Pulsed Laser Deposition cell for in-situ experiments with neutron reflectometry.

The work was done within the contract No 14.584.21.0028 between IKBFU and Russian Ministry of Education and Science. Unique Project identification number RFMEFI58417X0028

Dr. Alexander Goikhman

Immanuel Kant Baltic Federal University

Functional Nanomaterials
RESEARCH AND EDUCATION CENTER

Outline

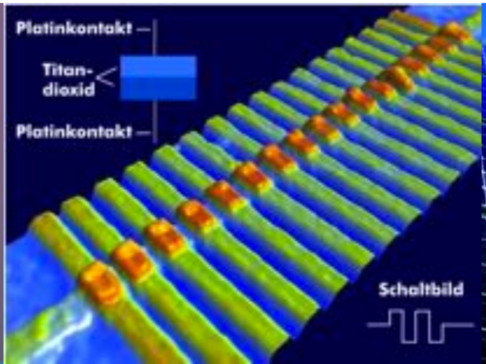
- Pulsed Laser Deposition technique
- Home PLD laboratory at IKBFU (Kaliningrad, Russia)
  - Examples of PLD structures
- PLD thin films Neutron Reflectometry
  - In-situ concept chambers
- Another concepts

Motivation

- ✓ Memory devices
- ✓ Sensors
- ✓ Solar cell elements
- ✓ Biocompatible materials
- ✓ Protective coatings
- ✓ Optic elements

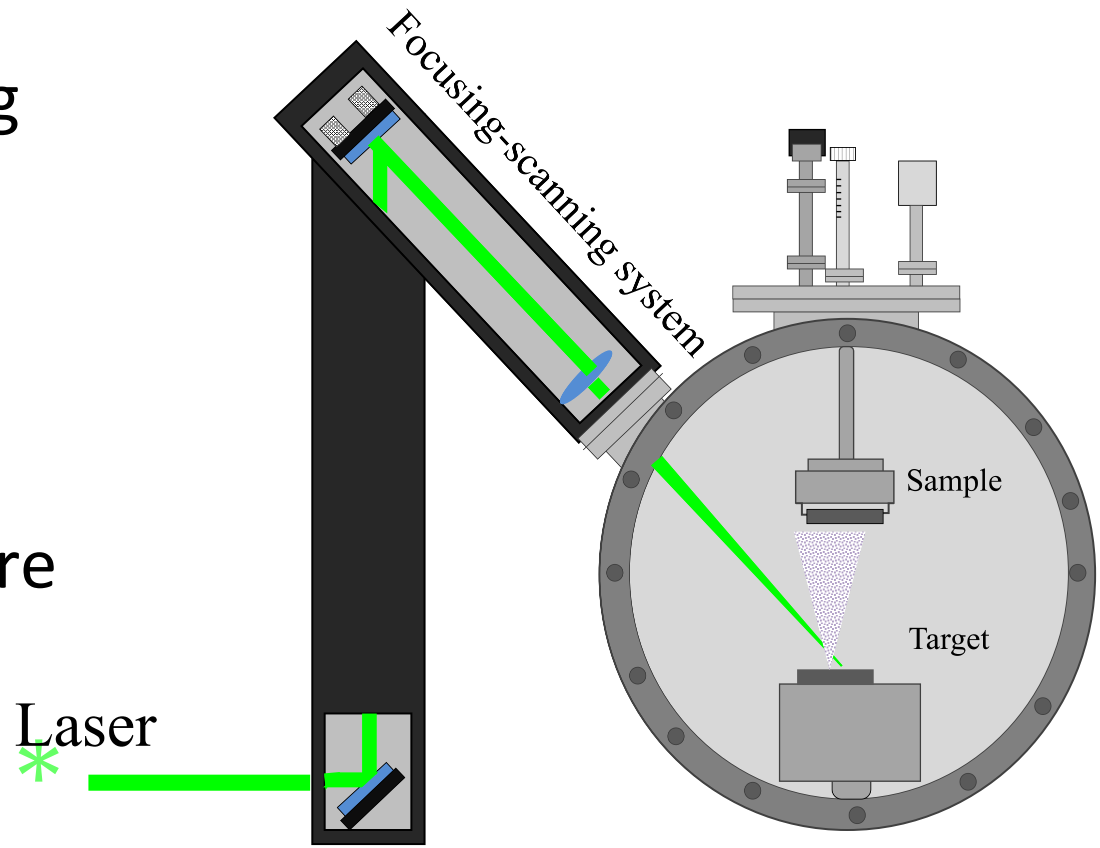
- Clean material without atmosphere contamination
- Exclude influence of top protective coating
- Material properties investigation depends on the thickness





Main parts of PLD

- Laser
- Focusing - scanning system
- Target
- Substrate
- UHV or low pressure gas atmosphere



Thin film deposition

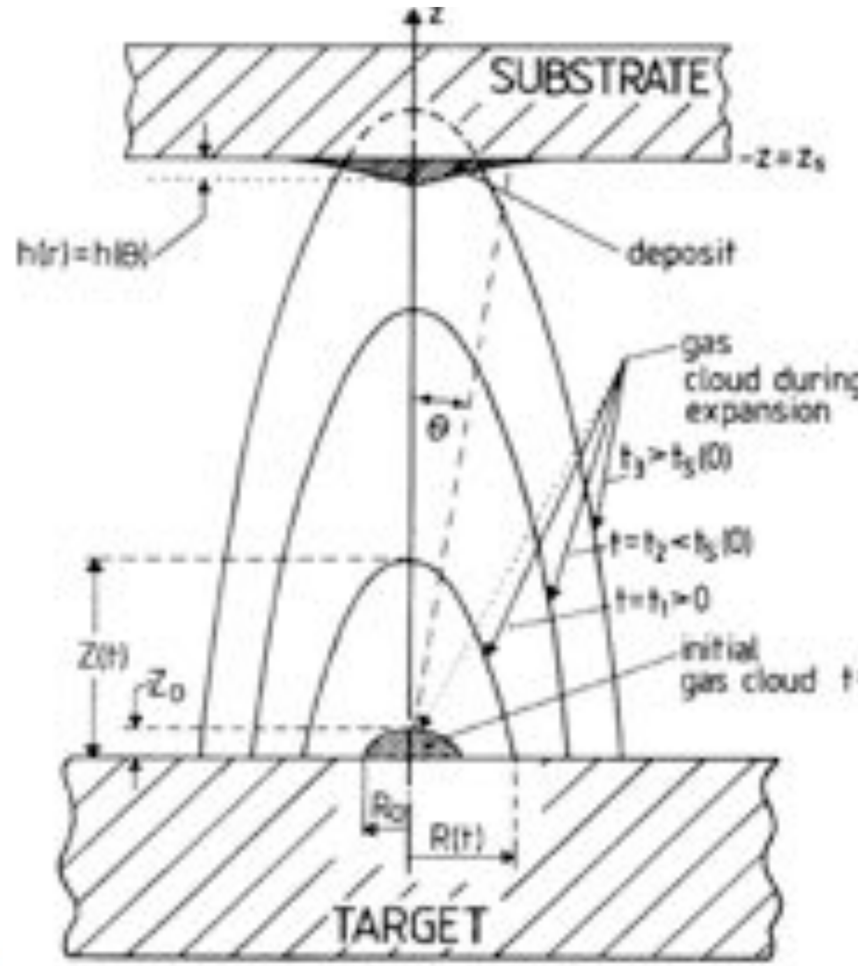
- Steps to thin film deposition:

t=0
- Creation of the initial gas

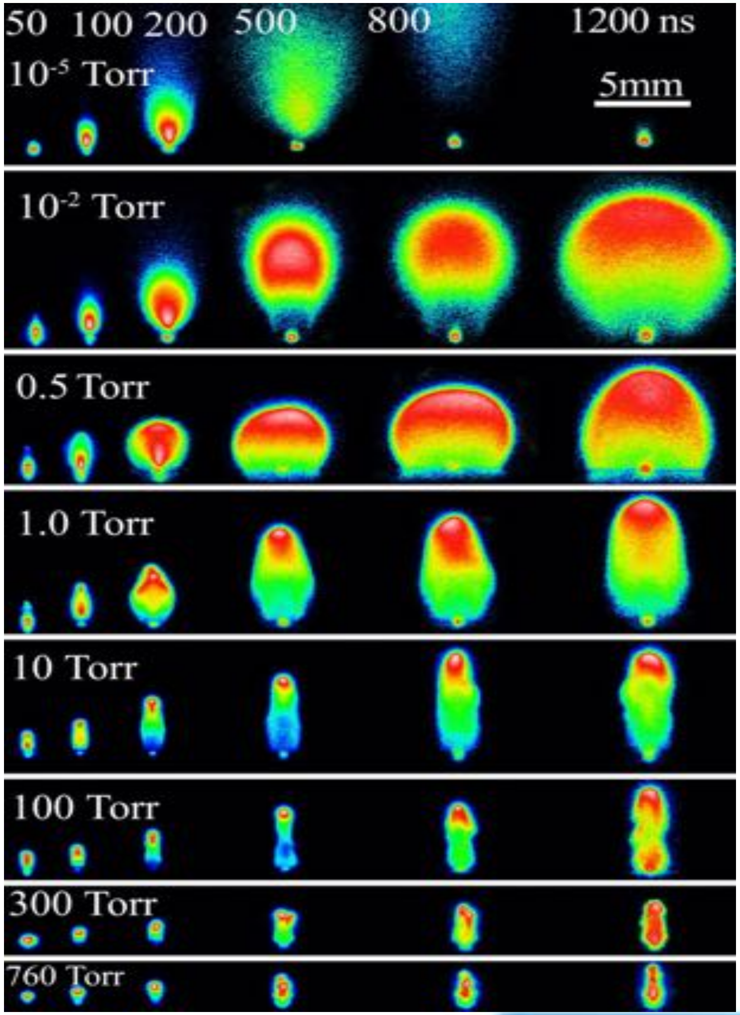
t>0
- Elliptical plasma expansion

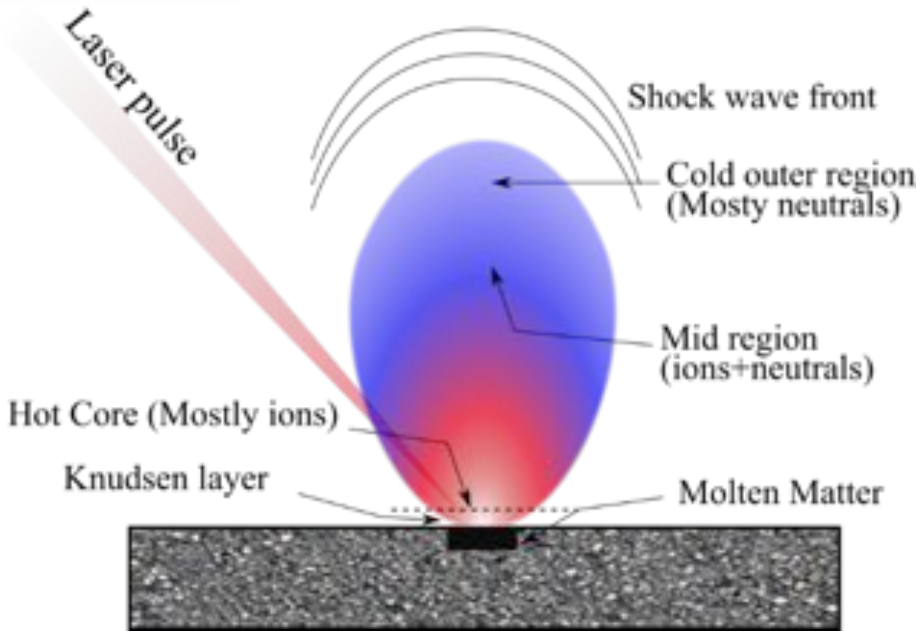
$Z = Z_s$: ablated material reaches the substrate

Flux of species ~ cos^{n}θ, n=5-7



Plasma plume study





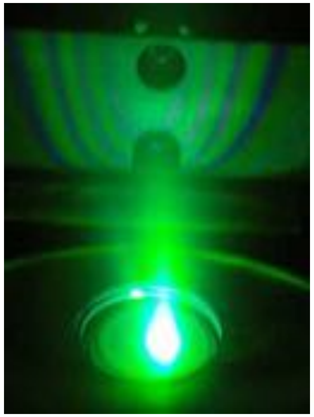
Plasma plume is confined by the gas pressure!

*Farid, N., et al. "Dynamics of ultrafast laser plasma expansion in the presence of an ambient." *Applied Physics Letters* 103.19 (2013): 191112.

Advantages - Disadvantages

- almost any condensed matter material can be ablated;
- the pulsed nature of PLD means that film growth rates may be controlled to any desired amount;
- small amount of evaporated target, exotic materials possible;
- the ability to produce species with electronic states far from chemical equilibrium;
- laser (the energy source) out of vacuum, great degree of flexibility geometrical arrangements.

- the production of macroscopic ejecta (causing the droplets formation);
- crystallographic defects in the film, caused by bombardment by high kinetic energy ablation particles;
- inhomogeneous flux and angular energy distributions within the ablation plume;



The main characteristic of thin films

- precise stoichiometric reproduction of complex materials into thin films;
- materials with high fusion temperature;
- high reproducibility and good control of deposition rates;
- high kinetic energy (50 eV to 500 eV) → long diffusion length on the surface → single crystals, nanowires,...

Why PLD?

- **Molecular Beam Epitaxy:**

Direct Industry

- hard to change target material
- technology transfer is impossible
- total chamber weight > 80kg
- non-flexible geometrical arrangements

Why PLD?

- **Magnetron sputtering:**

Torr International Inc.

- Target size from 1’’
- Each chemical element in a complex structure requires individual magnetron module
- total chamber weight > 80kg
- non-flexible geometrical arrangements

Why PLD?

