

Saint-Petersburg State Technological Institute (Technical University)





Was based in 1828 year by imperial command of Emperor Nicholas I

The origins of ML-ALD in the USSR-Russia: from V. B. Aleskovskii 'framework hypothesis' to precise synthesis of solids

A. A. Malygin

Saint-Petersburg State Technological Institute (Technical University)

Department of Chemical Nanotechnology and materials for electronics

malygin@lti-gti.ru

The fundamental basis of the method of molecular layering

Inventors of the molecular layering method, V.B. Aleskovskii (left) and S.I. Kol'tsov (early 2000)

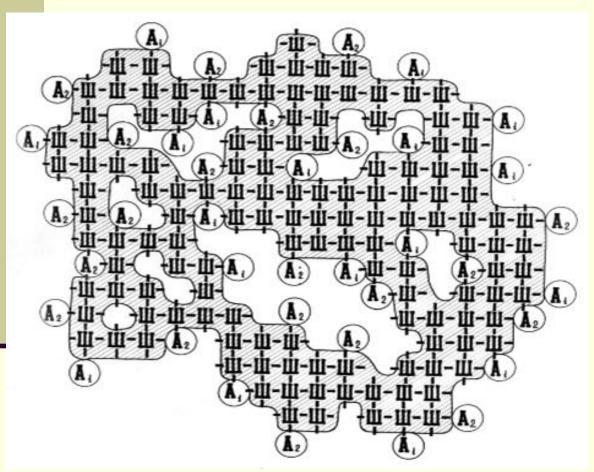
(03.06.1912 - 29.01.2006)



(30.08.1931 - 25.05.2003)



The chemical model of a solid as proposed by V.B. Aleskovskii's "framework" hypothesis (1952, Doctoral dissertation)



Formula of solid chemical model of V.B. Aleskovskii can be represented as

 $[W]_aA$

In the formula stoichiometric coefficient "a" indicates the amount of chemical equivalents "core" per one chemical equivalent of functional groups.

Schematic of the first molecular layering flow-type experimental setup by S.I. Kol'tsov (p. 44)

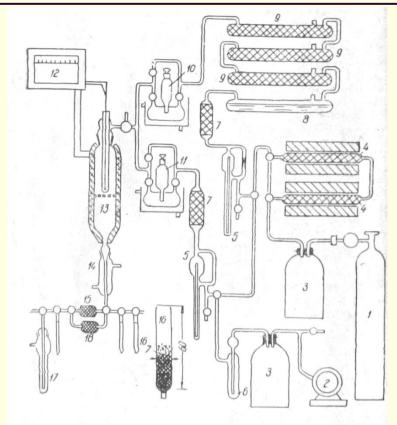


Рис. 9. Установка для изучения реакции разложения CCl_4 на силикагеле I-6алдов с азотом; 2- воздуходурка; 3-буферные емкости; 4- печи с поглотителем для очистки азота от примеси кислорола; 5- реометры; 6- поглотитель CO_6 ; 7.8, 9- поглотитель CO_6 ; 7.8, 9- поглотитель возота от примеси кислорола; 5- реометры; 6- поглотитель CO_6 ; 7.8, 9- поглотители возможное фосфора); 10, 11- "гуськи" с CCl_4 и 1_2O_5 ; 12- регулирующий потенциометр $2\Pi(I-O_9)$; 13- жварцевый реак тор; 14-колодильник; 15-18 — поглотители (гранулированиях цинковая пыль, "шелочно силикатель»; раствор гилорожено бария, гранулированиях трехсерицетая сурьма

Where 1 is the nitrogen tank; 2 is the blower; 3 is the buffer vessel; 4 is the oven with absorber for separating nitrogen from oxygen Impurities; 5 is the rheometer; 6 is the CO₂ absorber; 7,8,9 are H₂O absorbers (silica gel, concentrated sulfuric acid, phosphorus pentoxide); 10,11 are boats with CCl_4 and H_2O ; 12 is the regulating potentiometer; 13 is the quartz reactor; 14 is the refrigerator; and 15 to 18 are absorbers (granulated zinc powder, alkali silica gel, solution of barium hydroxide, granulated antimony sulfide).

