Санкт-Петербургский
Государственный
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ML-ALD seeks its niche in education, science and application

V. Drozd (SPbSU).

Helsinki
Baltic ALD 2014

The main principles of ML from S.I. Kol’tsov doc.n. thesis: “Synthesis of solids by Molecular Layering (ML) method, 383 p., Leningrad, 1971.

1. Reproductive synthesis – chemical build up of solid states – prescribed and adjusted compound composition and controlled chemical structure should be build upon irreversible during synthesis reactions of functional groups on the surface of solid state with molecules of low-molecular matter. At that time they have not react one to another that exclude parallel uncontrolled reactions in gas or liquid phase out of solid state surface.

2. Chemical build up of solid states should be carried out by multiple alternation of two or several reactions on the surface of substrate, nucleus which must be held in given sequence so that in result of each of them only one monolayer of a new functional groups will attach to surface and there chemical composition should be determined by nature of low-molecular matter been used. After reaction with functional groups of substrate they produced chemical bonds with under layer and thus joined to solid substrate as a new monolayer of structural units. These structural units as a part of low-molecular matter must contain atoms or groups of atoms which should be able to react and chemically bond in the next irreversible reaction with other low-molecular matter a new corresponding functional groups which must be able react in the next stage of synthesis. Each next reaction should be occur only after completion of previous reaction. On each stage of such process a new structural units will produce a new solid state in step-by-step manner. After all substrate may be moved off by chemical or mechanical way.

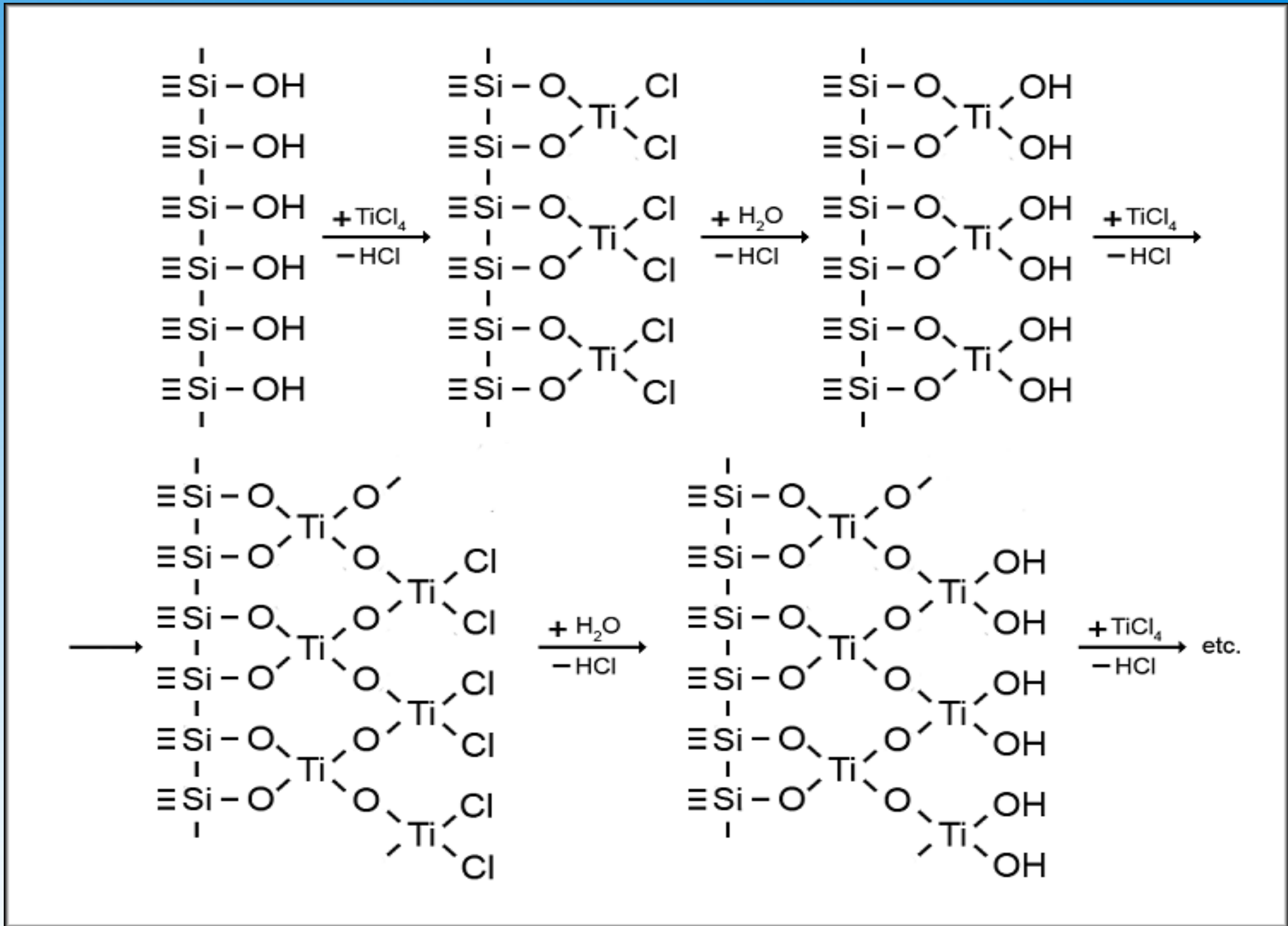
3. Convenience of solid state surface for chemical build up from “construction units” determined as in epitaxy by some structural conformity but in main part by presence of necessary amount of functional groups of desired chemical structure. Concentration and reciprocal position of these groups on the surface of initial substrate and on the surface of a grown new layer determined the role of a surface as a matrix on each stage of Molecular Layering. This process permits crosslinking of new attached atoms to produce 3D lattice of synthesized solid state.

Consequences from above:

1. Fulfil the necessary amount of cycles of Molecular Layering reactions it is possible to synthesize a layer, film of solid state of necessary thickness with accuracy of one monolayer.

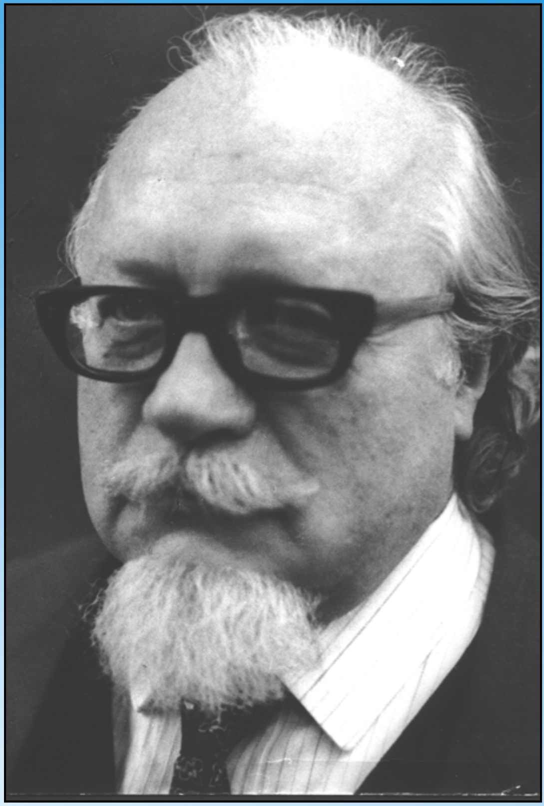
2. In a way of employing the different low-molecular compounds in a different stages of Molecular Layering it is possible to cover surface by one or few monolayers of one composition in adjusted sequence with monolayers of structural units of other chemical composition. That provides deposition of different chemically bonded atoms in a prescribed structure.

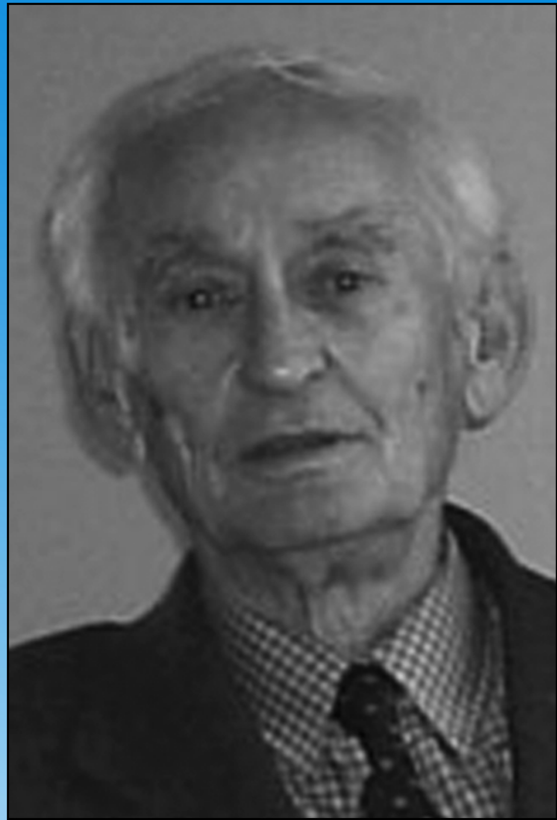
2D Scheme of Molecular Layering of TiO2 on SiO2 surface by S.I.Kol'tsov



Silicon atoms are normally 4 bonded, dotted vertical lines show border of substrate surface

