция «Новые способы получения и области применения газонаполнен-ных полимеров», 26-28 октября, НИИТЭХИМ, Черкассы, 1982, С. 81-81.
{Tsvetkova1982b} cyr

G. K. Shevchenko, E. N. Dolgova, A. Yu. Rodina, A.A. Malygin, S.I. Koltsov. New moisture scavengers based on the filled polymers. Conference "New methods of obtaining and spheres of application of gas-filled polymers", 26-28 October 1982, NIITEKHIM, Cherkassy 1982, P. 124-126.
Г. К. Шевченко, Е. Н. Долгова, А. Ю. Родина, А. А. Малыгин, С. И.Кольцов. Новые влагопоглотители на основе наполненных полимеров. Конференция «Новые способы получения и области применения газонаполнен-ных полимеров», 26-28 октября, НИИТЭХИМ, Черкассы, 1982, С. 83-84.
{Shevchenko1982} ru

A.A. Malygin, S.A. Trifonov, S.I. Koltsov, V.V. Barsova. Gas-filled polymeric materials of reduced combustibility. Conference "New methods of obtaining and spheres of application of gas-filled polymers", 26-28 October 1982, NIITEKHIM, Cherkassy 1982, P. 124-126.
А.А. Малыгин, С.А.Трифонов,С.И.Кольцов, В.В.Барсова. Полимерные газонаполненные материалы с пониженной горючестью. Конференция «Новые способы получения и области применения газонаполнен-ных полимеров», 26-28 октября, НИИТЭХИМ, Черкассы, 1982, С. 124-126.
{Malygin1982b} ru

Tsvetkova, M. N.; Yur'evskaya, I. M.; Malygin, A. A.; Kol'tsov, S. I. & Skorik, Yu. I.
Preparation of titanium oxide coatings on sodium borosilicate glass surfaces by molecular layering and study of the stability of the products obtained in aqueous medium
***Journal of Applied Chemistry of the USSR,* 1982*, 55 (2)*, 229-233.**
М. Н. Цветкова, И. М. Юрьевская, А. А. Малыгин, С. И. Кольцов, Ю. И. Скорик. Синтез методом молекулярного наслаивания титаноксидных покрытий на поверхности натриевоборосиликатных стекол и исследование устойчивости полученных продуктов в водной среде. Журнал прикладной химии. 1982, Т. 55, вып. 2, С. 256-261.
{Tsvetkova1982} en ru
In this work the molecular layering has been used to study the sealing effect of TiO2 coating on sodium borosilicate glass surfaces with the varying composition of Na2O and B2O3. Details of molecular layering process has not been given, but refereed to the Kol'tsov's 1969 work. The deposition has been done on the glass particles with the specific surface area of 0.5 m2/g. The sealing effect of TiO2 coating, as a function of number of TiO2 layers, has been studied by measuring the leached Na+ ions into the water. The paper provides valuable information about the effect of the glass substrate chemical composition on initial growth characteristics of ML TiO2. The observation was that the most rapid deposition occurs for low-alkali glass samples. The importance of this is seen as a sealing of the low-alkali glass substrate surface already after 4 to 6 TiO2 layers, which is shown as a gradual decrease of Na+ ions leached into the water.

E. A. Avrutina, A. V. Gusev, S. I. Koltsov, et al., Production of titaniferous zinc-oxide, J. Appl. Chem. USSR, Vol 55, Issue 4, Year 1982, pp 821-824.
Э. А. Аврутина, А. В. Гусев, С. И. Кольцов, Г. Н. Кузнецова, А. А. Малыгин, П. М. Сидоров. К вопросу получения титансодержащей окиси цинка. Журнал прикладной химии. 1982, Т. 55, вып. 4, С. 895-898.
{Avrutina1982} ru en

V. B. Kopylov, A. N. Volkova, A. P. Matveenko, L. V. Ivanova, V. N. Pak. Study of Styrene conversion on the surface of phosphor-containing silica. Zhurnal Prikladnoi Khimii, 1982, V. 55, I. 7, P. 1513-1517
В. Б. Копылов, А. Н. Волкова, А. П. Матвеенко, Л. В. Иванова, В. Н. Пак. Изучение превращения стирола на поверхности фосфор (III) содержащего кремнезема. Журнал прикладной химии. 1982, Т. 55, вып. 7, 1513-1517.
{Kopylov1982} ru

Della Mussia J. P., Electron. actual., 1982, 17(676) 16.
(no code)
Riikka Puurunen: This was referred to by Aidla and Tammik (1983), saying that here the decision of French company Sintra to use ALE-made electroluminescent displays on 40 x 40 cm substrates is told of.

Dergachov VF Development of technology for combined cycle process of modification of silica gel with vanadium : Diss . ... Candidate . techn . Science / TRL - L. , 1982 . - 148 p. (EAF) Дергачев В.Ф. Разработка технологии парогазового процесса модифицирования силикагеля ванадием: Дисс. ... канд. технич. наук/ ЛТИ - Л., 1982. - 148 с. (ДСП)
(no code)

N. Kopylov Structure and properties of ultrathin titania layers synthesized on the surface of single-crystal silicon in an electric field . : Diss ... Candidate . Chem. Science / TRL . - L., 1982 - 122c . (EAF) Копылов Н.Н. Структура и свойства сверхтонких титаноксидных слоев, синтезированных на поверхности монокристаллического кремния в электрическом поле.: Дисс…канд. хим. наук/ ЛТИ. - Л., 1982 - 122с. (ДСП)
(no code)

Kropachev AA Synthesis and study of physical and chemical properties of pyrolytic carbon : Diss . ... Candidate . Chem. Science / TRL - L. , 1982 . - 149 p. Кропачев А.А. Синтез и исследование физико-химических свойств пироуглерода: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1982. - 149 с.
(no code)

P. M. Vainshtein, Yu. K. Ezhovskii, S. I. Kol'tsov. A method of metals preparing before gluing. Description of invention for the author certificate № 975771. Claimed: 16.07.81. Published 23.11.82
П. М. Вайнштейн, Ю. К. Ежовский, С. И. Кольцов Способ подготовки металлов перед склеиванием. Описание изобретения к авторскому свидетельству 975771. Заявлено: 16.07.81, Опубликовано: 23.11.1982
{Vainshtein1982} ru

Busse, W.; Gumlich, H. E.; Tornqvist, R. O. & Tanninen, V. P.
ZERO-PHONON LINES IN ELECTRO-LUMINESCENCE AND PHOTO-LUMINESCENCE OF ZnS-Mn THIN-FILMS GROWN BY ATOMIC LAYER EPITAXY
Phys. Status Solidi A, **1983***, 76*, 553-558
{Busse1983} en
Hele Savin: The application here is a large area display. They make ZnS:Mn films by ALD, but not any details of the process are given (only deposition temperature 500C and film thickness 350 nm). The benefit of using ALD is to make the films more stable. They refer to paper Tanninen et al. 1981 for ALD technology but this is not very clearly stated.

Malygin, A. A.; Kol'tsov, S. I.
Some principles of the synthesis of two-component oxide layers by molecular stratification
Napravlennyi Sintez Tverdykh Veshchestv (1983), 1, 17-50.
А. А. Малыгин, С. И. Кольцов. О некоторых закономерностях синтеза двухкомпонентных оксидных слоёв методом молекулярного наслаивания. Направленный синтез твердых веществ. (Межвузовский сборник), 1983, вып. 1, Ленинград, изд-во ЛГУ. 17-50.
{Malygin1983} ru

A. A. Malkov, V. D. Ivin, I. B. Ternyaeva, R. M. Levit, L. V. Lashina. Effect of conditions of chlorine chemisorption on the stability of carbon fibers in oxidative environments. Zhurnal prikladnoy khimii, 1983, V. 56, № 4, P. 836-839
А. А. Малков, В. Д. Ивин, И. Б. Терняева, Р. М. Левит, Л. В. Лашина. Влияние условий хемосорбции хлора на поведение углеродных волокон в окислительных средах. Журнал прикладной химии, 1983, Т. 56, вып. 4, С. 836-839.
{Malkov1983} ru
Yury Koshtyal: ?not ALD.

L. V. Ivanova, Yu. K. Ezhovskii, A. V. Eliseev. Adhesion properties of surface modified by chromium oxides. Journal of Applied Chemistry of the USSR. V. 56, I 5, P. 1069-1071 1983
Л. В. Иванова, Ю. К. Ежовский, А. В. Елисеев. Адгезионные свойства поверхности модифицированной оксидами хрома. Журнал прикладной химии, 1983, Т. 56, вып. 5, С. 1137-1139.
{Ivanova1983} ru en
Riikka Puurunen: Chromium oxide grown from CrO2Cl2 and H2O/H2O2 in up to about ten cycles on aerosil and on glass-ceramic at 373 to 453 K. Strength of adhesion of "condensed" Cu and Al films is measured (it is not explained, how). The strength of adhesion increases about linearly with CrO3 cycles (/thickness), and after 4-5 cycles, the strength of adhesion saturates, which is ascribed to that a monolayer of chromium oxide has formed.

E. P. Smirnov, A. A. Malkov, A. V. Krasnobryzhy, S. K. Gordeyev. Control of the reactivity of carbon materials in the processes of thermooxidation. Khimicheskaya fizika. 1983, V. 2, №. 8, P. 1109-1113.
Е. П. Смирнов, А. А. Малков, А. В. Краснобрыжий, С. К. Гордеев. Управление реакционной способностью углреодных материалов в процессах термоокисления. Химическая физика. 1983, Т. 2, вып. 8, С. 1109-1113.
{Smirnov1983a} ru

P.M. Vainshtein, S. I. Kol'tsov, Yu. K. Ezhovskii, E. A. Ivanova. The interaction of Dychloromethylsilane with the surface of silica. Russian Journal of Physical Chemistry, 1983 V. 57, I. 7, P. 1046-1049.
П. М. Вайнштейн, С. И Кольцов, Ю. К. Ежовский, Е. А. Иванова Исследование взаимодействия метиллдихлорсилана с поверхностью кремнезема. Журнал физической химии, 1983, Т. 57, вып. 7, С. 1728-1733.
{Vainshtein1983} ru en

P.M. Vainshtein, S. I. Kol'tsov, Yu. K. Ezhovskii. The Interaction of Polyfuctional Silanes with a Silica Surface. Russian Journal of Physical Chemistry, V. 57, I. 7, P. 1049-1052, 1983
П. М. Вайнштейн, С. И Кольцов, Ю. К. Ежовский. Исследование взаимодействия полифункциональных силанов с поверхностью кремнезема. Журнал физической химии, 1983, Т. 57, вып. 7, С. 1733-1737.
{Vainshtein1983a} ru en

Damyanov, D. & Vlaev, L.
On the interaction of CrO2Cl2 vapor with the surface of gamma-alumina and the formation of a chromium oxide covering
Bull. Chem. Soc. Jpn., **1983***, 56*, 1841-1846
{Damyanov1983} en
Riikka Puurunen: This is an interesting paper, where results are presented for up to three reaction cycles of CrO2Cl2 vapor and hydrolysis by water vapour on gamma-Al2O3. What makes it especially interesting is that the ALD principles are followed, but there are no references to either the Russian or the Finnish works. In the Introduction, it is said: "there are no investigations on reactions of the Al2O3 surface with vapors of valatile halides or halide oxides of transition metals, which are known to ensure a more uniform deposition of a transition metal and a halogen on the surface than the classical methods of catalyst preparation. " Had the authors come up with the ideas independently, or did earlier works influence this? About the results: it is concluded that the HCl evolved in the CrO2Cl2 reaction reacts both with OH groups and with Al--O--Al bridges on gamma-alumina. CrOCl2 reacts with OH groups, but does not consume all of them. ClO2Cl2 reaction is carried out at 150°C, and McBain balance is used to follow the weight gain as function of time, giving interesting kinetic information for Al2O3 heat-treated at 250, 550 and 750°C. The temperature is chosen to avoid physisorption, observed at 25°C, and partial polymerization of ClO2Cl2 occurring (according to a reference) at 170°C. It is said that "with samples showing no weight gain, the residual chromyl chloride vapor and the gaseous products were removed by evacuation..." Thus, the saturation of the reactions as well as the purge/evacuation step needed for ALD, have been made.
Marja-Leena Kääriäinen: Damyanov and Vlaev, Bull. Chem. Soc. Jpn. 56 (1983) pp. 1841-1846: The interaction of chromyl chloride (CrO2Cl2) with surface hydroxyl groups of gamma-Al2O3 was studied by IR spectroscopy. The residual chromyl chloride vapor and gaseous products were removed by evacuation for 1 hr at 150C. The following reaction cycle was carried out: treatment of Al2O3 with CrO2Cl2 vapor; dehydration at 550C; hydrolysis at 100C with H2O; calcination at 550C. It is left unclear whether the evacuation is used in the last mentioned reaction cycle. Therefore the process sounds more like CVD than MLD.