(S.I. Kol'tsov, V.B. Aleskovskii, Silica Gel:Its Structure and Chemical Proprties. Goskhimizdat, Leningrad, **1963**, 94 pp (in Russian)).

S. I. Kol'tsov, V. B. Aleskovskii, Silica Gel:Its Structure and Chemical Properties. Goskhimizdat, Leningrad, 1963, 94 pp (in Russian)

In particular, when presenting the data on silica gel modification by reaction of its surface OH groups with different precursors, they noted that this way of producing silica "...with a new set of functional groups and thus with new properties" "...contains great potential because it enables reactions with a new functional groups to be carried out and affords a variety of reactions with organic and organo element compounds which have a great practical importance in the producing new rubber fillers, selective sorbents and catalysts" (pp. 19-20)

And later the authors note that "by removing organic ligands from the silicon-methylated surface of silica gel, and by supplying water to the liberated silicon atoms one arrives at a regenerated hydrated silica matrix..." (p. 28).

Early experiments on creating of structures on the surface of solids by the method of molecular layering

Some of the first publications mentioning the term "molecular layering"

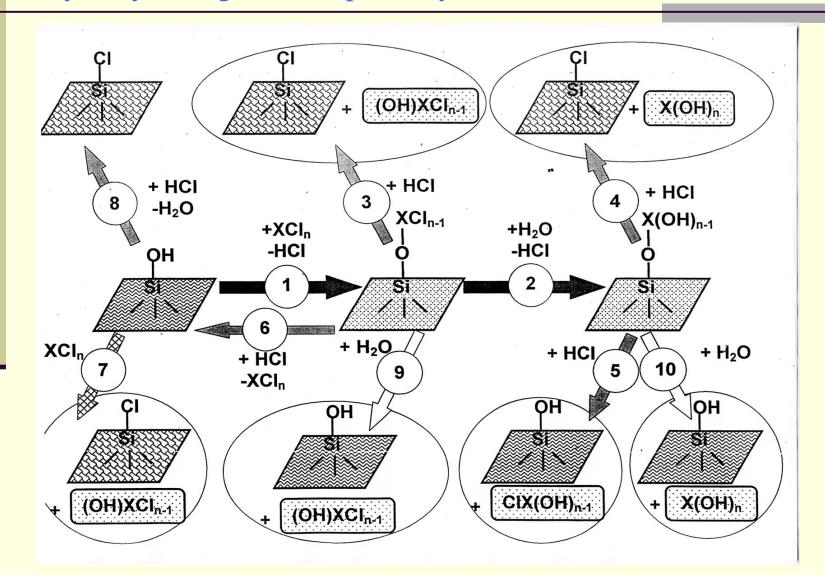
- S. I. Kol'tsov, Synthesis of "multilayered" inorganic polymers, Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad, 1963, p.27. (in Russian).
- S. I. Kol'tsov, Zh. Prikl. Khim. 1965, 38, 1384. [J. Appl. Chem. USSR 1965, 38, 1352.].
- V. B. Aleskovskii, S. I. Kol'tsov, Some aspects of molecular layering reactions. Abstract of Scientific and Technical Conference, Goskhimizdat, Leningrad, 1965, p.67 (in Russian).
- S. I. Kol'tsov, G. N. Kuznetsova, V. B. Aleskovskii, Zh. Prikl. Khim. 1967, 40, 2774. [J. Appl. Chem. USSR 1967, 40, 2644.].