World first Soviet inventors of Molecular Layering (ML) – ALD method



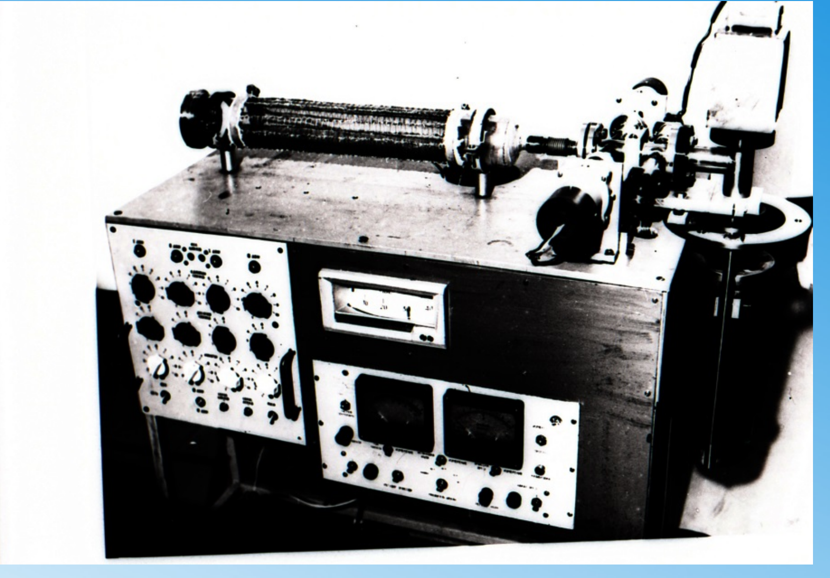


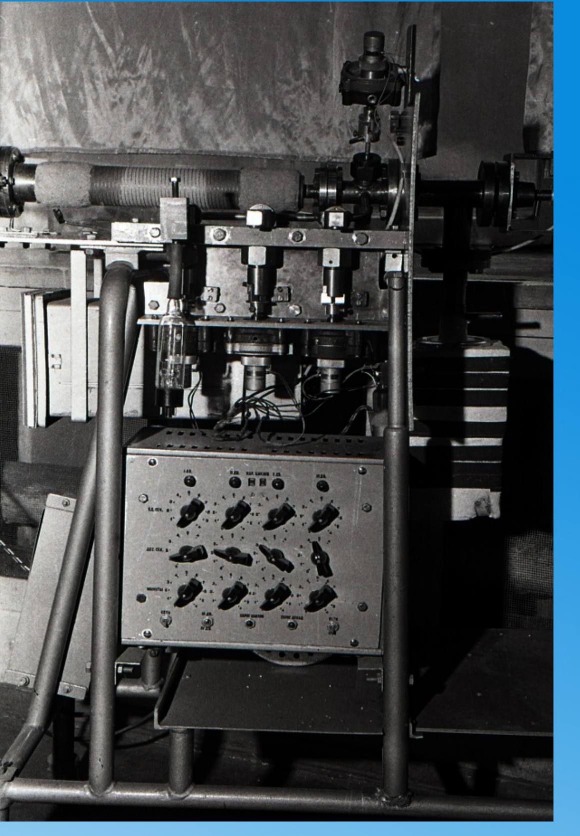
Kol’tsov S.I.

30.08.1931 - 26.05.2003

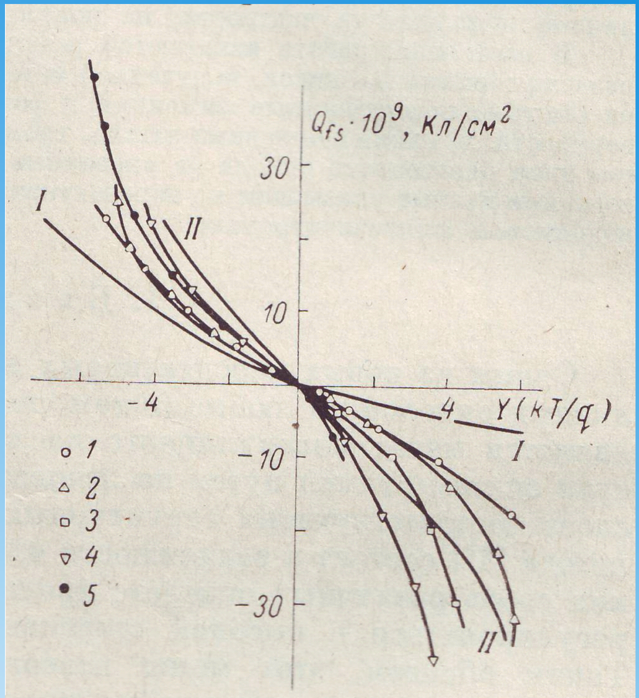
Aleskovskii V.B.

03.06.1912 - 29.01.2006



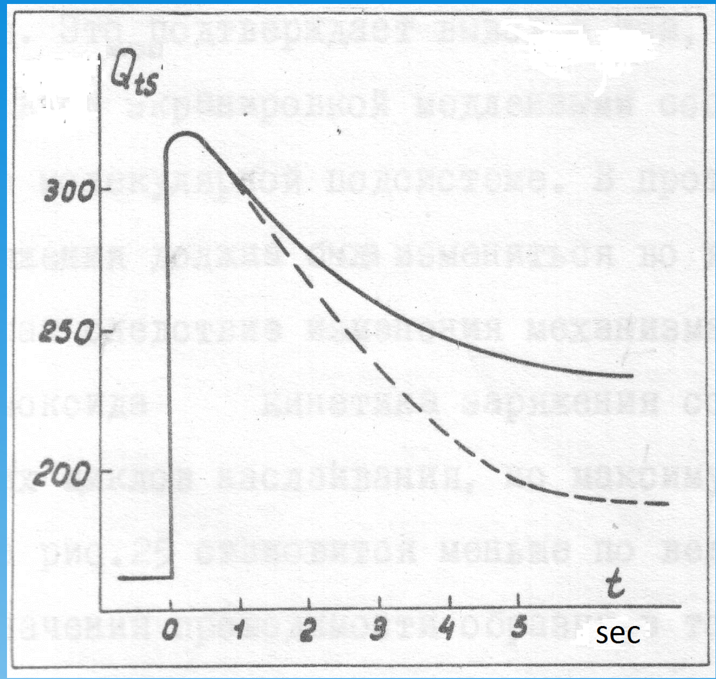


The first “computerized” vacuum flow-type devices for ML-ALD with analog programmable modules made on 1975-76 in Leningrad (now Sankt-Petersburg)

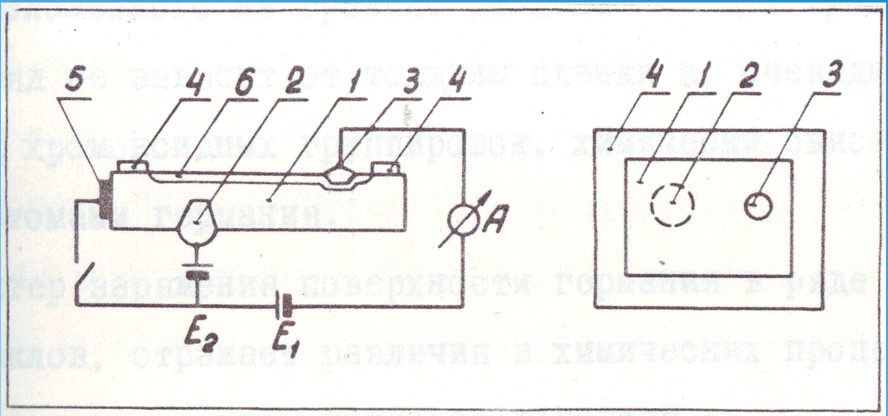


Density of charge traped on fss as
a function of surface potential Y:

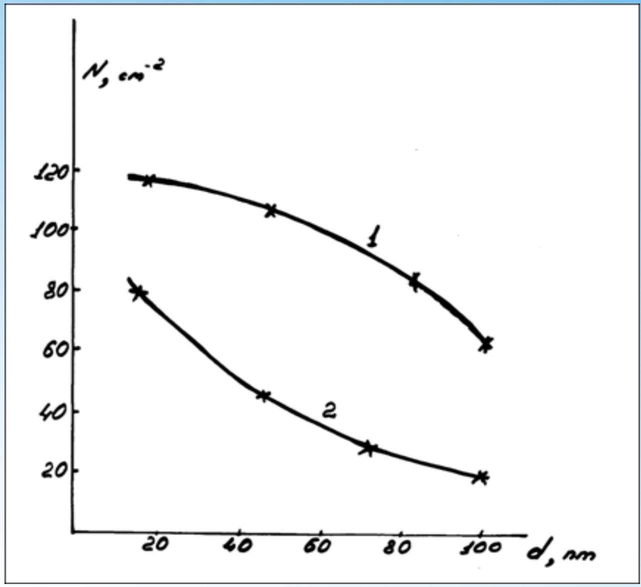
1. 20 ML of Cr2O3
2. 15 ML of TiO2
3. 4 ML of V205
4. Native surface of Ge
5. Annealed at 500K Ge surface



Kinetics of surface charge changing
during the layer growth on Ge surface
with different composition of precursors



Patented gas sensing structure which differed the sign (+ or -) of a surface charge, generated by adsorbed molecules (donor or acceptor ones)



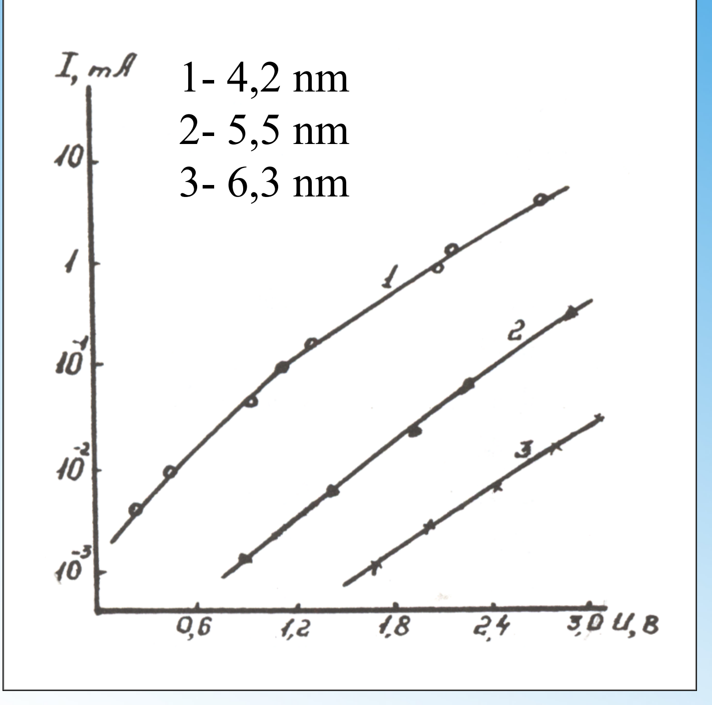
Decrease of porous density in thermal oxide on Si substrate after deposition of 1 (one) nm of Cr_2O_3 by ML-ALD