Kinney, J. B. & Staley, R. H.
Reactions of titanium tetrachloride and trimethylaluminum at silica surfaces studied by using infrared photoacoustic spectroscopy
J. Phys. Chem., **1983***, 87*, 3735-3740
{Kinney1983} en
Pia Sundberg: Much like the title says, the authors investigated the reaction between silica and TMA/TiCl4 by Fourier transform infrared photoacoustic spectroscopy. The silica was dried at 450 °C under vacuum and then transferred to the photoacoustic cell where it was exposed to TMA or TiCl4 vapor. Exposure time was 1 min, after which the reaction gas was evacuated. For complete reaction 4-6 repeated exposures was required. According to the authors, TMA "reacts quickly with siloxane groups and then also hydroxyl groups. In addition, bridged surface species are formed by reaction between the TMA and more than one reactive surface site". The group also concluded that TiCl4 reacts with silica in much the same way as TMA: both terminally bound and bridged species were said to be observed. The TMA and TiCl4 treated samples were also further exposed to TiCl4 and TMA, respectively. The occurring reactions were said to be similar to the reactions when clean silica was used. When the sample first treated with TiCl4 followed by reaction with TMA was further exposed to ethylene, rapid polymerization was observed. No polymerization was observed for the sample fabricated in reverse order, i.e. TMA followed by TiCl4 exposures. No repeated cycles were reported.
Ruud van Ommen: The reaction of TiCl4, TMA, and the combination of the two with silica surfaces is studied in light of the preparation of Ziegler Natta catalysts, used in polymerization. From the product code (Alfa Products no. 89376), it seems that the substrate is probably highly porous silica particles of about 50 micron. Although the paper is interesting for learning about the first half-cycle in the ALD schemes with TiCl4 and TMA, is does not treat ALD explicitly, and the second half-cycle is not dealt with. Nevertheless, it gives useful information about the different ways that TiCl4 and TMA can bind to a silica surface with abundant hydroxyl-groups, and to a silica surface with just surface oxygen-atoms (obtained after heating in a dry atmosphere).
Marja-Leena Kääriäinen: The reactions of titanium chloride (TiCl4) and trimethylaluminum (TMA) with high-surface-silica were studied by Fourier transform infrared photoacoustic spectroscopy. A peak at 980 cm-1 was assigned for the strained, surface siloxane bridge. Unreported peaks were found in the low-frequency region for various products of the surface reactions. The spectrum of an active Ziegler-Natta catalyst was examined. Reaction between surface TiClx and TMA gas has known to give an active olefin-polymerization catalyst. In this paper the chemisorption of TiCl4 and TMA onto dehydrated silica was examined. The silica substrate was exposed to TiCl4 and TMA vapors at 10 torr (13.3 mbar). First either TiCl4 or TMA was introduced to the chamber. The reacting gas was fed to the chamber for 1 min and then evacuated. This had to be repeated for 4-6 times to be able to monitor a complete reaction. After TiCl4 or TMA exposure the other of the two was introduced and let react. When TiCl4 was introduced first, the bridged SiO-TiOSi species reacted with TMA. When TMA was introduced first, -Si-O-AlMe2 species reacted with TiCl4. This paper clearly describes a MLD process although no process methods are mentioned in the paper by the authors.

Kuznetsova, G. N.; Shakina, T. V.; Malygin, A. A. & Kol'tsov, S. I.
Changes in the structure of dispersed silica during the molecular stratification of chromium oxide
***Kolloidn. Zh.,* 1983*, 45 (3)*, 574-577**
Г. Н. Кузнецова, Т. В. Шакина, А. А. Малыгин, С. Кольцов. Изменение структуры дисперсного кремнезема в процессе молекулярного наслаивания. Коллоидный журнал. 1983, Т. 45, вып. 3, С. 574-577.
{Kuznetsova1983} en ru

Pessa, M.; Huttunen, P. & Herman, M. A.
ATOMIC LAYER EPITAXY AND CHARACTERIZATION OF CdTe-FILMS GROWN ON CdTe (110) SUBSTRATES
J. Appl. Phys., **1983***, 54*, 6047-6050
{Pessa1983} en
Hele Savin: Requirements met for film growth by ALD. They refer to Suntola's patent (1977) as the origin of ALD. The paper reports the first attempt to grow by ALD sc CdTe and CdMnTe thin films (deposition parameters 540K, 0.8Å/s, 10nm). The ALD results on superior structural quality of the films and additional surface smoothing is observed.
Timo Sajavaara: In this paper CdTe films were successfully deposited on (110)CdTe wafers using an MBE chamber with Knudsen cells for Cd and Te. The depositions were made in high vacuum environment, which more resembles MBE than ALD. What is striking in this more than 30 year old article is the quality of elemental and chemical analysis tools they used. In this single article AES, XPS and angle resolved XPS were used to measure the composition and crystalline quality of the grown films and surfaces. They also give clear upper limits for impurities (few thousands of ppm) based on the instrumental sensitivities.

Törnqvist, R. O.; Antson, J.; Skarp, J. & Tanninen, V. P.
HOW THE ZnS-Mn LAYER THICKNESS CONTRIBUTES TO THE PERFORMANCE OF AC THIN-FILM EL-DEVICES GROWN BY ATOMIC LAYER EPITAXY (ALE)
IEEE Trans. Electron Devices, **1983***, 30*, 468-471
{Tornqvist1983} en
Tommi Kääriäinen: The paper is about the performance of AC ZnS:Mn TFEL device grown by atomic layer epitaxy as a function of active ZnS:Mn layer thickness. The importance of the active layer thickness for optimal devise structure has been emphasized, which justifies the usage of ALE. The process details of ALE Al2O3 and ZnS:Mn used to built up the device have not been given. The paper provides information about the change in crystallinity of ZnS:Mn layer as a function of layer thickness. For example the poor crystallinity of the first 35 nm of the film has been reported to coincide with the dead layer seen in luminance. After the dead layer the luminance depends sublinearly on the thickness of ZnS:M layer. Know industrial application of ALD.

Drozd, V. E.

Study of some properties of oxide coatings prepared by molecular stratification on the surface of semiconductors
Napravlennyi Sintez Tverdykh Veshchestv, Volume: 1, Pages: 78-90, **1983**
В. Е. Дрозд Исследование некоторых свойств оксидных покрытий, полученных методом молекулярного наслаивания на поверхности полупроводников. Направленный синтез твердых веществ. (Межвузовский сборник), 1983, вып. 1, Ленинград, изд-во ЛГУ. 78-90.
{Drozd1983} ru

V. N. Postnov Synthesis of inorganic matrix on the base of silica by chemical assembly method. Napravlennyi Sintez Tverdykh Veshchestv, Volume: 1, Pages: 118-126, **1983**
В. Н. Постнов Синтез неорганических матриц на основе силикагеля методом химической сборки. Направленный синтез твердых веществ. (Межвузовский сборник), 1983, вып. 1, Ленинград, изд-во ЛГУ. 118-126.
{Postnov1983} ru

V. M. Smirnov Chemical Assembly - the way of directed synthesis (construction) of heterogeneous catalysts. Napravlennyi Sintez Tverdykh Veshchestv, Volume: 1, Pages: 90-109, **1983**
В. М. Смирнов Химическая сборка - путь направленного синтеза (конструирования) гетерогенных катализаторов. Направленный синтез твердых веществ. (Межвузовский сборник), 1983, вып. 1, Ленинград, изд-во ЛГУ. 90-109.
{Smirnov1983} ru

R. V. Sushko, A. V. Gemme, I. F. Mironyuk, A. A. Chuyko. Structural transformations in titanium-bearing silicates // Journal of Applied Chemistry of the USSR. – 1983. – V. 56, № 6. – P. 1155-1159.
Изучение структурных превращений в титаносодержащих кремнезёмах / Р. В. Сушко,
А. В. Гетте, И. Ф. Миронюк, А. А. Чуйко, // Журнал прикладной химии. – 1983. – Т. 56, вып. 6. – С. 1230-1234.
{Sushko1983} ru en

Tanninen, V.-P.; Oikkonen, M. & Tuomi, T.
COMPARATIVE-STUDY OF THE CRYSTAL PHASE, CRYSTALLITE SIZE AND MICROSTRAIN IN ELECTROLUMINESCENT ZnS-Mn FILMS GROWN BY ATOMIC LAYER EPITAXY AND ELECTRON-BEAM EVAPORATION
Thin Solid Films, **1983***, 109*, 283-291
{Tanninen1983} en
Gloria Gottardi: The paper is focused on the comparison of the microstructural properties (crystal phase, crystallites size, microstrain,...) of EL ZnS:Mn films grown by Atomic Layer Epitaxy and by Electron Beam Evaporation. ALE reveals to be a promising method for the production of EL devices, as it allows the deposition of films with better microstructural properties (larger crystallites, lower microstrain, lower dislocation density, lower defects density) which may significantly influence the performance and the degradation of the devices.