Synthesis of solids with simple (3.1.) and complex (3.2) chemical composition and structure by the method of molecular layering

(S.I. Kol'tsov, 1971, Doctoral dissertation, p. 222)

Possible reaction routes of a silica surface with a

chloride precursors1, 2 - one ML cycle; 3 - 8 - surface chlorination routes; 9, 10 - hydrolytic degradation pathways



Chemical constructing of nanostructures with different chemical composition on the surface of solids

1)
$$2(=Si - OH) + TiCl_4 - = Si - O Ti Cl + 2HCl$$

$$2) = Si - O$$
 Cl $+ 2 H2O - = Si - O$ OH $+ 2HCl$ и т.д.

2) [C]
$$CH_3 + CCl_4 - [C] - C_1 - C_1 - C_1 + 3HCl$$
 и т.д.

1)
$$[Si] - SeH_2 + Cd(CH_3)_2 - [Si] - Se Cd + 2CH_3$$

Molecular layering of chromium oxide layer with using of redox reactions.

$$2(\equiv Si-OH) + CrO_2Cl_2 \rightarrow (\equiv Si-O-)_2CrO_2 + 2HCl$$

$$(\equiv Si-O-)_2CrO_2+ 3/2 H_2 \rightarrow (\equiv Si-O-)_2CrOH+ H_2O$$

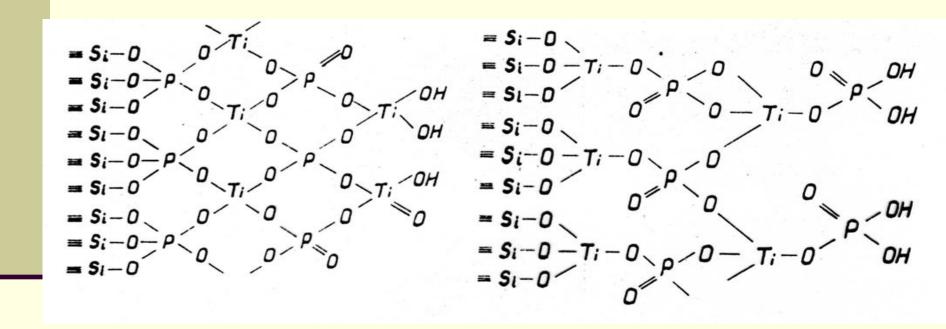
$$(\equiv Si-O-)_2CrOH+CrO_2Cl_2\rightarrow (\equiv Si-O-)_2CrOCrO_2Cl+HCl$$

$$(\equiv Si-O-)_2CrOCrO_2CI+H_2O \rightarrow (\equiv Si-O-)_2CrOCrO_2(OH) +HCI$$

 $(\equiv Si-O-)_2CrOCrO_2(OH)+H_2\rightarrow (\equiv Si-O-)_2CrOCr(OH)_2+1/2H_2O$

The chemical structure of the products of molecular layering of phosphorus and titanium oxides on silica gel

(A.N. Volkova, candidate dissertation, p. 148)

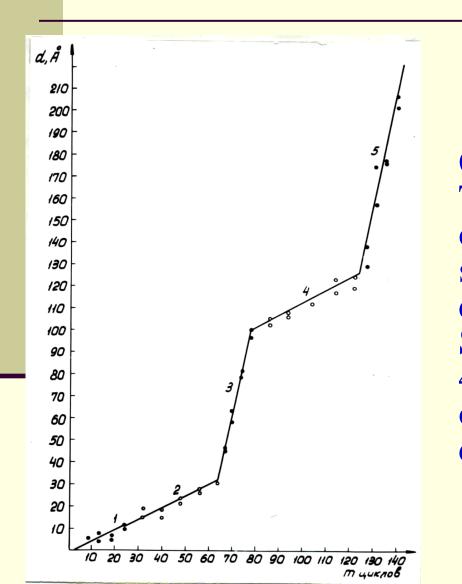


P-Ti-P-Ti

Ti-P-Ti-P

Ellipsometry film thicknes vs. cycle number

(G.V. Sveshnikova, candidate dissertation, 1971, p.145)