- **Atomic Layer Deposition:**
  - Expensive precursors
  - Growth technology is individual for each chamber
  - Safety limitations

About lasers

Nd:YAG diode pump laser

Excimer laser – 248

Laser characteristics

Nd:YAG Laser (LOTIS TII):

- 532 nm, 266nm;
- Energy range:
  up to 435 mJ (532nm),
  up to 129 mJ (266nm);
- frequency up to 10 Hz;
- pulse duration 6-7 ns;
- crystal for *second* harmonic - KTP
- crystal for *fourth* harmonic - BBO;
- one laser beam path for both harmonics;
- laser mirror for both wavelength;
- holder for mirror with motors;
- focusing lens

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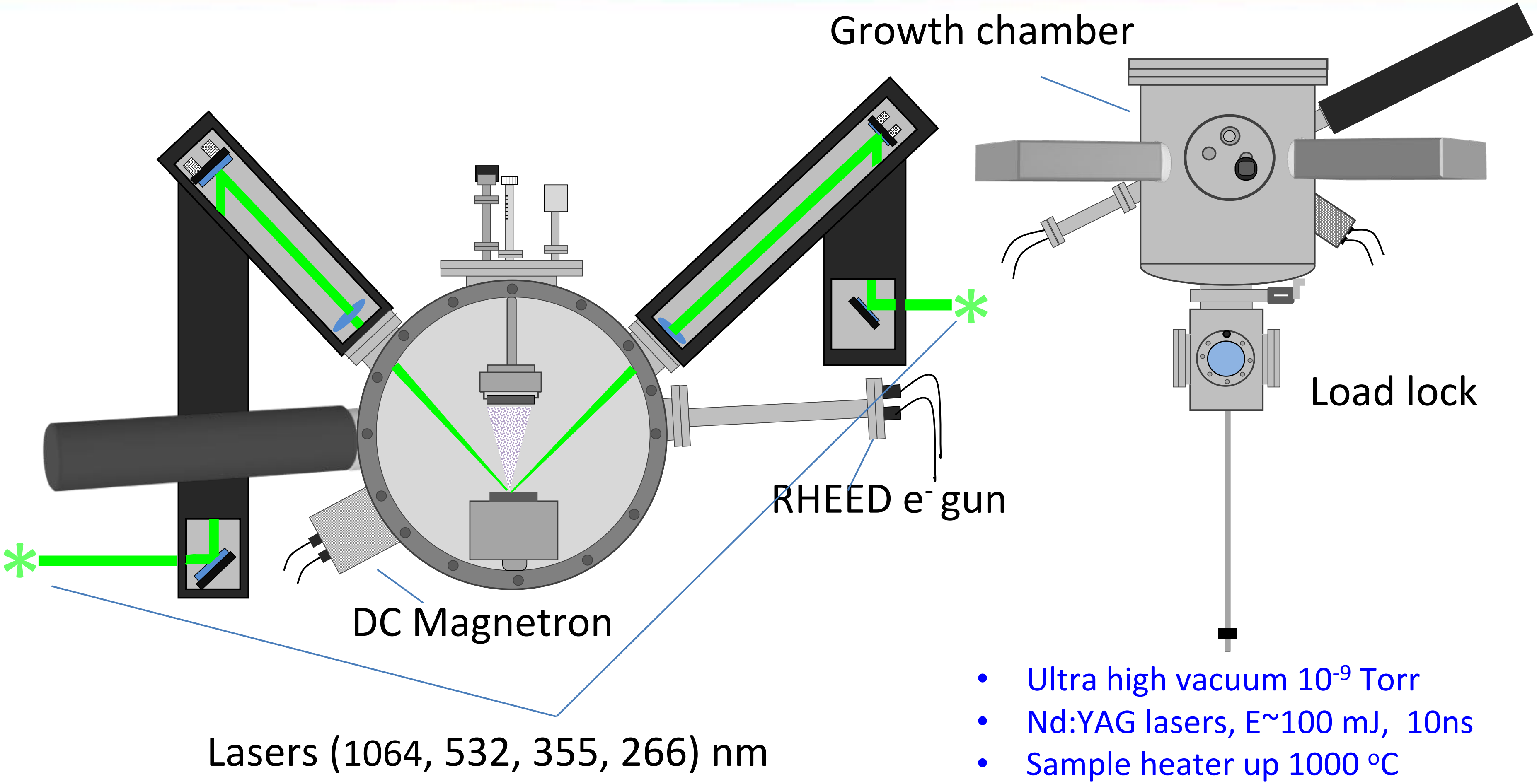
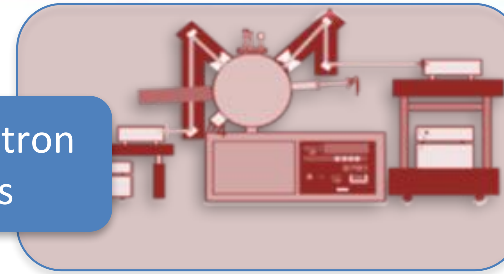
Experimental PLD Setup



- Ultra high vacuum 10^{-9} Torr
- Nd:YAG lasers, E~100 mJ, 10ns
- Sample heater up 1000 ^{o}C
- Magnetic Field annealing

Home lab

Thin film formation & investigation *in-situ* complex



Low energy electron dif-fraction

Pulsed laser deposition

Auger electron analysis

Atomic Layer Deposition

Magnetron sputtering

Sample pre-paration

UHV Atomic forc e microscope

Time of Flight mass-spectroscopy

Refractive high energy electrons diff

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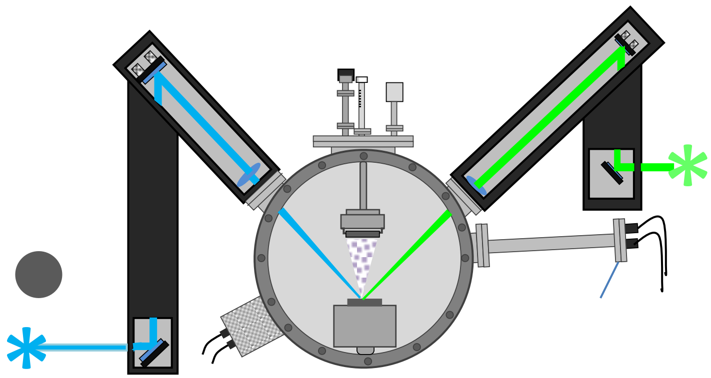
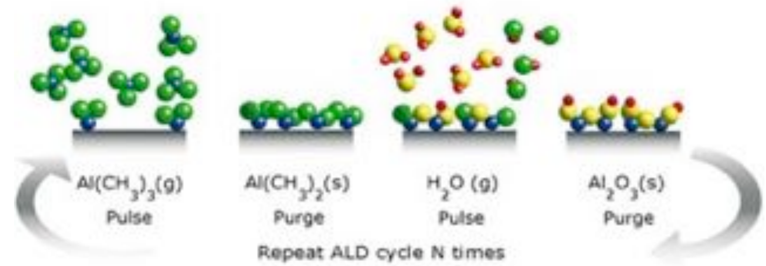
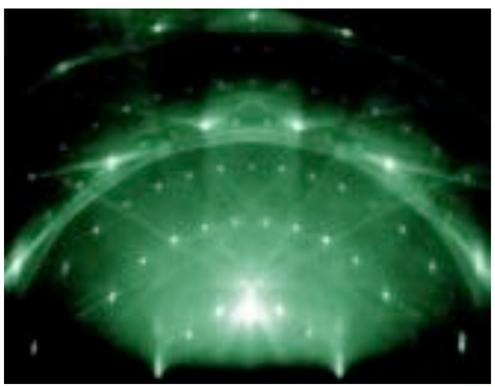
Thin film formation & investigation *in-situ* complex



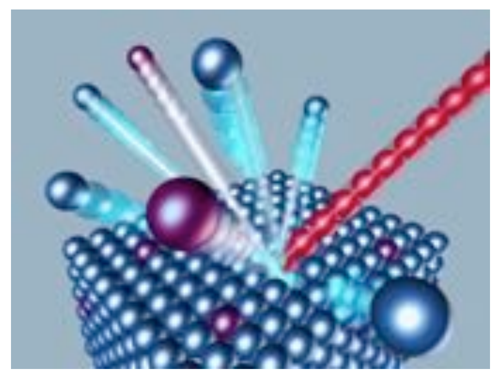
2 Nd:YAG lasers co-deposition system



Atomic layer depostion in situ



Refractive high energy electrons diffraction



Time of Flight secondary ion mass-spectroscopy

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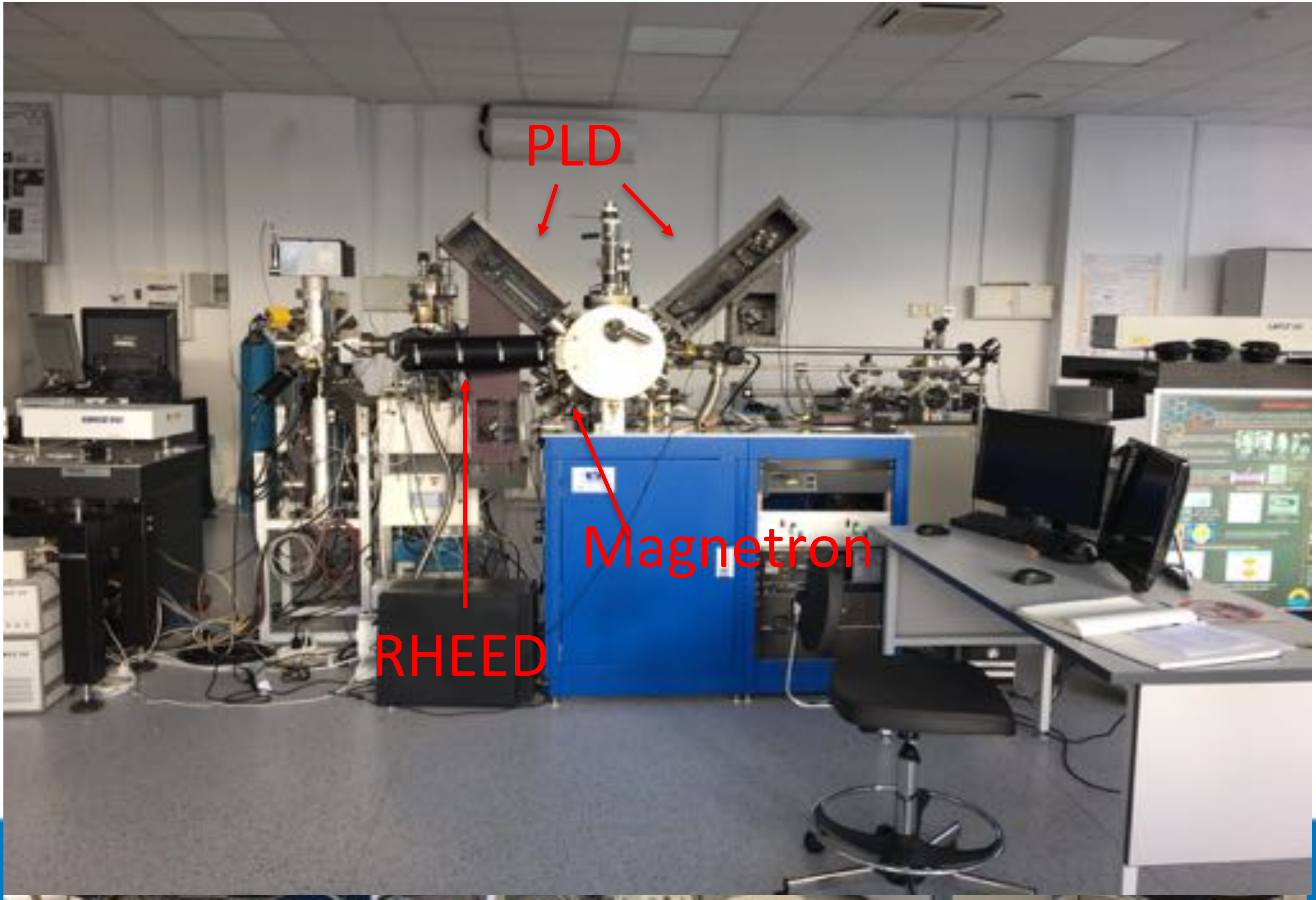
Thin film formation & investigation in-situ complex



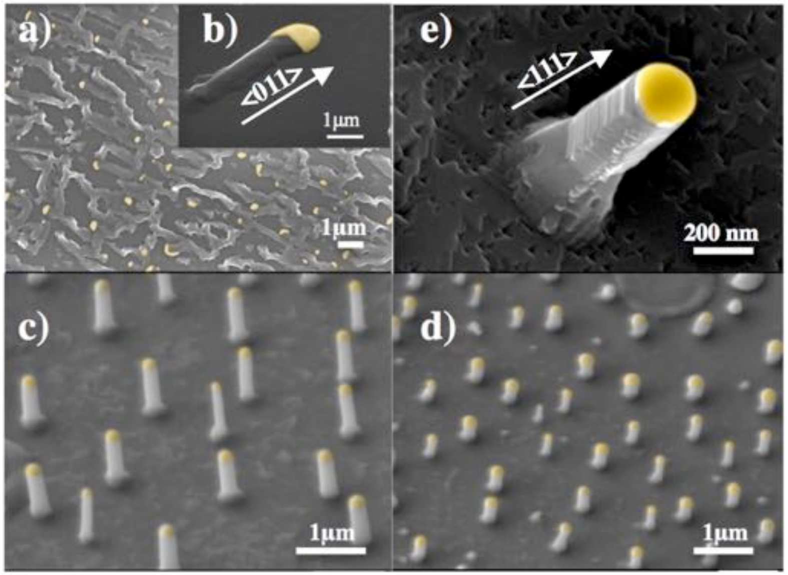
Thin film formation & investigation *in-situ* complex

Si:Au nanowhiskers for nanoelectronic devices

GROWTH METHOD

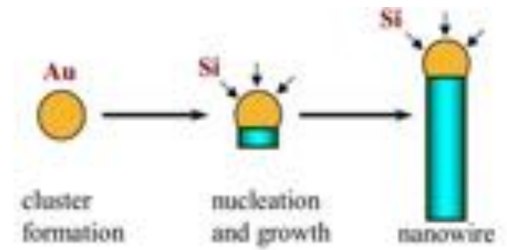
Pulsed Laser Deposition (PLD)

