



ACHIEVEMENTS AND PERSPECTIVES IN NANO MATERIALS AND NANOTECHNOLOGIES

IN

**THE NATIONAL INSTITUTE FOR LASERS,
PLASMA AND RADIATION PHYSICS**

NILPRP



HUMANE RESOURCES:

- number of working persons : 113 (~45%)
- number of scientists : 94
- referees in international journals: 8
- EU experts for FP7 NMP projects: 2
- number of young researchers (PhD students or Post Doc) with international grants: 18
- number of scientific papers published in the last five years: over 250



LABORATORIES:

LASER PHOTOCHEMISTRY

Dr. I. Morjan

NANOMETRIC POWDERS, QUANTUM DOTS AND NANOSTRUCTURES THIN FILMS

Dr. C. Grigoriu

NONLINEAR NANOPHOTONICS

Acad. V.I.Vlad

PHOTONIC PROCESSING OF ADVANCED MATERIALS

Dr. M. Dinescu

LASER-SURFACE-PLASMA INTERACTIONS

Dr. I.N. Mihailescu

PLASMA PROCESSES, MATERIALS AND SURFACES

Dr. G. Dinescu

PLASMA SURFACE ENGINEERING

Dr. C. Ruset

ELEMENTARY PROCESSES IN PLASMA AND APPLICATIONS

Dr. C. Lungu

LASER SPECTROSCOPY

Dr. M. L. Pascu

SOLID STATE LASERS

Dr. M. Zamfirescu



LABORATORY OF LASER PHOTOCHEMISTRY

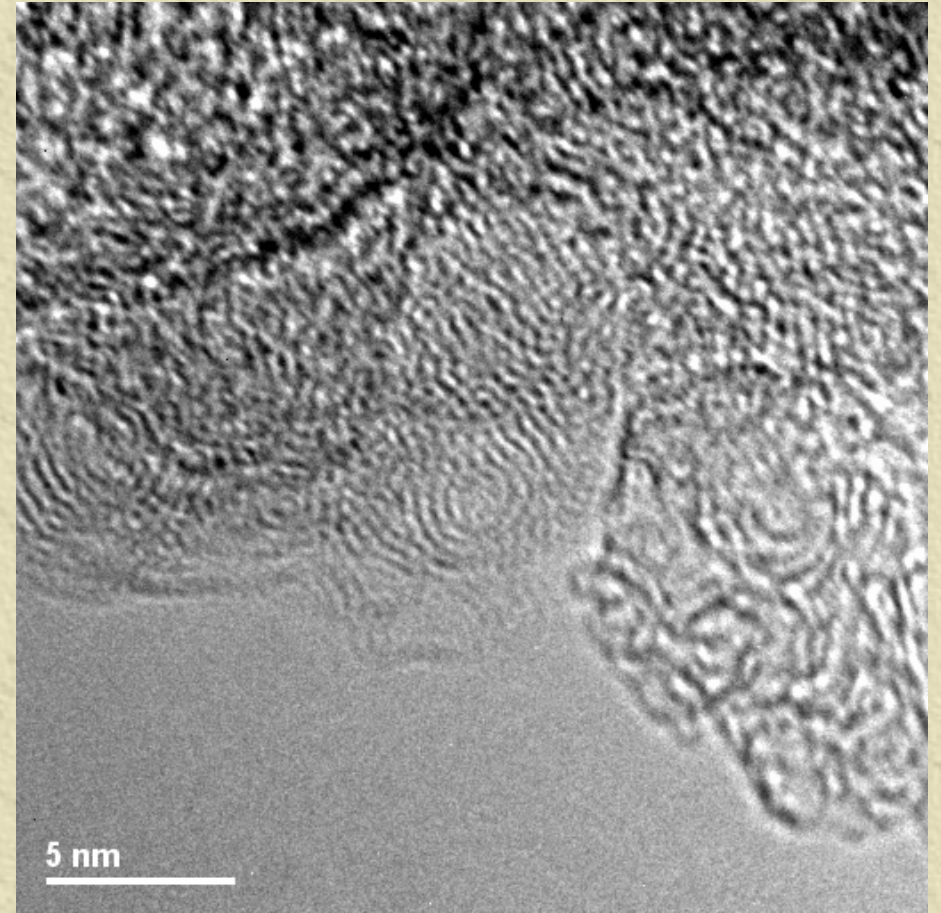
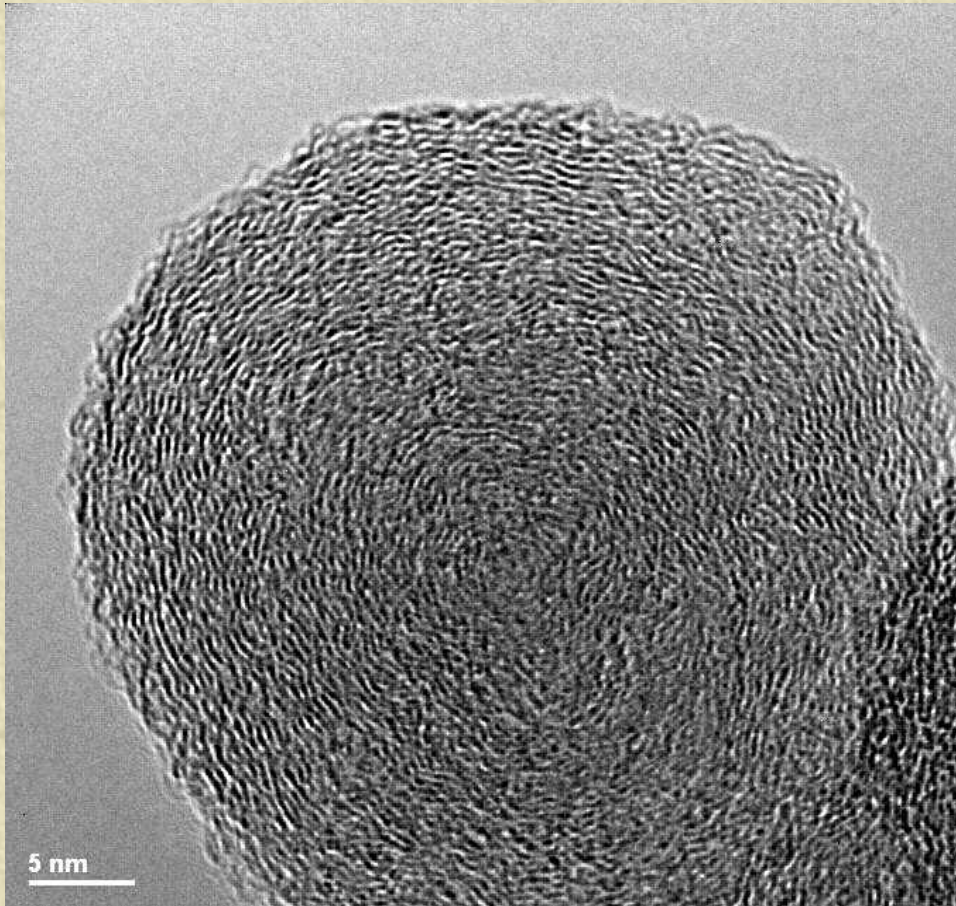
EXPERTISE:

1. *The synthesis of nanomaterials with controlled composition and structure by laser pyrolysis*
2. *Thin films production by LCVD*
3. *The characterization of nanomaterials produced by laser pyrolysis and LCVD*