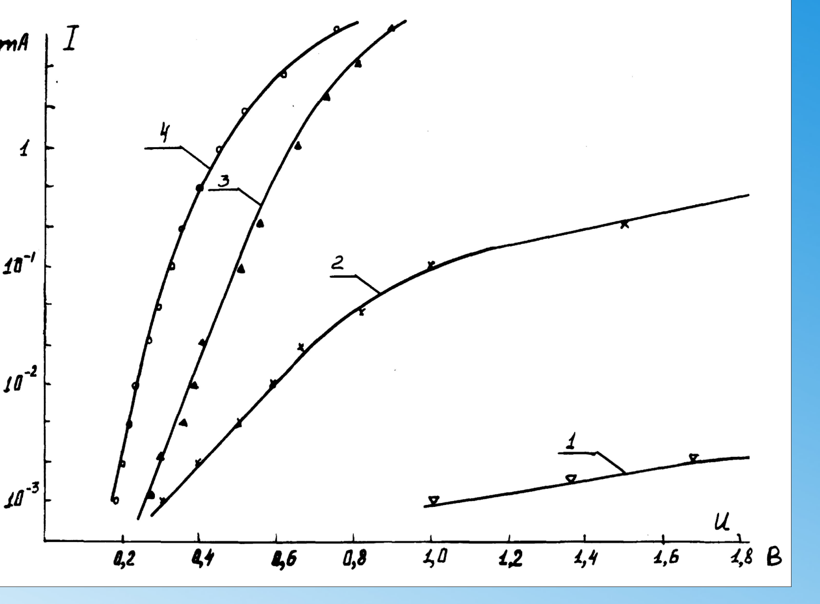
Influence of tunnel-thin layers of chromium oxide introduced into metal-semiconductor contacts interface by ML-ALD on I-V of Shottky diodes

$[I = I_s [\exp(qV/nkT) - 1]$.

1. As grown

2. Annealed at 770 K during:
1.- 3min., 2.- 8min., 3.- 15min.,
4.- 25min.





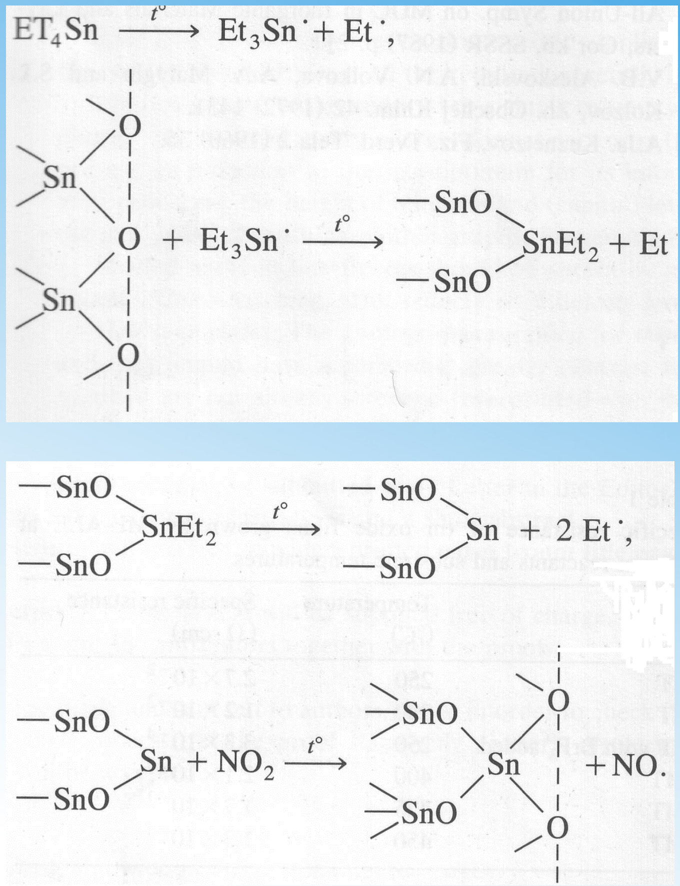
Comparison of the barrier's heights in MIS structures contains ML-ALD grown interlayers of different composition of oxides on Si with Me-Si contacts of the same metals (literature data)

oxide interlayer composition	interlayer thickness (nm)	barrier height (eV)	barrier Si-Me (eV)
Cr_2O_3	3.0	0.64	0.57 - 0.61
	1.0	0.59	
V_2O_5	4.0	0.57	0.60
	1.5	0.48	
TiO_2	5.0	0.47	0.45 - 0.51
	2.5	0.48	
ZrO_2	2.0	0.45	0.50
HfO_2	2.0	ohmic	ohmic
WO_3	2.0	0.55	0.56 - 0.60
Nb_2O_5	2.0	0.60	0.58 - 0.62

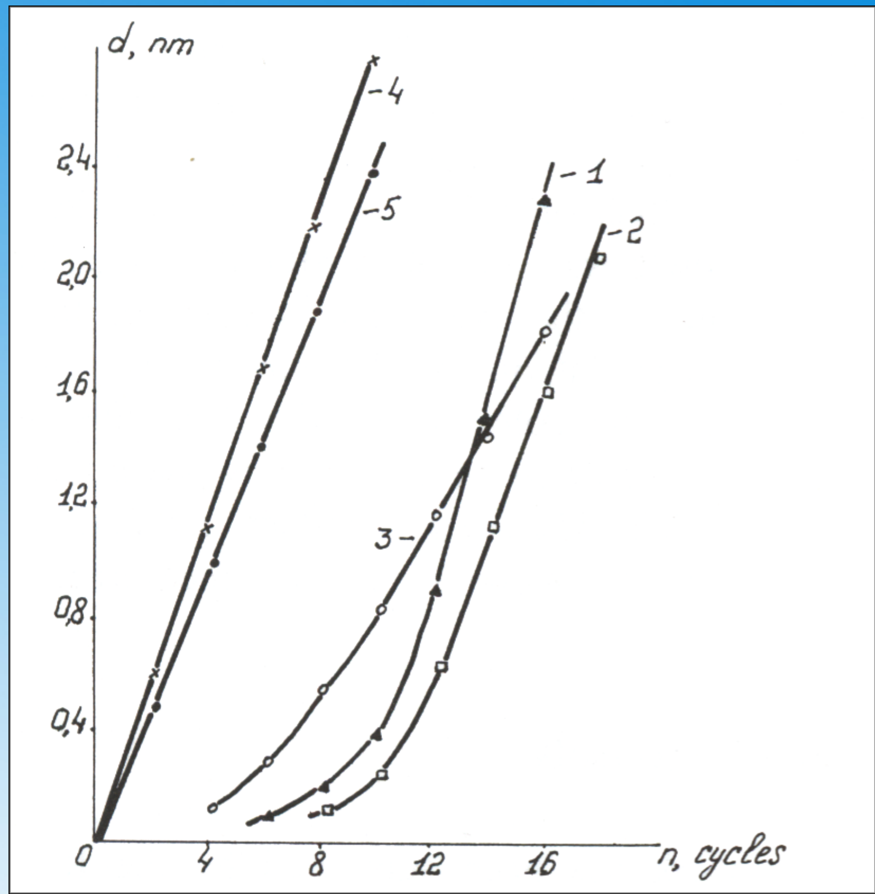
1. Influence of substrate “chemistry” on the synthesis of tin oxide (model).
2. “Delay” of the tin oxide growth on Si substrate with different sublayers:

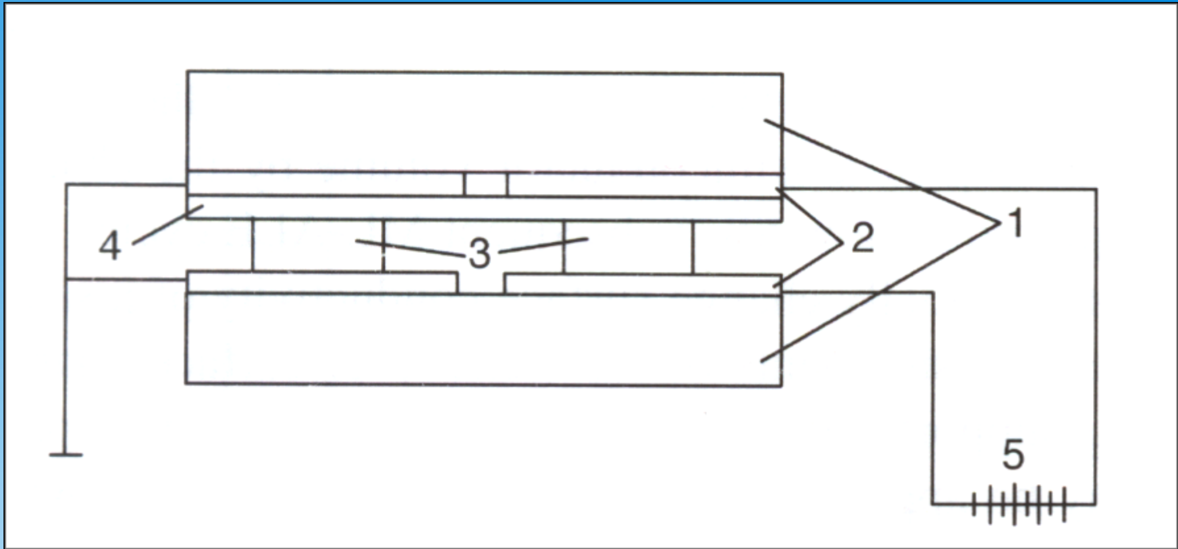
1- pure Si; **2**- one nm of SiO2; **3**- one nm of Al2O3; **4**- two nm of TiO2; **5**- two nm of VOx

1.