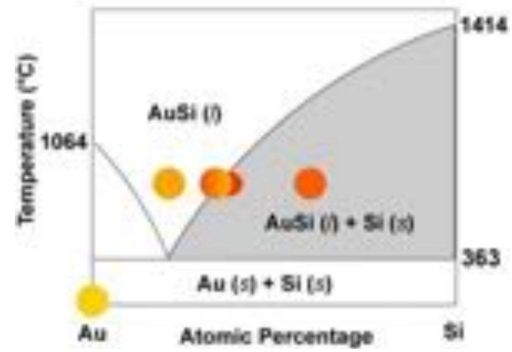
- High particles energy in the plasma plume (up to 50keV);
- Precise thickness control (~0.1ML/pulse)
- realization of experiment in the different gas atmosphere (O_2: Ar, N_2);
- Laser harmonics: 1064nm; 532nm; 355nm; 266nm;
- Possibility growth heterostructures in one vacuum cycle;



GROWTH MECHANISM

vapor–liquid–solid method (VLS)





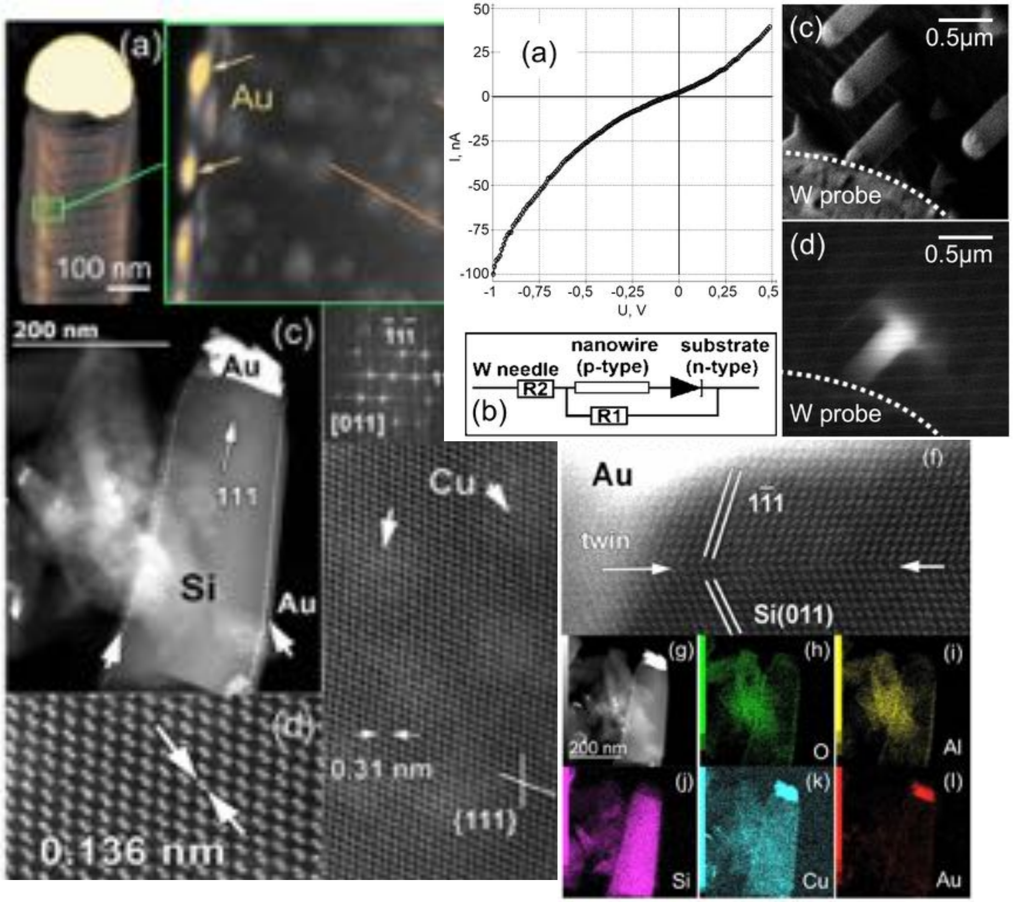
CONCLUSIONS

- Possibility of gold clusters formation by PLD. Higher substrate temperature – larger size of the separate cluster.
- Au clusters crystallized in (111) orientation;
- Si:Au NW is possible to growth by PLD on Si(111) substrate in a special conditions (vac. pressure, laser energy, …).

ACS Omega 3, 2, 1684-1688

Copper-stabilized Si:Au nanowhiskers for advanced nanoelectronics application

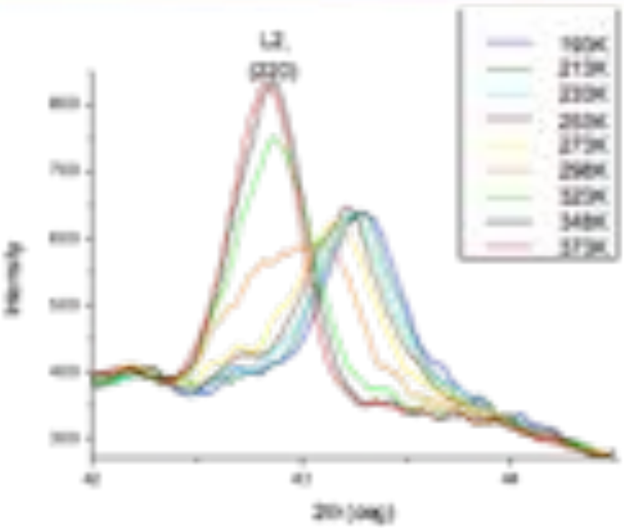
- For the first time, we demonstrate that this method could be employed to control the size and shape of silicon NWs by using a two-component catalyst material (Cu:Au~1:60).
- During the NW growth, copper is distributed on the outer surface of the nanowhisker, while gold sticks as a droplet to its top.
- The measurements of the electrical transport properties revealed that in contact with the substrate, individual NWs demonstrate typical I-V diode characteristics.

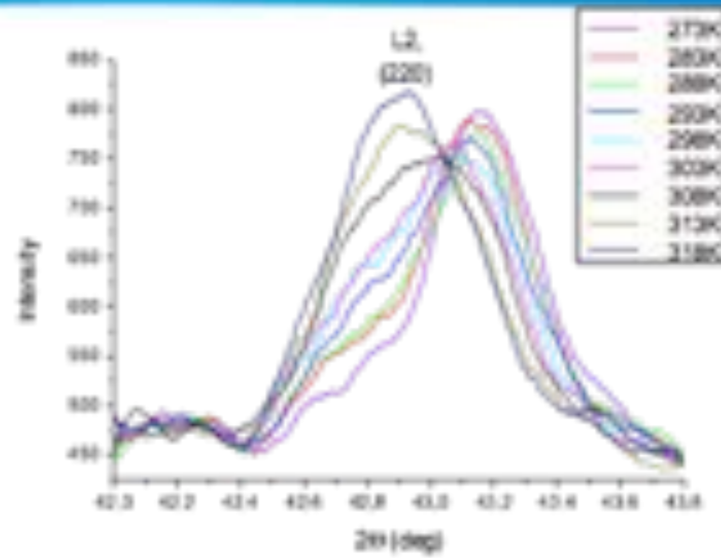


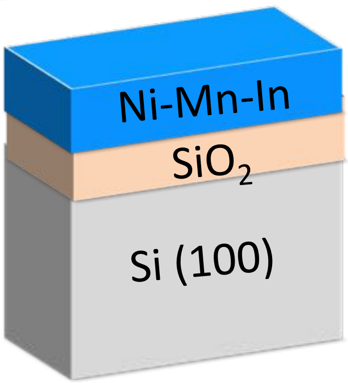
ACS Omega 3, 2, 1684-1688

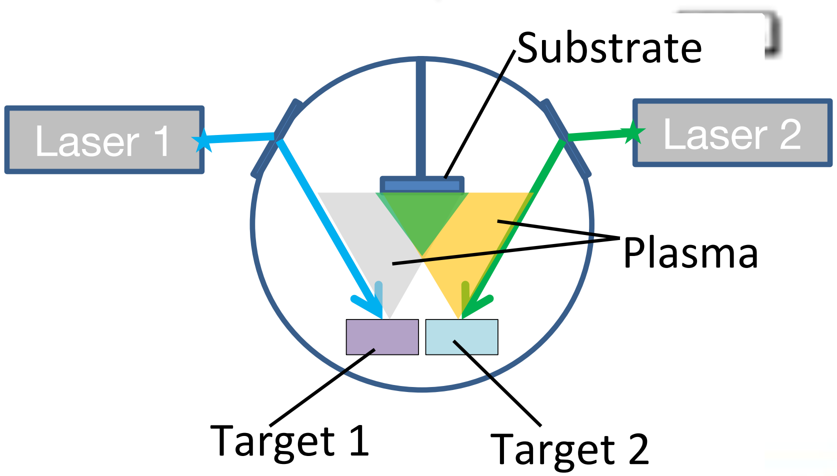
Functional Nanomaterials

Thin $Ni_{51}Mn_{33}In_{16}$ film XRD investigation









- Near-room martensitic transition.
- Narrow temperature interval of the martensitic transition (~30K).
- Transition temperature ~310K.

by Alexey Grunin

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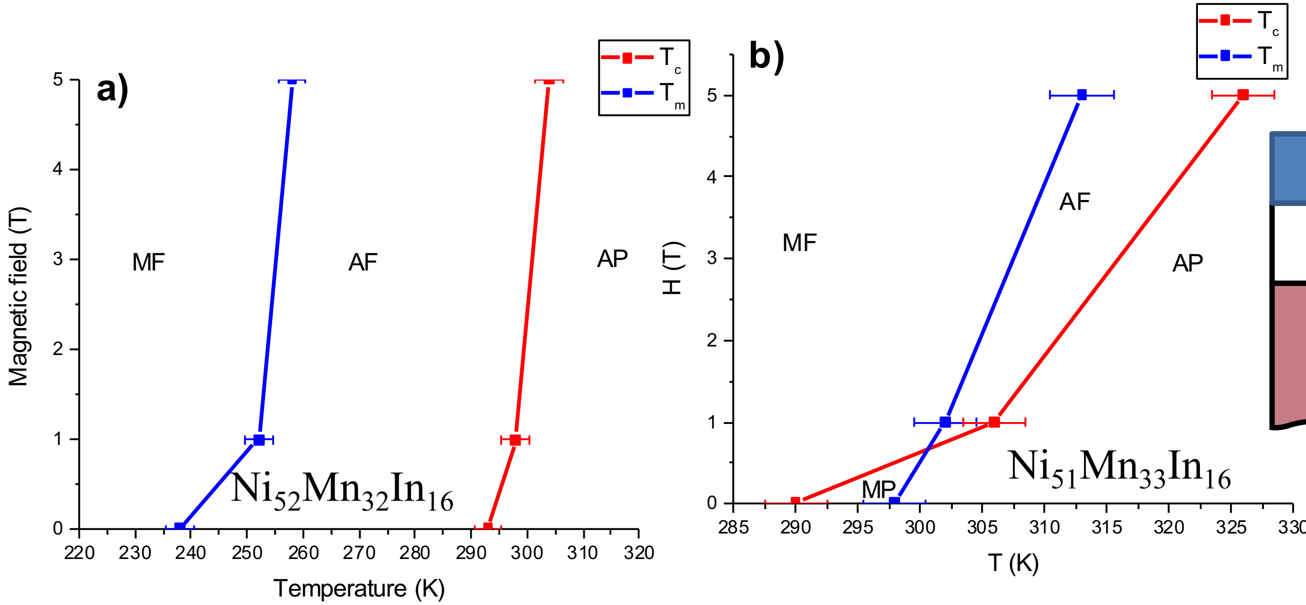
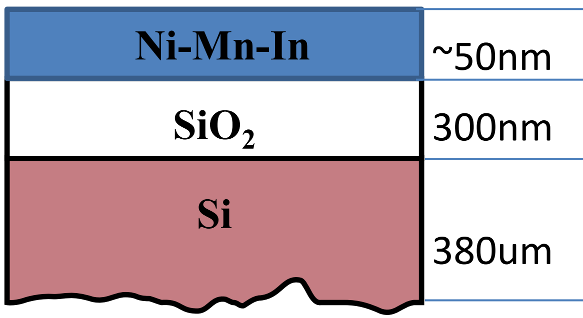
Magnetostructural transformations in Ni-Mn-In thin films

Properties of martensitic transition are investigated by X-Ray diffraction at different temperatures, magnetometery and HAXPES





Phase diagrams for samples $Ni_{52}Mn_{32}In_{16}$ (a) и $Ni_{51}Mn_{33}In_{16}$ (b)

M – martensitic phase, A – austenite. F – ferromagnetic, P - paramagnetic

*Alexei Grunin thesis defense 25.10.17

YIG(111)/GGG(111) Structures by PLD

Thin yttrium iron garnet films grown by pulsed laser deposition: Crystal structure, static, and dynamic magnetic properties

N. S. Sokolov,[1,a)] V. V. Fedorov,[1] A. M. Korovin,[1] S. M. Suturin,[1] D. A. Baranov,[1] S. V. Gastev,[1] B. B. Krichevtsov,[1] K. Yu. Maksimova,[2] A. I. Grunin,[2] V. E. Bursian,[1] L. V. Lutsev,[1] and M. Tabuchi[3]
[1]*Ioffe Physical-Technical Institute of Russian Academy of Sciences, St. Petersburg 194021, Russia*
[2]*Immanuel Kant Baltic Federal University, Kaliningrad 236041, Russia*
[3]*Synchrotron Radiation Research Center, Nagoya University, Nagoya 464-8603, Japan*