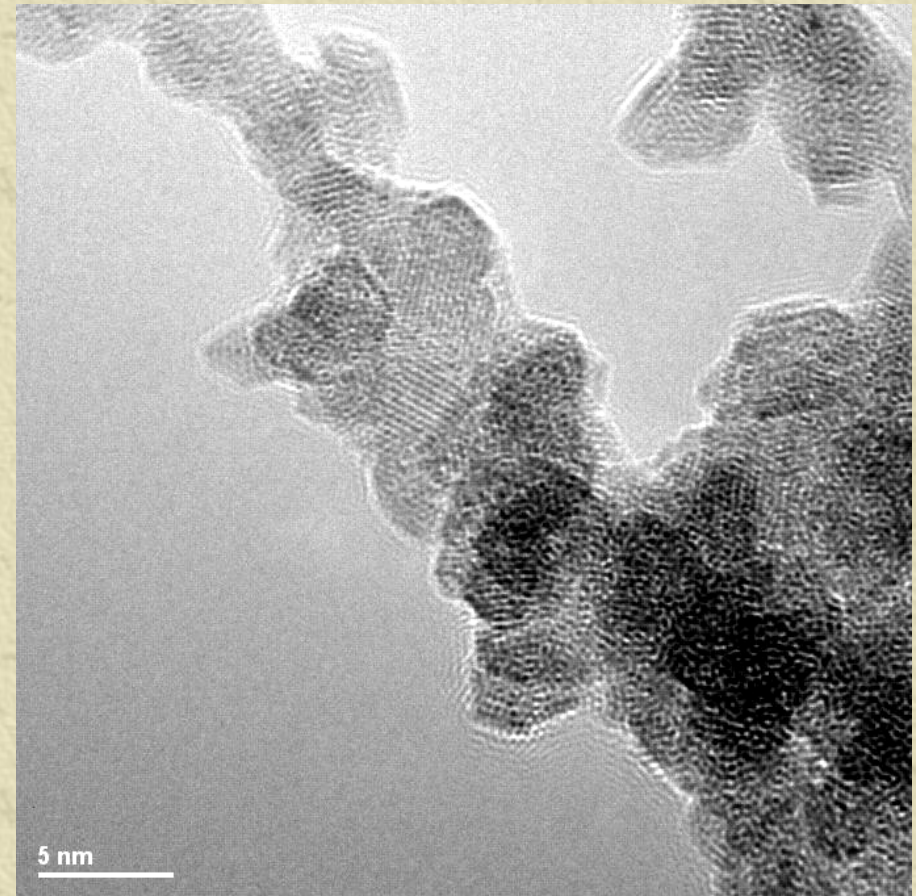


THE SYNTHESIS OF CARBON NANOMATERIALS



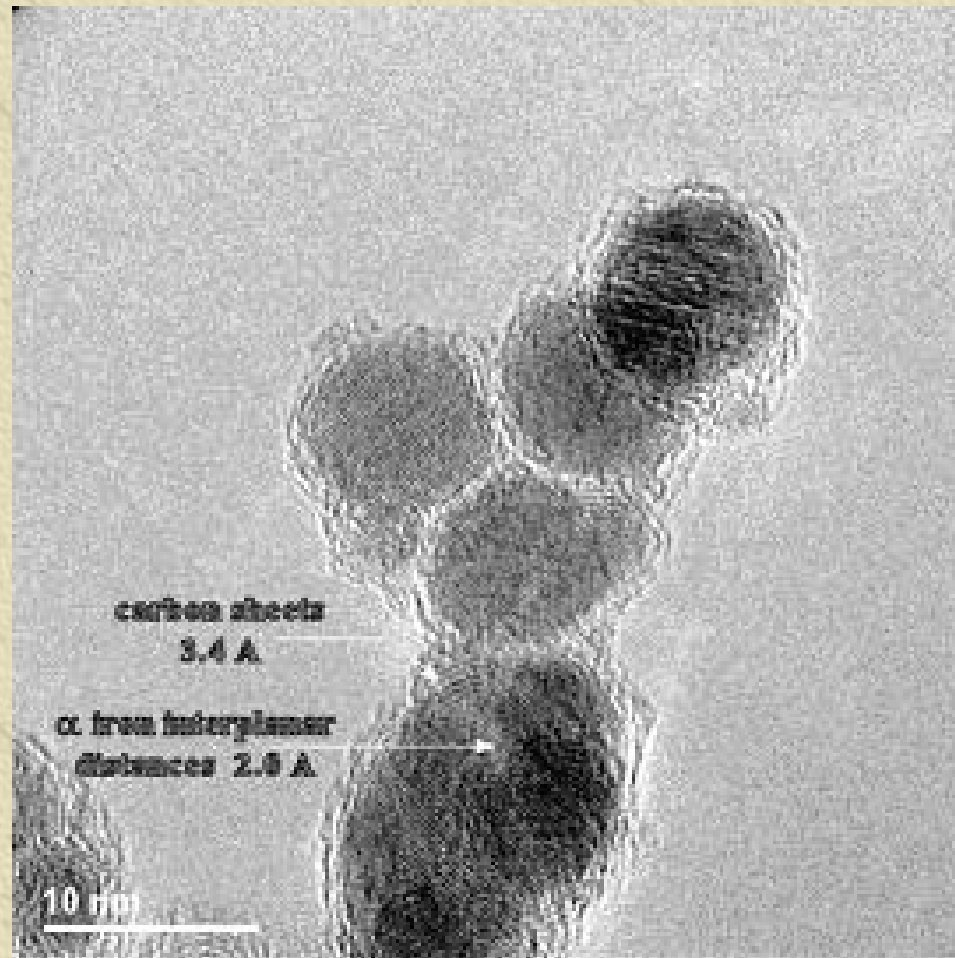


THE SYNTHESIS OF γ -Fe₂O₃ NANOPARTICLES



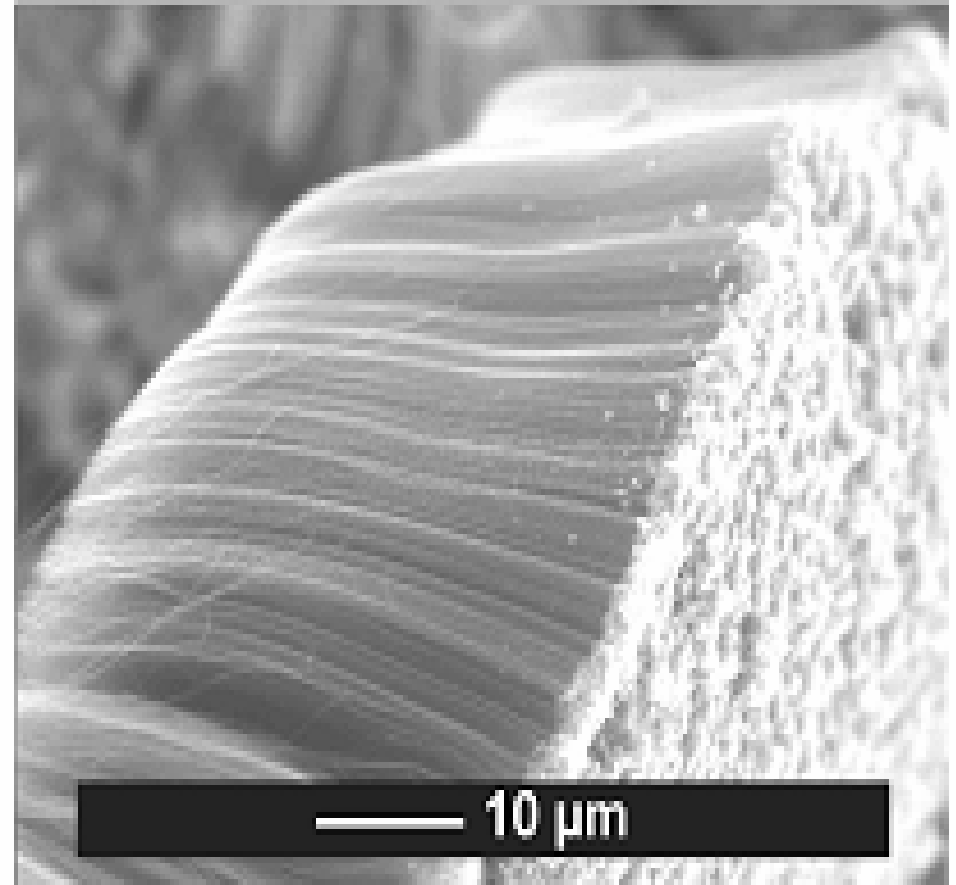
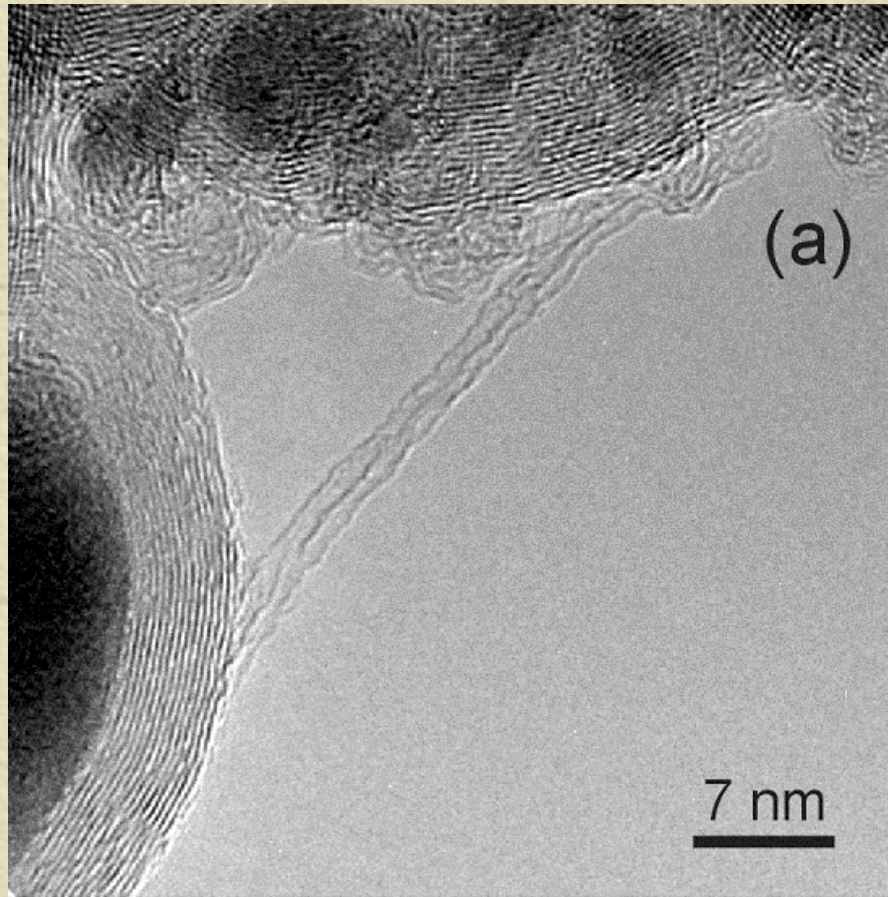


CORE-SHELL IRON-CARBON NANOCOMPOSITES





CARBON NANOTUBES



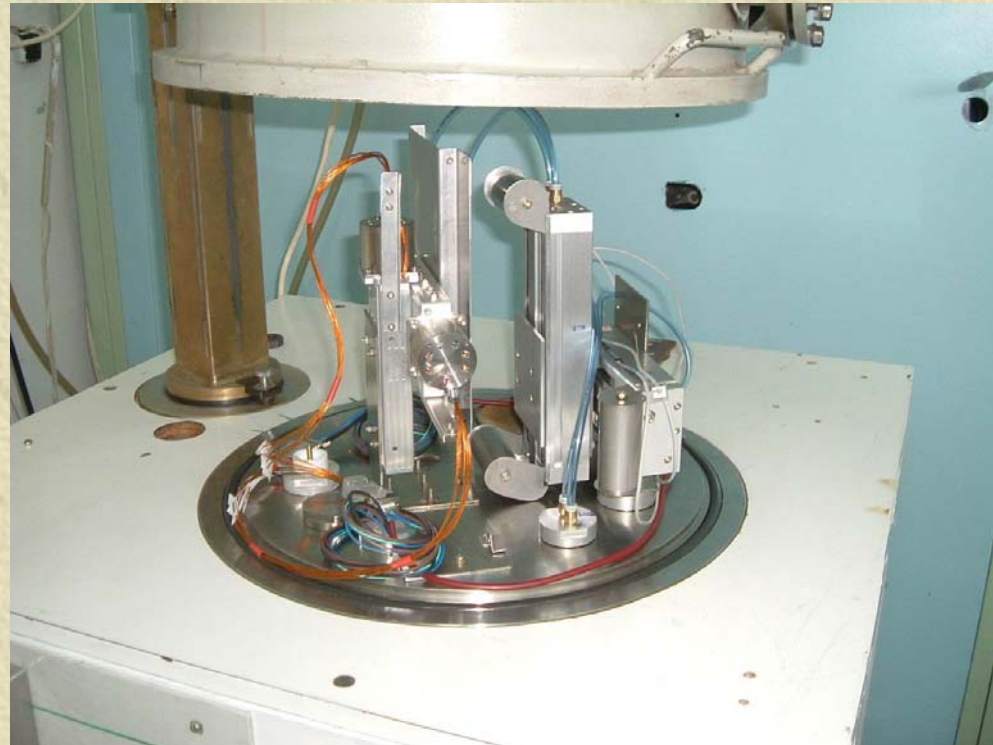


NANOMETRIC POWDERS, QUANTUM DOTS AND NANOSTRUCTURES THIN FILMS

EXPERTISE:

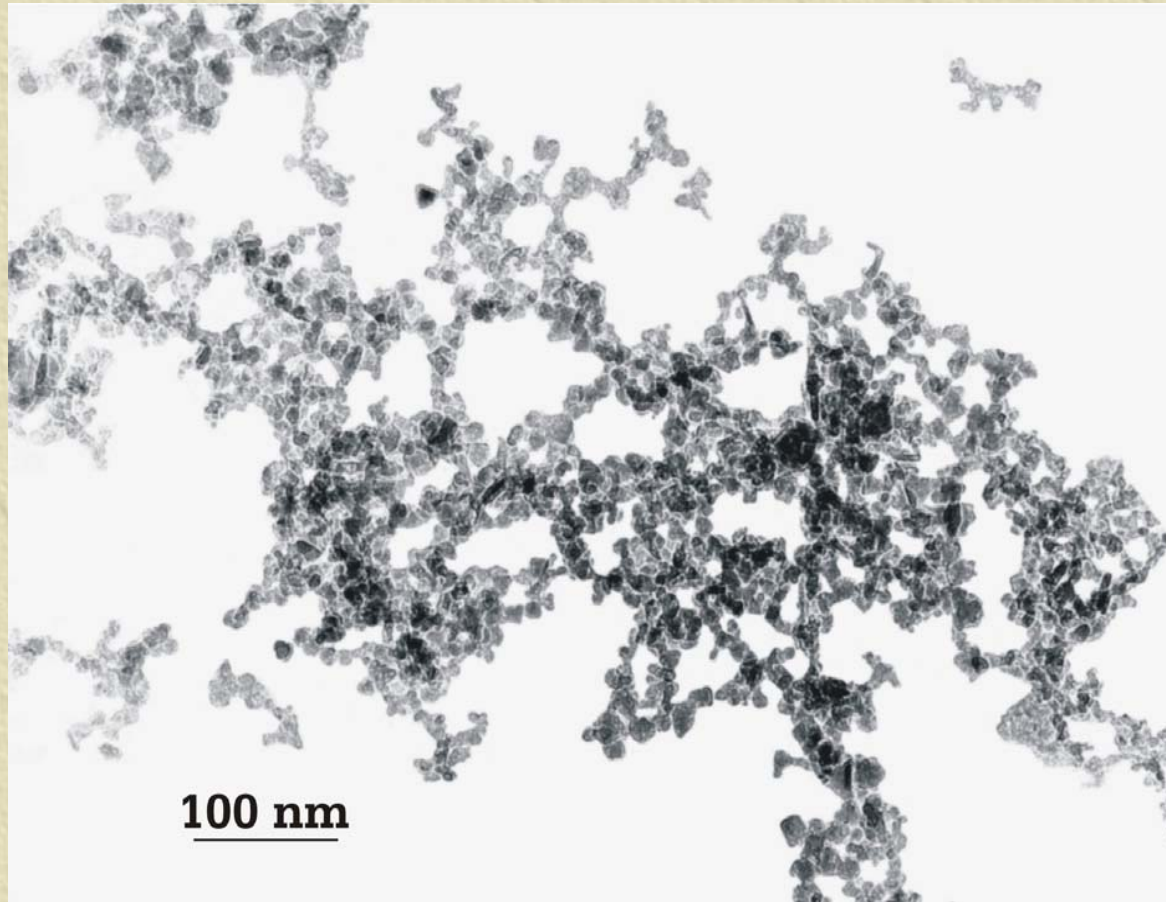
1. *Nanometric ceramic and metallic powder synthesis*
2. *Quantum Dots*
3. *Thin films for photonic crystals*

SYNTHESIS EQUIPMENT FOR NANOMETRIC POWDERS AND FILMS



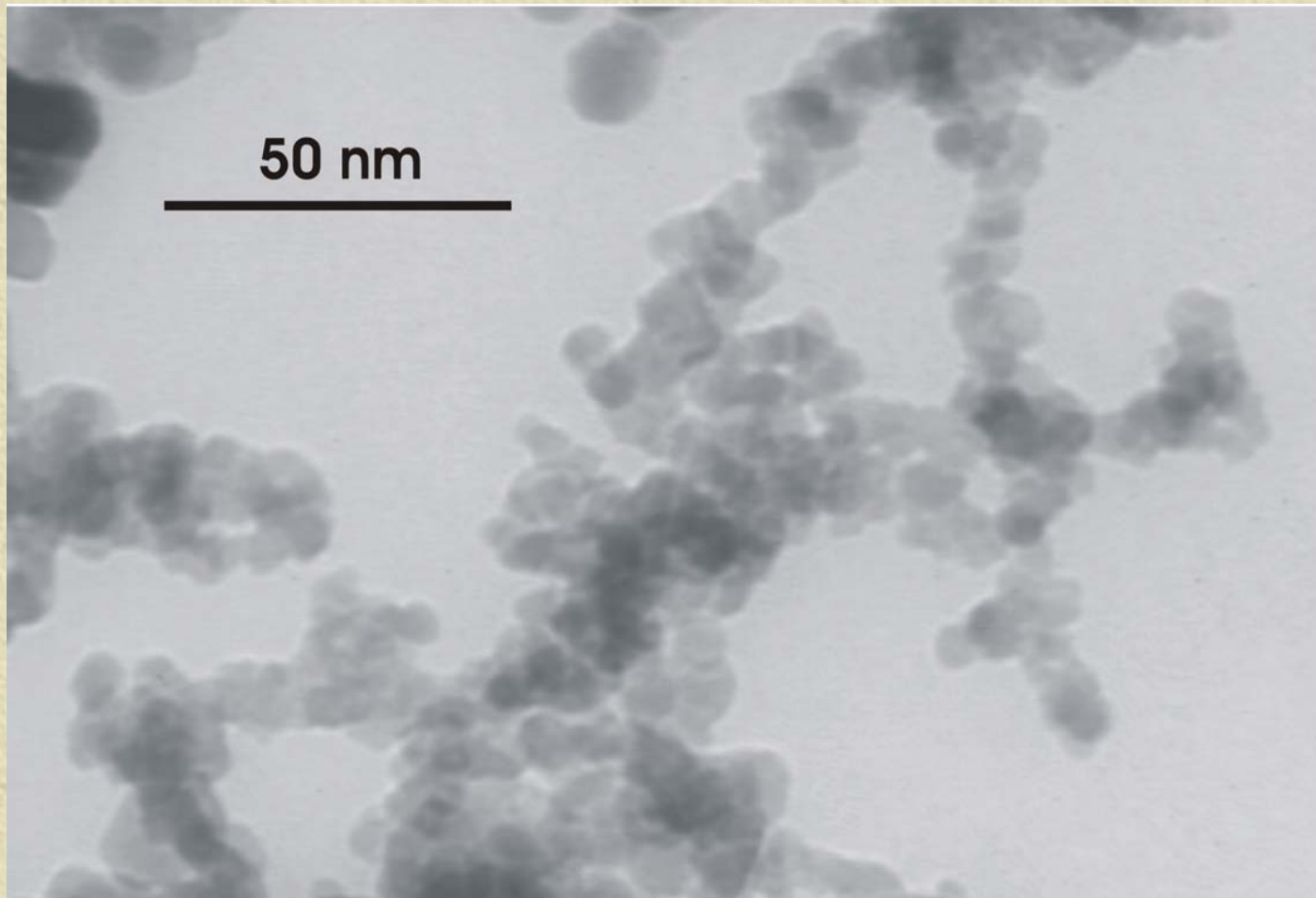


AIN NANOMETRIC POWDERS



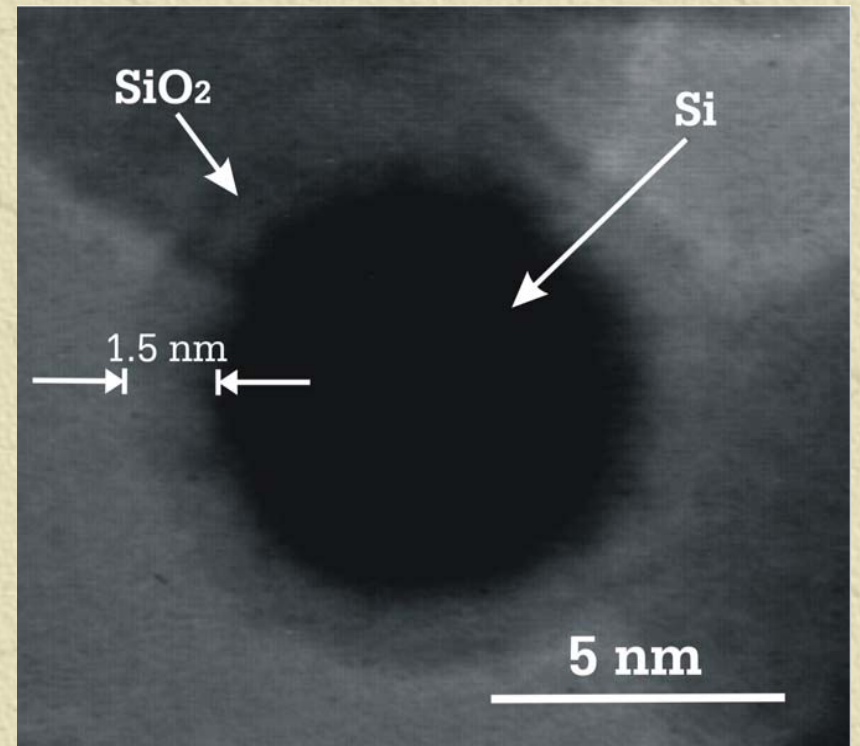
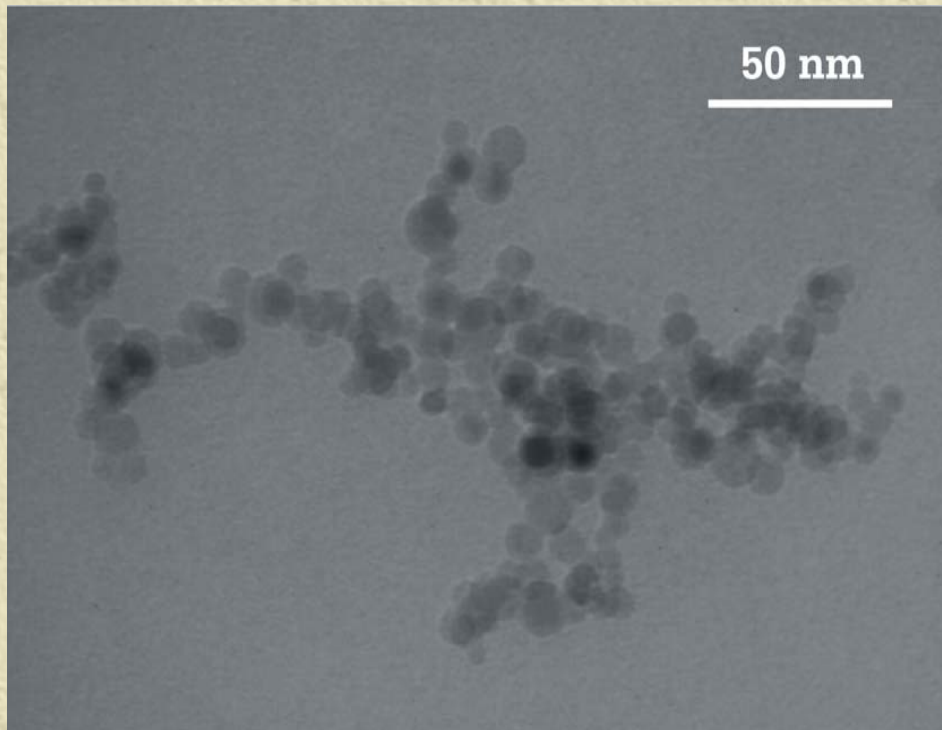