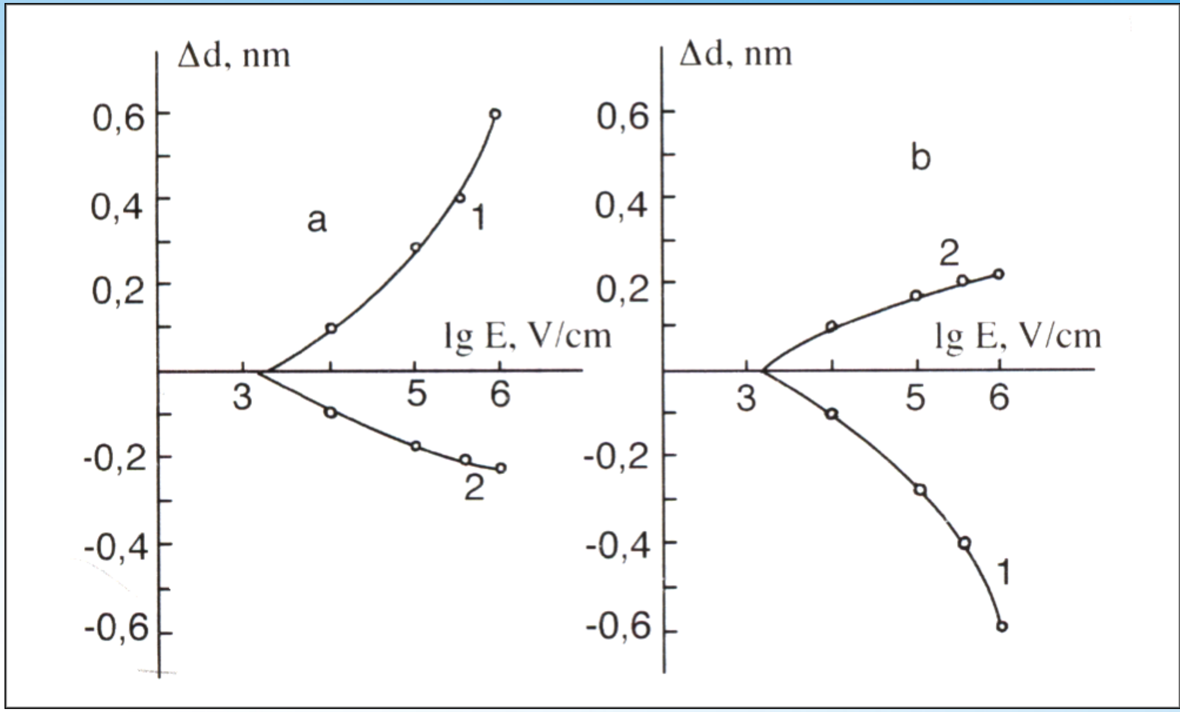


2.





Scheme of the cell for the growth of TiO_2 by ML-ALD In electric field.
(1)Quartz plate,
(2)Metal electrodes,
(3) Si substrate,
(4) Mica plate



The electrical field effect on the growth of titanium oxide layers by ML-ALD at 300K on silicon.
a-field directed from the substrate
b-field directed to the substrate
1-field during water inlet
2-field during $TiCl_4$ inlet

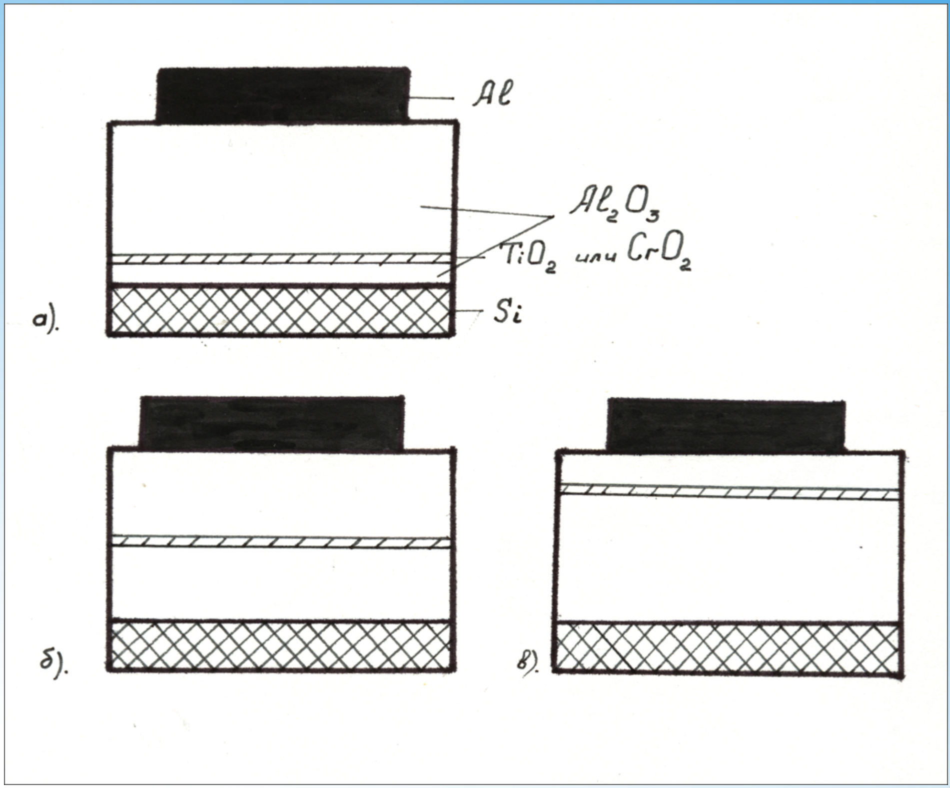
Heterooxide of 1,0 nm TiO_2 or CrOx interlayer introduced into 100nm Al_2O_3 matrix in different space position to the Si substrate.

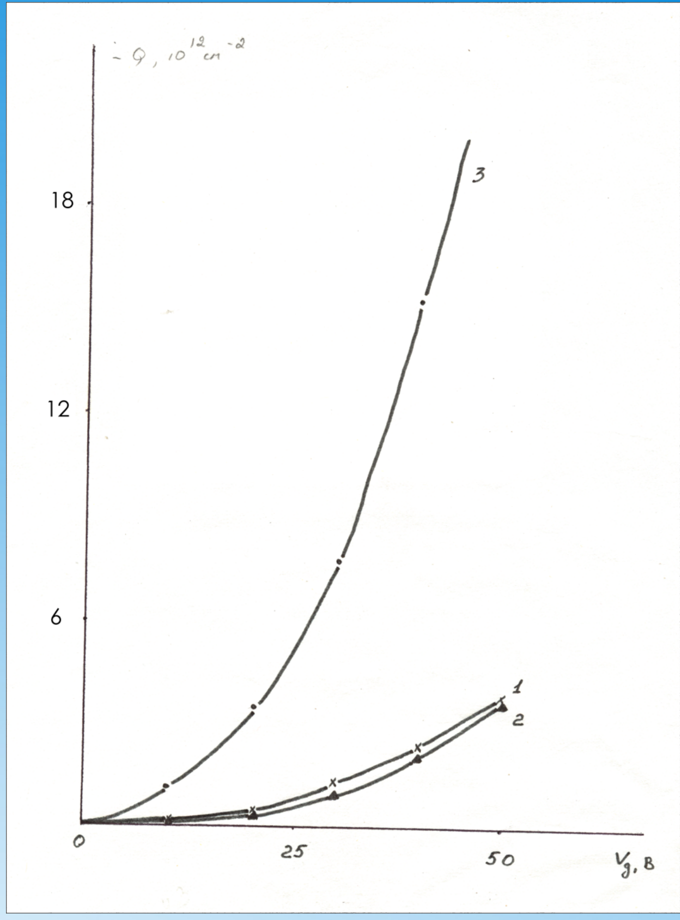
Charge trapping in these structures.

1-heterooxide close to Si (5 nm)

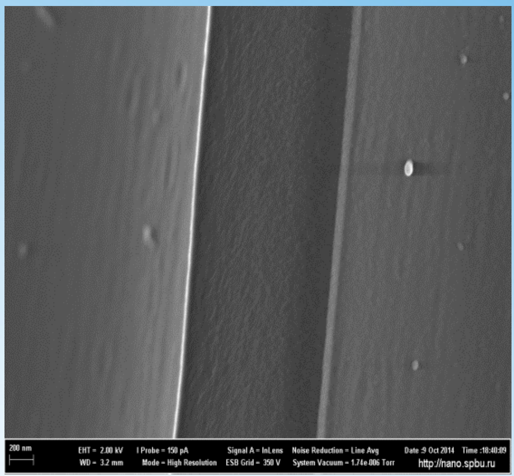
2-heterooxide in the middle

3-heterooxide close to Al (5 nm)

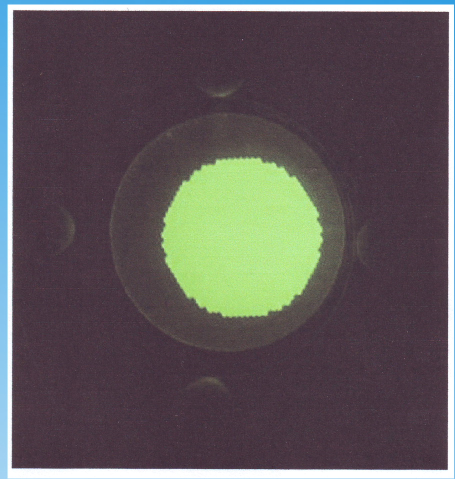




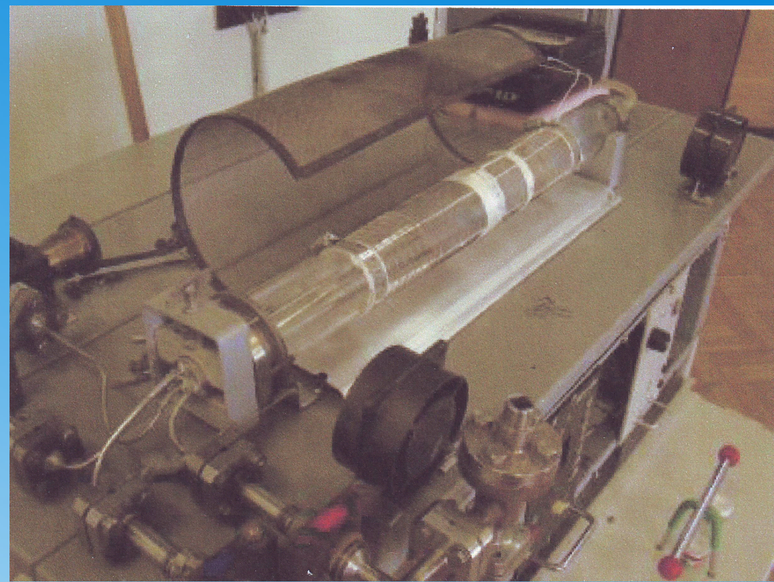
ML-ALD of oxides in Micro Chanel Plates (MCP) in SPb in the end of 90-s