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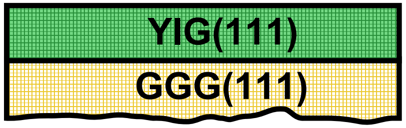
Pulsed laser deposition has been used to grow thin (10–84 nm) epitaxial layers of Yttrium Iron Garnet $Y_3Fe_5O_{12}$ (YIG) on (111)–oriented Gadolinium Gallium Garnet substrates at different growth conditions. Atomic force microscopy showed flat surface morphology both on micrometer and nanometer scales. X-ray diffraction measurements revealed that the films are coherent with the substrate in the interface plane. The interplane distance in the [111] direction was found to be by 1.2% larger than expected for YIG stoichiometric pseudomorphic film indicating presence of rhombohedral distortion in this direction. Polar Kerr effect and ferromagnetic resonance measurements showed existence of additional magnetic anisotropy, which adds to the demagnetizing field to keep magnetization vector in the film plane. The origin of the magnetic anisotropy is related to the strain in YIG films observed by XRD. Magneto-optical Kerr effect measurements revealed important role of magnetization rotation during magnetization reversal. An unusual fine structure of microwave magnetic resonance spectra has been observed in the film grown at reduced (0.5 mTorr) oxygen pressure. Surface spin wave propagation has been demonstrated in the in-plane magnetized films.
 [http://dx.doi.org/10.1063/1.4939678]



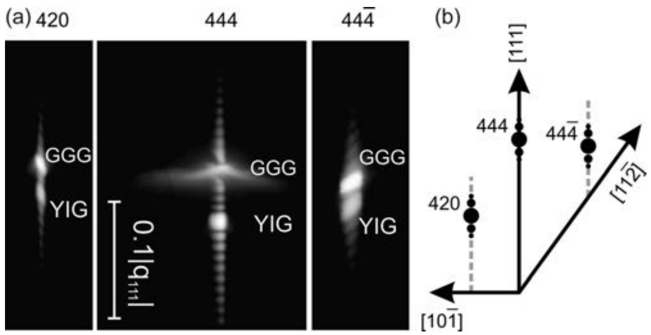
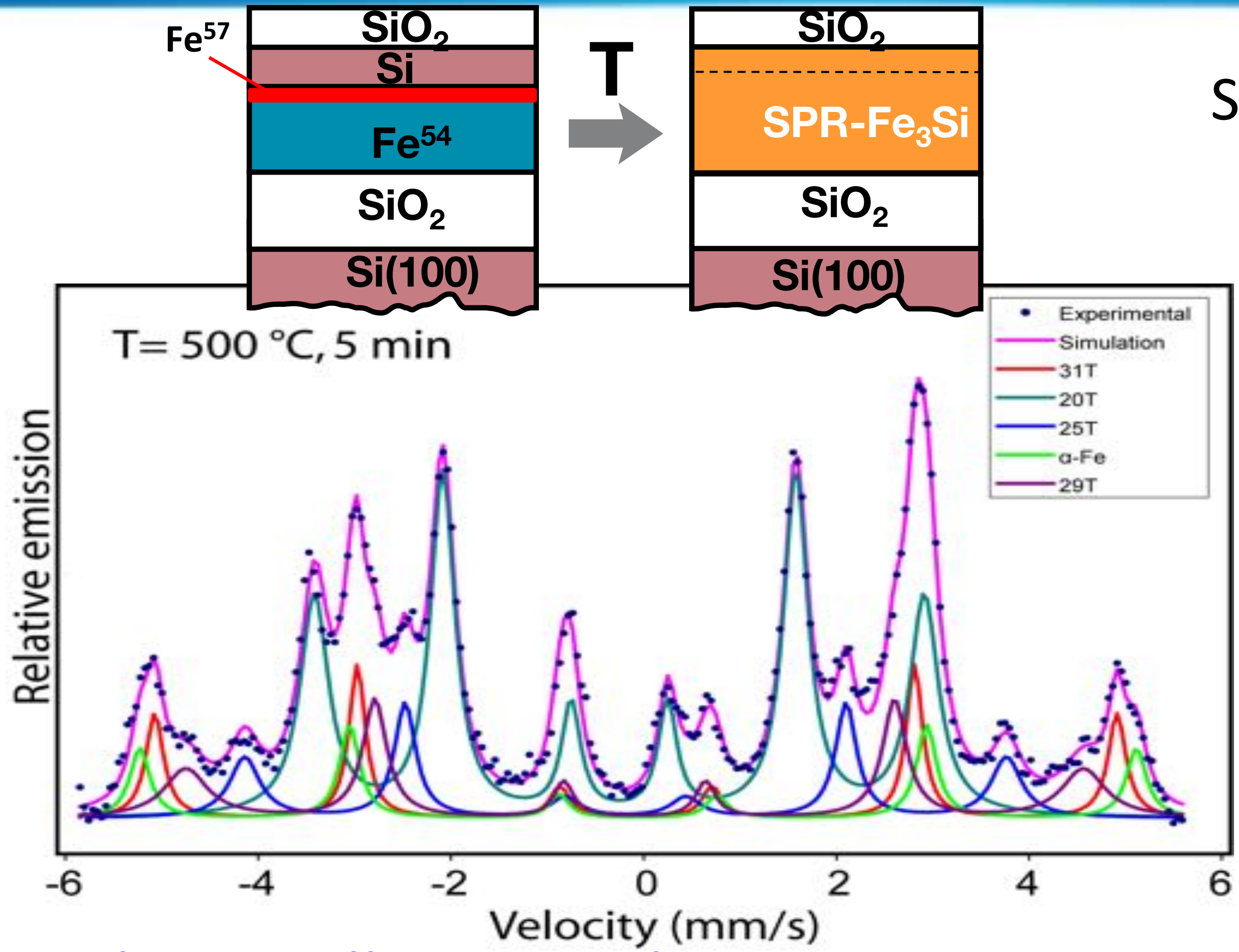


FIG. 2. 3D reciprocal space maps in the vicinity of GGG (420), (444), and (44-4) reflections of the sample with 84 nm YIG film (a) and schematic drawing of the corresponding crystal truncation rods (b).

The origin of the magnetic anisotropy is related to the strain in $\mathbf{Y_3Fe_5O_{12}}$ films observed by XRD

Fe_3Si/SiO_2 interface: ex *situ* CEMS

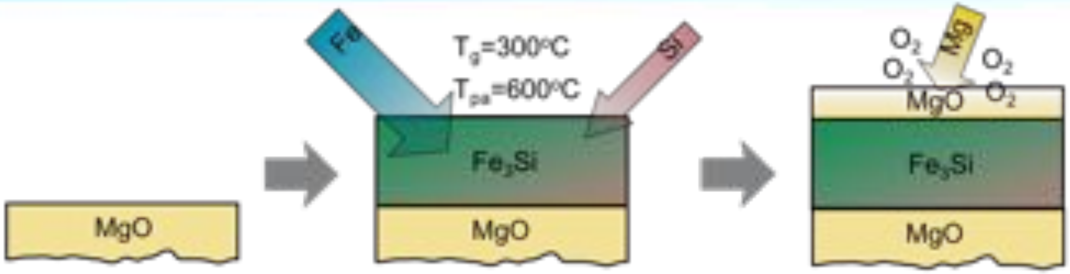


Solid Phase Reaction (SPR)

*R. Mantovan et. al, Phys. stat. sol. (a), 1– 5 (2008)

- Polycrystalline stoichiometric Fe_3Si in contact with SiO_2

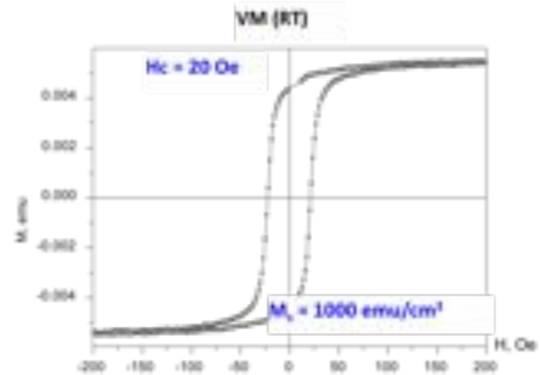
Epitaxial Fe_3Si/MgO growth



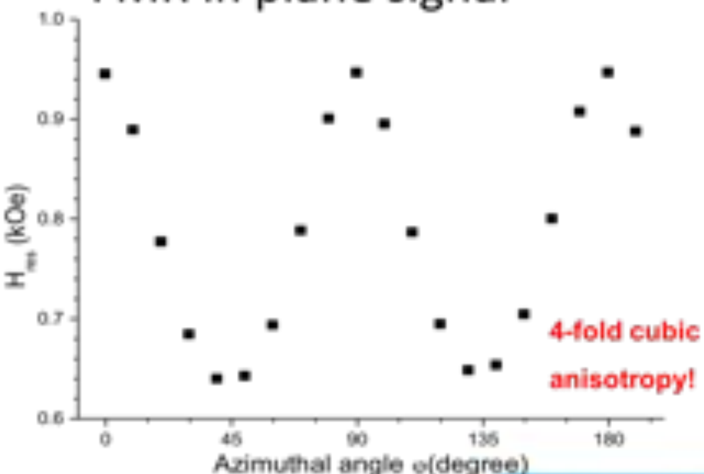
MgO(001)/Fe3Si(001) (Δa/a≈2.7%)

$[110]_{Fe3Si}$ || $[010]_{MgO}$

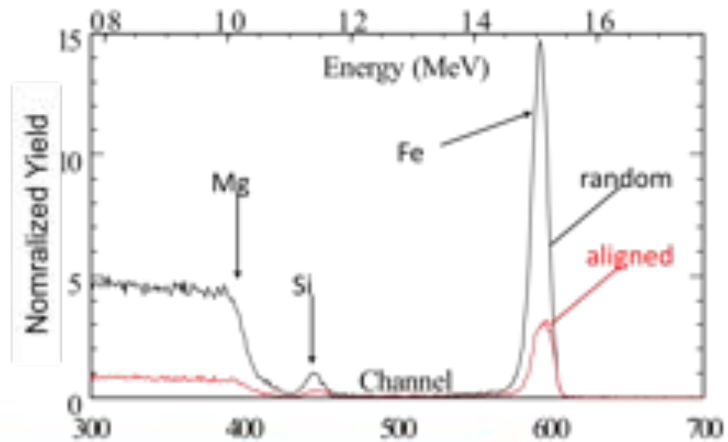
$(001)_{Fe3Si}$ || $(001)_{MgO}$



FMR in plane signal



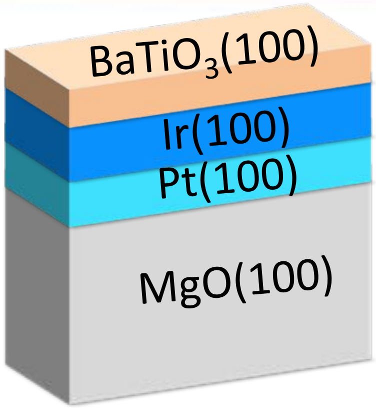
RBS/Chenneling χmin~ 20%

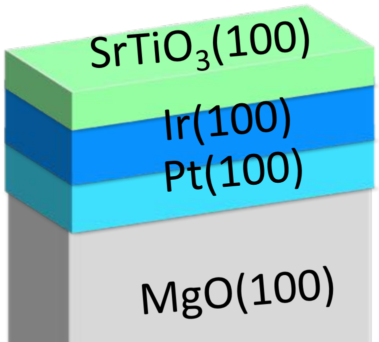


* A. Goikhman et al., Thin Solid Films Volume 652,28-33 Doi: 10.1016/j.tsf.2017.11.008

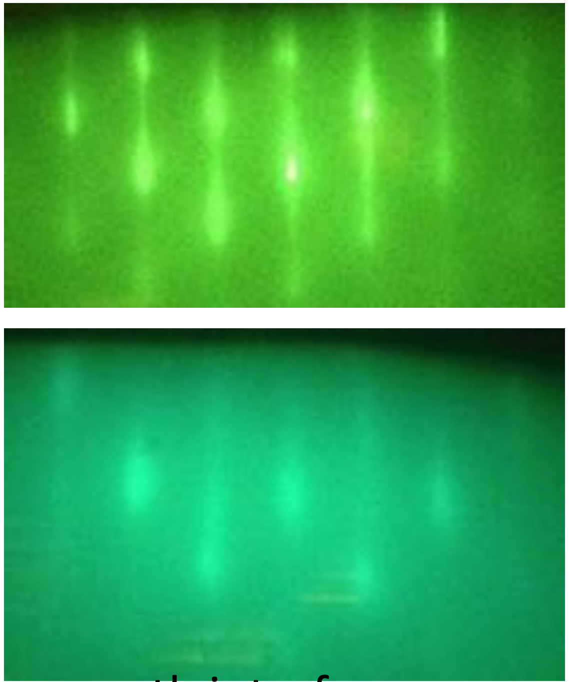
BTO and STO epitaxial growth by PLD

BTO and STO tetragonal

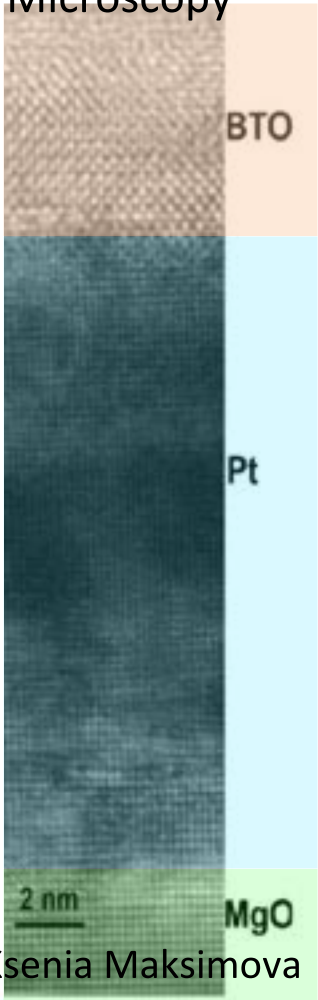




Reflection High Energy Electron Diffraction



Transmission Electron Microscopy



by Ksenia Maksimova

- Layer-by-layer growth with smooth interfaces;
- Lattice mismatch $BaTiO_3$/Ir= 2.1%; Fe/$BaTiO_3$= 3.3%;
- Lattice mismatch $SrTiO_3$/Ir= 1.7%; Fe/$SrTiO_3$= 3.7%;