Cu NANOMETRIC POWDER



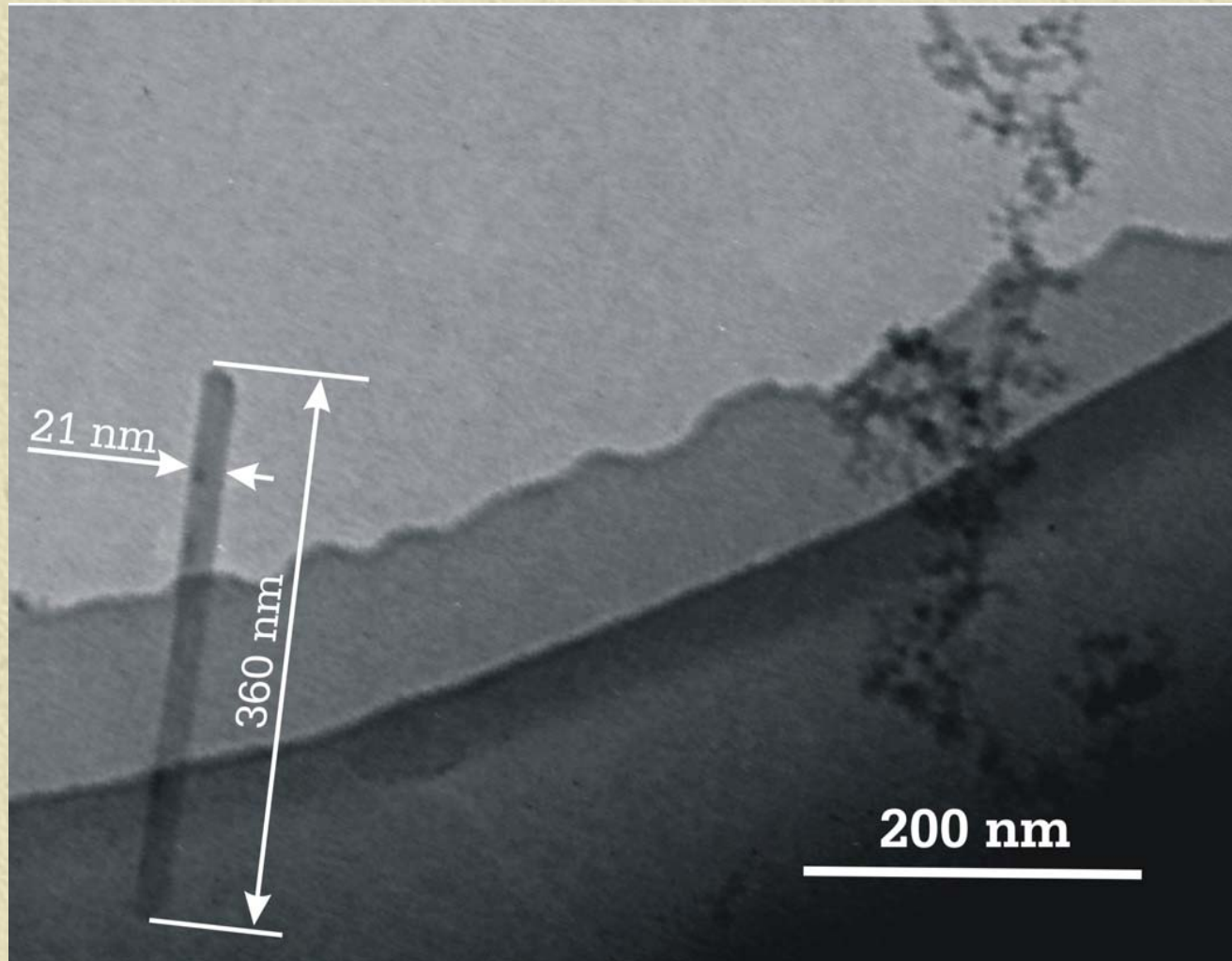


Si QUANTUM DOTS





Si NANOTUB





NONLINEAR NANOPHOTONICS

1. Amplificarea puternica a raspunsului nelinier ultra-rapid al Siliciului-pe-izolator (SOI) nano-structurat periodic masurata prin metoda RZ-scan cu un femto-laser

- Prima masurare cantit. a raspunsului nelinier de ord.3 a nano-structurilor SOI
- Elaborarea unei noi proceduri pentru discriminarea intre NLO de tip electronic si termic: **Dublu Z-scan (DZ-scan)** (colab. ENS, Paris si Univ. "La Sapienza" Roma)

2. Controlul raspunsului nelinier al Siliciului nano-poros prin porozitate

- * Modelare (Brueggeman) simplificata
- Prima masurare cantitativa a raspunsului nelinier de ord.3 prin RI-scan si verificare a predictiei teoretice Bruggeman (colab. IMT)

3. Neliniaritatea de ordinul trei a "punctelor cuantice" ("quantum dots", QD) in regim de confinare cuantica puternica

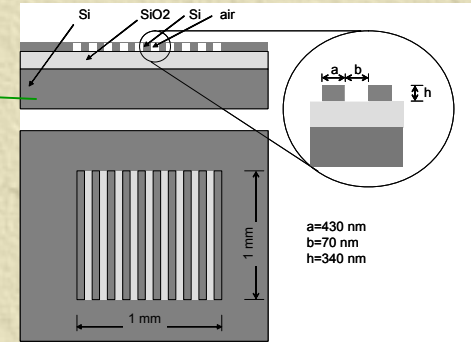
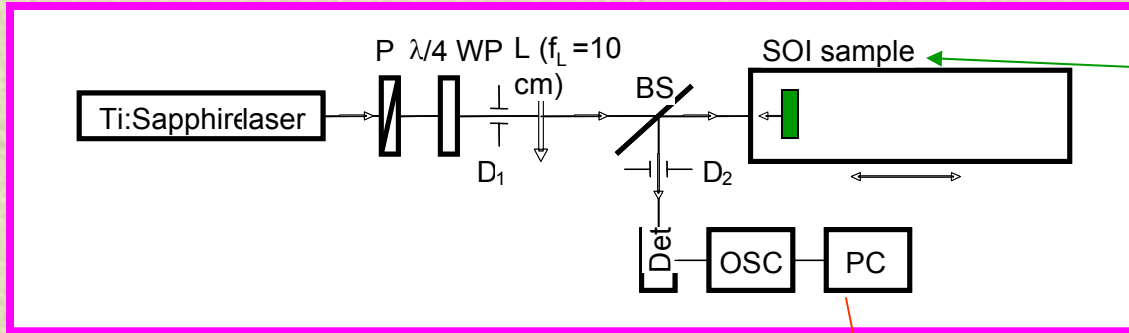
- Masurarea cresterii uriase a raspunsului nelinier al QD de CdTe in comparatie cu materialul masiv in regim de confinare cuantica puternica
- **Controlul raspunsului optic nelinier prin dimensiunea QD** si a saturatiei acestuia la nivele mici de intensitate

4. Nano-imaging

- **AFM+SNOM cu impulsuri laser cu durate de femtosecunde** – NL single QDs
- Studiul proprietatilor structurale ale nano-starturilor de a-Se (depose prin PLD) folosind metoda **extractiei diferential-evanescente** a luminii din ghidul format de nanostrat (colab. A. Peled – Holon Inst. Technol., Israel si I. N. Mihailescu, G. Socol s.a.)

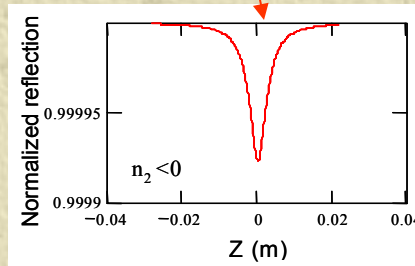


Amplificarea puternica a raspunsului nelinier ultra-rapid (femto-sec) al SOI nano-structurat periodic, masurata prin met. dublului RZ-scan



SOI: Si (340 nm)-SiO₂(2 μm)-Si(0.5 mm)

Laser Ti:Sapphire : $\lambda=800\text{nm}$
 $P_{av}=265\text{mW}$, **75 fs**, 76 MHz



Metoda si formula puterii reflectate Vlad et al:

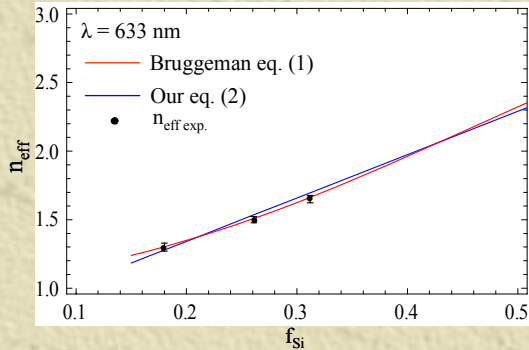
$$P(z) \sim 1 + \frac{2n_2 I_0}{n_0^2 - 1} \cdot \frac{1}{1 + (z/z_0)^2} = 1 + \frac{2\Delta n}{n_0^2 - 1} \cdot \frac{1}{1 + (z/z_0)^2}$$

Raspunsul nelinier electronic SOI nano-structurat ~ 20 x Raspunsul nelinier al Siliciului
=> Dispozitive fotonice neliniare ultra-rapide in tehnologia siliciului cu proprietati controlate prin nano structurare

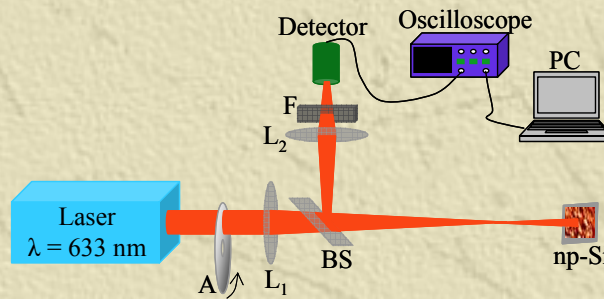
Colaborare INFLPR – Univ. “La Sapienza” di Roma si Ecole Normale Superieure Paris, in cadrul Retelei de Excelenta a UE PHOREMOST



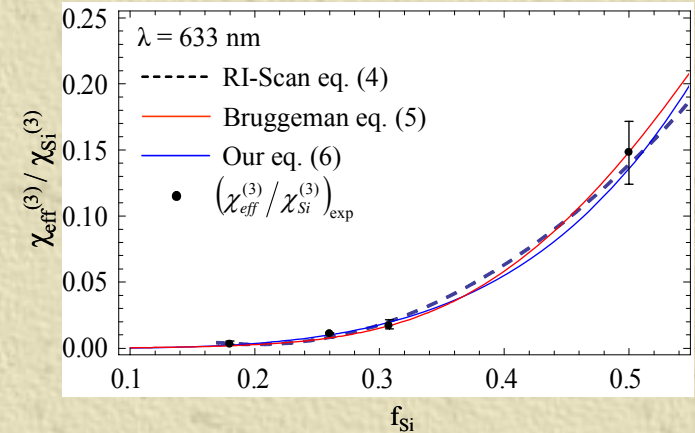
Optical linear and third-order nonlinear properties of nano-porous Si



$$n_{eff} \approx 3.19 \cdot f_{Si} + 0.73, \text{ for } \lambda = 633 \text{ nm}, \epsilon_{Si} = 15$$



$$R(I) \approx 1 + \frac{0.04}{n_{eff}^2} \cdot \frac{\chi_{eff}^{(3)} \cdot I}{(n_{eff}^2 - 1)}$$



Susceptibilitatea dielectrica de ord.3 in masuratori RI-scan (Vlad, Bazaru et al, JOAM, 2010):

$$\frac{\chi_{eff}^{(3)}}{\chi_{Si}^{(3)}} \approx \frac{R_{np-Si} - 1}{R_{Si} - 1} \cdot \frac{1}{209} \cdot (3.16 \cdot f_{Si} + 0.71)^2 \cdot [(3.16 \cdot f_{Si} + 0.71)^2 - 1]$$

Controlul raspunsului nelinier electronic Si prin nano-structurat =>

Dispozitive fotonice neliniare ultra-rapide in tehnologia siliciului cu proprietati controlate prin nano structurare

Colaborare INFLPR – Actiunea COST MP0702 “Towards Functional Sub-Wavelength Photonic Structures” ; Colab. IMT Bucuresti



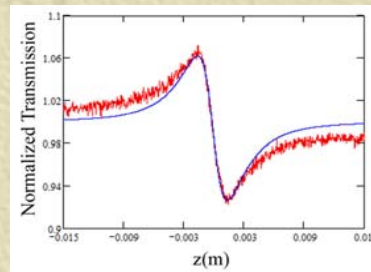
Neliniaritati de ordinul trei uriase ale “punctelor” cuantice de CdTe in regim de confinare puternica (de sute de mii de ori mai mari decat in volumul cristalelor)