Oxides - Al2O3 and others



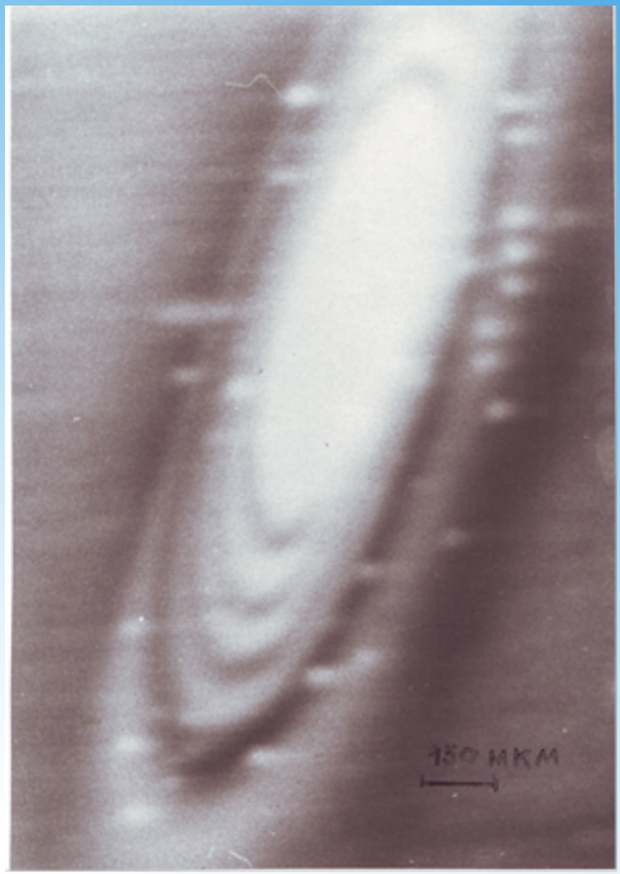
Increase of time stability
by 10 to 25 %

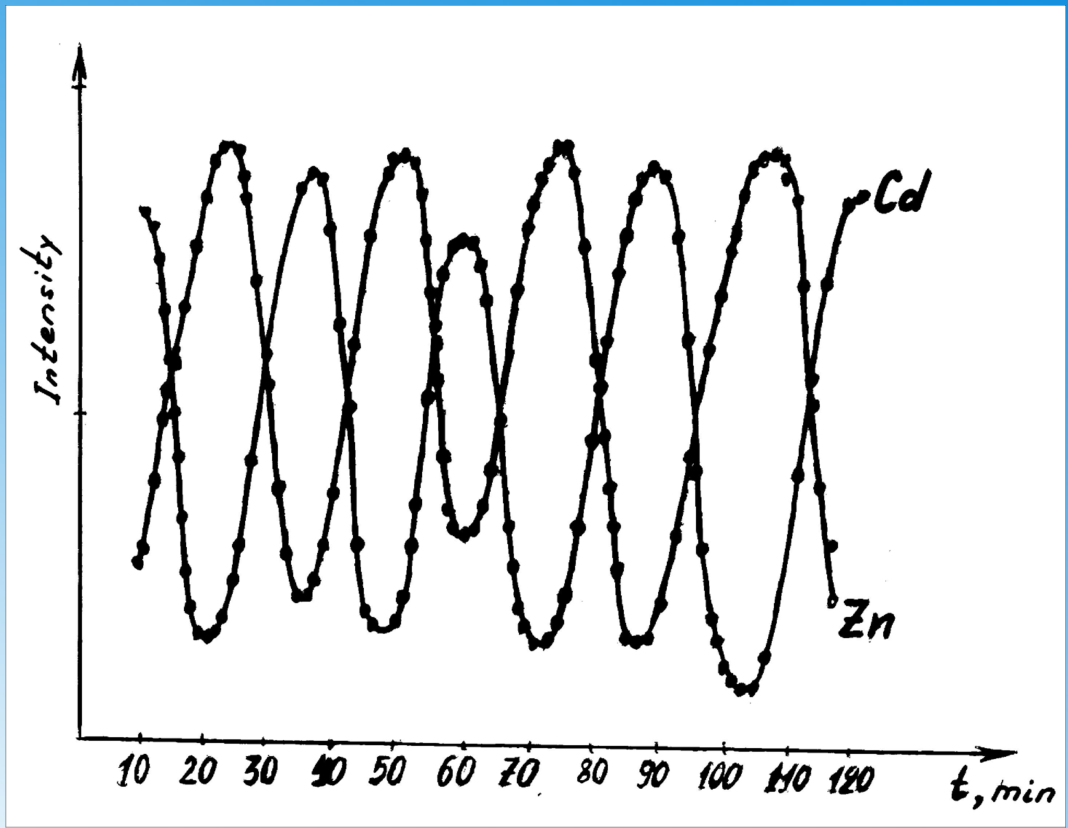


Device for MCP processing by ML-ALD

Multilayers of ZnSe-CdSe grown by ML-ALD and Auger spectra during ion etching.

Spacing of layers – 10 nm. (SPbSU, middle 80s)





Spatial ALE of GaAs in NCSU in the end of 80-s by S.M.Bedair and colleagues
(1-st International Symposium on ALE, Helsinki, 1990).

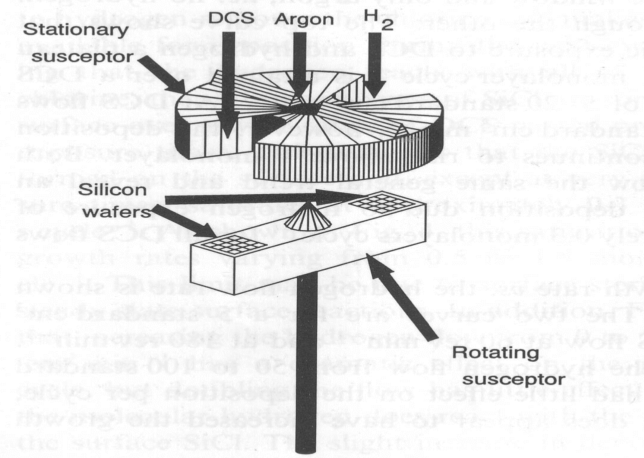


Fig. 1. Graphite susceptor design.

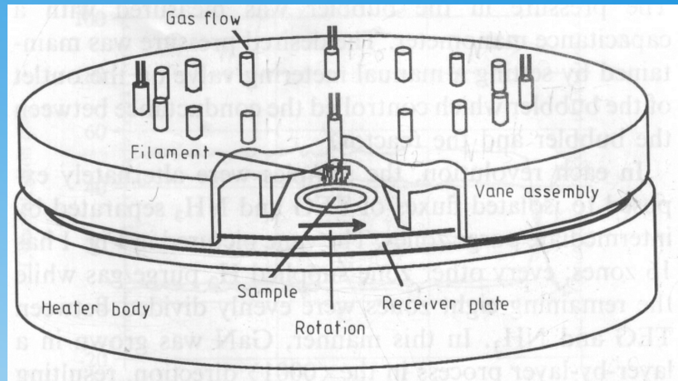
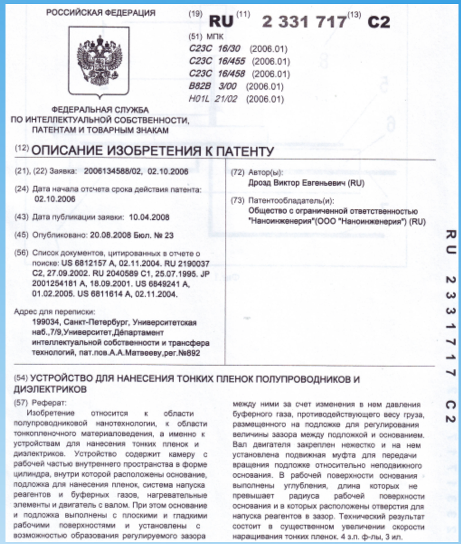


Fig. 1. Major internal components of ALE system. View into group V element supplying zone.