Tolmachev, V. A. & Okatov, M. A.
Investigation of the synthesis process and properties of titanium-oxide films, formed by molecular deposition method
***Sov. J. Opt. Technol.,* 1983*, 50(11)*, 706-708.**
В. А. Толмачев, М. А. Окатов. Исследование процесса синтеза и свойствтитаноксидных пленок, получаемых методом молекулярного наслаивания Оптико-механическая промышленность (Оптический журнал) 1983, вып 11, С. 38-41.
{Tolmachev1983} en ru
Riikka Puurunen: Up to 50 cycles of TiO2 by the TiCl4/H2O ALD process (called "molecular deposition (MD)" in the English translation) at 180°C on "silica optical glass" and "chemically unstable TK8 and TF7 glasses". From the abstract: "It is shown to be possible to use a gravimetric method and an emission spectral microanalysis to investigate the reactions of the synthesis. The deposition process and the optical and protective properties of titanium-oxide layers are investigated." The reactor is described; reaction pressure is 10^-4 Torr. Different types of growth curves are observed for deposition at different temperature and on different substrates. TiO2 is concluded to work as a protective film, protecting "the surface of unstable glasses from the action of an acid medium."
Marja-Leena Kääriäinen: "Investigation of the synthesis process and properties of titanium oxide films formed by molecular deposition method". This study by Tolmachev has been published one year after Tolmachev, Zhrnal Prikladnoi Khimii 55 (1982) p. 1410. Interestingly, instead of referring molecular layering as "abstracts of lectures by Kol'tsov" as in the 1982 paper; the references for "molecular deposition" and MD as "alternate treatment of chlorides and water with intervening evacuation" are "V.B. Aleskovskii, Khimia tverdykh veshchestv Vyssh. Shkola Press Moscow 1978" and "Yu.K.Ezhovskii et al Sov. Pat. No 789,452, Byull, Izobret,. Tov. Znakov No 47 (1980), respectively. The apparatus for the molecular depositions has been presented in a schematic. Quartz springs are used again for in situ gravimetric studies. Three different types of glass are used as substrates. The deposition process, optical and protective properties of titanium oxide have been studied. The results show that the growth of titanium oxide is linear on 'KUI" glass. The investigators report that the process on KUI at 20C shows a high growth rate "due to the incomplete removal of the products (TiCl4 and H2O) from the surface". The porosity of TF7 glass is noticed by a decrease in the growth rate after 2 cycles of deposition. In addition the investigators report a gradual decrease in transmission in the UV region as the number of cycles increases. At deposition cycles of 60 the transmission cuts at lambda=340nm. This is close to the cut wavelength of anatase of lambda=384nm. The refractive index of titanium oxide is found to be n=2.44. Further the TiO2 layers improved the chemical stability of the unstable glass substrate against the action of acid medium. An ALD article.

Aidla, A.; Tammik, A.-A. (1983). About a New Method for Producing Electroluminescent Thin Film Structures. Tartu Riikliku Ülikooli Toimetised, 655, 120 - 130.
{Aidla1983} ru
Riikka Puurunen: This is to my understanding the first Estonian publication on ALD. It is written in Russian and it presents a literature study of the Finnish atomic layer epitaxy method used to make high-quality electroluminescent displays. I find especially the literature citations interesting (total of ten cited papers). The authors refer to Finnish, American and British patents on ALE, but not the Soviet patent---were they not aware of them? Also, the authors refer to a paper by Nishizawa from 1981. It is their Ref. 8 and is copied exactly here: "Nishizawa J - Electron. Parts. and Mater., 1981, 20, 12, 119." I have not yet managed to find this in any search engine. The authors also say that according to Nishizawa's paper, already 26 companies are discussing with the Finnish company Oy Lohja about the possibilities of using ALE. And that according to their Ref. 10, the French company Sintra is the first customer, who has decided to use the technology for 40 x 40 cm substrates. Ref. 10 is: "Della Mussia J. P. - Electron. actual., 1982, 17, 676, 16."
Tuomo Suntola has told me about the licensing of ALE display technology to France---this is the first written evidence that I find of it, very nice to find it here!
Jonas Sundqvist: According to theis reference from 1999 (http://www.indiana.edu/~hightech/fpd/papers/ELDs.html A History of Electroluminescent Displays) The french company Sintra was part of Alcatel.

Brykalov AV Synthesis of silica-based hemosorbents by the molecular layering method and their physico -chemical properties: Diss ... Candidate . Chem. Science / TRL . - L. , 1983 . - 153c . (EAF) Брыкалов А.В. Синтез гемосорбентов на основе кремнезема методом молекулярного наслаивания и их физико-химические свойства: Дисс…канд. хим. наук/ ЛТИ. – Л., 1983. – 153с. (ДСП)
(no code)

Egorov, AL Synthesis of oxide films on the surface of tantalum and gallium arsenide , their structure and properties: Diss ... Candidate . Chem. Science / TRL . - L., 1983 - 201c . Егоров А.Л. Синтез оксидных пленок на поверхности тантала и арсенида галлия, их структура и свойства: Дисс…канд. хим. наук/ ЛТИ. - Л., 1983 - 201с.
(no code)

Marja Hamilo, TUTKIMUKSIA EPÄPUHTAUKSISTA ATOMIC LAYER EPITAXY -MENETELMÄLLÄ VALMISTETUISSA ELEKTROLUMINENSSIOHUTKALVORAKENTEISSA, M. Sc. thesis, Helsinki University of Technology, Department of Chemical Technology
(no code)

Veli-Pekka Tanninen, X-ray diffraction studies of aluminium powder and electroluminescent zinc sulphide thin films, Doctoral Dissertation, Helsinki University of Technology, Acta Poly. Scandinavica, Appl. Phys. Ser., Ph 355-2721, 1983.
(no code)

R. Törnqvist, Electroluminescence in ZnS:Mn thin film structures grown with atomic layer epitaxy, Doctoral Dissertation, Helsinki University of Technology, Acta Poly. Scandinavica, Appl. Phys. Ser., Ph140, 1983, 34 pages.
(no code)

Yu. K. Ezhovskii, S. I. Kol'tsov, A. V. Eliseev, L. V. Ivanova. A method of treatment of silicate supports surface. Description of invention for the author certificate № 988786. Claimed: 05.06.81. Published 15.01.83
Ю.К. Ежовский, С. И. Кольцов, А. В. Елисеев, Л. В. Иванова. Способ обработки поверхности силикатных подложек. Описание изобретения к авторскому свидетельству 988786. Заявлено: 05.06.81, Опубликовано: 15.01.83
{Ezhovskii1983} ru

First Symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, 1984, 45 p.
abstract: The proceedings contains the invited papers presented at the First Symposium on Atomic Layer Epitaxy, held on December 13-14, 1984 in Espoo. Most of the papers have been devoted to this novel growth method. Related growth techniques, methods of layer characterization and potential applications account for the rest of the content. The contributions represent the growing number of research groups active in this area in Finland.
{Paananen1984} en
Riikka Puurunen: Proceedings of the first Finnish conference on ALE, organized by VTT, in Espoo, Finland. The papers contained in the proceedings are by the following authors: Pessa, Antson, Hiltunen, Koskinen, Leskelä, Niinistö, Tammenmaa, Grassbauer, Stingeder, Tuomi, Pakkanen, Lindblad, Nevalainen, Hyvärinen, Suni, Asonen, Vulli, Jylhä, and Hautojärvi. These proceedings will have historical significance, as most likely, the conference proceedings report for example the very first quantum chemical studies on ALE/ALD (or maybe there could be earlier Russian works, who knows). It is interesting that it is only through this ALD history project that I have become aware of this symposium, it is not generally mentioned in the existing reviews on ALD.

M. Pessa, Research and development of thin film technology in Finland, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 6-6.
{Pessa1984a} en

H. Antson, L. Hiltunen, T. Koskinen, M. Leskelä, L. Niinistö, M. Tammenmaa, M. Grassbauer, G. Stingeder, Characterization of electroluminescent thin film structures by analytical techniques, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 7-10.
{Antson1984} en

T. Tuomi, X-ray and optical studies of the formation of zinc sulfide thin films grown by atomic layer epitaxy, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 11-13.
{Tuomi1984} en

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
Riikka Puurunen: The first Finnish quantum chemical modelling report on ALD. ZnCl2 reaction with ZnS surface and H2S reaction with the ZnCl2-modified ZnS surface. "A maximum growth rate of one layer with three ZnCl2-H2S cycles" is concluded on the basis of the modelling, commenting also that on real zinc sulphide, the growth process is more complicated than assumed in the modelling.
Simon Elliott: A report of quantum chemical and graphical modelling of ZnCl2+H2S ALE. The brevity of the proceedings format makes it hard to assess which of the conclusions are based on computed data, rather than on reasonable supposition. Bonding of ZnS with surface or neighbouring groups is stated (without evidence) as a pre-requisite for HCl desorption - this is also seen in recent atomic-scale calculations.

M. Tammenmaa, T. Koskinen, L. Hiltunen, M. Leskelä, L. Niinistö, Growth of ZnS thin films using zinc acetate as zinc source and manganese and lanthanoid beta-diketonates as activator sources, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 18-21.
{Tammenmaa1984} en

J. Hyvärinen, Development trends in ALE and thin film electroluminescent displays, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 22-26.
{Hyvarinen1984} en

I. Suni, III-V compounds for semiconductor technology, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 27-31.
{Suni1984} en

H. Asonen, Applications of thin films grown by MBE technique, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 32-34.
{Asonen1984} en

M. Vulli, H. Asonen, M. Pessa, Possibilities and plans to prepare cadmium-mercury-telluride (CMT) semiconductor thin films with MBE- and ALE-methods, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 35-39.
{Vulli1984} en

O. Jylhä, Growth and characterization of CdTe-based thin semiconductor films, quantum well heterostructures and superlattices, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 40-43.
{Jylha1984} en

P. Hautojärvi, The use of slow positrons to study semiconductor surfaces and interfaces, Proceedings of the First symposium on Atomic Layer Epitaxy (VTT Symposium 54), Ed. Riitta Paananen, Valtion teknillinen tutkimuskeskus, Espoo, Finland, 1984, pp. 44-45.
{Hautojarvi1984} en

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. Journal of Applied Chemistry of the USSR, 1984, V. 57, I. 1, P. 153-155.
Б. З. Моценят, Ю. К. Ежовский, Л. М. Леванькова, Н. В. Михайлова. Образование и реакции гидроксильных групп поверхности полиимида с тетрахлоридом титана. Журнал прикладной химии, 1984, Т. 57, вып. 1, С. 166-168.
{Motsenyat1984} ru en
Pia Sundberg: The main focus of this work is the etching of polyimide surface first with NaOH and then with an acid (not sure which one). The aim was to form hydroxyl groups on the surface, enabling further reaction with TiCl4. Different etching temperatures and NaOH concentrations were tried during the experiments. Lastly the etched polyimide was treated with TiCl4, followed by water vapor.

Yu. K. Ezhovskii, A. L. Egorov, S. I. Kol'tsov. Formation and structure of titanium-dioxide layers on the surface of tantalum. Inorganic Materials. 1984. V. 20, I. 2, P. 211-214.
Ю. К. Ежовский, А. Л. Егоров, С. И. Кольцов, Формирование и структура титанкислородных слоев на поверхности танатала. Неорганические материалы (Изв. Академии наук СССР). 1984, Т. 20, вып. 2, С. 253-256.
{Ezhovskii1984} ru en
Cagla Ozgit-Akgun: In this manuscript, authors investigated the influence of the conditions of synthesis and thickness on the structural characteristics of TiO2 films, synthesized on a Ta support (high purity polished Ta and Ta films 0.8 micron thick obtained on glass-ceramic plates by plasma ion sputtering). Before the TiO2 deposition, supports were treated with H2SO4:H2O2:H2O = 1:1:3, washed with DI-water, and heated in vacuum. Ellipsometric measurements showed that 2-3 nm thick oxide layer remains on the surface, which ensures the hydroxylation of the surface necessary for ALD. TiO2 was deposited on Ta supports via ALD, in a vacuum reactor using H2O and TiCl4 vapors. Excess reagents and reaction products were removed after each half-cycle. Using ellipsometry, it was found that in the temperature range 400-500 K (temperature of the support), thickness of TiO2 layer increases linearly with the number of cycles. GPC was determined as 0.22+/-0.01 nm (authors emphasized that this value is close to the distance between the opposite ribs of the TiO2 tetrahedron, which is the structural unit of an amorphous oxide). It was further determined that each TiCl4 reacts preferentially with 2 surface hydroxyl groups. Increase in the thickness of the TiO2 layer was accompanied by a change in its structure. Electron diffraction analysis showed that up to a thickness of 10 nm, the TiO2 films are amorphous; with further increase in thickness, polycrystalline anatase phase appears. It has been further shown by the authors that the mean size of the crystallites increases, but does not exceed 10 nm at a thickness of 40 nm.