Raza “punctelor” cuantice (“atomi” artificiali) sintetizati special pentru a avea nivelele excitonice rezonante cu lungimea de unda a laserului utilizat este:

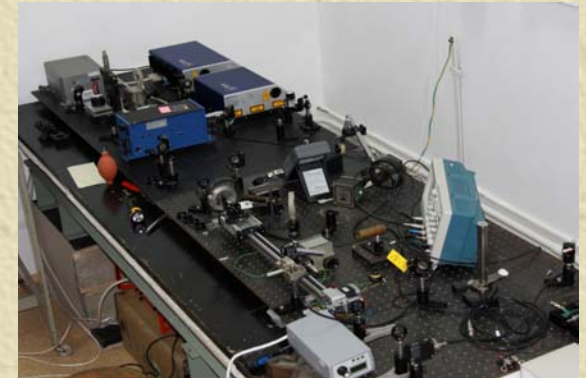
$$R_{\text{QD}}=2 \text{ nm} < R_{\text{BohrCdTe}}=7.5 \text{ nm} \Rightarrow \text{Confinare cuantica puternica}$$

Am masurat neliniaritati uriase (la concentratii ale “punctelor” cuantice infime $\sim 10^{-4} \text{cm}^{-1}$): de $\times 10^5$ ori marimea neliniaritatilor din cristalele masive de CdTe:

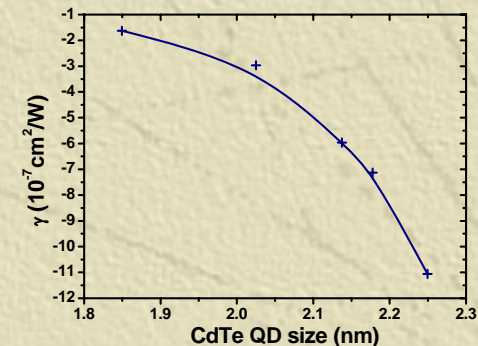
$$n_{2e} = -5.3 \times 10^{-8} \frac{\text{cm}^2}{\text{W}}$$



Aceste neliniaritati pot fi controlate prin dimensiunea “atomilor” artificiali, avantaj fata de neliniaritatile oferite de materialele optice naturale si au un mare potential in obtinerea unor **comutatoare fotonice ultra-rapide (femto-secunde) la scara nano-metrica** (Dancus, Vlad et al, Optics Letters, 2010)



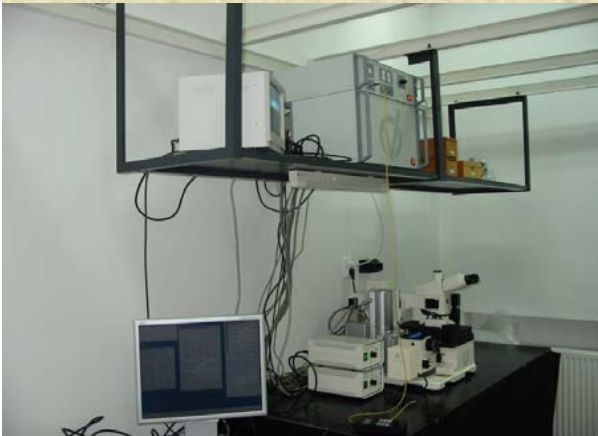
Montajul experimental de Z-scan



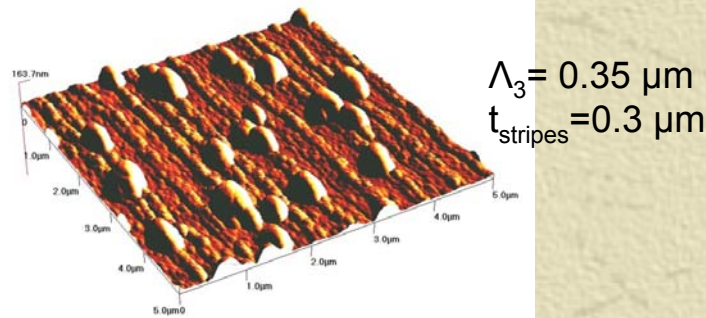
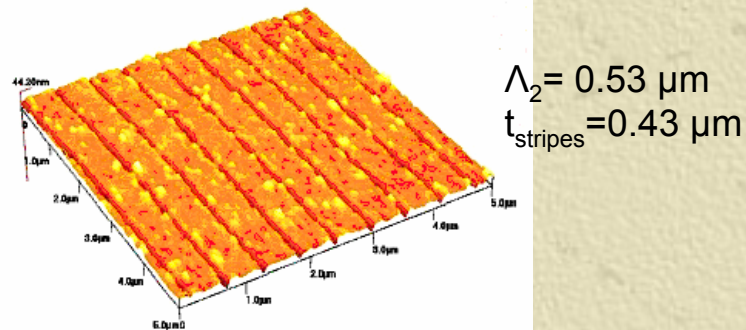
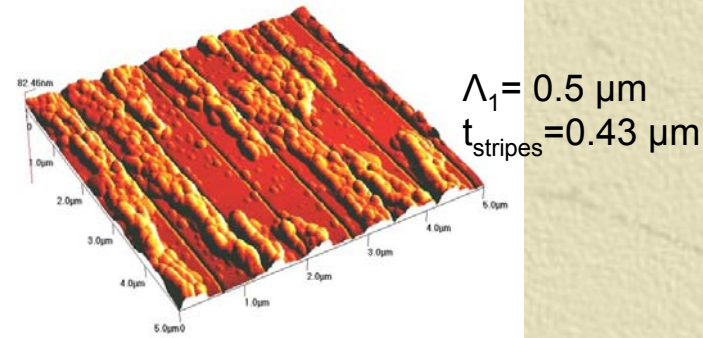
Colaborare INFLPR – TU Dresden in cadrul Retelei de Excelenta a UE PHOREMOST



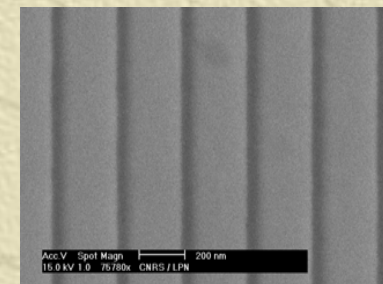
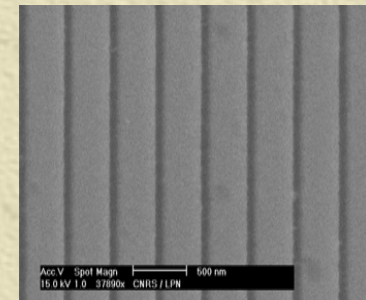
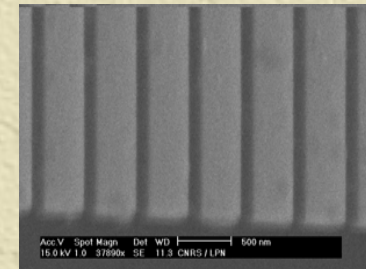
Caracterizarea SOI nanostructurat folosit pentru cresterea raspunsului optic nelinier cu AFM/SNOM si SEM



Imagini AFM/SNOM



Imagini SEM

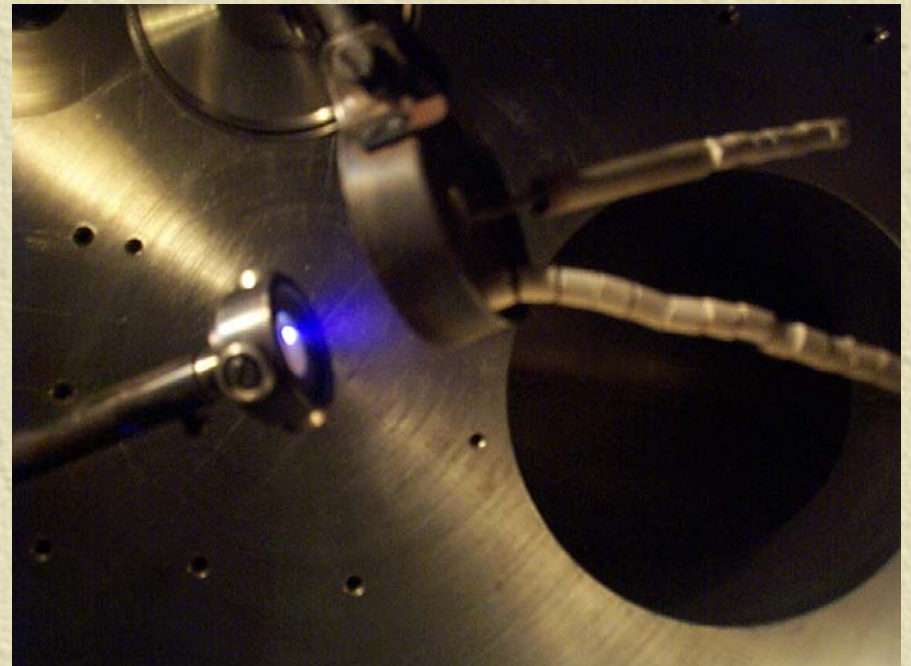
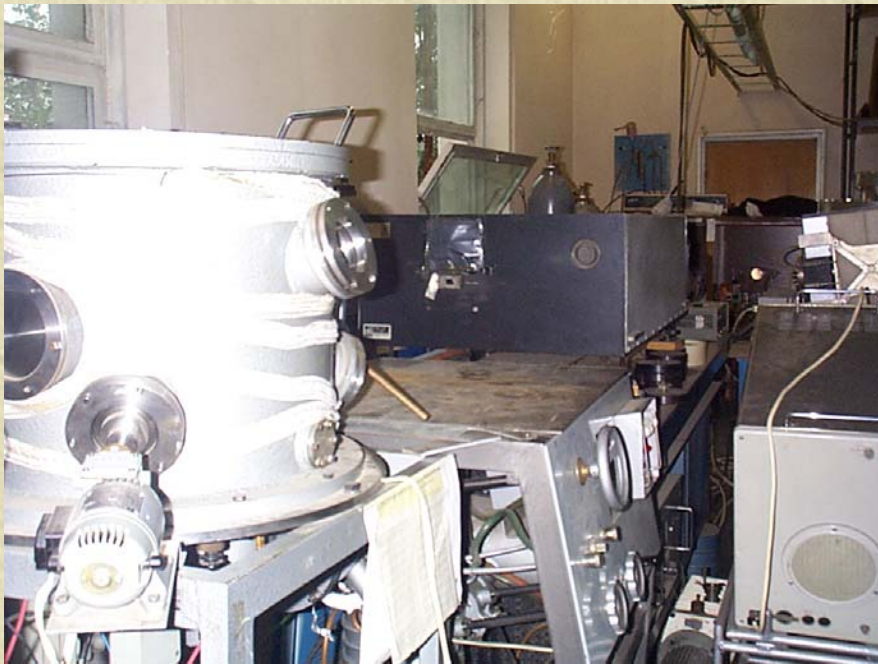




LASER-SURFACE-PLASMA INTERACTIONS

EXPERTISE:

1. *Pulsed laser deposition of thin layers in chemically-active media*
2. *Laser radiation interaction with metals and semiconductors in chemically –active atmospheres*
3. *Nitriding, carbiding and oxidation of metals and semiconductors in coherent radiation field.*





PHOTONIC PROCESSING OF ADVANCED MATERIALS

The group was organized starting with 1996 and in present contains 17 qualified scientists and 2 technicians.