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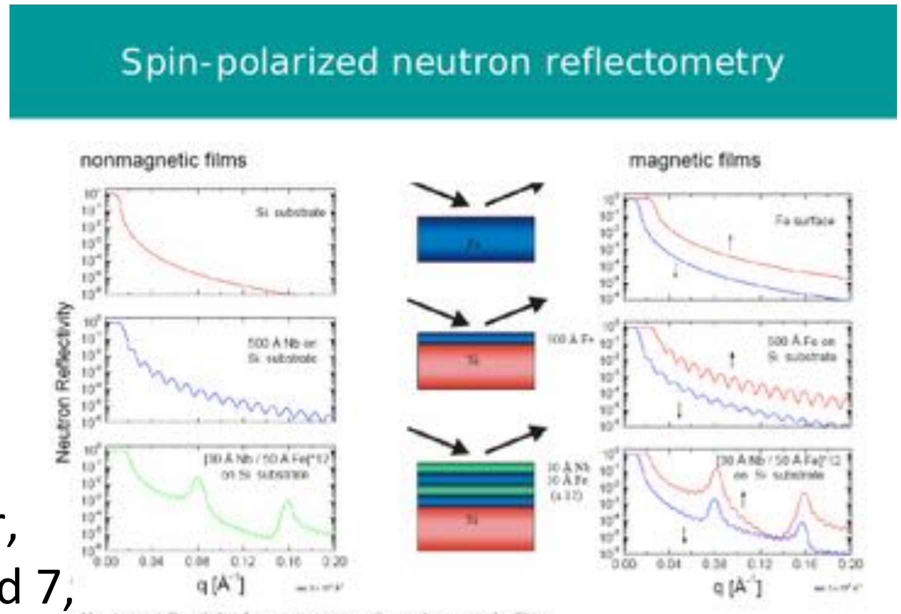
In-situ neutron investigations

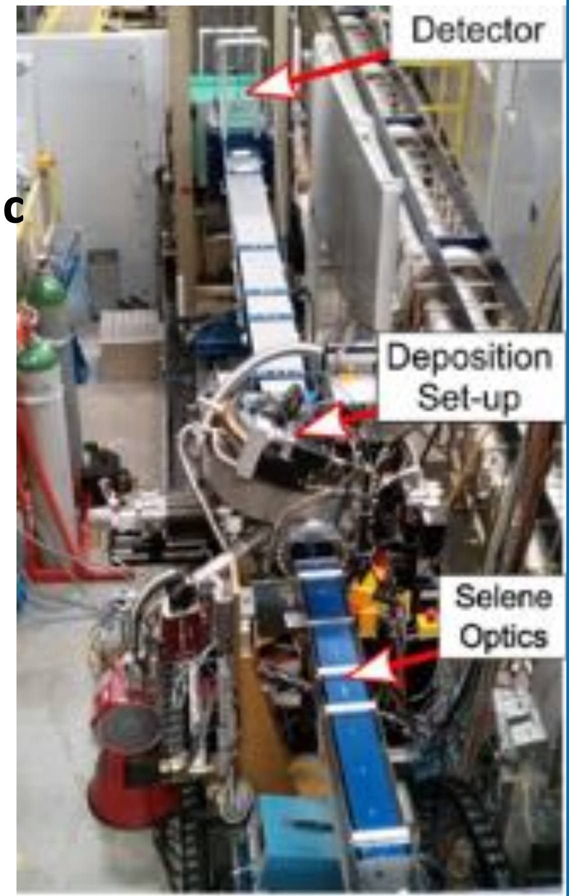
✓**The aim – to investigate the properties of materials at early stages of thin films growth.**

Polarized Neutron Reflectometry (PNR) is very sensitive technique for structural and magnetic properties with atomic resolution.



Neutron reflectivity from nonmagnetic and magnetic films
http://www.orau.org/council/02presentations/klose.pdf

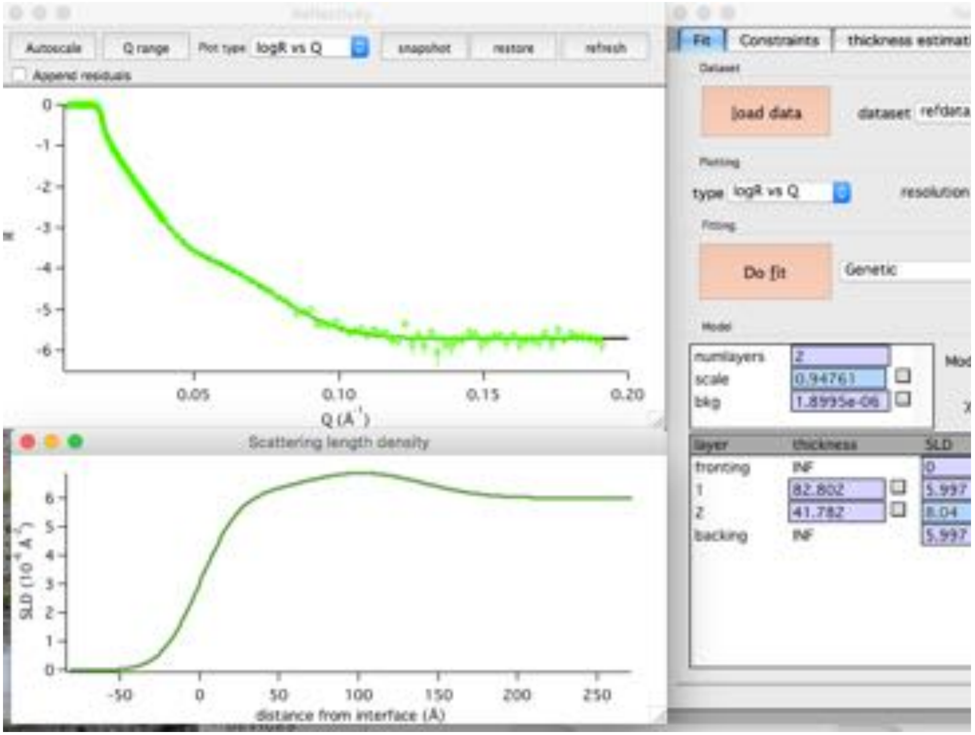
W. Kreuzpaintner, Phys. Rev. Applied 7, 054004, 2017



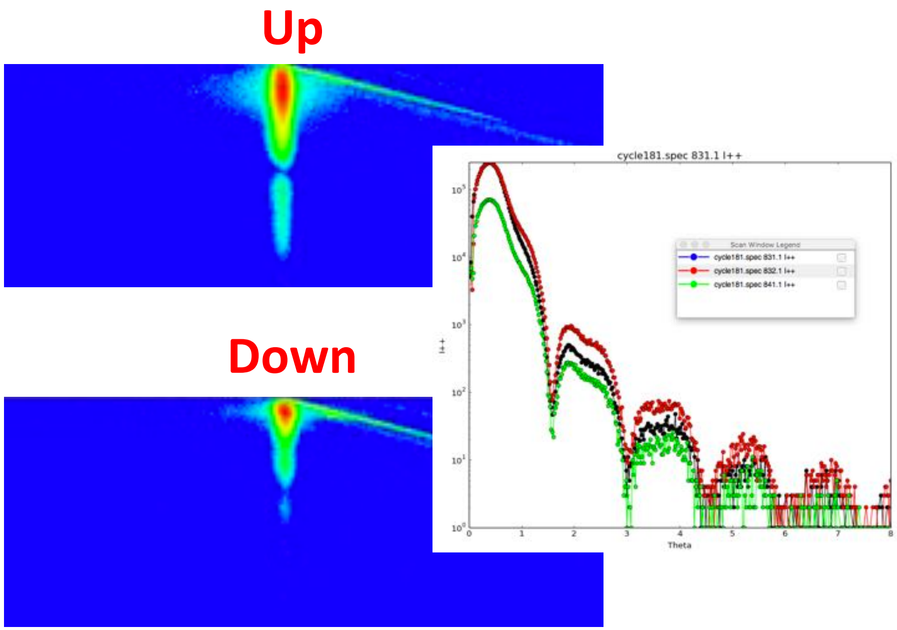
In-situ magnetron sputtering system at Swiss neutron spallation source SINQ

Neutron Reflectometry on PLD samples

MgO(4nm)/Fe(13nm)//MgO (@MARIA)

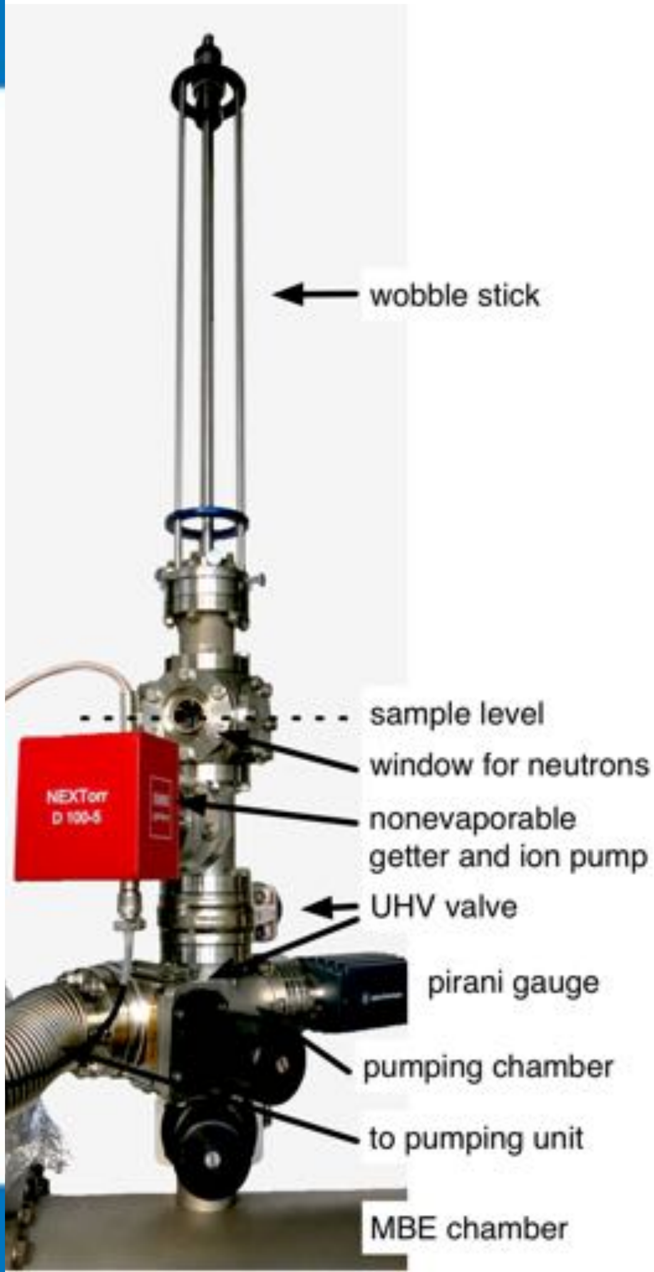


SiO2(10nm)/Fe(9.9nm)//SiO2/Si (@SuperAdam)



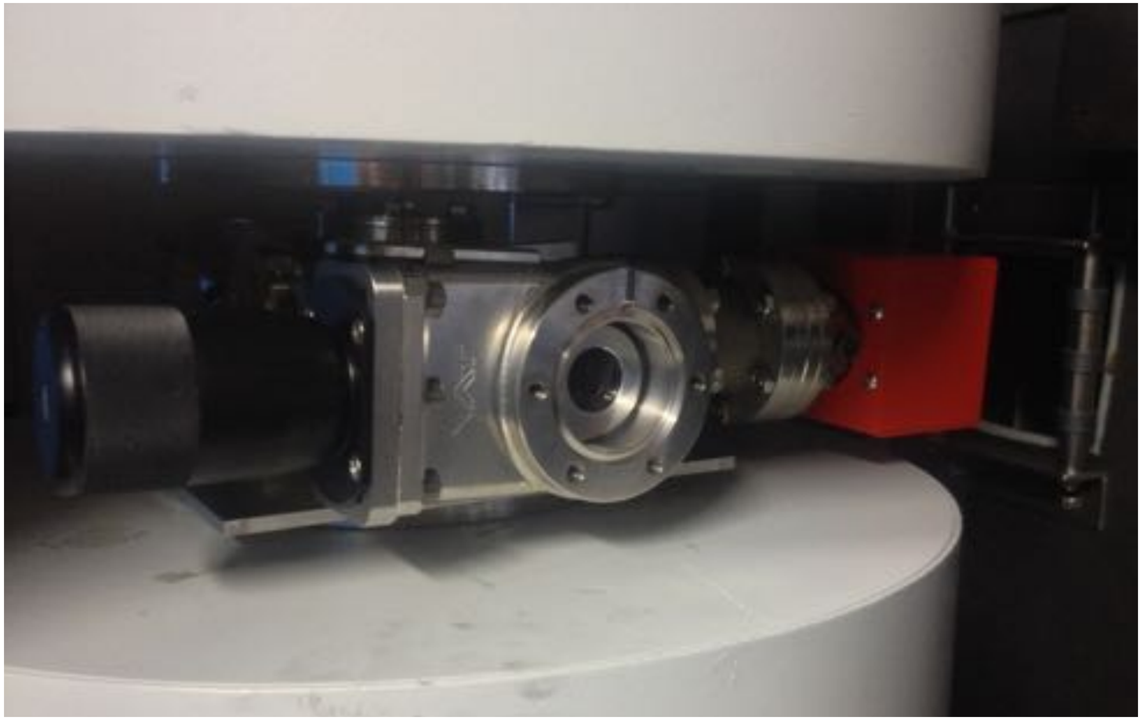
- **PLD samples are uniform till 10x10 cm**
- **Thickness might be controlled with the very high accuracy**
- **Surface roughness <0.5 nm**