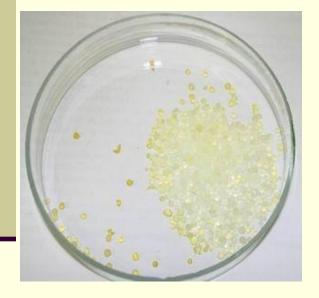
Growth of alternating films of TiO₂ and SiO₂ (nanolaminates) on the surface of single crystal silica (five zone system): 24 cycles of TiO₂ (1) - 40 cycles of SiO₂ (2) - 14 cycles of TiO₂ (3) - 44 cycles of SiO₂ (4)- 18 cycles of TiO₂ (5) (G.V. Sveshnikova, candidate dissertation, p.145)

Fundamental effects in the materials obtained by the ML method

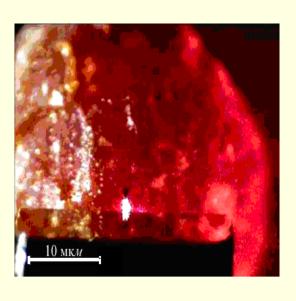
- The "monolayer effect" which observed sharp change in the material properties of the surface after just 1-4 ML cycles had been applied;
- The substrate shielding effect that observed complete physical coverage of a matrix surface after at least 4-6 ML cycles;
- Effects related to multi-component systems;
- Effects related to the mutual structural coordination between a substrate surface and an ML thin film.

The first materials used in industry

Change of the color of silica with vanadium oxide monolayer on the surface when contact with water vapor







Humidity indicator of gases (IVS-1)

Relative water content reduced to 20°C,%	0.05	0.5	1.6÷ 4.5	6÷10	10÷13	15÷45	48÷60	70÷ 95
Concentration	0.008	0.095	0.28÷	1÷1.7	1.7÷2.2	2.5÷	8.2÷	11.9÷
of water			0.76			7.6	10.4	16.2
vapours, mg/l								
Dew point, °C	-60	-40	-30÷	-18 ÷ -13	-12 ÷- 10	-9÷+6	+8÷	+13 ÷
			-20				+11	+19
Grain color	slightly-	lemon-	yellow	light-	dark-	red	brown	black
	vellow			orange	orange			

Moisture capacity of initial and of phosphorus-containing silica gel (P/Ps=0,7; T = 22°C) (reagents are POCl₃ and H₂O),

Sample	The number of cycles of molecular layering	Adsorption capacity, %		
silica gel	0	6		
FS-I	1	20		
FS-II	2	25		
FS-III	3	35		
FS-IV	4	35		

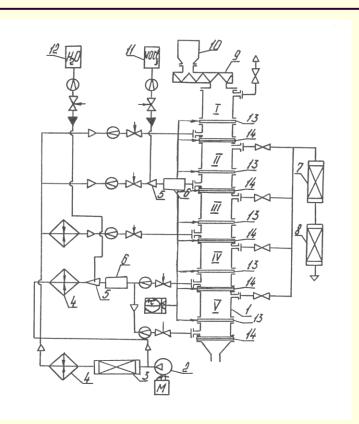
Full capacity on ammonia of silica gel and of sorbent FS-N after different cycles of molecular layering (reagents are $POCl_3$ and H_2O), $T = 22^{\circ}C$

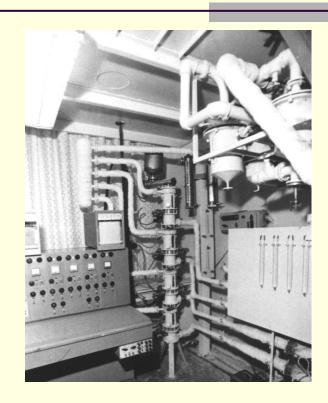
Sample	The number of cycles of molecular layering	Contents of NH ₃ (mmol/g of sorbent)
Silica gel	0	0,60
FS-I	1	1,00
FS-II	2	2,77
FS-III	3	4,51
FS-IV	4	4,16