Notes: Within the manuscript, ALD was named as "chemical build-up" and "molecular stratification". In the first paragraph, advantages of ALD (over conventional methods) have been given as: "temperature of the process can be considerably decreased, it is possible to control the thickness and the composition down to a monolayer of structural units". These references are worth checking out (they are not listed in ALD-history-evolving-file): [5] V. E. Drozd, S. I. Kol'tsov, and T. A. Redrova, "Ellipsometric study of condensation reactions on semiconductor surfaces (molecular stratification reactions)," in: Modern Problems of Ellipsometry [in Russian], (edited by A. V. Rzhanov), Manua, Novosibirsk (1980), p. 134. [6] G. V. Sveshnikova, S. I. Kol'tsov, and V. B. Aleskovskii, "Ellipsometric study of multilayer systems on silicon surface," in: Modern Problems of Ellipsometry [in Russian], (edited by A. V. Rzhanov), Manua, Novosibirsk (1980), p. 141. (Riikka 10.6.2014: these references have been added in the list.)

Egorov, A. L.; Ezhovskii, Yu. K.; Kol'tsov, S. I. & Anikeev, G. V.
Formation of titanium dioxide films in the course of chemical assembly
***Journal of Applied Chemistry of the USSR,* 1984, *57*, 2395-2396**
А. Л. Егоров, Ю.К. Ежовский, С. И. Кольцов, Г. В. Аникеев. Особенности формирования пленок двуокиси титана в процессе химической сборки. Журнал прикладной химии, 1984, Т. 57, вып. 11, С. 2593-2594.
{Egorov1984} en ru
Luca Lamagna: The paper presents a study on the formation of TiO2 films by means of low temperature molecular layering carried out under vacuum conditions. TiO2 films are deposited on GaAs(100) substrates which are prepared by a gas phase etching (hydrogen-halogen halide) and followed by H2O vapor hydroxilation. Films are deposited using TiCl4 and H2O using fixed inflow pressure (100 Pa) and vapor residence time (5 min) in the reactor. The aim of the paper is the investigation of selected technological parameters (i.e. growth conditions) on the film formation mechanism, growth rate and structure of the oxide. The baseline of the experimental structure is defined at the beginning of the work when the authors claim that, with some fixed technological parameters (they do not explain which ones), the thickness of TiO2 is a linear function of the number of treatments/cycles. The growth parameters that are actually varied and therefore investigated are the residual pressure of the reactants, varied between 0.13 and 13.3 Pa, and the deposition temperature, varied between 323 and 573 K. The discussion of the experimental data results in a complete picture that describes the dependence of the growth rate on the increase of pressure or temperature. Two process windows in which the growth rate remains constant are finally highlighted. The authors clearly refer to condensation, gas phase reactions or hydrolysis of adsorbed reactants while discussing the mechanism of the film formation thus addressing the “ALD window” concept.
Tommi Kääriäinen: The paper studies molecular layering of TiO2 on gallium arsenide substrate at low temperature (323...573 K) using TiCl4 and water. It describes the effect of residual pressure of the reactants and the growth temperature on the film growth rate constant. In flow pressure and the residence time of the reactants were fixed parameters. The main observations are that at temperature above 470 K and residual pressure below 1 Pa the formation of TiO2 layer proceeds by the chemisorption of the TiCl4 followed by the hydrolysis of chloride groups, and that the monolayer growth of TiO2 by the condensation mechanism of ML proceeds at temperature above 520 K.
Cagla Ozgit-Akgun: Authors reported on the growth (chemical assembly, molecular layering) of TiO_2 on GaAs (100) substrate (whose surface was first etched to remove surface oxide layer and then hydroxylated with water vapor prior to TiO_2 deposition) in a vacuum system using $TiCl_4$ and H_2O. The growth of TiO_2 was monitored using an ellipsometer. Temperature, pressure of the incoming reactant vapor, residence time of the components in the reactor, and their residual vapor pressure were defined as the important parameters, which determine the film formation mechanism, growth rate and film structure. For a set of fixed parameters, TiO_2 growth was linear. Authors defined the parameter “growth-rate constant, d_0”, which is simply GPC. $d_0(TiO_2)$ was plotted (1) as a function of residual pressure (P = 0.13-13.3 Pa) of the reactants at various temperatures (T = 323-573 K), and (2) as a function of temperature at various residual pressures of the reactants, from which the growth mechanisms were determined. At T > 470 K and P < 1 Pa oxide layer forms by the chemisorption of $TiCl_4$ and subsequent hydrolysis of Cl groups. Under these conditions d_0 is independent of the residual pressure and is determined only by the temperature and reaction time. This paper resembles Ezhovskii1985_en.

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.
Translated from: ZPH, 57(4) 738-741, 1984.
Егоров А. Л., Ежовский Ю. К. Получение ультратонких пленок двуокиси кремния на поверхности тантала методом химической сборки. Журнал прикладной химии. 1984, Т. 57, вып. 4, С. 738-741
{Egorov1984a} en ru
(Original article submitted June 7, 1982)
Riikka Puurunen: From the English translation: “The aim of the present work was to carry out a chemical build-up of silicon dioxide on a tantalum surface, using an electron-donor agent with the ability to increase the chemical activity of the surface hydroxyls. Triethylamine was chosen as such an agent.” Substrate was 0.8 micrometers of tantalum, deposited on silicon-tantalum plates by cathode arc sputtering. Ellipsometry was used for thickness analysis and x-ray photoelectron spectroscopy for chemical composition. Nickel electrodes for electrical characterization. Just before deposition, Ta films were etched with HCl at 530K to remove the native oxide, and the surface was rehydroxylated in a steam flow at 440°C. For ALD, SiCl4 reaction was carried out in the prescence of triethylamine, and hydrolysis. Linear dependency of film thickness on the number of cycles for deposition at 380-440K, 0.11 nm. Catalytic action of triethylamine lasted until 445-450 K. Film thickness up to about 14 nm is shown in a figure. In the discussion of the results, term “steric hindrance” is used to explain why less than a monolayer is deposited.
Claudia Wiemer: In the present work "purging" was done by "vacuum evacuation", it is not so clear at which stage of the cycle this purging was done.
Interestingly, the concept of "steric hindrance" is introduced to explain the incomplete filling of the surface
Jonas Sundqvist. Is this the first study on “catalytic ALD”`? “electron-donor agent with the ability to increase the chemical activity of the surface hydroxyls” → the basis for all the work on using HCDS/pyridine/H2O, SiCl4/NH3/H2O etc. We need to review the papents that have been made later on these types of processes.

Herman, M. A.; Jylhä, O. & Pessa, M.
ATOMIC LAYER EPITAXY OF Cd$_1-X$Mn$_X$Te GROWN ON CdTe (111)B SUBSTRATES
J. Cryst. Growth, **1984**, *66*, 480-483
{Herman1984} en
Luca Lamagna: The paper presents Atomic Layer Epitaxy of a ternary magnetic semiconductor Cd(1-x)MnxTe. Thermally generated molecular beam are employed here in an ultra high vacuum system; therefore, the physical MBE-type growth is discussed here. Mn, Cd and Te beams are generated by effusion cells and the film are deposited on CdTe(111) substrates. LEED and XPS are employed to assess the heteroepitaxy and the core level binding energies of the layer. Saturation (ALD-like) is not mentioned. Indeed, alloying Mn with Cd is achieved varying pulse lengths and beam intensities thus indicating a physical growth.

A. V. Krasnobryzhii, E. P. Smirnov, S. K. Gordeev, S. G. Zhukov. Hydrolysis of titanium chloride groups synthesized on the surface of technical carbon (carbon black), Journal of Applied Chemistry of the USSR 1984, V. 57, I. 1, P. 68-70.
А. В. Краснобрыжий, Е. П. Смирнов, С. К. Гордеев, С. Г. Жуков. Гидролиз титанхлоридных группировок, синтезированных на поверхности технического углерода. Журнал прикладной химии, 1984, Т. 57, вып. 1, С. 76-78
{Krasnobryzhii1984} ru en
Tanja Kallio: Technical carbon (TC) oxidized with HNO3 resulting in functional groups (carboxyl and hydroxyl) 0.48 mmol/g. Reagents: TiCl4 (0.4 kPa, 420 K, 3 min), TC and H2O (470 K, 0.5 kPa) in vacuum so that extra TiCl4 was removed before H2O addition > ALD. Conditions for TiCl4 from A.V. Krasnobryzhii et al “Adsorption of titinaium tetrachloride on the surface of technical carbon” Zh. Prikl. Khim. 54 (1981) 1605
In TiCl4 reaction C–O2TiCl2 is formed on the C surface. In H2O reaction cleavage of Ti-Cl bonds C–O2TiCl2 > C–O2Ti(OH)2 + 2 HCl
Effect of temperature: 43 % is hydrolyzed at room temperature and full reaction takes place at 500 K.
completely new?

Pessa, M. & Jylhä, O.
GROWTH OF Cd1-XMnXTe FILMS WITH 0<x<0.9 BY ATOMIC LAYER EPITAXY
***Appl. Phys. Lett.,* 1984, *45*, 646-648**
{Pessa1984c} en
Henrik Pedersen: This is not an ALD paper to me but a paper on pulsed MBE. The authors describe that they do the depositions in their new MBE system an that elemental Cd, Te and Mn is heated to produce atomic beams. However, the authors describe the growth as selflimiting since the substrate is to hot to allow for Cd-Cd / Te-Te bonds and thus restricts the depostion to monolayers of Cd or Te.

Pessa, M.; Jylhä, O. & Herman, M. A.
Atomic layer epitaxy of CdTe on the polar (111)A and (111)B surfaces of CdTe substrates
***J. Cryst. Growth,* 1984, *67*, 255-260**
{Pessa1984b} en

Henrik Pedersen: To me, this is not ALD as we see it today - I would call it pulsed MBE. The authors describe the deposition mechanism as beeing controlled by surface chemistry, but the growth species are atomic Cd and diatomic Te, so the surface chemistry does not resembles what we call ALD chemistry today.

Pessa, M.; Jylhä, O.; Huttunen, P. & Herman, M. A.
Epitaxial growth and electronic structure of CdTe films
***J. Vac. Sci. Technol., A* , 1984, *2*, 418-422**
{Pessa1984} en
Henrik Pedersen: The first historic ALD paper from the "Suntola-branch" that I read in the VPHA. It seems to me that the approach here is physical rather than chemical - there are no discussion on surface chemistry or molecular precursors but rather discussions on how Cd and Te can be evaporated for the CdTe films deposited with Atomic Layer Epitaxy (ALE), as the technique is named in this paper. It seems to me as the work stems from MBE.

Postnova, A. M.; Postnov, V. N. & Kol'tsov, S. I.
Study of catalytic systems synthesized by the molecular layering method Journal of Applied Chemistry of the USSR, 1984, *57 (7)*, 1360-1364.
А. М. Постнова, В. Н. Постнов, С. И. Кольцов. Изучение каталитических систем, синтезированных методом молекулярного наслаивания. Журнал прикладной химии, 1984, Т. 57, вып. 7, 1465-1469
{Postnova1984a} ru en
Jaana Kanervo: This concerns ALD research for a specific catalytic application, namely oxidation of benzene to maleic anhydride. As known, vanadium oxide is a selective catalyst for this reaction. This article demonstrates how activity and selectivity can be further modified by the order and the number of molecular layers of specific other oxides such as phosphorus oxide on silica gel substrate. Figure 1 in article shows graphically how the number of phosphorus oxide monolayers under the vanadium oxide surface layer affect the maleic anhydride yield. The strongest yield-boosting effect is observed from zero to one layers of phosphorus oxide deposited on SG beneath the vanadium oxide layer. The effect from one to two layers is still significant after which the boosting effect appears to level off. This would imply that the catalytic properties are being electronically modified at least through 2-3 monolayers. Altogether this is a significant ALD work which I was not familiar with before.