UHV-Transfer: quasi in-situ

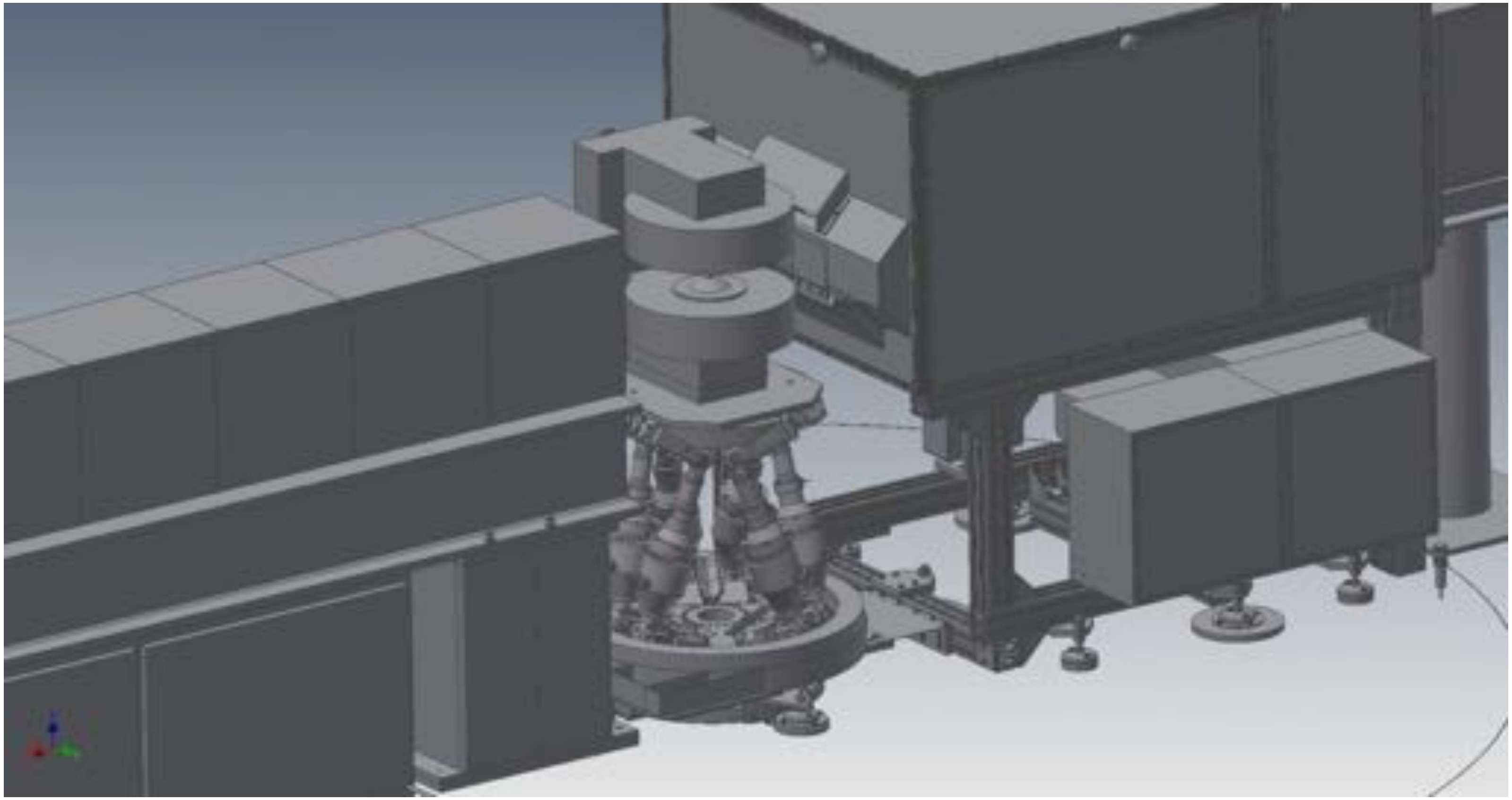


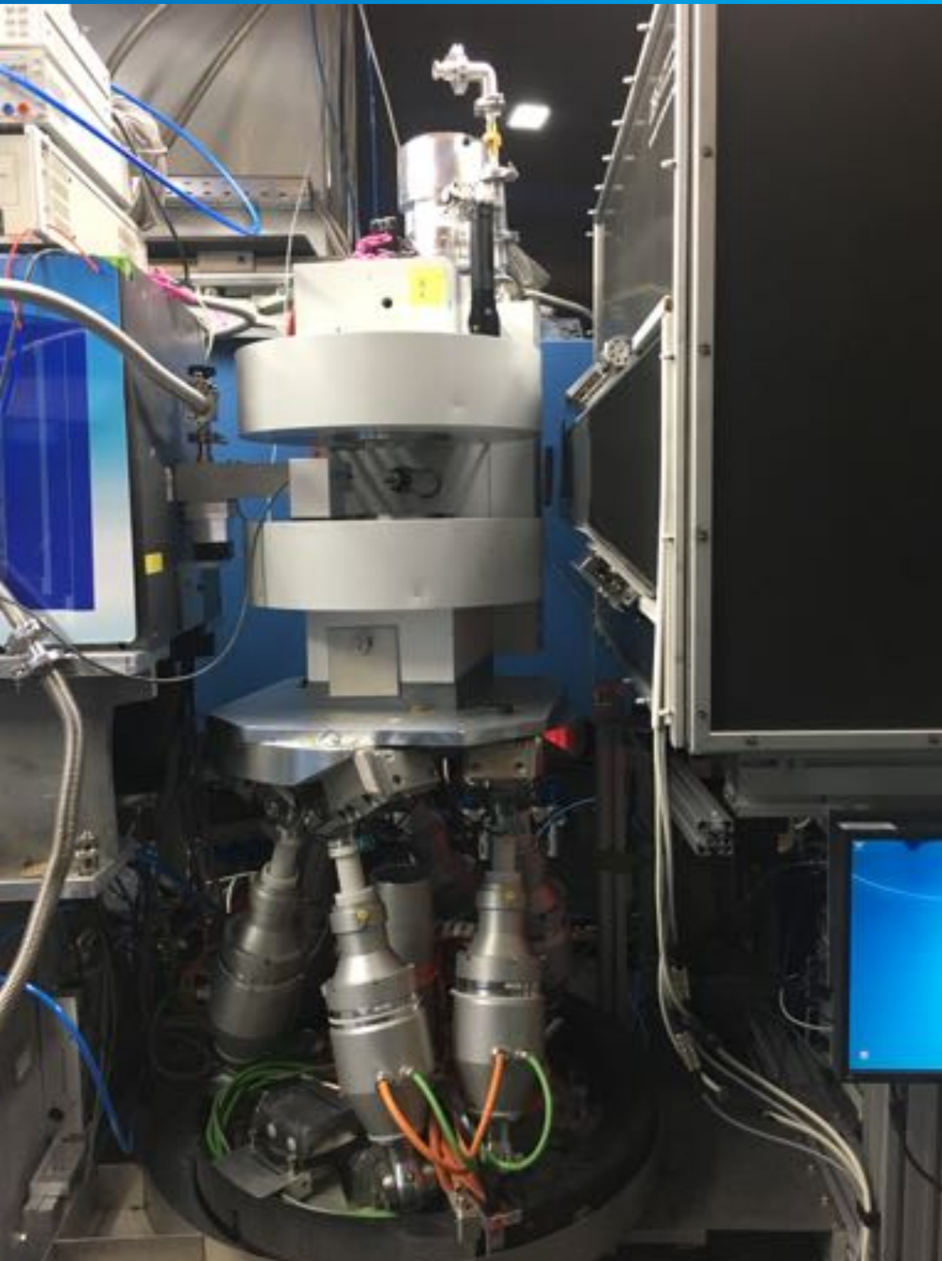
- DN CF-40 cube serves as main chamber
- two sapphire windows for the neutron beam
- a wobble stick, which serves also as a sample holder for samples of up to 1 cm2
- a DN CF-40 tee
- a nonevaporable getter and ion pump type Nextorr D 100-5 (SAES Getters SpA)
- DN CF-40 valve with window (for adjusting

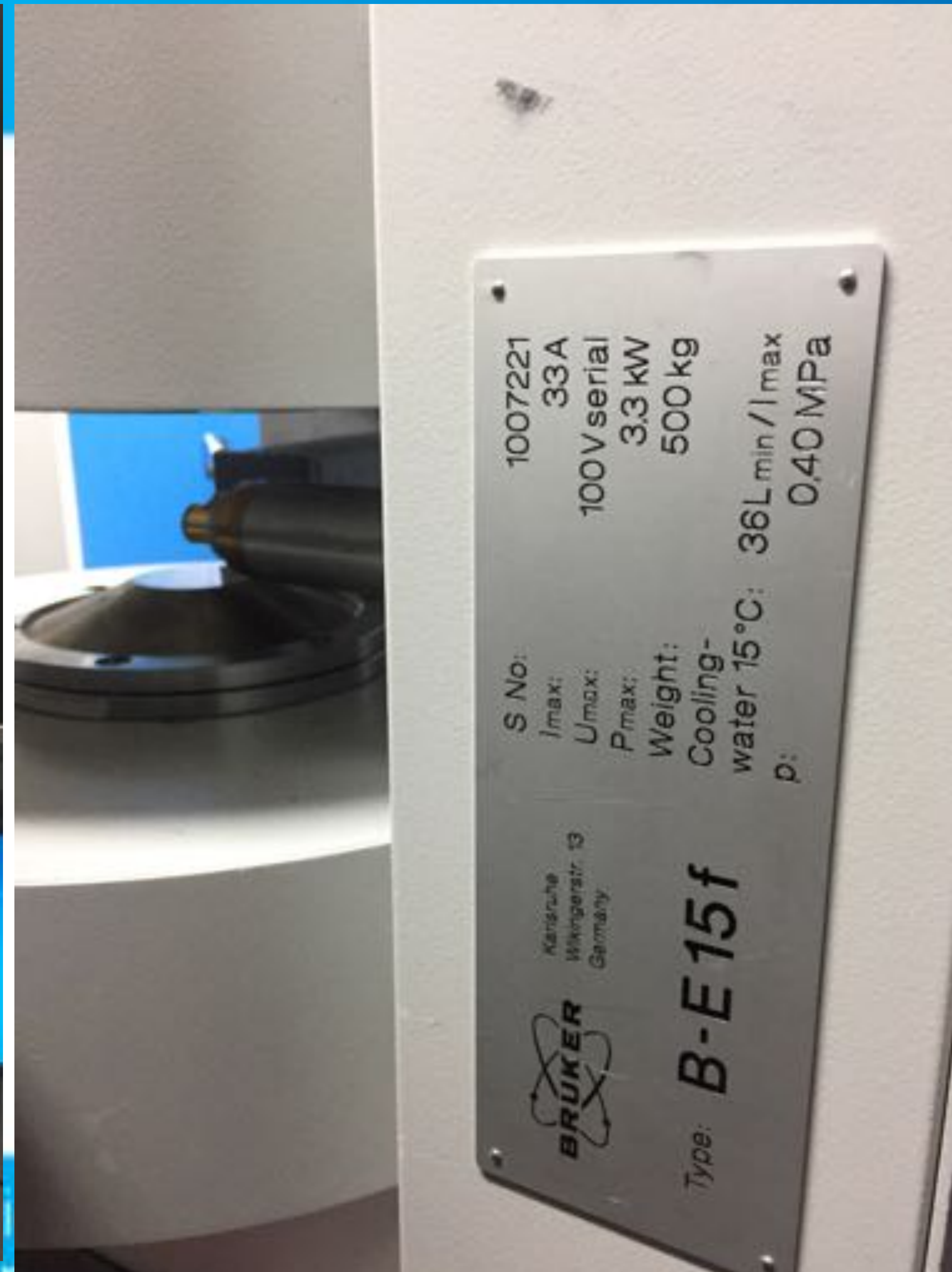
➜base pressure 2・10-10 mbar



MARIA sample environment

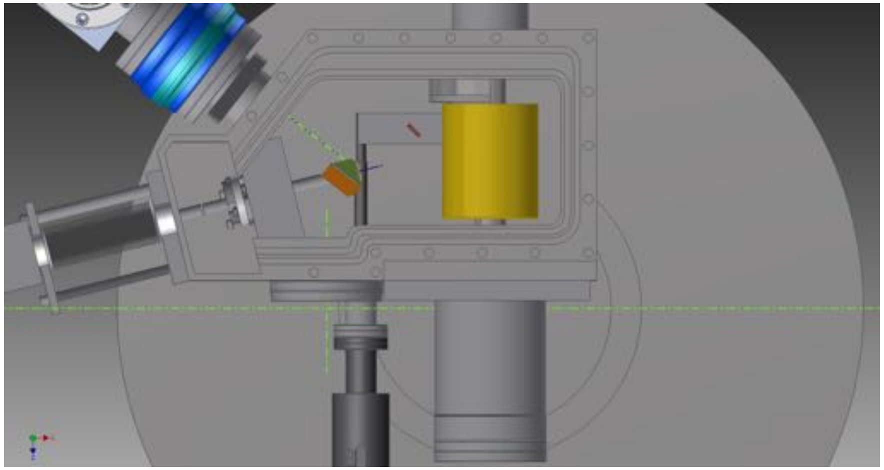


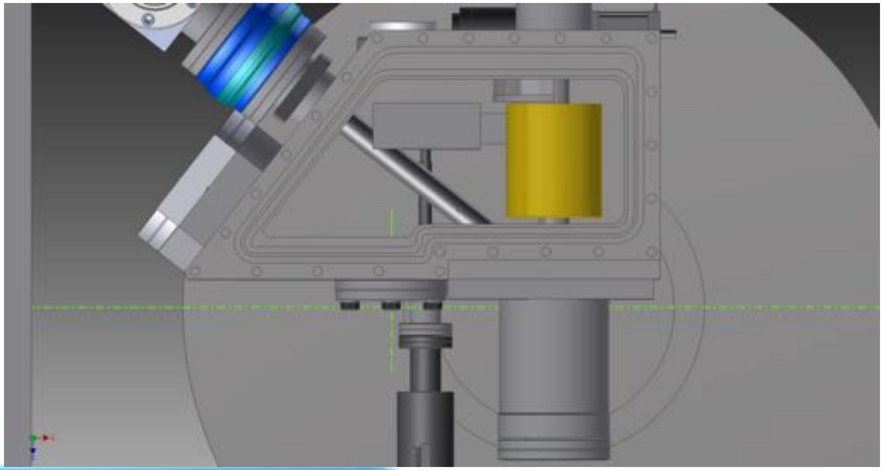



BRUKER
Karlsruhe
Wikingerstr. 13
Germany
Type: B-E 15 f
S No: 1007221
Imax: 33 A
Umax: 100 V serial
Pmax: 3,3 kW
Weight: 500 kg
Cooling-water 15°C: 36 Lmin / lmax
p: 0,40 MPa