Aviation flight director with sorbents IVS-1 and FS-1-3 installed



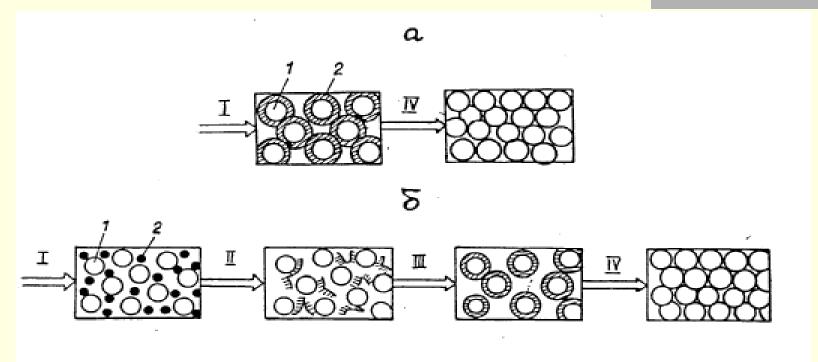
Schematic representation of the apparatus for IVS-1 production (left) and photography (right) of pilot scale ML installation for production of IVS-1 (1982)],





1 - ML reactor; 2 - blower; 3 - dehumidifier; 4 - heater; 5 - spray gun; 6 - mixer; 7, 8 - absorbers; 9 - feeder; 10, 11, 12 - tanks with silica gel, vanadium oxochloride and water; 13 - gas distribution device; 14 - isolating septum

Sintering of doped ceramics powder



Doping of ceramics powder:

- a synthesis of nanolayers by the Molecular Layering Method:
- b mixing of components; 1 particle 2 additive

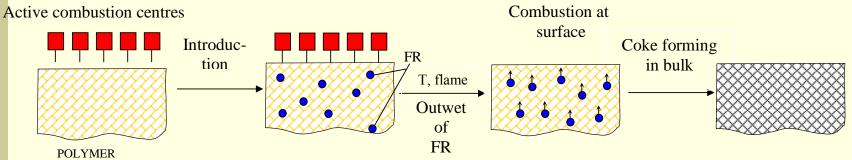
Nanodoped blend for ceramic insulators used in X-ray tubes (2010)



Some new promising directions today developed by the Department of chemical nanotechnology and electronics materials

Reduction of combustibility of polymers

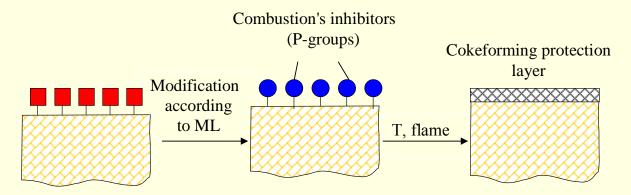
I. Introduction of flame retardants (FR).



II. Surface modification according to ML method

$$n(R-OH) + PCl_3 \rightarrow (R-O-)_nPCl_{3-n} + nHCl$$

where R - organic solid; PCl_3 - modificator



Combustibility of P-containing polymers

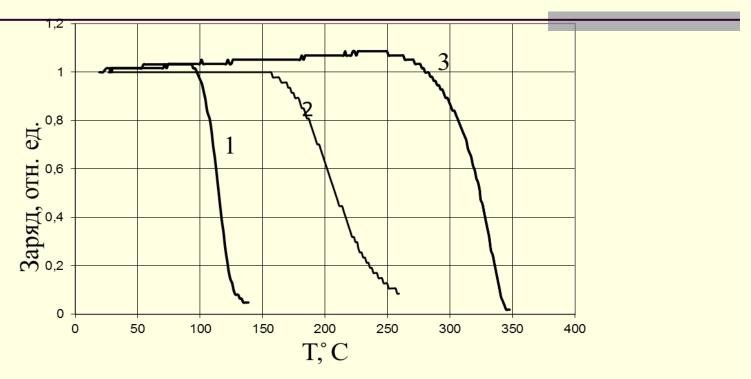
Number of treatment by vapours of PCI ₃ and H ₂ O	Containing of P, mmol/g	Setting fire time, s	Time of indepe-ndent combustion, s	Mass loss, %
PEN - I				
0		8	221	45,0
1	0,12	10	55	8,6
3	0,49	20	40	5,5
5	0,83	55	20	3,9
7	1,18	150	0	2,9
PPS				
0	_	13	1500	97,5
1	0,55	50	25	9,8