Spatial ML-ALD in SPb in the middle of 90-s



РОССИЙСКАЯ ФЕДЕРАЦИЯ

ФЕДЕРАЛЬНАЯ СЛУЖБА ПО ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ, ПАТЕНТАМ И ТОВАРНЫМ ЗНАКАМ

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(54) УСТРОЙСТВО ДЛЯ НАНЕСЕНИЯ ТОНКИХ ПЛЕНОК ПОЛУПРОВОДНИКОВ И ДИЭЛЕКТРИКОВ

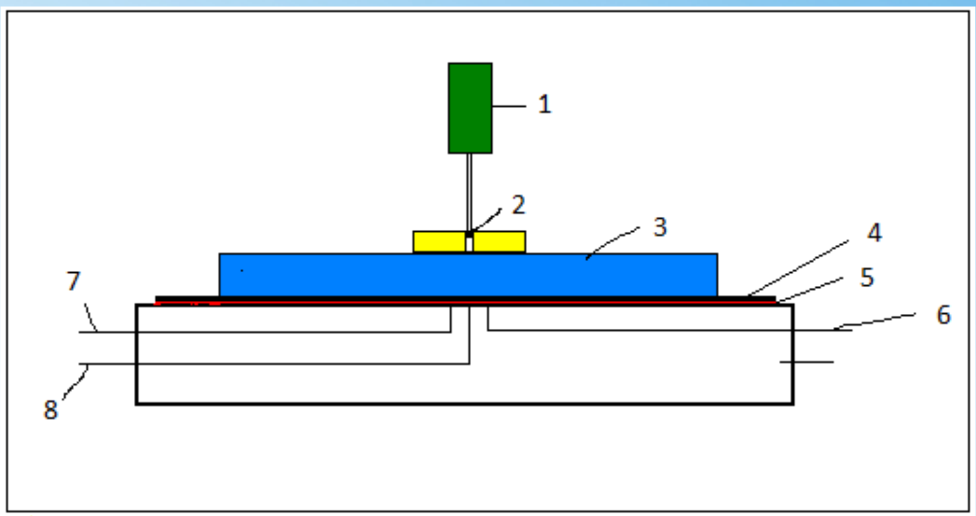
(57) Реферат:

Изобретение относится к области полупроводниковой нанотехнологии, к области тонкопленочного материаловедения, а именно к устройствам для нанесения тонких пленок и диэлектриков. Устройство содержит камеру с рабочей частью внутреннего пространства в форме цилиндра, внутри которой расположены основание, подложка для нанесения пленок, система напуска реагентов и буферных газов, нагревательные элементы и двигатель с валом. При этом основание и подложка выполнены с плоскими и гладкими рабочими поверхностями и установлены с возможностью образования регулируемого зазора между ними за счет изменения в нем давления буферного газа, противодействующего весу груза, размещенного на подложке для регулирования величины зазора между подложкой и основанием. Вал двигателя закреплен нежестко и на нем установлена подвижная муфта для передачи вращения подложке относительно неподвижного основания. В рабочей поверхности основания выполнены углубления, длина которых не превышает радиуса рабочей поверхности основания и в которых расположены отверстия для напуска реагентов в зазор. Технический результат состоит в существенном увеличении скорости наращивания тонких пленок. 4 з.п. ф-лы, 3 ил.

RU 2331717 C2

Russian Patent # 2331717
from 02.10.2006

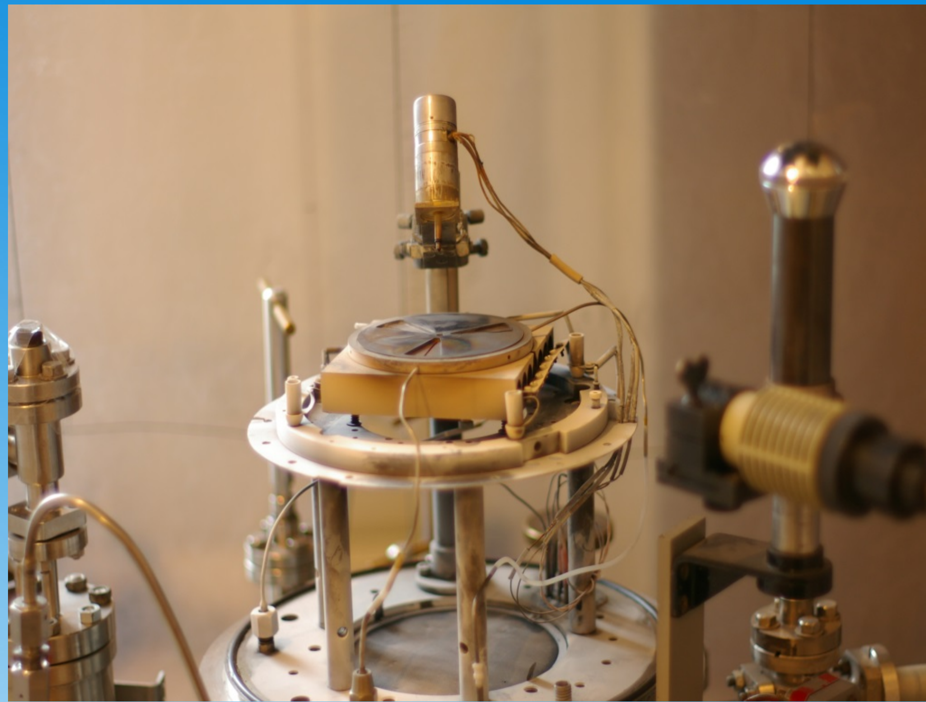
Growth rate of CdTe
films ~ 6 mkm/h



1-motor
2-muff
3-suspender
4-Si plate
5-clearance
8-channel for argon (He)

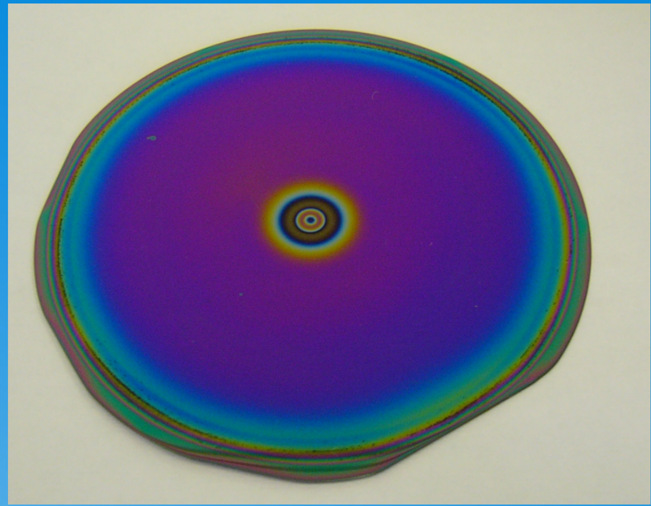
6-channel for MATe
7-channel for Cd(Me)2
-stationary plate

Spatial ML-ALD for CdTe and oxides growth

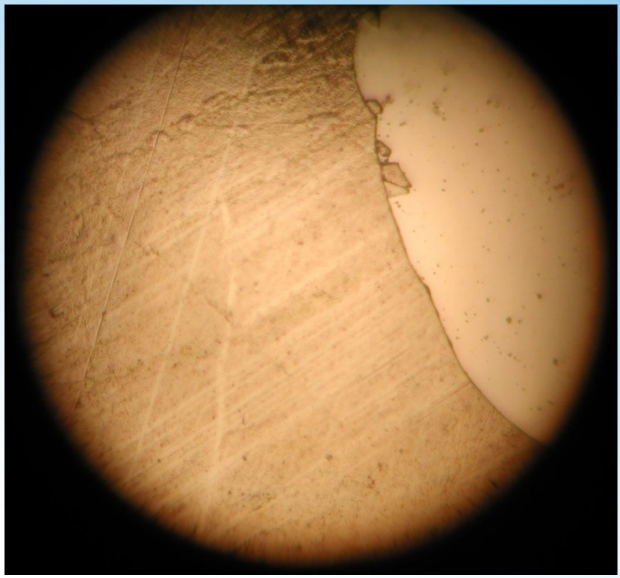


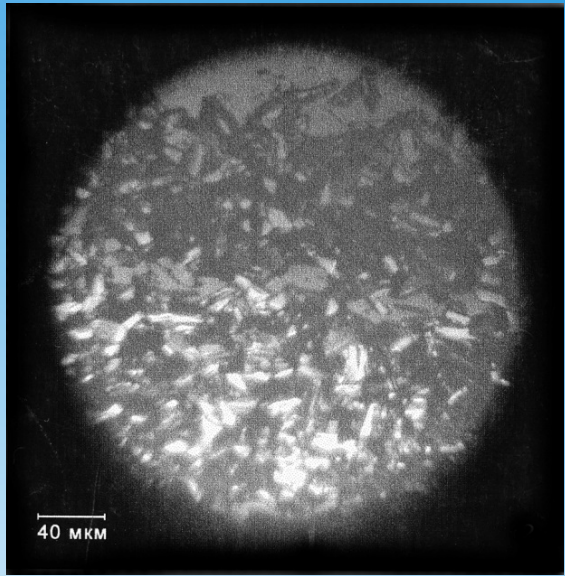
High growth rate and good uniformity of layers by patented gas-pillow technique with clearance less than 10 nm between stationary plate and substrate, controlled by gas pressure in space. (made in SPbSU in middle of 90-ths)