In-line PLD concept @MARIA

- Movement of sample from ablation position to analytical position
- IR laser \ lamp sample heating
- Cold finger sample T=10K
- Ablation position T=600K
- Vacuum chamber height= 80 mm.
- Base Pressure 10x -8Pa
- Ultra compact setup design





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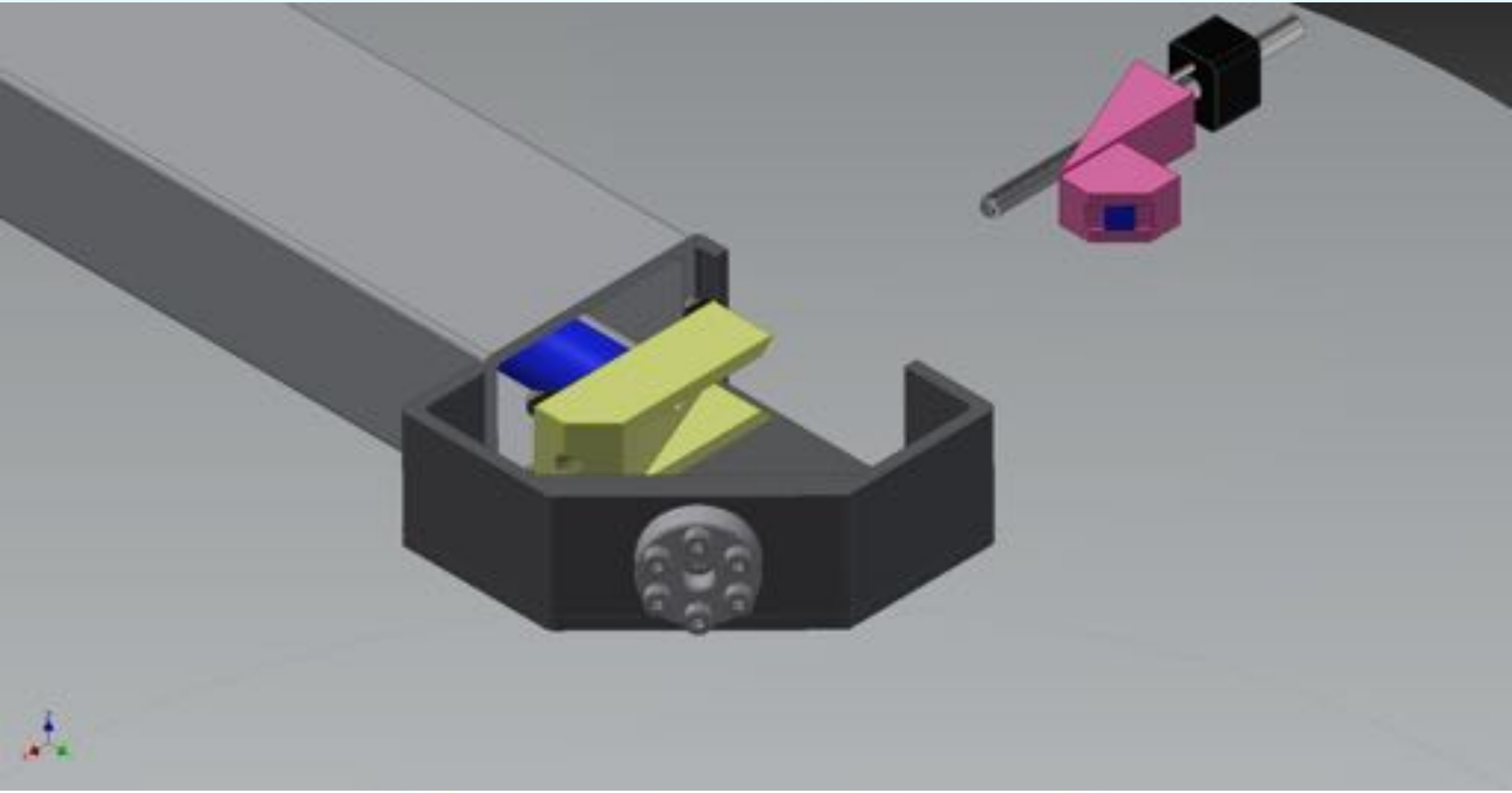
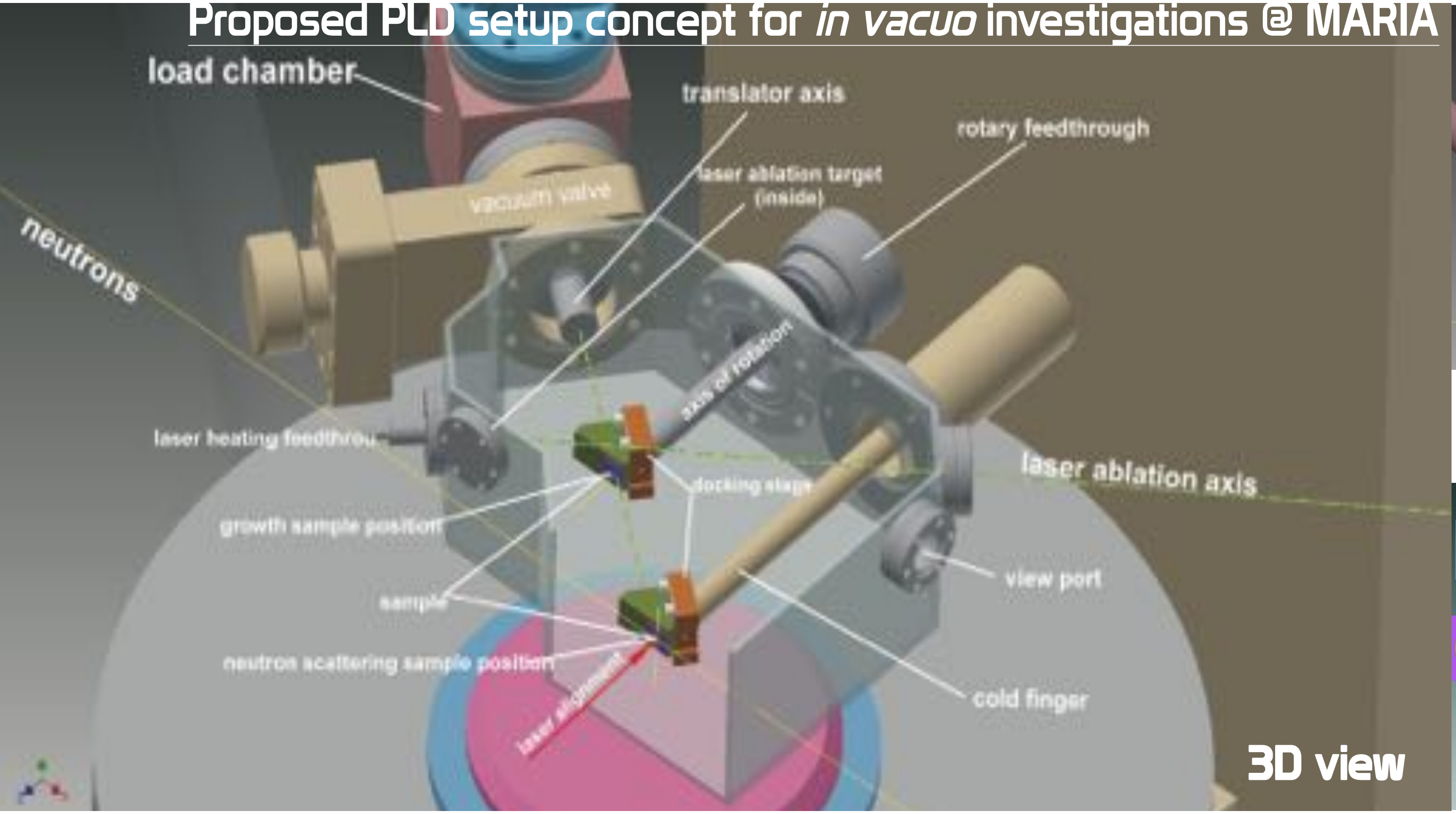
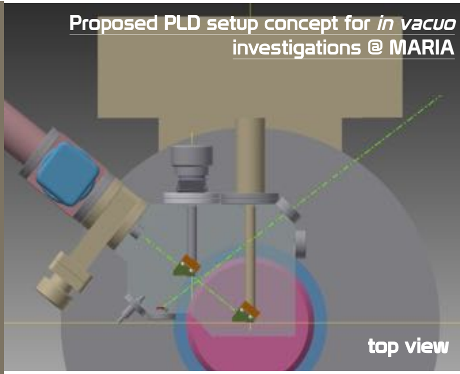
Heater Concept