Combustibility of PEN-I with P(V)-containing structures on the surface

Sample	Setting fire time, s	Time of independent combustion, s	Mass loss, %
V	10	120	63,0
P	10	55	8,6
VP	8	13	4,0
PV	5	30	6,0
VPV	5	24	5,2
PVP	5	8	4,9
VPVP	150	0	3,3
PVPV	8	12	4,1

The thermal stability of the positive charge on the surface of the fluoropolymer films (F4)

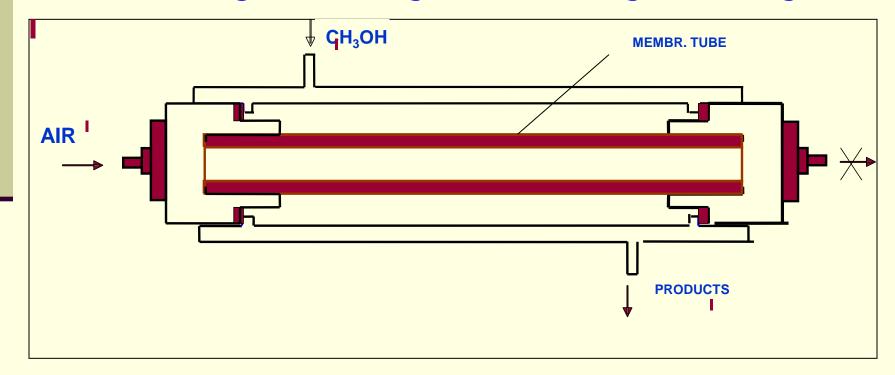
(electret properties)



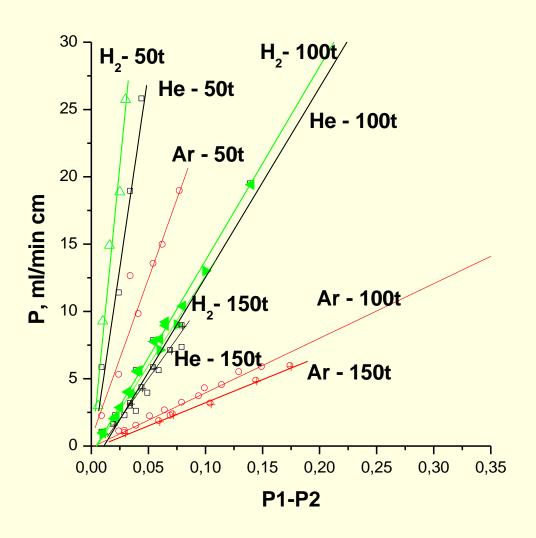
1 – the original film of F4, 2 – modified pairs of TiCl₄ and H₂O, 3 – processed in a plasma with subsequent gas-phase modification of pairs of TiCl₄ and H₂O;