Topic

The activity is focused on laser processing of matter, with applications in thin films and nanostructures with functional properties, functional polymers, protein and cell transfer for tissue engineering, chemical sensors for the detection of warfare agents.

Expertise:

Thin films and heterostructures obtained by PLD and RF-PLD for different electronic applications :

- Ferroelectrics, piezoelectrics and relaxors for electronic, microwave and optoelectronic applications: titanates (PZT, La doped PZT, BTO, BST, etc), niobites (SBN, PMN, NKN), tantalates (SBT, BZT, NBT).
- Zinc oxide (ZnO): piezoelectric, n-type semiconductor, p-type semiconductor- $ZnO/Mg_xZn_{1-x}O$ and $Mg_xZn_{1-x}/ZnO/Mg_xZn_{1-x}$
- III-V compounds: AlN, InN, GaN and their combinations.
- Heterostructures: PMN/LSCO; PZT/TiN; CN/SiCN/SiC; SBN/STON.
- High-k dielectric materials: ZrO_2 , $ZrSi_xO_y$, HfO_2 , $HfSi_xO_y$, Nb_2O_5 , $NbSi_xO_y$, Ta_2O_5 , $TaSi_xO_y$.
- Wide band gap semiconductor metallic oxide: WO_x .

Nanomaterials for catalytic and biological applications:

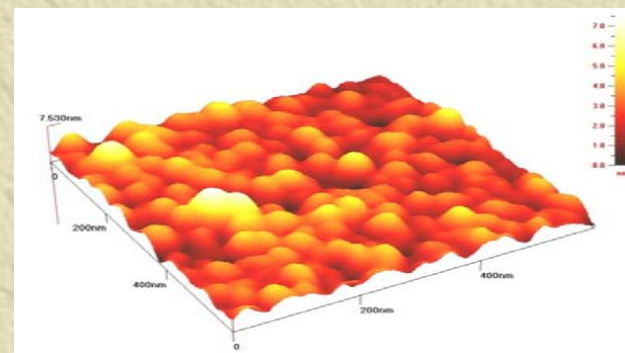
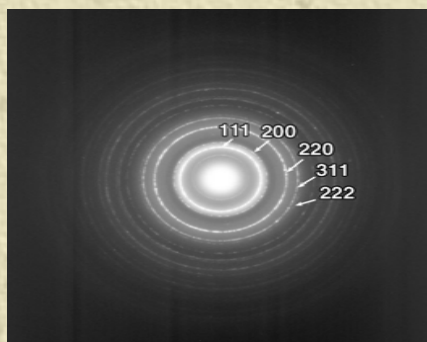
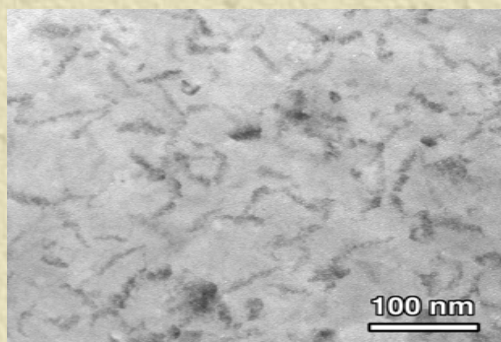
- catalytic systems and porous materials fabrication by laser and conventional techniques.
- nanomaterials for drug delivery.

132 papers in nanoscience and nanotechnology field, published in **ISI journals and 4 contributions in Springer and Wiley & Sons's published handbooks.**



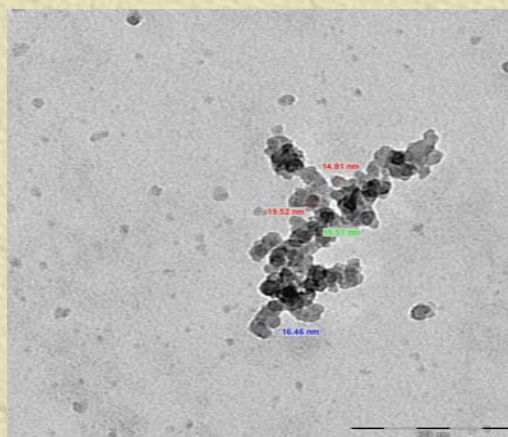
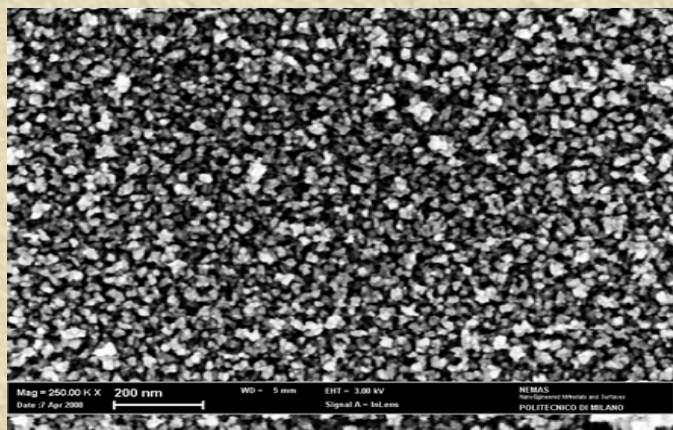
Nanostructured zirconia thin films grown by Pulsed Laser Deposition (PLD)

• ZrO_2 thin film on Si (100) deposited at room temperature, at 5×10^{-2} mbar oxygen, 6 J/cm^2 laser fluence: it can be observe a mixture of amorphous ZrO_2 and nanocrystallites; cubic crystallization phase ($a=0.5135$) even it is known that at room temperature the stable crystallization phase is monoclinic.



WO_3 nanoclusters obtained by PLD

• Surface microstructure of a film WO_3 deposited at 9 mbar oxygen pressure and substrate temperature at 873 K



-M. Dinescu, M. Filipescu, P.M. Ossi, N. Santo,,
Thin Solid Films (2009)

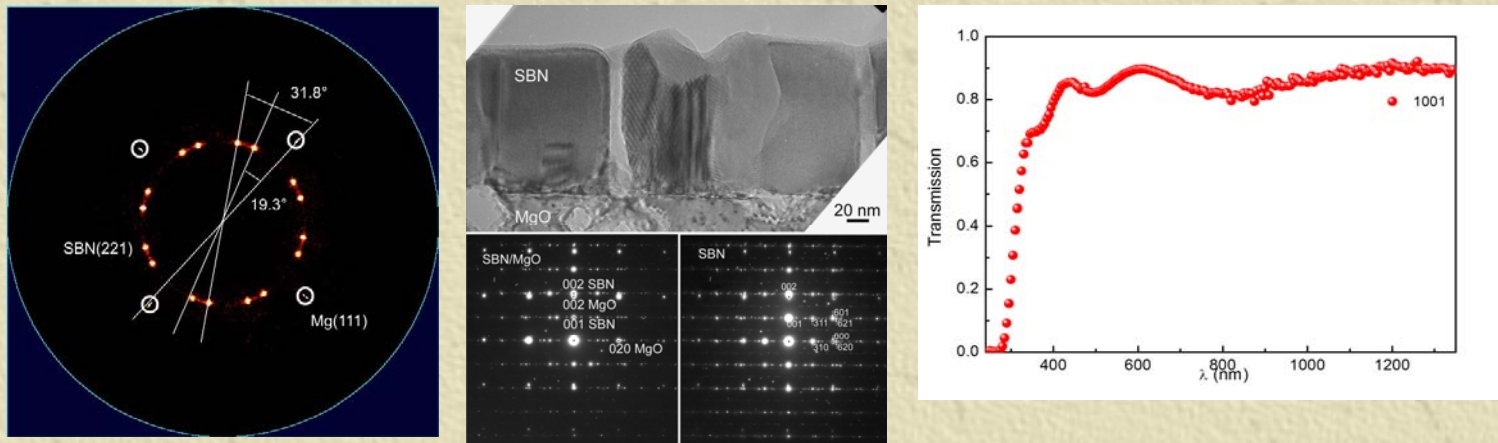
-M. Filipescu, P.M. Ossi, N. Santo, M. Dinescu,
Applied Surface Science 255 (2009) 9699–9702

-Filipescu M, Scarisoreanu N, Craciun V, Mitu
B, Purice A, Moldovan A, Ion V, Toma O,
Dinescu M, *APPLIED SURFACE SCIENCE* 253
(19): 8184-8191 (2007);

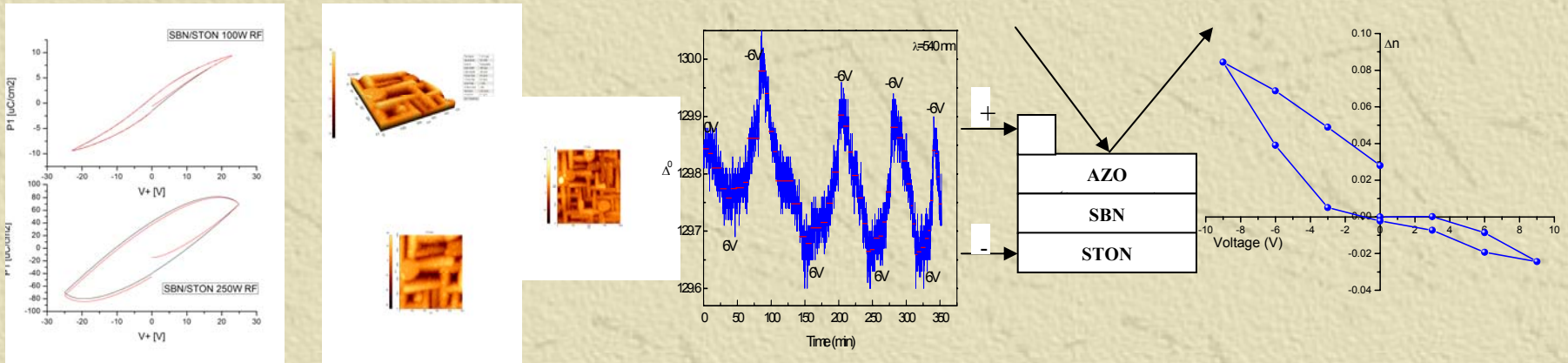


Electro-optic and ferroelectric properties of lead-free ferroelectric $Sr_xBa_{1-x}Nb_2O_6$ (SBN) thin films obtained by PLD and RF-PLD.

-SBN/MgO – highly crystalline structure , reproducibility and transmission.



-SBN/STON – good dielectric and ferroelectric properties, high electro-optic behavior: $r_{33}=36.5$ pm/V .