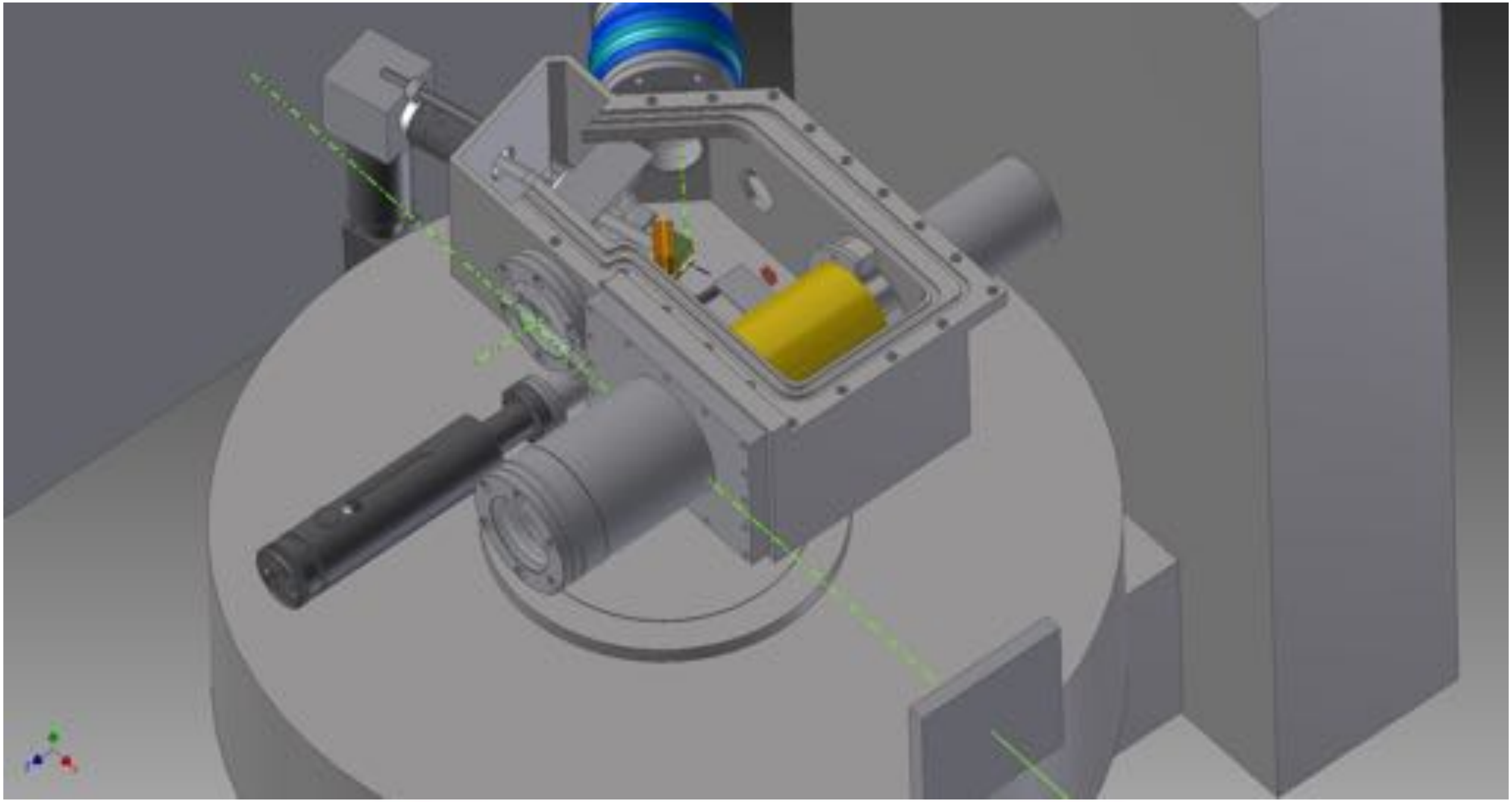


Neutron in-line chamber concept I





Neutron in-line chamber concept II



Functional Nanomaterials

Conclusions

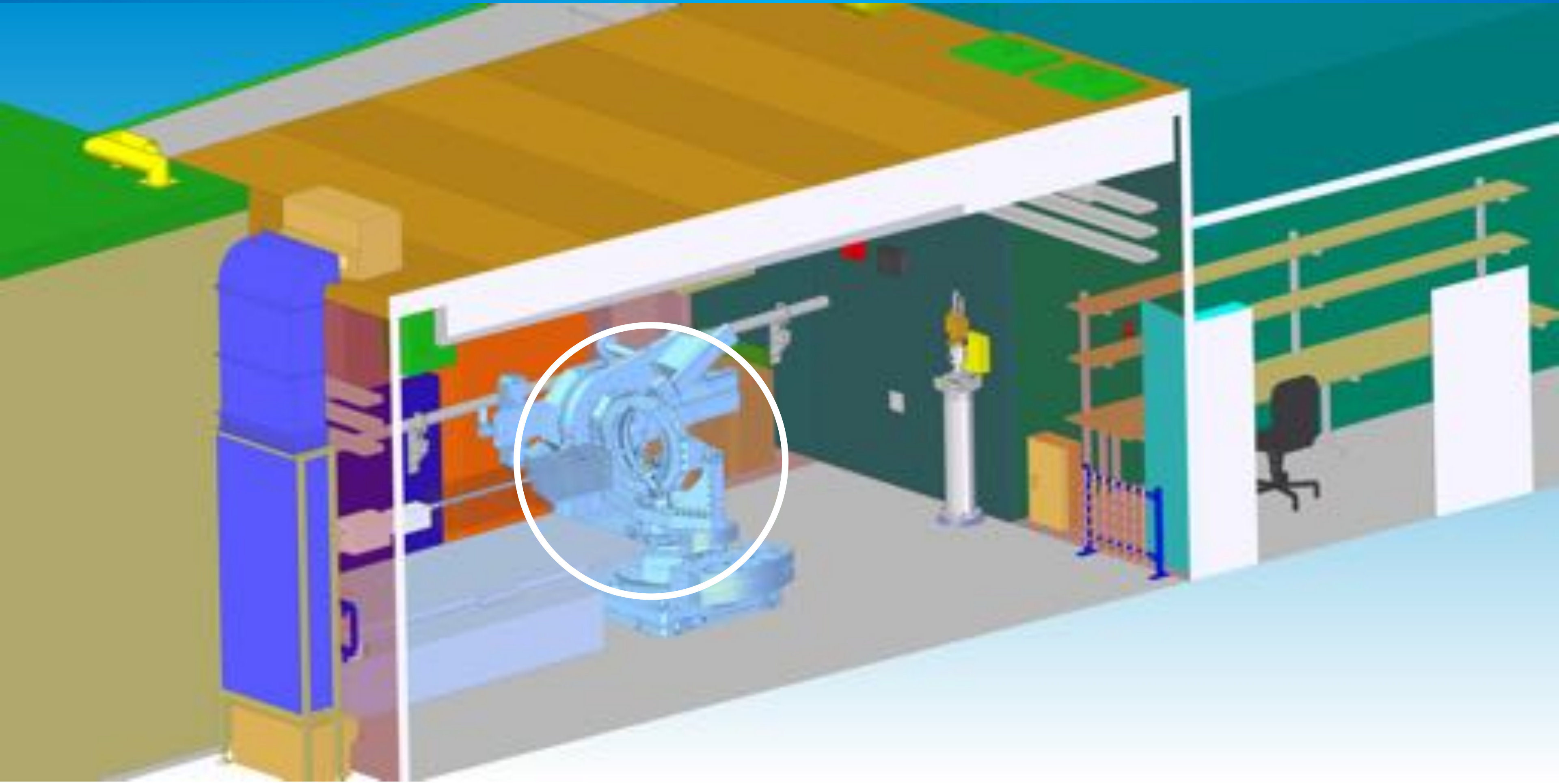
- Possibility of creating a Pulsed Laser Deposition setup in the conditions of an extremely stained space - in the gap between the poles of an electromagnet equal to 80 mm

- The possibility of in situ growth and investigation in low temperature and high-power magnetic fields conditions of a thin-film sample was demonstrated, as well as the method of transferring the sample from the growth zone to the cold finger of the cryostat.

Outline

- Pulsed Laser Deposition technique
- Home PLD laboratory at IKBFU (Kaliningrad, Russia)
  - Examples of PLD structures
- PLD thin films Neutron Reflectometry
  - In-situ concept chambers
- Another concepts

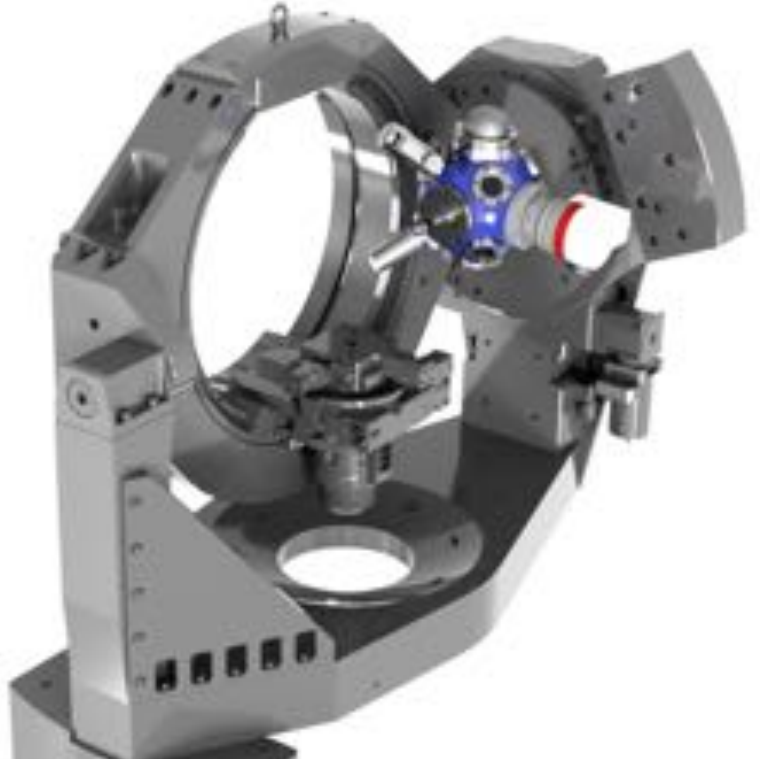
DESY, PETRA III, P23 (Russian-German)



- Thin film deposition system concepts for *in situ* investigations

DESY, P23 Russian-German Beamline: PLD chamber concept

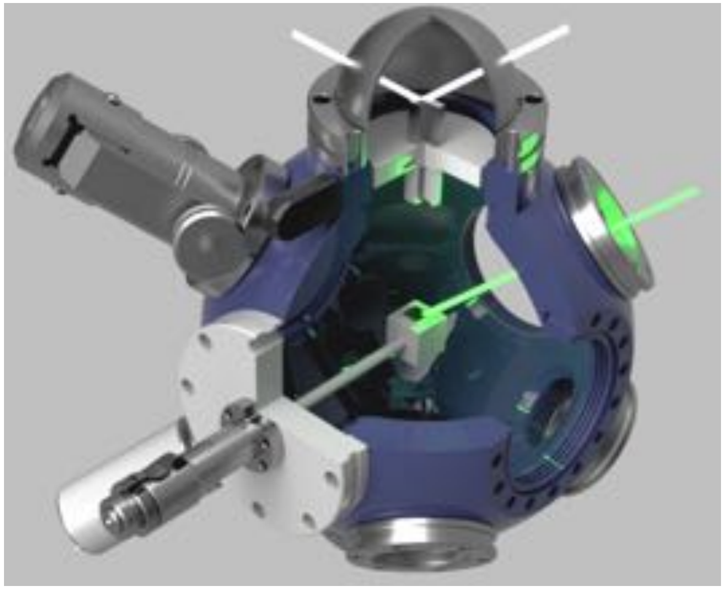
Russian-German beamline P23

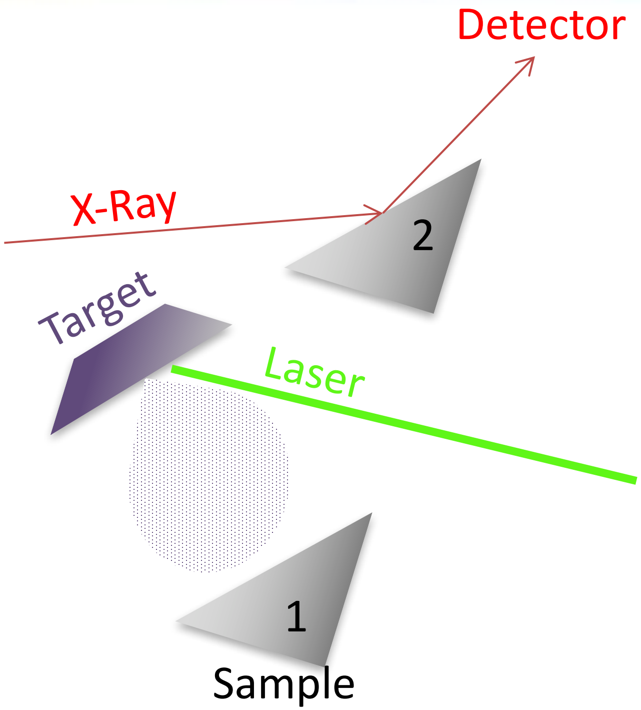


Goniometr EH1, for light chamber

by Ksenia Maksimova

DESY, P23 Russian-German Beamline: PLD chamber concept





Main features:

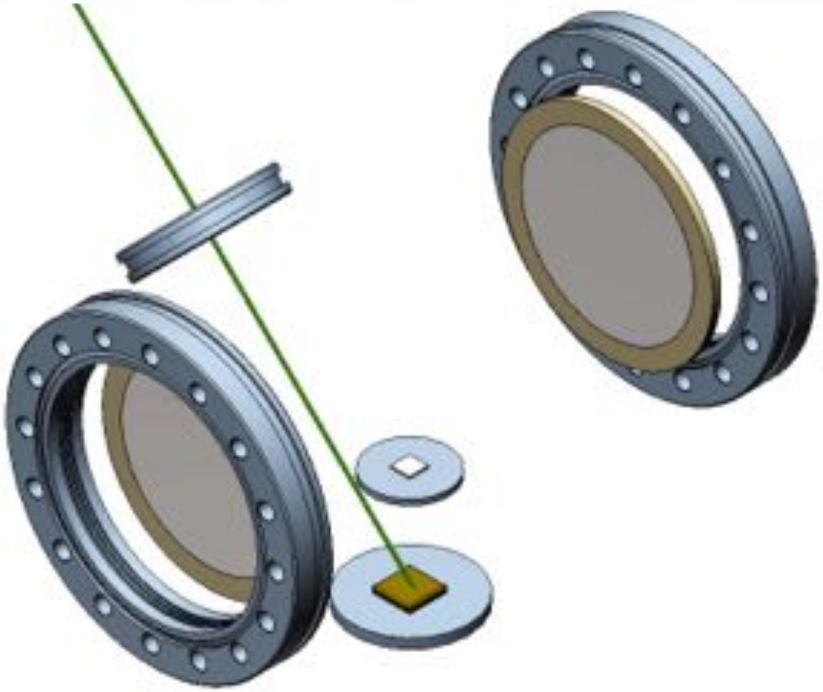
- chamber material: titanium
- Ultra High Vacuum chamber;
- Be-dome for *in situ* X-Ray experiments;
- adjustable leaks to $1x10^{-10}$ Torr l/sec

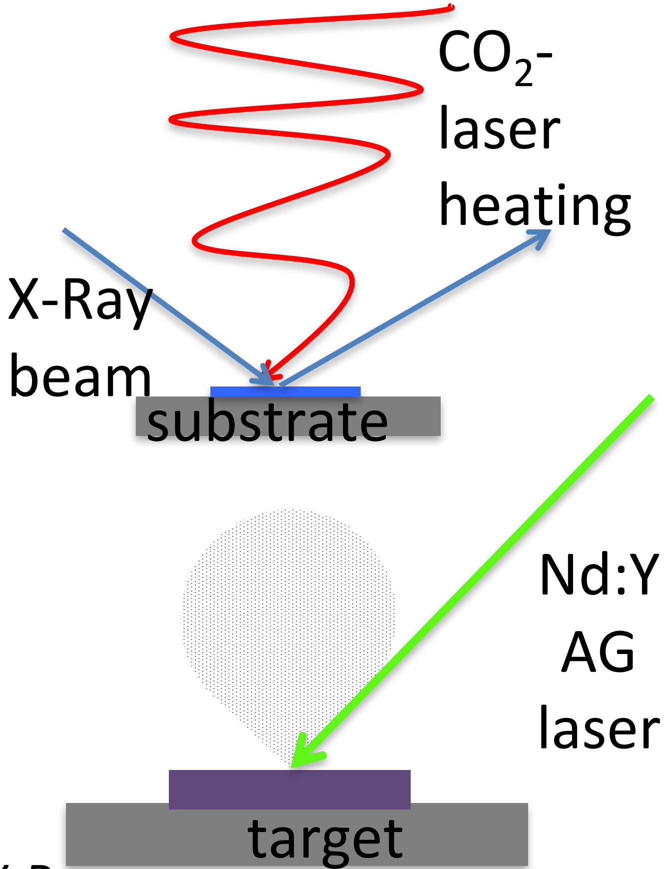
- the sample is displaced from 1-deposition to 2- X-Ray investigation positions

by Ksenia Maksimova

Portable PLD chamber: design III

"Shadow" thin film deposition:





- Very slow growth speed;
- Absence macroparticles;
- Possibility doing X-Ray investigation during growth

«Functional Nanomaterials»

20 persons, responsible A. Goikhman

- 5 Ph. D students (O. Yurkevich, O. Dikaya, U. Koneva, D. Serebrennikov, A. Grunin)
- 3 Master Students (A. Kozlov, E. Maznitsyna, A. Shapilov)
- 4 Postdocs and researchers: E. Klementyev, P. Shvets, K. Maksimova, A. Vinichenko
- 7 Engineers: (P. Prokopovich, D. Efimov, V. Kolesniskiy, A. Dolgoborodov, V. Molchanov, E. Severin, V. Fedotov

Functional Nanomaterials

E. Klementyev

Strongly Correlated Systems Lab

- High pressure cells
- Models and methods for electronic systems calc

K. Maksimova

Magnetron+UHV **Pulsed Laser Deposition** SVTA(2010)

Ion Beam Deposition (2008)

Atomic Layer Deposition SVTA(2011)

Be Magnetron Sputtering

AFM/MFM UHV JEOL(2008)

ToF SIMS Oxford Instruments (2011)

RF/DC Large Area Magnetron Sputtering (2013)

AES + HR-SEM JEOL(2009)

SEM +EDS JEOL(2009)

TEM JEOL + sample preparation

XRD/XRR with GISAXS+GID Bruker D8 (2011)

Raman-AFM complex Horiba LabRAM+AistNT (2012)

UV-IR Sph Shimadzu (2010)

D. Efimov

Ion Beam sector

HVEE Van der Graff accelerator (RBS, ion implantation)
He+, protons, liquid and solid ion sources

Engineering group

- Equipment support
- Drawings
- New Facilities Development

P. Prokopovich

Secretary group

- Project time management
- Applications
- Trips organization

I. Smirnova

Thank you for your attention

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Alexander Goikhman

AYGoikhman@gmail.com