Tolmachev, V. A.; Okatov, M. A. & Pal'chevskii, V. V.
Molecular layering of titanium oxide layers and their effect on the chemical stability of optical glass. *Sov. J. Opt. Technol.,* 1984, *51(6)*, 368-370
В. А. Толмачев, М. А. Окатов, В. В. Пальчевский. Молекулярное насливание титанкислородных слоев и их влияние на химическую устойчивость оптического стекла. Оптико-механическая промышленность (Оптический журнал), 1984, вып. 6, С. 57-59.
{Tolmachev1984} en ru
Luca Lamagna: The general aim of the paper is to discuss the protective properties of TiO2 films deposited by using the molecular layering method. The growth are carried out using TiCl4 and H2O, the temperature is varied between 20 and 210 °C; no details on pulses or pressure are reported. Two main paragraphs of the paper discuss first the chemical stability of TK8 glass, covered with a different and increasing number of TiO2 cycles, and then the consequent activation energy that is required for the glass dissolution process. TiO2 synthesis at 180 °C clearly improve the glass chemical stability even after few cycles. The authors address the deposition temperature effect on the TiO2 structure correlating it to different protective properties. For this specific item in molecular layering they recall Ref 6 [Aleskovski]; however in Fig. 2 the growth linearity for the TiO2 process is shown and it is underlined that between 100 and 210 °C a sort of constant deposition rate is achieved. The paper does not provide an understanding or a characterization of the molecular layering process; nevertheless ALD concepts are mentioned in it.
Hele Savin: I agree with Luca. I could only add that in this paper they also refer to Kol'tsov paper from 1969 as origin of ALD technique. In addition, the novelty here is that this is a first study on ALD coating of optical materials, but as Luca mentions, no details of ALD itself are given except precursors, it is just mentioned.

V. A. Tolmachev, M. A. Okatov. Investigation of process for synthesizing ultrathin titanium-oxide layers in porous glass. Opt. Mekh. Promst. 1984 V. 51, I. 2, P. 38-41.
В. А. Толмачев, М. А. Окатов. Исследование процесса синтеза сверхтонких слоев титаноксида в пористом стекле. Оптико-механическая промышленность (Оптический журнал). 1984, № 2, С. 38-41.
{Tolmachev1984a} ru

Tsvetkova, M. N.; Pak, V. N.; Malygin, A. A. & Kol'tsov, S. I.
Coordination state of modifier cations on the surface of glass fillers, Izv. Akad. Nauk SSSR,
Neorg. Mater., **1984**, *20*, 144-147
М. Н. Цветкова, В. Н. Пак, А. А. Малыгин, С. И Кольцов. Координационное состояние катионов-модификаторов на поверхности стеклянных наполнителей. Неорганические материалы (Известия Академии Наук СССР), 1984, Т. 20, вып. 1, С. 144-147.
{Tsvetkova1984a} ru

J. Nishizawa, ___, Oyo Butsuri 53, 516 (1984).
(no code)
title missing
Riikka Puurunen: J.-I Nishizawa refers back to this in a later paper (Nishizawa1985). I assume that this paper is in Japanese.

Suntola, T., Atomic layer epitaxy, in “Extended Abstracts of the 16th Conference on Solid State Devices and Materials,” p. 647, Kobe, Japan (1984).
(no code)
Reference from the Nishizawa1985 paper. Suntola1985 refers to this as: Suntola, T. 1984. Proc. 16th Int. Conf. Solid State Devices & Mater., Kobe, pp. 647-50.
Riikka Puurunen (writing on what Suntola has told): Suntola gave an invited talk in a grand conference organized by Jun-ichi Nishizawa. The ALE activities in Japan were very significant at this time, for example the lecture room was not large enough to accommodate all interested people. Suntola was interviewed for the Japanese TV, too, along with attending the conference.

Jarmo I. Skarp, Combination film, in particular for thin film electroluminescent structures, Patent US4486487 A, Priority date: May 10, 1982, Publication date: Dec 4, 1984.
(no code)
Riikka Puurunen: This is the work where the ATO nanolaminates (ATO = Al2O3/TiO2) were demonstrated to have beneficial dielectric strength.

Bedair, S. M.; Tischler, M. A.; Katsuyama, T. & El-Masry, N. A.
ATOMIC LAYER EPITAXY OF III--V binary compounds
Appl. Phys. Lett., **1985**, *47*, 51-53
{Bedair1985} en
Timo Sajavaara: This paper reports for the first time ALD of III-V compounds. For the deposition of GaAs AsH3 and TMG were used as precursors and AlAs was deposited using AsH3 and TMA. The carrier gas was H2. The precursors were not pulsed but a rotating disc with binary exposure to the input fluxes was used. The film quality was characterized by PL emission measurements and TEM studies, which proved the grown films to be single crystal GaAs and AlAs. A growth rate of 8 Å/cycle and 3 Å/cycle are reported fro GaAs and AlAs, respectively.

Ellestad, O. H. & Blindheim, U.
Reactions of titanium tetrachloride with silica gel surfaces
J. Mol. Catal., **1985**, *33*, 275-284
{Ellestad1985} en
Riikka Puurunen: A paper dealing with the chemistry that has been investigated in USSR from the 1960s. Indeed, the author refer to the works by Koltsov et al., in Refs. 9 and 10.

Herman, M. A.; Vulli, M. & Pessa, M.
Surface morphology of CdTe films grown on CdTe (111) substrates by atomic layer epitaxy
J. Cryst. Growth, **1985**, *73*, 403-406
{Herman1985} en
Timo Sajavaara: The growth of CdTe is now studied in more detail than in 1983 CdTe paper with variable pulse lengths. Again the depositions were made in high vacuum environment using variable opening times of the Knudsen cells. The main observation was that the surface morphology of the films, as studied using SEM, varied with different pulsing parameters. Smooth surfaces were only obtained if one monolayer of is present during one half-cycle.

V. D. Ivin, A. A. Malkov, R. M. Levit, E. P. Smirnov. Reaction of various carbon fibers with chlorine. Khimiya tverdogo topliva. 1985, № 5, P. 135-138.
В. Д. Ивин, А. А. Малков, Р. М. Левит, Е. П. Смирнов. Взаимодействие углеродных волокон различной природы с хлором. Химия твердого топлива. 1985, № 5, С. 135-138.
{Ivin1985} ru
Yury Koshtyal: ?not ALD

V. D. Ivin, R. M. Levit, A. A. Malkov, E. P. Smirnov. Interaction of methane with the chlorinated surface of carbon fibers. Journal of Applied Chemistry of the USSR. 1985, V. 58, № 3, P. 592-595.
В. Д. Ивин, Р. М. Левит, А. А. Малков, Е. П. Смирнов. Взаимодействие метана с хлорированной поверхностью углеродных волокон. Журнал прикладной химии. 1985, Т. 58, вып. 3, С. 659-661.
{Ivin1985a} ru en

Lahtinen, J. A.; Lu, A.; Tuomi, T. & Tammenmaa, M.
EFFECT OF GROWTH TEMPERATURE ON THE ELECTRONIC-ENERGY BAND AND CRYSTAL-STRUCTURE OF ZnS THIN-FILMS GROWN USING ATOMIC LAYER EPITAXY
J. Appl. Phys., **1985**, *58*, 1851-1853
{Lahtinen1985} en
Hele Savin: Application mentioned here is EL display (as in many papers). The goal is to find optimal crystalline properties for ZnS to improve the efficiency of EL. Not so much information about ALD process itself (temperature 300-500C, thickness 200-410nm, precursors:zinc acetate, ZnCl2, H2S). Suntola San Diego conference paper 1982 mentioned as reference for ALD. The main result here is that the crystal structure of ZnS depends on the growth temperature and source materials.

Miroshnichenko, L. V.; Malygin, A. A. & Kol'tsov, S. I.
Thermal oxidation of silicon carbide with surface modification by the molecular layering method
***Ogneupory,* 1985, *26*, 22-24**
Л. В. Мирошниченко, А. А. Малыгин, С. И. Кольцов. Термоокисление карбида кремния с поверхностью модифицированной методом молекулярного наслаивания. Огнеупоры, 1985, Вып. 2, С. 22-24.
{Miroshnichenko1985} en ru
Cagla Ozgit-Akgun: Thermal oxidation behavior of powdered SiC (avg. grain size of 40-63 um) samples - after they have been subjected to repeated (from 1 to 4 times) alternating treatment with vapors of halides (or oxyhalides) and water (or hydrogen) - were studied. $SiCl_4$, $POCl_3$, $VOCl_3$, $TiCl_4$, and CrO_2Cl_2 were used for the molecular layering of respective oxide layers. Effect of the chemical nature and concentration of the surface oxide layer on its thermal oxidation resistance was investigated by the thermogravimetric method. Treating powdered SiC with vapors of CrO_2Cl_2 increased its resistance during heating to 1500 °C in air by 20-23%. References [16], [20], [21], and [22] are not listed in the ALD-history-evolving-file. These references seem to be related to molecular layering.

Nicolau, Y. F.
SOLUTION DEPOSITION OF THIN SOLID COMPOUND FILMS BY A SUCCESSIVE IONIC-LAYER ADSORPTION AND REACTION PROCESS
Appl. Surf. Sci., **1985**, *22*, 1061-1074
{Nicolau1985} en

Nishizawa, J.; Abe, H. & Kurabayashi, T.
MOLECULAR LAYER EPITAXY
J. Electrochem. Soc., **1985**, *132*, 1197-1200
{Nishizawa1985} en
Hele Savin: They give a weird reference (3rd. in the reference list) J. Nishizawa Oyo Butsuri 53, 516 (1984) as a reference for the ALE. I cannot find this paper from this document. Also Ahonen 1980 paper is given in the references.
In this paper they want to make a difference between ALE and MLE. They explain this difference as follows: they 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. So in practice there is not much difference I would say.
This is a first report on ALD growth of GaAs film (AsH3 and TMG as precursors). The main purpose of this paper is to study if photoepitaxy and MLE can be combined. They found out that this is possible and as a result were able to improve the surface morphology and electrical properties of the film.

Tammenmaa, M.; Koskinen, T.; Hiltunen, L.; Niinistö, L. & Leskelä, M.
Zinc chalcogenide thin films grown by the atomic layer epitaxy technique using zinc acetate as source material
Thin Solid Films, **1985**, *124*, 125-128
{Tammenmaa1985} en
Cagla Ozgit- Akgun: ZnS (ZnO) thin films were deposited on soda glass plates (5 cm x 20 cm) by atomic layer epitaxy (ALE) within the temperature range of 290-360 C using anhydrous zinc acetate (Zn(CH3COO)2) and H2S (H2O). For both ZnS and ZnO, growth rate was slightly dependent on the temperature. Growth rate of ZnO was approx. one-fifth of that of ZnS (rate for ZnS: 5-6.5 nm/min). XRD patterns obtained from various positions along the substrate indicated an uniform crystalline quality. ZnS thin films were highly oriented and they had an excellent crystalline quality, although it could not be determined whether the structure is cubic or hexagonal. The ZnS film thickness decreased from 204 to 199 nm along the sample length, indicating highly uniform thin films over a large substrate area. ZnO thin films were found to be hexagonal - (100) and (101) reflections appeared in its XRD pattern. A comparison of the film thicknesses and diffraction intensities for ZnS and ZnO suggested that ZnO films have rather poor crystallinity. ZnS films were doped with Mn(II) and Te(III) ions, resulting in yellow and green photoluminescence, respectively. Films doped with Mn showed a much higher emission intensity.