Chemical assembling of V-O-P nanolayers on the surface of membrane catalytic reactor

$$(\equiv Zr-O-)_3VO + PCI_3 \rightarrow (\equiv Zr-O-)_3VO \leftarrow PCI_3$$

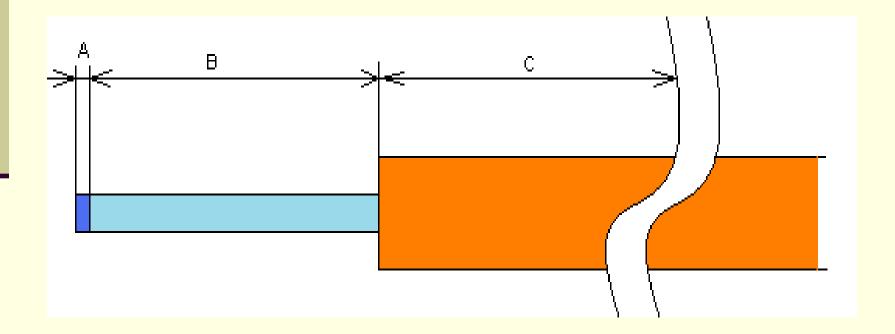


The dependence of the rate of permeability of gases from the pressure differential on the membrane after different number of cycles ML titanium oxide nanolayer

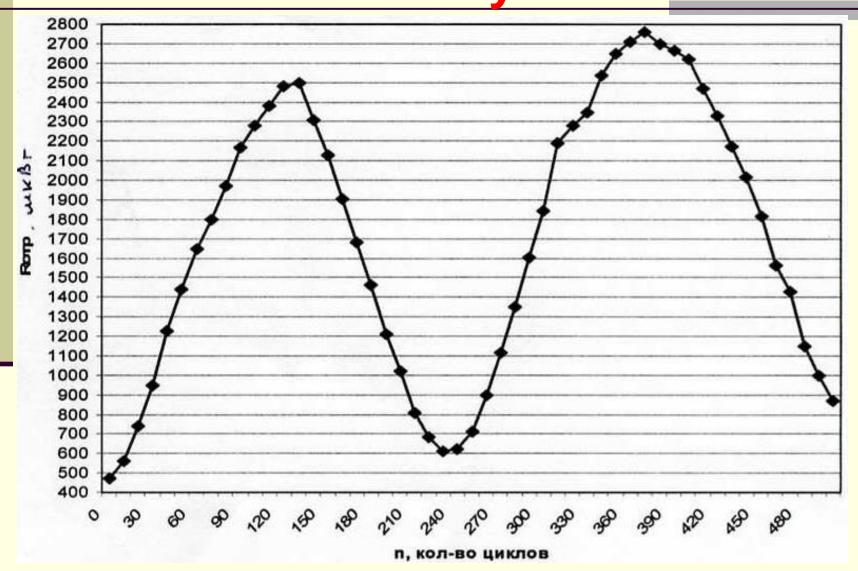


Nanotechnology ML in the creation of fiberoptic sensors (FOS)

Diagram of the FOS element
A – functional nano-coating; B – quartz optical fiber; C - optical fiber with a polymer coating)



The magnitude of power of the reflected light depending on the number of cycles ML



A flow-vacuum automated system for deposition of functional thin films on quartz fibers used for manufacturing of fiber-optic sensors (2011)



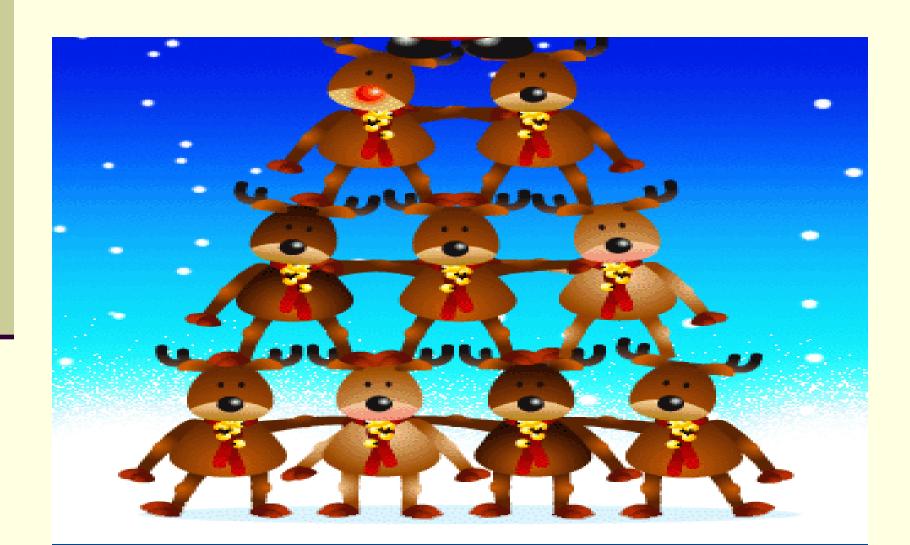
Project of a new flow-vacuum ML unit "Ales-1" for the manufacture of supercapacitor components (joint venture between SPbSTI and "Chemical Assembly of Nanomaterials", LLC) (2014)