Te crystals grown
by spatial ML-ALD

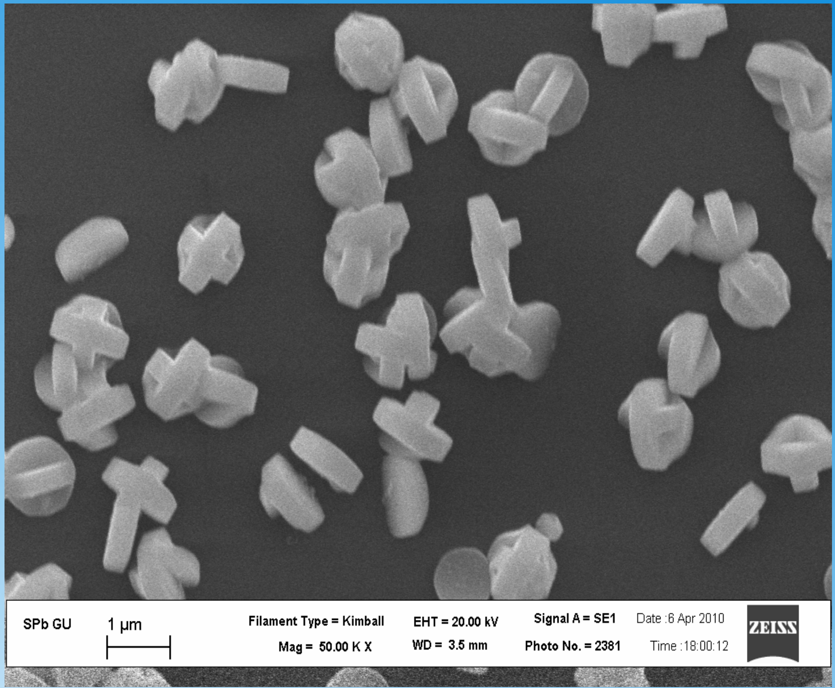


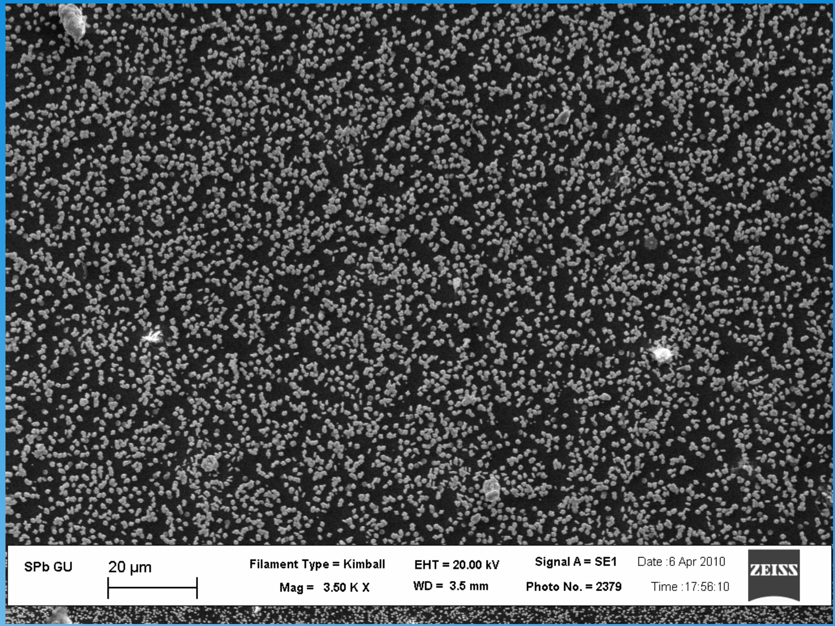
CdTe film on Si
by spatial ML-ALD



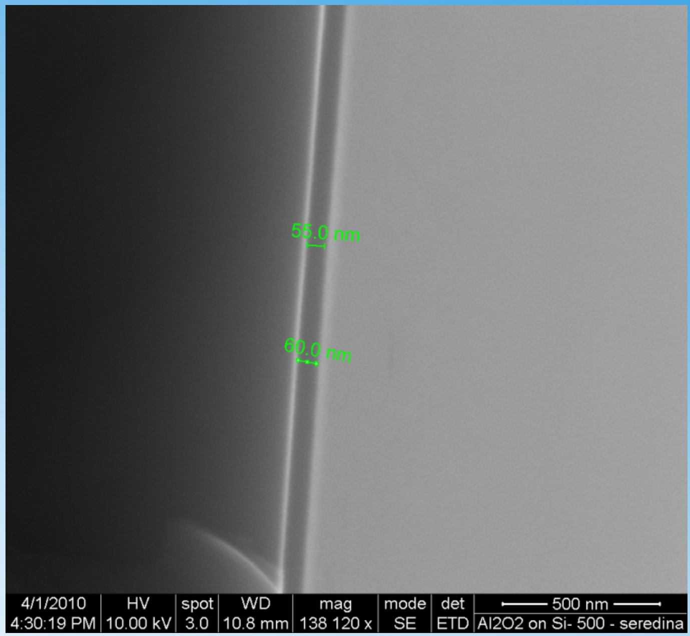


Ta2O5 film grown
by spatial ML-ALD





Growth of 0-D and 2-D structures as the example of ML-ALD synthesis of Ta_2O_5 on the Si substrate by spatial process



CdTe films grown from DMC and MATe by spatial ML-ALD

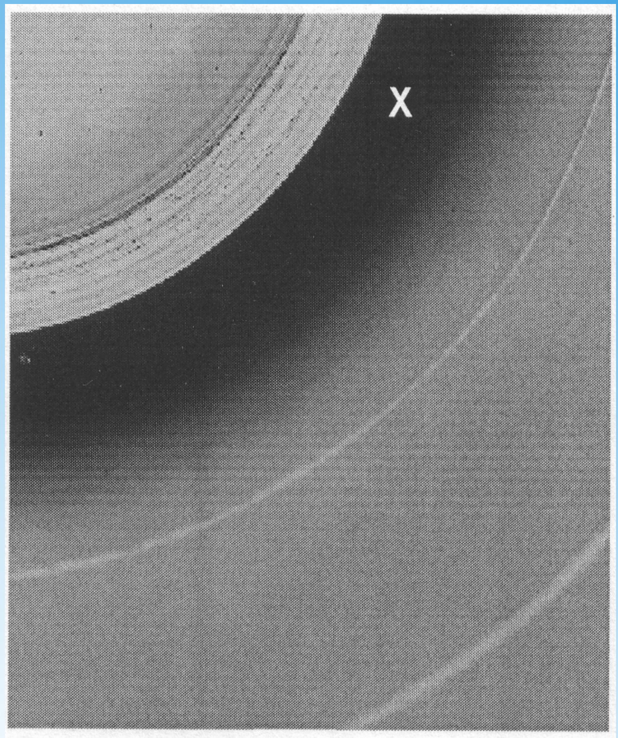


Fig.1 - conventional ML-ALD

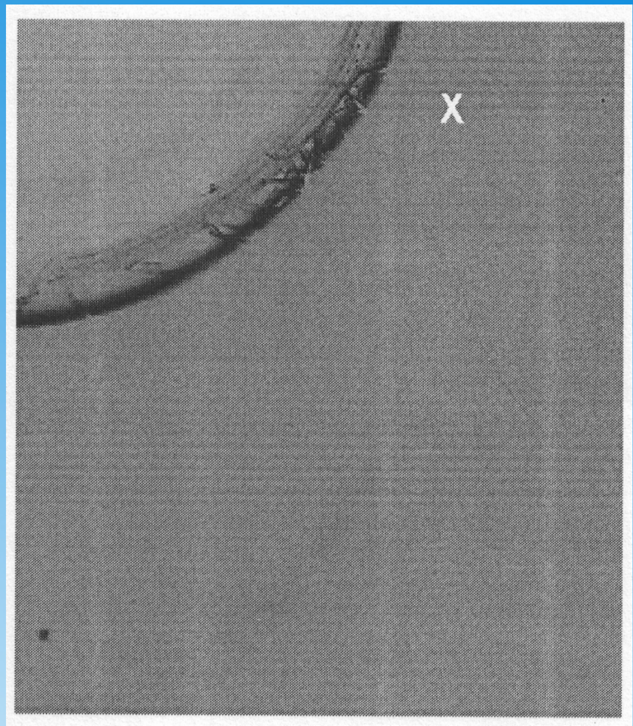
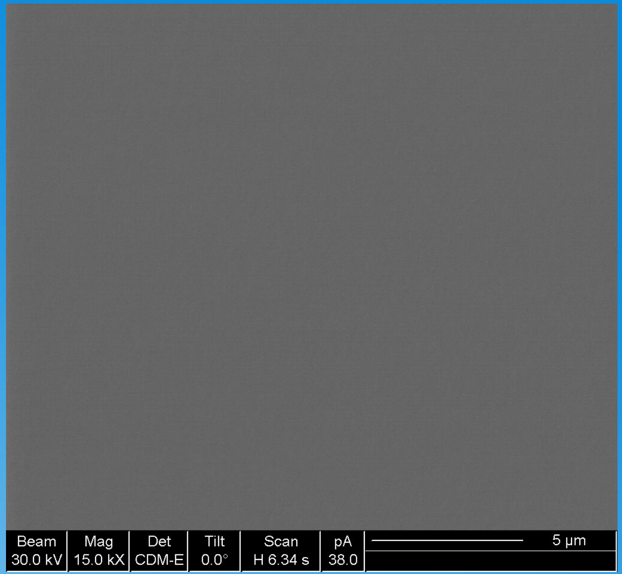
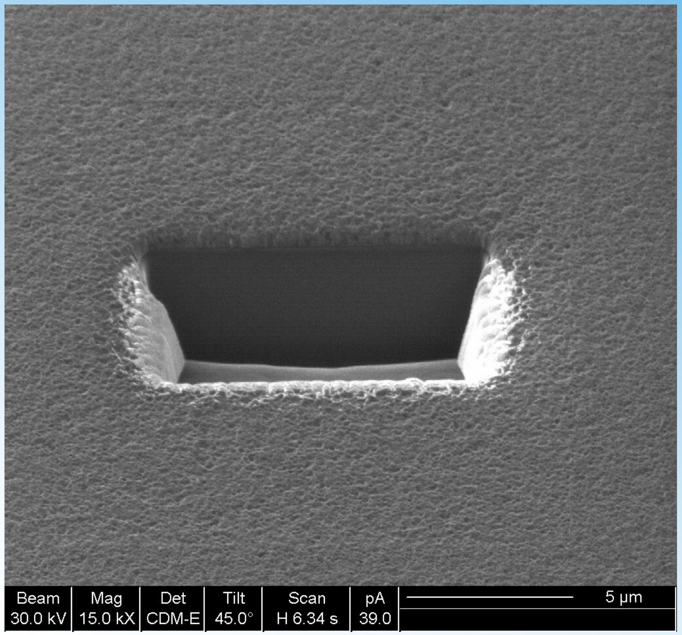
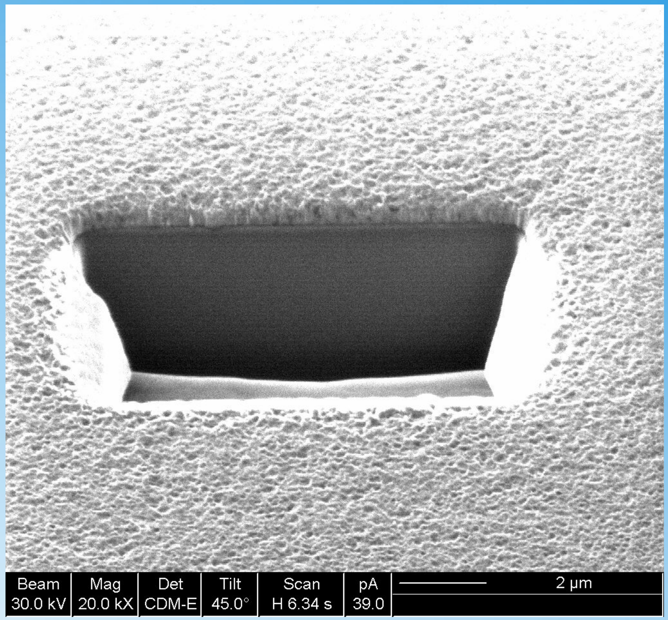