S.A. Trifonov, A.A. Malygin, V.A.Nikolaev, M.V.Vinogradov, V.A.Yakovlev. Thermo-oxidative stability of PA-6 with phosphorus-containing additives in the surface layer (in Russian). Plasticheskie massy. 1985, I. 6, P. 21-23.
С. А. Трифонов, А. А. Малыгин, В. А. Николаев, М. В. Виноградов, В. А. Яковлев. Термоокислительная стойкость ПА-6 с фосфорсодержащими добавками в поверхностном слое. Пластические массы. 1985, № 6, С. 21-23.
{Trifonov1985} ru

A.A. Malygin, S.A. Trifonov, S.I. Kol’tsov, M.V.Vinogradov, V.V. Barsova. Temperature resistance of epoxy - phenolic polymers with oxygen phosphorus-containing additives in the surface layer (in Russian). Plasticheskie massy, I 8, 1985, C. 15-17.
А.А. Малыгин, С.А.Трифонов, С.И.Кольцов, М.В.Виноградов, В.В.Барсова. Термостойкость фенолформальдегидных и эпоксифенольных полимеров с фосфоркислородсодер-жащими добавками в поверхностном слое. Пластические массы, № 8, 1985, С. 15-17.
{Malygin1985} ru

Oikkonen, M.; Blomberg, M.; Tuomi, T. & Tammenmaa, M.
X-ray diffraction study of microstructure in ZnS thin films grown from zinc acetate by atomic layer epitaxy
Thin Solid Films, **1985**, *124*, 317-321
{Oikkonen1985} en
Cagla Ozgit-Akgun: An XRD study was carried out in order to reveal the microstructure of ZnS thin films (110-1350 nm) grown by ALE (290-330 °C) using anhydrous zinc acetate ($Zn(CH_3COO)_2$) and hydrogen sulphide. The growth these films was reported in {Tammenmaa1985} en. The films were shown to possess a strong preferred orientation (only one intense peak was observed, which can either be cubic (111) or hexagonal (002) reflection). Line profile analysis was applied to XRD patterns. Average crystallite sizes were found to range from 40 to 80 nm depending on film thickness. The relative microstrain in the films was found to be $(1\text{-}2)x10^{-3}$. The results (obtained from ZnS film deposited at 300 °C) were compared to those obtained from ZnS thin films (1) grown by ALE using zinc chloride and hydrogen sulfide at 500 °C, (2) deposited using electron beam evaporation at 190 °C.

Seitmagzimov, A. A.; Pak, V. N. & Kol'tsov, S. I.
Change in potential of anodized aluminum upon its modification with titanium dioxide
***Journal of Applied Chemistry of the USSR,* 1985*, 58(1)*, 85-87.**
А. А. Сейтмагзимов, В. Н. Пак, С. И. Кольцов. Измение потенциала анодированного алюминия при его модифицировании диоксидом титана. Журнал прикладной химии. 1985, Т. 58, вып. 1, С. 92-95.
{Seitmagzimov1985} en ru

G. K. Shevchenko, A. A. Malygin, A. Yu. Rodina, N. V. Maltseva, S. I Kol'tsov. Adsorption parameters and porous structures of products from the interaction of ShSMG silica gel with POCl3 and H2O vapors. Journal of Applied Chemistry of the USSR. 1985, V. 58, №2, P. 212-216.
Г. К. Шевченко, А. А. Малыгин, А. Ю. Родина, Н. В. Мальцева, С. И Кольцов. Адсорбционные свойства и пористая структура продуктов взаимодействия силигагеля ШСМГ с парами $POCl_3$ и H_2O. Журнал прикладной химии. 1985, Т. 58, вып. 2, С. 250-254.
{Shevchenko1985} ru en

Suntola, T. & Hyvärinen, J.
Atomic layer epitaxy
Annu. Rev. Mater. Sci., **1985***, 15*, 177-195
{Suntola1985} en
Riikka Puurunen: This review, which is (to my understanding) the first review article written by Tuomo Suntola, gives an interesting view on the development of ALD from the ALE perspective, and a snapshot of ALE/ALD research in 1985. Early ALE (ALD) 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 UHV MBE reactor, with which the first scientific ALE growth studies were carried out in Tampere. Term "growth rate" is used for the amount of material deposited per cycle ("growth per cycle" is not used). It is noted that in ALE (ALD), only two-dimensional nucleation takes place (assumingly as compared to 3D nucleation in other methods). The on-going modeling of the ZnS process by Pakkanen and co-workers in Joensuu is mentioned. Also so are the plans of in situ mass spectrometry measurements, which are made 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". (I would like to see quantum chemical calculations which would predict the temperature range, where a particular process works!) XRD studies of ZnS by Prof Tuomi and Tanninen are mentioned. 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, which is one third of the value reported for conventional deposition methods, which is an important factor for EL efficiency. It is also mentioned that the substrate material influences the texture of the film. Several oxide ALE processes are mentioned: Al2O3 process from AlCl3/H2O (works at 200-600°C) used to grow ion barrier, dielectric, and passivation film; Ta2O5 reaction mechanism investigation; Al2O3-TiO2 mixture as dielectric; TaxTiyOz mixed dielectric; and ITO (In2O3-SnO2) 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." Also, Suntola and Hyvärinen predict the coming of PEALD: "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."

Postnova, A. M.; Zhdanova, T. N.; Kol'tsov, S. I.

Study of the proton-donor properties of aluminum-containing silica gels synthesized by the molecular stratification method
Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, Volume: 28, Issue: 3, Pages: 69-70, **1985**
А. М. Постнова, Т. Н. Жданова, С. И. Кольцов. Изучение протонодонорных свойства алюминийсодержащих силикагелей, синтезированных методом молекулярного наслаивания. Известия высших учебных заведений, Химия и химическая технология, 1985, Т. 28, вып. 3, С. 69-70.

{Postnova1985} ru

A. A. Abakumov, Yu. K. Ezhovskii, S.I. Koltsov. Chemical assembly of a silicon-nitrogen layer on silicon. Journal of Applied chemistry of the USSR. 1985, V. 58, I. 8. P. 1718-1721.
А. А. Абакумов, Ю. К. Ежовский, С. И. Кольцов. Химическая сборка кремнийазотного слоя на кремнии. Журнал прикладной химии. Т. 58, вып. 8, С. 1867-1870.
{Abakumov1985} ru en
Riikka Puurunen: Silicon nitride on Si (111) by SiCl4 and NH3 in up to 40 cycles at 250, 300, 400, 450°C. Thickness up to 8 nm, GPC up to 0.2 nm. Saturation curves presented; SiCl4 saturates faster than NH3 (time scale is minutes). The authors conclude that "chemisorption of ammonia is the determining step in layer growth" and that "monomolecular growth of silicon-nitride layers in this system is possible at T_S = 450-500°C".
Jonas Sundqvist: I need to get hold of this paper. I could not grow SiN using that precursor combination 400 to 500°C. I used an ASM A412 Large Batch ALD 250 mTorr, 10-60s SiCl4 and NH3 pulses on TiN.

P. M. Vainshtein, S. I. Kol'tsov, Yu. K. Ezhovskii. Rearrangement reactions on the surface of modified silicas. Journal of Applied Chemistry of the USSR. 1985, V. 58, I. 4, P. 670-674.
П. М. Вайнштейн, С. И. Кольцов, Ю. К. Ежовский. Реакции перегруппировки на поверхности модифицированных кремнеземов. Журнал прикладной химии, 1985, Т. 58, вып. 4, С. 740-745.
{Vainshtein1985} ru en
Simon Elliott: Detection of surface species after treatment of silica with chlorosilanes. Conclude that exchange reactions are not significant. No explicit reference to ALD, although the reactions considered would be the desired growth reaction and a deleterious etching side-reaction in ALD.

Yu. K. Ezhovskii, A. L. Egorov, S. I. Kol'tsov. Chemical Preparation of Silicon and Titanium Oxides. Russian Journal of Physical Chemistry, 1985 V. 59, I. 3, P. 391-392.
Ю. К. Ежовский, А. Л. Егоров, С. И. Кольцов. Исследование процессов химического получения оксидов кремния и титана. Журнал физической химии, 1985, Т. 59, вып. 3, С. 683-686.
{Ezhovskii1985} ru en
Cagla Ozgit-Akgun: Authors studied the effects of substrate temperature and vapor pressure of gaseous reactants on the characteristics of TiO_2 (and SiO_2) growth on GaAs (110) (just before the deposition GaAs was etched to remove surface oxide layer) using $TiCl_4$ (or $SiCl_4$) and H_2O. The processes described in this article are definitely ALD: "...alternate treatment of the surface with water vapor and with metal halide vapor and removal of the excess of reagent and of the reaction products at each stage…" The growth was monitored by an ellipsometer. Authors plotted film thickness as a function of number of cycles, and showed that growth of both TiO_2 and SiO_2 at 150 °C and 250 °C are linear. They further defined the parameter "growth constant, d_0" as the increment of thickness produced by one cycle. d_0 was then plotted, for both TiO_2 and SiO_2, as a function of substrate temperature for different vapor pressures of reagent, from which authors commented on the reaction mechanism. They stated that at high residual pressures (p > 10 Pa) and low temperatures (< 400 K) the layers grow mainly by the interaction of the reagents in the physisorbed state. On the other hand, for both TiO_2 and SiO_2, d_0 at T = or > 500 K is close to the thickness of a monolayer of the respective oxide and only weakly dependent on pressure, suggesting the formation of oxide layers via molecular layer mechanism. This paper resembles Egorov1984_en.

A. V. Krasnobryzhii, E. P. Smirnov. Synthesis of chrome oxide structure on the surface of technical-grade carbon. Journal of Applied Chemistry of the USSR, 1985. V. 58, №. 2, P. 227-230.
А. В. Краснобрыжий, Е. П. Смирнов. Синтез хромоксидной структуры на поверхности технического углерода. Журнал прикладной химии, 1985. Т. 58, вып. 2, С. 266-270
{Krasnobryzhii1985} ru en

Evdokimov A.V. Synthesis of multicomponent elementoxides monolayers on the surface of silica and features of their structure and cross-functional interactions : Diss . ... Candidate . Chem. Science / TRL - L. , 1985 . - 193 p. (EAF) Евдокимов А.В. Синтез многокомпонентных элементоксидных монослоев на поверхности кремнезема и особенности их строения и межфункциональных взаимодействий: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1985. - 193 с. (ДСП)
(no code)

Seytmagzimov AA Chemical modification of the surface properties of the anode and aluminum oxides and titanium : Diss . ... Candidate . Chem. Science / TRL - L. , 1985 . - 177 p. (EAF) Сейтмагзимов А.А. Химическое модифицирование и поверхностные свойства анодных оксидов алюминия и титана: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1985. - 177 с. (ДСП)
(no code)

Vitkovskaja TA Surface modification by the molecular layering method of photo phosphor : Diss ... Candidate . Chem. Science / TRL , Institute of phosphors and high-purity substances. - L. , 1985 . 158 pp . (EAF) Витковская Т.А. Модифицирование поверхности фотолюминофоров методом молекулярного наслаивания: Дисс…канд. хим. наук/ ЛТИ, ВНИИ люминофоров и особо чистых веществ. – Л., 1985. 158с. (ДСП)
(no code)

G. V. Anikeev, Yu. K. Ezhovskii, A. I. Klusevich. Chemical deposition of layers of aluminium oxide on silicon. Journal of applied chemistry of the USSR, 1986, V. 59, I. 12, P. 2431-2434.
Г. В. Аникеев, Ю. К. Ежовский, А. И. Клусевич. Исследование химической сборки слоев оксида алюминия на кремнии. Журнал прикладной химии, 1986, Т. 59, вып. 12, С. 2661-2664.
{Anikeev1986} ru en
Maria Berdova: The work describes the principle of molecular layering (citations are mainly to Aleskovsky works). Al2O3 growth with aluminium bromide and water precursors on Si (111) at 370-670 K is shown. Thickness is evaluated by ellipsometry.