The main centers of ML-ALD in Russia

- Saint-Petersburg State Technological Institute (Technical University),
- Department of Chemical Nanotechnology and materials for electronics (over 60 years);
- Saint-Petersburg State University, Department of Chemistry of Solid (over 30 years);
- Moscow Physical-Technical Institute (State University), Department of General chemistry and Laboratory of functional materials and structures for nanoelectronics (over 10 years)

Thank you very much for attention!



Additions

The first candidate dissertations in ML

- S.I. Kol'tsov, 1963, The study of interaction of carbon tetrachloride with silica gel, LTI by Lensovet
- G.N. Kuznetsova, 1965, Study of a reaction products between hydrated silica and metal ions by IR spectroscopy, LTI by Lensovet
- A.N. Volkova, 1969, Interaction of some chlorides with silica gel reaction of molecular layering, LTI by Lensovet
- G.V. Sveshnikova, 1971, Synthesis and study of thin oxide layers on the silicon surface, LTI by Lensovet
- R.R. Raczkowskii, 1972, Synthesis and study of thin oxide layers on the surface of single-crystal silicon, LTI by Lensovet
- A.A. Malygin, 1973, Interaction of oxychlorides of vanadium, chromium and phosphorous with silica gel - reaction of molecular layering, LTI by Lensovet
- V.M. Smirnov, 1973, Synthesis and activity study of a thin oxide layers on the silica gel surface, LTI by Lensovet
- T.V. Tuz, 1974, Synthesis and stability of thin oxide layers on the silica gel surface, LTI by Lensovet
- E.P. Smirnov, 1974, Synthesis of carbon and titanium oxide layers on carbon surface by the molecular layering method, LTI by Lensovet

Some of the important of Doctoral dissertations in ML

- V. B. Aleskovskii, 1952, Framework hypothesis and experience the preparation of certain active catalysts, LTI by Lensovet
- S. I. Kol'tsov, 1971, Synthesis of solids by the Molecular Layering Method, LTI by Lensovet
- V.N. Pak, 1982, Element oxide polyhedral structure and physicochemical properties of the surface oxides, LTI by Lensovet
- D. Damyanov, 1988, Growth by molecular layering of a catalytically active phase on the oxide surfaces, Burgas Institute of Technology, Bulgaria
- A.A. Malygin, 1991, Theoretical and experimental bases of surface modification technology of dispersed and porous materials by the molecular layering method, SPbSTI
- V.M. Smirnov, 1994, Chemistry of surface chemical compounds of polydioxide silica (dispersed silica gel), SPbSU
- A.P. Alekhin, 1999, Chemical and technological bases of low temperature interphase boundaries formation between insulator and semiconductor, Research Institute of Physical Problems by N.F. Lukin (Moscow, Zelenograd)
- Y.K. Yezhovskii, 2002, Correlation analysis in surface chemistry of solids and matrix synthesis of nanostructures, SPbSTI
- V.B. Kopylov, 2007, Chemical structure and the role of electron-excited states in the properties of oxides, SPb State Pedagogical University
- V.P. Tolstoy, 2009, Synthesis of inorganic nanolayers using "layer by layer" approach at the solid-liquid interface, SPbSU