Fig.2 - patented three steps ML-ALD

FIB etched CdTe film grown in spatial ML-ALD reactor in the end of 90-s

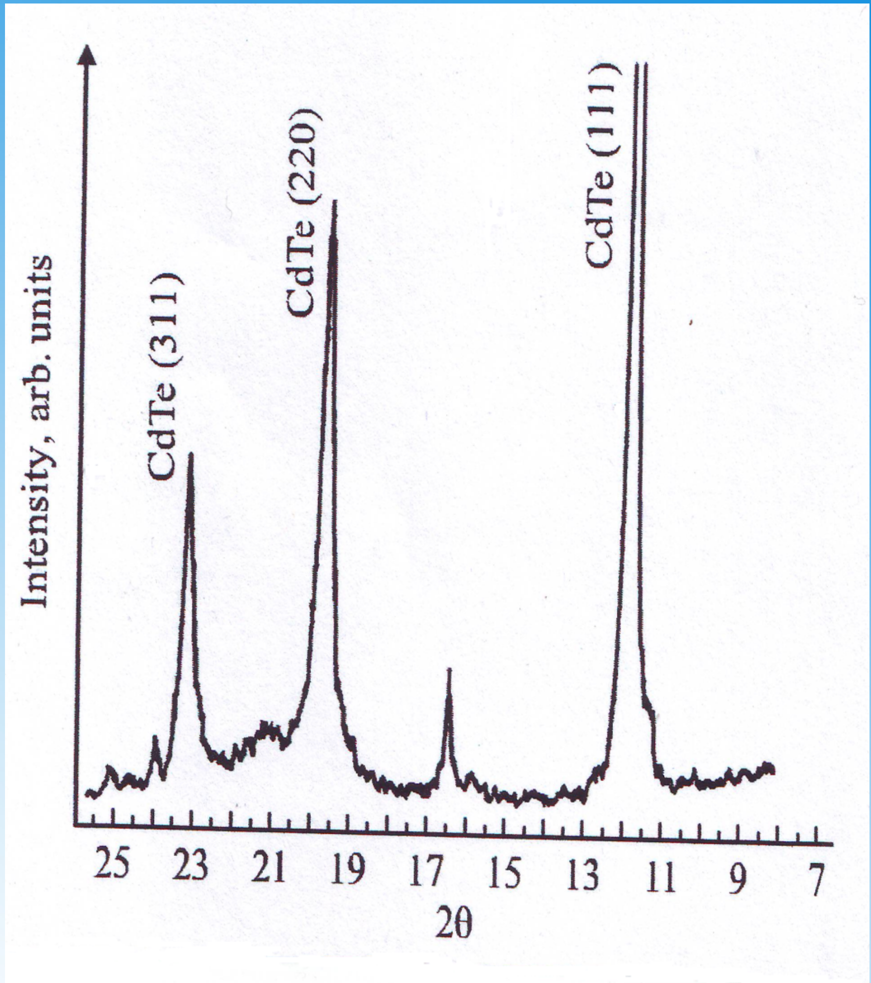


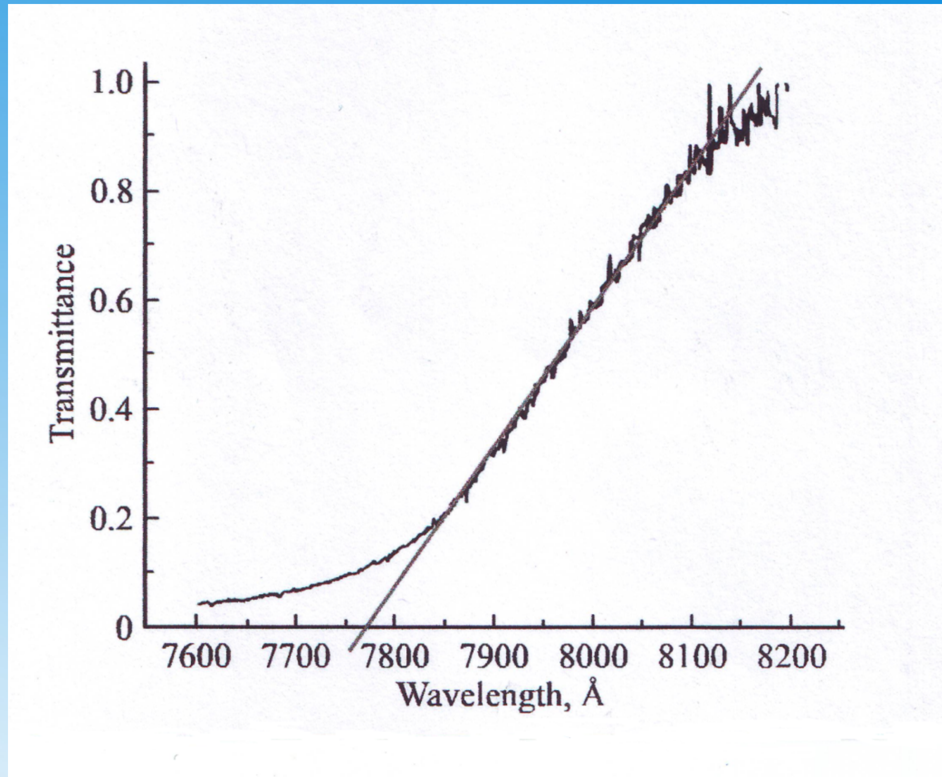


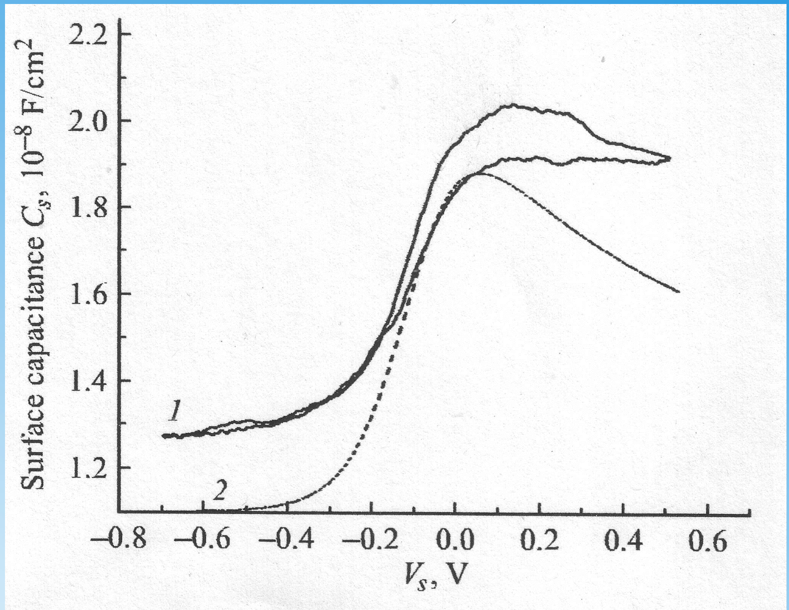


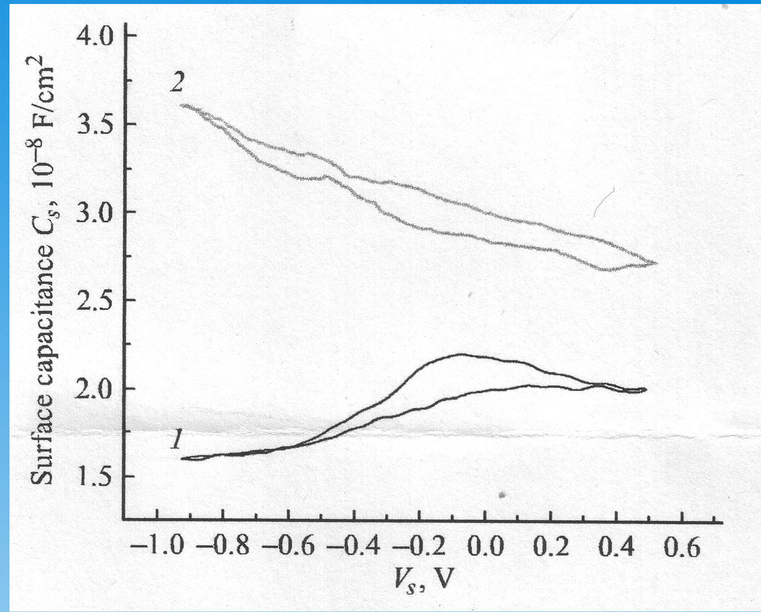
XRD and IR of CdTe films (3 microns) grown in high-rate spatial ML-ALD process

EG = 1.57 эВ









C-V of CdTe on Si substrate

$1/C = 1/C_{CdTe} + 1/C_{si}$

P = 6.3 · 10^{16} см−3

C-V of CdTe layer in 1 M $CdCl_2$ in H_2O

1. Dark capacitance
2. Under illumination of AM1

ML-ALD devices made in SPb in nowaday and got started in SPbSU education and investigation process

Liquid and
Solid precursors,
5 sources,
8 inch x 8 inch
substrates

ML-ALD device made in the beginning of 90-s for education process in SPbSU

ML-ALD device made in the beginning of 00-s in SPb for scientific institute.

ML-ALD device for the large substrate with load-lock camera In the 00-s in SPbSU

Spatial ML-ALD device for investigation in II-VI and III-V compounds. Mid of 90-s SPbSU.