A. A. Abakumov, Yu. K. Ezhovskii, S. I. Kol'tsov. Study of thin silicium-nitrogen layers by XPS and IR-spectroscopy. Zh. Prikl. Khimii, 1986, V. 59, I. 11, P. 2613
А. А. Абакумов, Ю. К. Ежовский, С. И. Кольцов. Исследование тонких кремнийазотных слоев методами рентгеноэлектронной и ИК спектроскопии. Журнал прикладной химии, 1986, Т. 59, вып. 11, С. 2613
Fulltext: VINITI AN SSSR, № 900 B-96 10.02.1986.
{Abakumov1986} ru
Maria Berdova: In this work silicon-nitrogen films were chemically deposited on different semiconductors. The films were obtained by sequence of ammonia and silicon tetrachloride pulses. The chemical composition depended on deposition temperatures.
Jonas Sundqvist: to my experince working with doping TiN with silicon to grow TiSiN, SiCl4/NH3 ALD is a self-terminating ALD process at temperatures </= 500°C (probably also much higher). You can conformally dope but not grow an actuall film. Are there any details on the experimental for this study? What is the process temperature?

Brykalov, A. V.; Kol'tsov, S. I.; Koval'kov, V. I. & Postnova, A. M.
The acidic properties of silochrom S-120 coated with various oxides by molecular layering
Russ. J. Phys. Chem., **1986***, 60*, 564-566
А. В. Брыкалов, С. И. Кольцов, В. И. Ковальков, А. М. Постнова. Исследование кислотных свойств силохрома С-120, модифицированного элементоксидными слоями методом молекулярного наслаивания. 1986, Т. 60, вып. 4, С. 950-952.
{Brykalov1986} en ru
Ruud van Ommen: The authors study molecular layering / ALD of silica gel and silochrom (a porous type of silica used in chromatography) with TiCl4, AlCl3, and ZiCl2; water is used as the oxidizer. For TiCl4 they go up to four ALD cycles, and show that the process is rather linear in the amount of Ti deposited. For the other two precursors, only 1 cycle is studied. The goal of the study is to show that molecular layering / ALD can be used to modify the acidity of the silica sorbents. The acidity does not just depend on the type of coating, but also on the coating thickness.

P. M. Vainshtein, Yu. K. Ezhovskii, S. I. Kol'tsov Effect of the Thickness of Oxide Layer on the Activity of Silanol Groups on the Surface of Monocrystalline Silicon. Russian Journal of Physical Chemistry. 1986, V. 60, I. 3, P. 414-417.
П. М. Вайнштейн, Ю. К. Ежовский, С. И Кольцов, Влияние толщины оксидного слоя на активность силанольных групп поверхности монокристаллического кремния. Журнал физической химии, 1986, Т. 60, вып. 3, С. 701-705.
{Vainshtein1986} ru en

Doi, A.; Aoyagi, Y. & Namba, S.
Stepwise monolayer growth of GaAs by switched laser metalorganic vapor phase epitaxy
Appl. Phys. Lett., **1986***, 49*, 785-787
{Doi1986} en
(Riikka Puurunen: I have listed this; may be other than ALD, too---should be checked)

Goodman, C. H. L. & Pessa, M. V.
Atomic layer epitaxy
J. Appl. Phys., **1986***, 60*, R65-R81
{Goodman1986} en
Riikka Puurunen: An interesting view on ALD, written by persons other than the inventors of the method. Written in the view of increased interest of ALE (ALD) films in "low-dimensional" structures, with thicknesses in the range 1-10 nm.
- In ALE, two modes are distinguished, the MBE-type growth based on heated elemental source materials, and the CVD-type growth, relying on sequential surface exchange reactions between compound reactants. ALE (ALE) should not be considered as a new method but as a special mode of these well-established growth techniques.
- It is concluded that ALE (ALD) "is a self-regulatory process which, in its simplest form, produces one complete molecular layer in an operational cycle." In my view, statements like this bring the names, ALE and ML, very close to each other.
- The term "growth per cycle" (GPC) seems to have been introduced for the first time in this work, as Goodman and Pessa stated: "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." (To my understanding, the term GPC started to become more widely adopted from the modeling works, Chem. Vap. Deposition 9 (2003) 249-257 and 327-332.)
- The early scientific investigations of ALD growth at the Tampere University of Technology in 1979-1980 are mentioned.
- Interestingly, reference is given (Ref. 7) to works by Herman et al., where weakly bound states and partial re-evaporation are used, requiring careful control of the timing. It is noted that this represents a considerable departure from the ideal ALE model, but "does retain the basic growth per cycle that is the distinctive feature of ALD". To me, this gives good caution when reading the cited works, as I assume always the target in ALE to be saturation.
- The modeling by Pakkanen et al. for ZnCl2/H2S is commented on, the only publication still being the 1984 proceedings.
- Somewhat surprisingly, it is noted that for ALE, "a flat perfect substrate is needed". At that time, then, film conformality on 3D topography has not been considered.
- A list is given of the materials grown by ALE by that time (not listing those made under the name ML, of course, as there was no info on them yet): cadmium telluride (CdTe), cadmium manganese telluride [Cd_(1-x)Mn_xTe], gallium arsenide (GaAs), zinc sulfide (ZnS), zinc telluride (ZnTe), and oxides: ZnO from Zn(CH3COO)2 + H2O; Ta2O5 from TaCl5/H2O; Al2O3 from AlCl3/H2O (at ca. 450°C), mixture of Al2O3-TiO2, and SnO2 from SnCl4/H2O; and ITO. Detailed review is given of the results for CdTe, Cd_(1-x)Mn_xTe, GaAs and ZnS.
- Perhaps the most interesting part of this review to me is the outlook of future extensions of ALE to other materials. Following the general schemes metal halide + H2O or O2 --> oxide; metal halide + H2S or sulfur vapor --> metal sulfide; metal halide + H2Se or selenium vapor --> metal selenide, one can preview a long list of new compounds, as many chlorides will most likely will work in ALE similarly as the chlorides already used: CdCl2, HgCl2, CaCl3, InCl3, SiCl4, GeCl4, ZrCl4, NbCl5, and also other transition metal halides, e.g. FeCl3. Thus, the processes for the future high-k materials were largely foreseen. Metalorganics (TMG, TEG, TMA) are commented upon as new development, but a note of caution is given related to the thermal stability. NH3, PH3, AsH3 are also pointed out as pathways to nitrides, phosphides, and arsenides. Finally, more complex materials are envisioned, such as ferrites with special magnetic properties, multilayers with ferrites combined with non-magnetic films giving "two-dimensionality" on magnetic properties. Also the growth of elements such as silicon is foreseen.

Tsvetkova, M.N. and Malygin, A.A., Strengths of Glass Microspheres with Ultrathin Oxide Coatings. Journal of applied chemistry of the USSR, 1986, V. 59, no. 11, pp. 2279–2281
М. Н. Цветкова, А. А. Малыгин. Прочность стеклянных микросфер с ультратонкими элементоксидными покрытиями. Журнал прикладной химии, 1986, Т. 59, Вып. 11, С. 2472-2475.
{Tsvetkova1986} ru en
Cagla Ozgit-Akgun: Authors deposited oxides of Ti, Cr and V on glass microspheres (using $TiCl_4$, CrO_2Cl_2 and $VOCl_3$), with an ultimate aim of strengthening the glass, which suffer from defective surfaces (cracks, inhomogeneities and inclusions arising during manufacture) acting as failure sources. The ALD or "molecular layering" process was referred in the introduction part without mentioning its name: "One can use the reactivity of the groups in a solid for simple reagents in chemical modification of the surface to a given composition and structure, which provides for deliberate control of physicochemical properties [4]." Ref. 4 is: V. B. Aleskovskii, Solid-Compound Stoichiometry and Synthesis [in Russian], Nauka, Leningrad (1976), 140 pp. I couldn't find this reference among the ones listed in this document. In the experimental section, authors referred to Ref. 4 and 5 ("A standard method was used [4, 5].") instead of explaining the details of ALD (or ML) processes. (Ref 5 is {Koltsov1969a} en ru.) Single cycle deposition of the metal oxides on glass microspheres increased the strength by 40-60%. The strength increased more slowly as the number of layer became larger. The increased strength was due to the vertices of submicrocracks being healed by the barrier oxide groups.

V. B. Aleskovskii, V. E. Drozd, V. I. Gubaidullin, A. I. Romanychev. Deposition of A2B6 thin solid films with constant composition by method of chemical assembly. Dokl. Akad. Nauk SSSR, serija: Khimija. 1986. V. 291, P. 136-139.
В. Б. Алесковский, В. Е. Дрозд, В. И. Губайдуллин, А. И. Романычев. Получение тонких пленок соединений постоянного состава типа A^2B^6 методом химической сборки. Доклады АН СССР, серия: Химия, Т. 291, С. 136-139.
{Aleskovskii1986} ru

Herman, M. A.; Jylhä, O. & Pessa, M.
Growth mechanism in atomic layer epitaxy. 2. A model of the growth process of CdTe on CdTe(111) substrates
Cryst. Res. Technol., **1986***, 21*, 969-974
{Herman1986b} en
Simon Elliott: Expression proposed for surface coverage during ALD of CdTe as a function of incident flux, evaporation rates and pulse times. No evaluation of sample data or validation against experiment. Interesting proposal of a "transition region, 3-4 ML thick, intermediate between chemisorbed and bulk-like film", in which diffusion and evaporation are more favourable. This idea resonates with very recent first principles calculations on oxide ALD.

Herman, M. A.; Jylhä, O. & Pessa, M.
Growth mechanism in atomic layer epitaxy. 1. RE-EVAPORATION OF Cd AND Te FROM CdTe(111) SURFACES MONITORED BY AUGER-ELECTRON SPECTROSCOPY
Cryst. Res. Technol., **1986***, 21*, 841-851
{Herman1986c} en
Timo Sajavaara: This paper reports the differences of re-evaporation rates of Cd and Te on bulk Cd or Ca films and CdTe-surfaces as measured with AES. The studied films were deposited under UHV condition using Knudsen-like effusion cells.
The re-evaporation rates were found to be two orders of magnitude smaller for the region near the substrate-overlayer interface than in the amorphous buld Cd or Te.

Herman, M. A.; Pessa, M.; Suntola, T. & Nishizawa, J.-i.
Molecular layer epitaxy
J. Electrochem. Soc., **1986***, 133*, 1269-1269
{Herman1986} en
Riikka Puurunen: This is an interesting comment-response pair. Herman, Pessa and Suntola commented on an article written by Nishizawa, Abe and Kurabayashi (J. Electrochem. Soc. 132 (1985) 1197-1200), and Nishizawa responded. Nishizawa et al. have in their 1985 paper called their technology "molecular layer epitaxy (MLE)", making thus a distinction between their technique and ALE. Herman, Pessa and Suntola describe how there are two alternative modes of operation of ALE (basically, from elemental reactants or from chemical compounds), and how the MLE of Nishizawa et al. "follows in every detail the procedure of the original ALE model (mode ii)," and that they "feel no need for renaming ALE." Nishizawa admits that, with some exceptions, "MLE is the same method as mode ii of ALE," but maintains that a separate name, MLE, should better be used. Nishizawa says for example that "we have no intention to ignore what you have achieved with your idea," justifying the use of MLE with that "there is no state in which an atomic layer is adsorbed on the surface" and that "we feel … that the difference between the real phenomena and the name of "ALE" is too large."

Horikoshi, Y.; Kawashima, M. & Yamaguchi, H.
LOW-TEMPERATURE GROWTH OF GaAs AND AlAs--GaAs QUANTUM-WELL LAYERS BY MODIFIED MOLECULAR-BEAM EPITAXY
Jpn. J. Appl. Phys., Part 2, **1986***, 25*, L868-L870
{Horikoshi1986} en
Hele Savin: They claim to invent a new method called "MEE Migration-Enhanced Epitaxy" and don't refer to any ALD papers probably since they are not aware of them. In principle RHEED is used to characterize the monolayer growth. They grow GaAs layers both at 580C and 300C with thickness up to 4000 monolayers. Is this ALD? They report that if the "pulse" length is not sufficient to fulfill all surface sites, island growth appears while if the number of Ga atoms is equal to the surface sites, monolayer growth takes place. They do not report what happens if they have excess of Ga atoms. So, if they do not know about ALD, does it mean they also invent this independently? Benefts mentioned as compared to MBE: sharp doping profiles, conformality on finely structured surfaces.

Malygin, A. A.; Dergachev, V. F. & Kol'tsov, S. I.
The concentration factor in production of vanadium-containing silica gel
Journal of applied chemistry of the USSR*, 1986, 59(2)*, 392-394
А. А. Малыгин, В. Ф. Дергачев, С. И. Кольцов. Концентрационный фактор при получении ванадийсодержащего силикагеля. Журнал прикладной химии, 1986, Т. 59, вып. 2, С. 430-432.
{Malygin1986a} ru en

Petrova, L. I.; Malkov, A. A. & Malygin, A. A.
Reaction of TiCl4 and H2O Vapor Products with A Mica Surface
Journal of applied chemistry of the USSR*, 1986, 59*, 6, 1131-1133
Л. И. Петрова, А. А. Малков, А. А. Малыгин Исследование продуктов взаимодействия паров TiCl4 и H2O с поверхностью слюды. Журнал прикладной химии, 1986, Т. 59, вып. 6, С. 1224-1227.
{Petrova1986a} ru en
Robin Ras: This publication concerns the deposition of titanium oxide (TiCl4/H2O process at 200°C) on mica particles (more specifically on muscovite). Mica belongs to the family of lamellar aluminosilicates, and the powder has high surface area. Deposition on both dry and wet powder were carried out. The Ti content per unit surface was higher on dry powder than on wet powder, because the dry powder had significant breakdown of lamellar structure. Up to ten cycles were deposited, and film growth occurred linearly. It was noticed that chlorine remained present after deposition.

Tammenmaa, M.; Leskelä, M.; Koskinen, T. & Niinistö, L.
ZINC-SULFIDE THIN-FILMS DOPED WITH RARE-EARTH IONS
J. Less-Common Met., **1986**, *126*, 209-214
{Tammenmaa1986} en
Bechelany: The paper by Tammenmaa et al. describes the synthesis of zinc sulfides thin films doped with rare earth ions using atomic layer epitaxy. The authors show that the crystallinity of the thin film changed as the functions of the zinc source and the growth temperature. The films doping could be controlled within large limits by the pulsing technique. This paper does not give a lot of details about the synthesis process but it focus on the luminescence properties of these thin films.

Tischler, M. A.; Anderson, N. G. & Bedair, S. M.
Ultrathin InAs/GaAs single quantum well structures grown by atomic layer epitaxy
Appl. Phys. Lett., **1986**, *49*, 1199-1200
{Tischler1986c} en
Bechelany: This paper reports the synthesis of extremely thin InAs/GaAs single quantum well structures by ALE. The wells were 2 and 4 InAs monolayers thick. Again the same set up as in the “Journal of Crystal growth 77 (1986) 89-94” has been used to growth the III-V compound thin film. In this paper, the spatial thickness uniformity has been studied on large sample (1.5 cm on a side). The photoluminescence measurement shows that ALE has the capacity to grow uniform, high quality material with excellent control of layer thickness and interface abruptness on large substrates.

Tischler, M. A. & Bedair, S. M.
Growth and characterization of compound semiconductors by atomic layer epitaxy
J. Cryst. Growth, **1986**, *77*, 89-94
{Tischler1986} en
Bechelany: This paper by Tischler et al. describes the synthesis of III-V compound thin films using atomic Layer epitaxy. This paper gives a very nice introduction about Atomic layer epitaxy and the conditions needed to achieve a monolayer per cycle. The deposition set up is well described. The substrate sits in the rotating part of the susceptor. The susceptor has two openings windows in the fixed part through which the gases flow. The precursor gases impinge on the wafer when the substrate is rotated in the opening. So the wafer is alternatively exposed to precursor gases for the accurate control of the thickness of the thin film. The exposed time to the stream is 0.3 s and the time per cycle is 2.6 s. This paper described as well the mechanism of the selflimiting growth of III-V compound.

Tischler, M. A. & Bedair, S. M.
Self-limiting mechanism in the atomic layer epitaxy of GaAs
Appl. Phys. Lett., **1986**, *48*, 1681-1683
{Tischler1986b} en
Bechelany: The paper described the self-limiting mechanism observed for the growth of GaAs deposited by ALE. The thickness of the deposited films was found to be independent of the mole fractions of the precursors in the gas phase. The same system of deposition as in the “Journal of Crystal growth 77 (1986) 89-94” has been used. The obtained GaAs is single crystal as showed by TEM. This paper is similar to the work reported by the same author in Journal of Crystal growth with a longer explanation of the self-limiting mechanism.

Tischler, M. A. & Bedair, S. M.
Improved uniformity of epitaxial indium-based compounds by atomic layer epitaxy
Appl. Phys. Lett., **1986**, *49*, 274-276
{Tischler1986d} en
Bechelany: At this paper, Tischler et al. synthesized another type of III-V based thin film: the indium based compounds by ALE. Again the same set up as in the “Journal of Crystal growth 77 (1986) 89-94” has been used to grow the thin films and a mechanism of self-limiting has been found which control the thickness deposited per cycle independent of the flux.

Usui, A. & Sunakawa, H.
GaAs atomic layer epitaxy by hydride VPE
Jpn. J. Appl. Phys., Part 2, **1986**, *25*, L212-L214
{Usui1986} en
Gloria Gottardi: The paper provide an interesting example of Atomic Layer Epitaxy of GaAs films accomplished by using a dual-growth chamber reactor. Differently from the standard ALE proposed by Suntola, the alternative adsorption of reactant gas molecules onto the growing surface is not obtained by the sequential introduction of the two precursors in the same reaction chamber (eventually separated by a purging step), but switching the position of the substrate between two separate chambers, each of which contains the specific precursor. The physical separation of the two chambers ensures the separation of the two half-reactions.

Yao, T.
Dynamic Reflection High-Energy Electron Diffraction Observations of the Atomic Layer Epitaxy Growth of Zn Chalcogenides
Jpn. J. Appl. Phys., Part 2, **1986**, *25*, L942-L944
{Yao1986b} en
Gloria Gottardi: The paper is fully focused on the use of the RHEED (reflection high energy electron diffraction) technique to investigate atomic layer epitaxy growth of Zn chalcogenides films. One period of the RHEED intensity oscillation corresponds to a monolayer growth of the crystal. The work demonstrates the power of this tool for an in situ investigation of the growth dynamics, by allowing the measurement of the adsorption times of the different beam fluxes and the calculation of some thermodynamic values relevant to surface kinetics.

Yao, T.
The Effect of Lattice Misfit on Lattice Parameters and Photoluminescence Properties of Atomic Layer Epitaxy Grown ZnSe on (100)GaAs Substrates
Jpn. J. Appl. Phys., Part 2, **1986**, *25*, L544-L547
{Yao1986c} en
Pia Sundberg: This is a XRD and photoluminescence study of ALE grown ZnSe using (100)GaAS as substrates. Of the growth process details only substrate temperature is given (280 °C); the thickness of the films varied between 60 to 350 nm. In conclusion, it was said that thinner than 170 nm films suffered complete tetragonal distortion, while thicker than 170 nm films showed relief from the misfit strain. In thin films the deep emission was said to be prominent while in the thicker films the deep emission became very weak.

Yao, T. & Takeda, T.
Growth process in atomic layer epitaxy of Zn chalcogenide single crystalline films on (100)GaAs
Appl. Phys. Lett., **1986**, *48*, 160-162
{Yao1986} en
Gloria Gottardi: The paper investigates the initial and successive stages of the Atomic Layer Epitaxy growth of Zn chalcogenides films (ZnSe and ZnTe) on a (001) GaAs substrate. The deposition is performed using a conventional molecular beam epitaxy system, where each constituent element was alternatively deposited onto the substrate as molecular beam pulses of Zn, Se and Te_2 from separated sources. In particular the authors’ main purpose is to clarify the initial and successive stages of the growth process by in situ RHEED analyses. What comes out from such investigation is that three-dimensional growth mechanism dominates the initial stage of the epitaxy, while, after the deposition of at least 50 monolayers, the film becomes smooth due to the coalescence of islands on the surface and the establishing of a two-dimensional growth mechanism. This is mainly due to the chemical bond mismatch between the substrate (GaAs) and the overgrowth, which does not favor the two-dimensional growth.
Honestly, even if the authors claims that one atomic layer is grown during the open period of a constituent element, the three dimensional growth appears to me rather far from a real ALD growth mechanism. I’m doubtful about the paper conclusions.

Yao, T.; Takeda, T. & Watanuki, R.
Photoluminescence properties of ZnSe single crystalline films grown by atomic layer epitaxy
Appl. Phys. Lett., **1986**, *48*, 1615-1616
{Yao1986d} en

Jidkov AB Kinetics of heterogeneous synthesis of titanium carbide and nitride from a gas phase on the surface of carbon materials : Diss . ... Candidate . Chem. Science / TRL - L. , 1986 . – 202 Жидков А.Б. Кинетика гетерегенного синтеза карбида и нитрида титана из газовой фазы на поверхности углеродных материралов: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1986. - 202 с. (title translated by Riikka Puurunen)
(no code)

Jukka A. Lahtinen, Electro-optical studies of semiconductor compounds for electroluminescent and laser devices, Doctoral dissertation, Helsinki University of Technology, **1986**, 51 p + 6 publications. Acta Polytechnica Scandinavica, Ph, Applied Physics Series.
(no code)

Lviva TB Chemical modification of the coal from the gaseous phase compounds of vanadium (V), chromium (VI), phosphorus (III) and the study of properties of the obtained adsorbents : Diss . ... Candidate . Chem. Science / TRL - L. , 1986 . - 186 p. (EAF) Львова Т.Б. Химическое модифицирование углей из газовой фазы соединениями ванадия (V), хрома (VI), фосфора (III) и исследование свойств полученных адсорбентов: Дисс. ... канд. хим. наук/ ЛТИ - Л., 1986. - 186 с. (ДСП)
(no code)