PLASMA PROCESSES, MATERIALS AND SURFACES

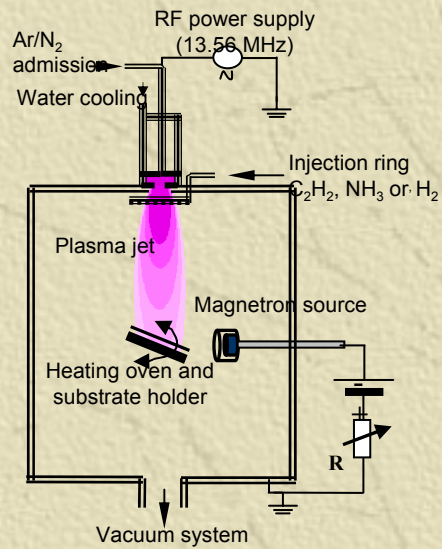


EXPERTISE:

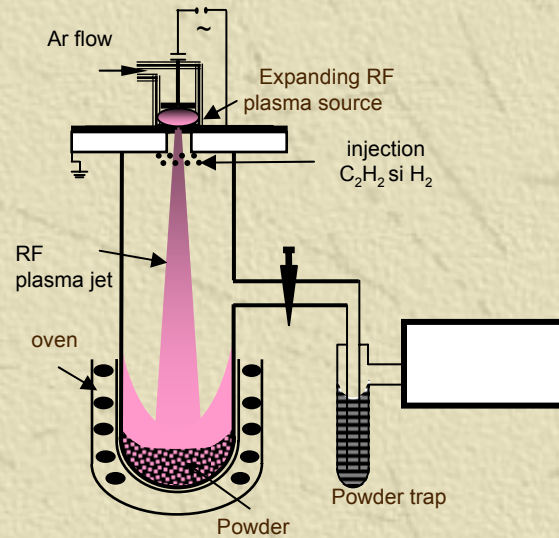
- *functional and nanostructured materials (polymeric composites, carbon nitride, carbonaceous structures, ceramic oxides) obtained by plasma assisted chemical vapor deposition;*
- *protective thin film deposition for application in optics, microelectronics, and biology;*
- *surface functionalisation of polymer-in plasma materials for the modification of hydrophilic, adherent and porosity properties*
- *carbon nanowalls, nanotubes, nanofibers obtained by plasma techniques and their applications*

Techniques developed for carbon nanostructures synthesis

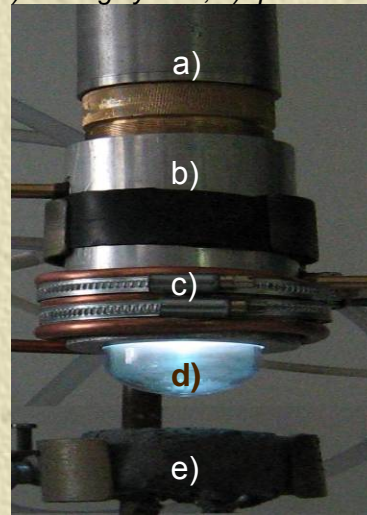
Combined RF jet for PECVD with DC magnetron sputtering



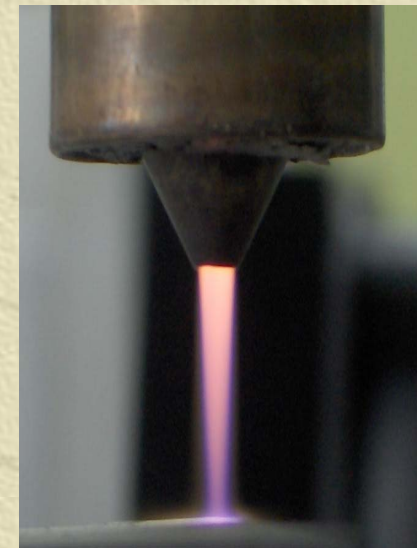
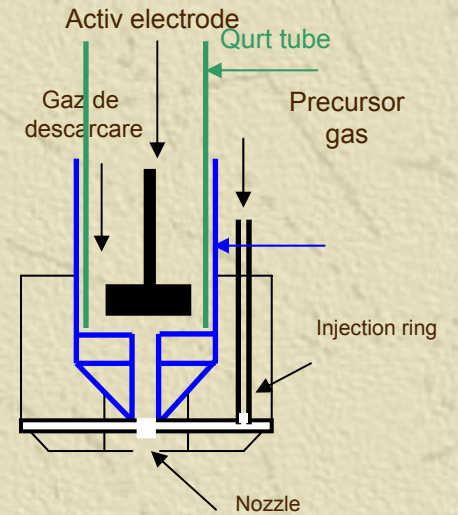
RF expanding plasma & fluidized bed reactor



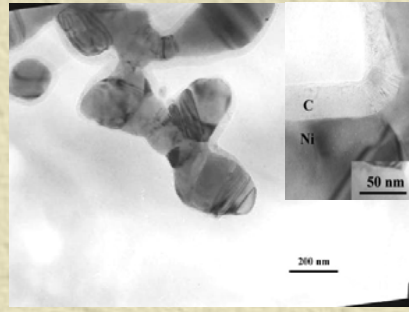
a) plasma source, b&e) oven, c) cooling system, d) quartz reactor



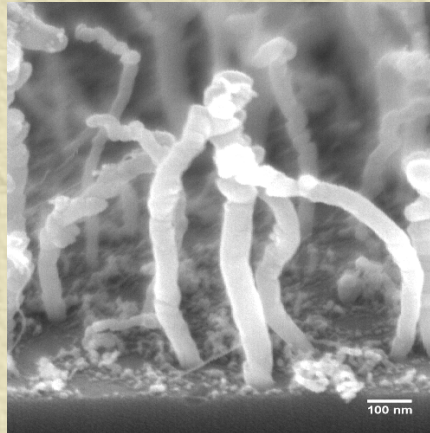
Atmospheric pressure plasma jet



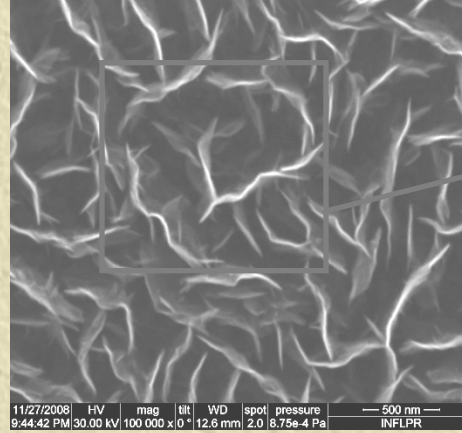
Obtained carbon based nano-materials



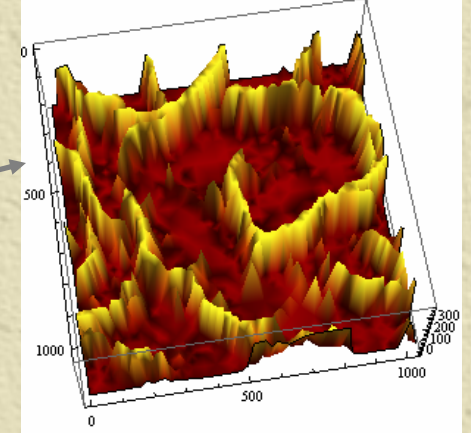
Core-shell nanoparticles embedded in graphitic layers



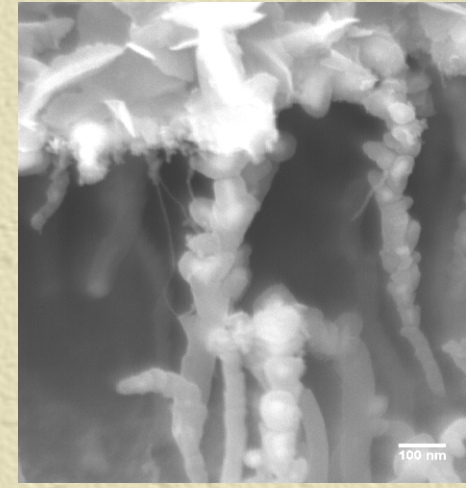
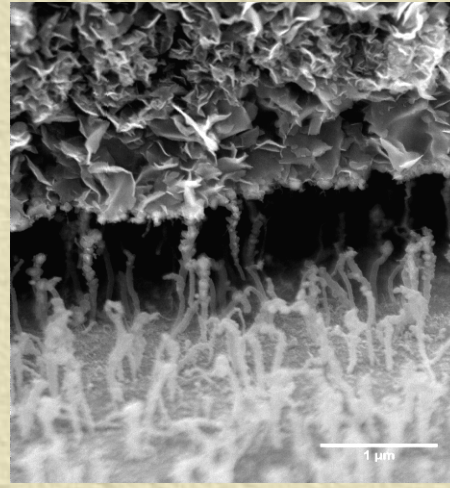
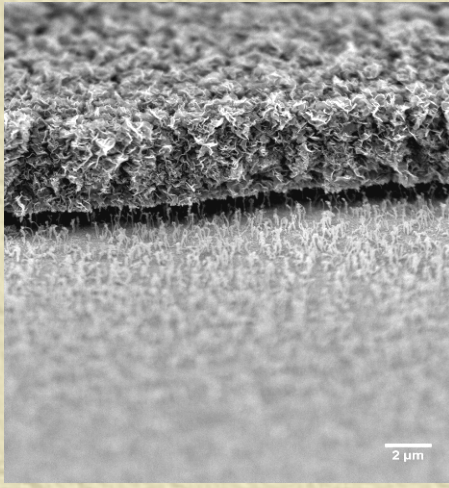
Carbon nanofibers (CNF)



Carbon nanowalls (CNW)



Combined CNT and CNW growth

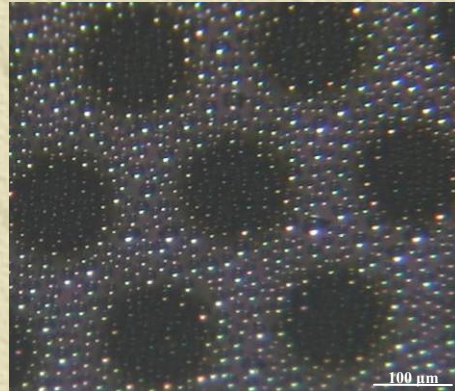


Applications

✓ CNW superhydrophobic materials



Optical Image of water drop on CNW



water vapor condensation on a cold patterned Si/SiO₂/CNW

✓ CNW- inhibitors of cell growth

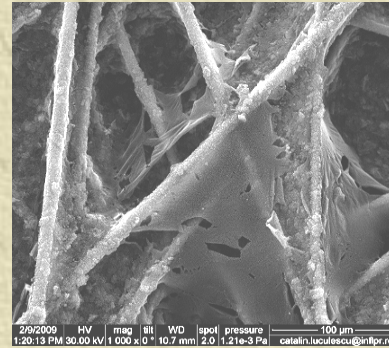
L929 fibroblast cells 2 days after seeding on Si/SiO₂ witness (a)

a

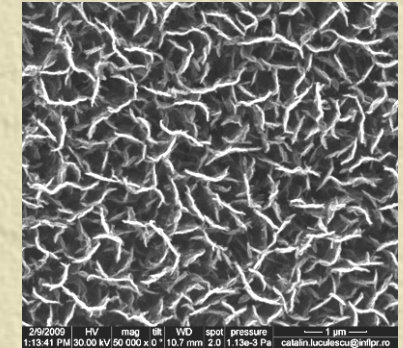
Si/SiO₂/CNW patterned films (b)

Under investigation:

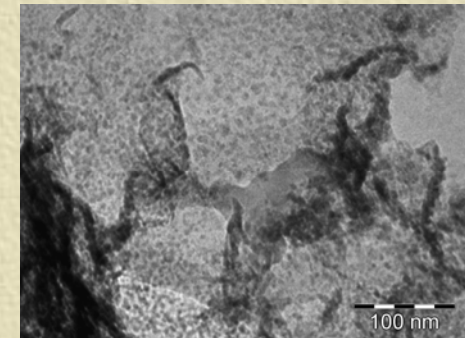
✓ Support for fuel cell catalyst



CNW on Carbonic paper as support



Magnifications of CNW growth between CP fibers



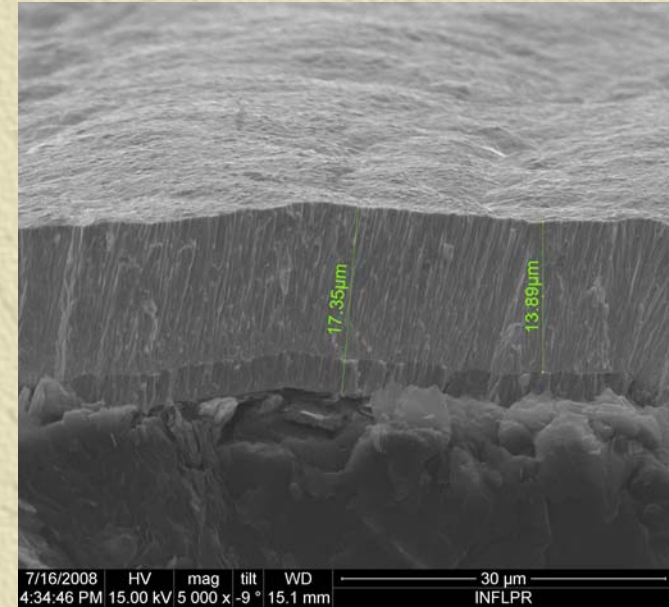
Ni nanoparticles grown onto CNW surface

✓ Field emission & gas sensors

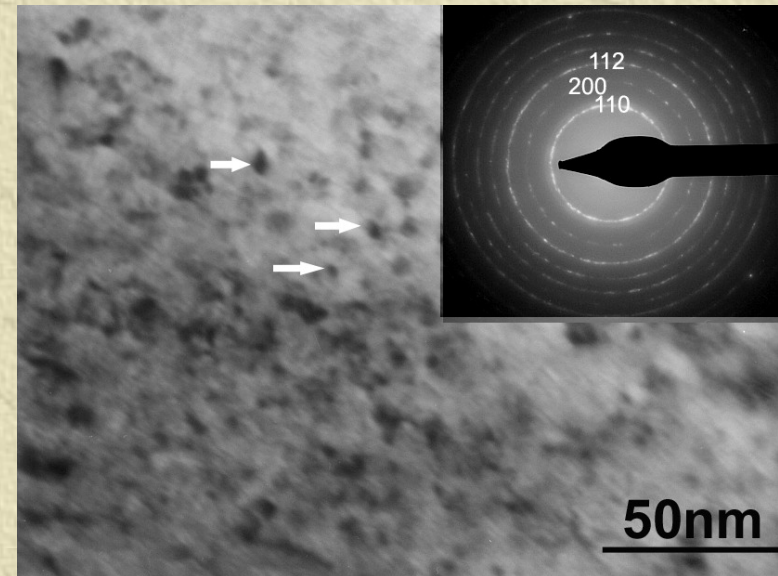
PLASMA SURFACE ENGINEERING

Nano-structured W coatings - from research to production

- Coating technology: **Combined Magnetron Sputtering and Ion Implantation (CMSII)**
- High energy ion bombardment
 - $U_{HV} = 30-70 \text{ kV}$; $\tau \sim 20 \mu\text{s}$; $f = 25 \text{ Hz}$
 - increase the surface mobility
 - high densification of the coating
- **Nano-crystalline structure**
- A Mo interlayer is used to **adjust the mismatch of thermal expansion coefficients** between CFC and W
- Due to the high energy ion bombardment a **stress relief** occurs into the coating and consequently relative thick coatings (**10-50 μm**) can be produced.



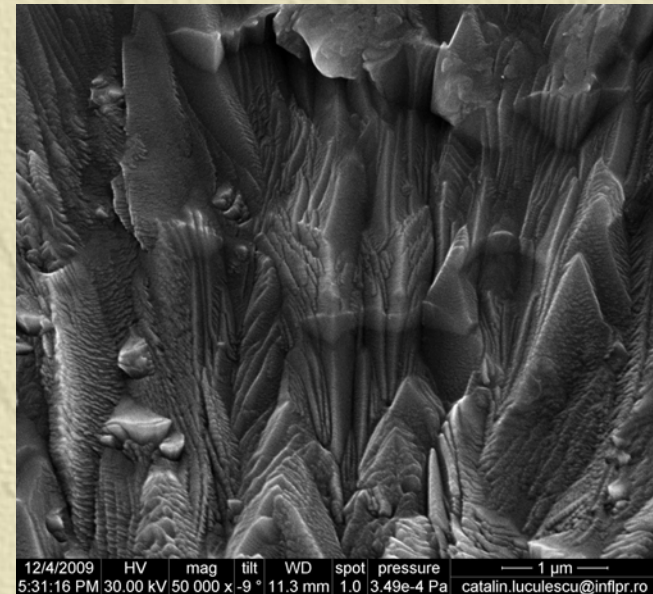
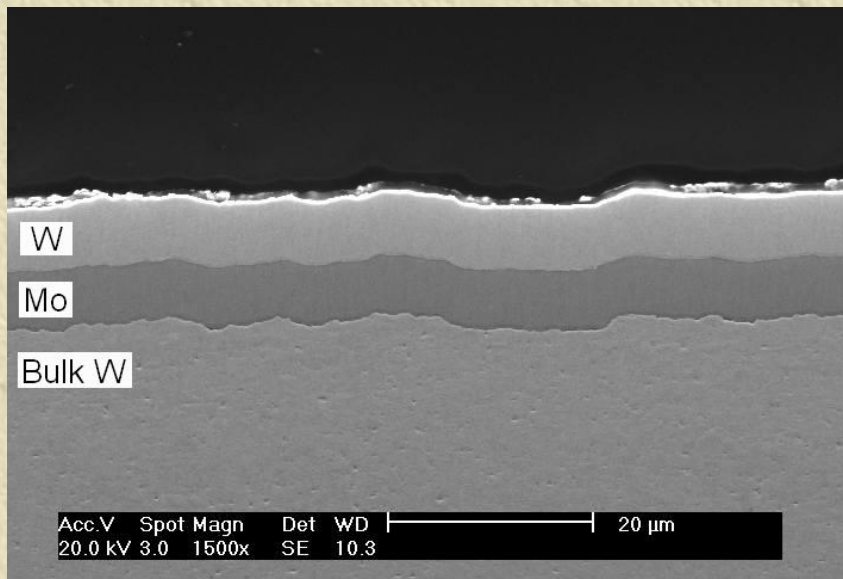
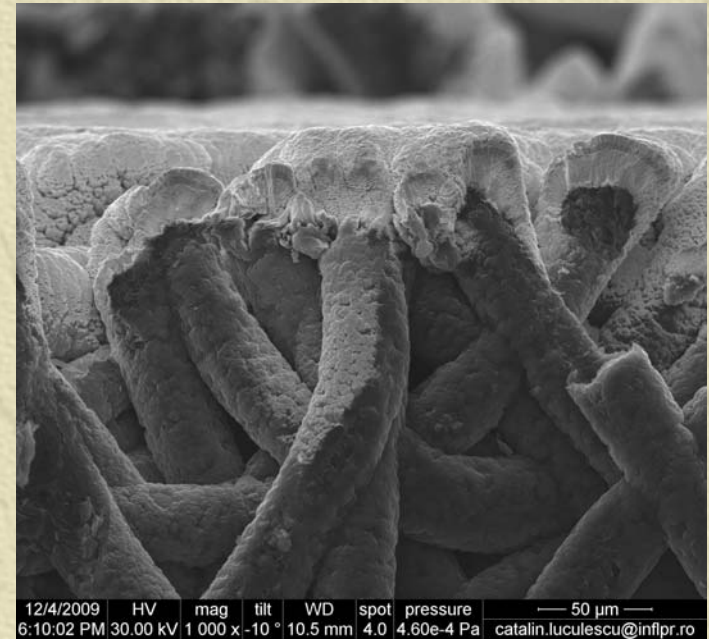
SEM micrograph



TEM micrograph

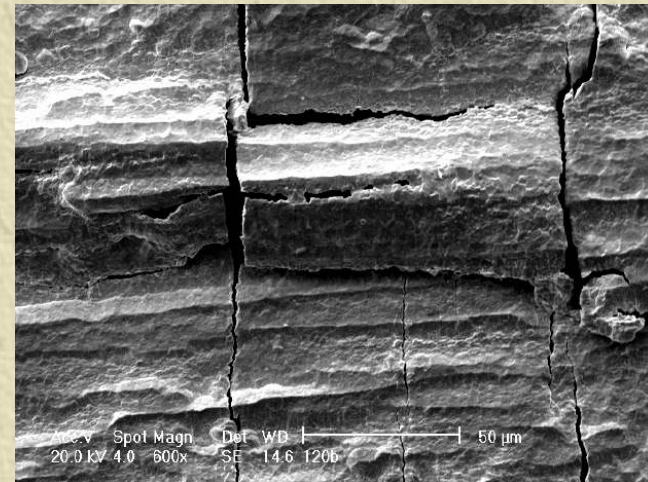
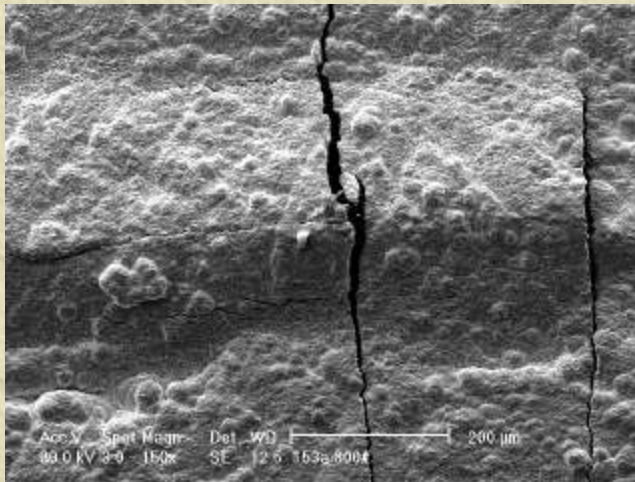
Specific characteristics of CMSII coatings

- W coating penetrates into the gapes between fibers, surrounding the fibers → **very good adhesion**
- The W coating appears to be more compact than bulk W

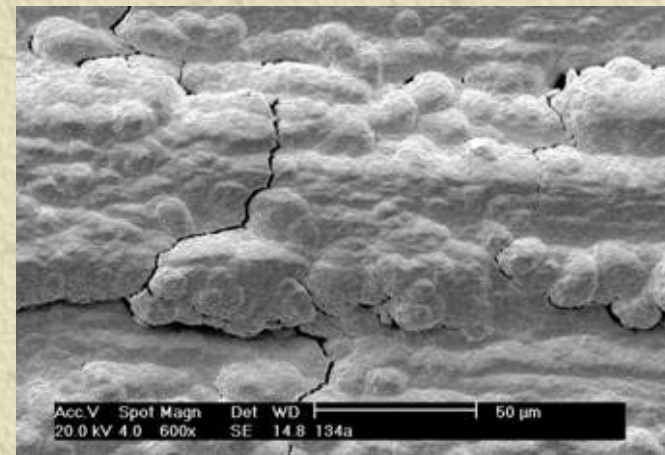
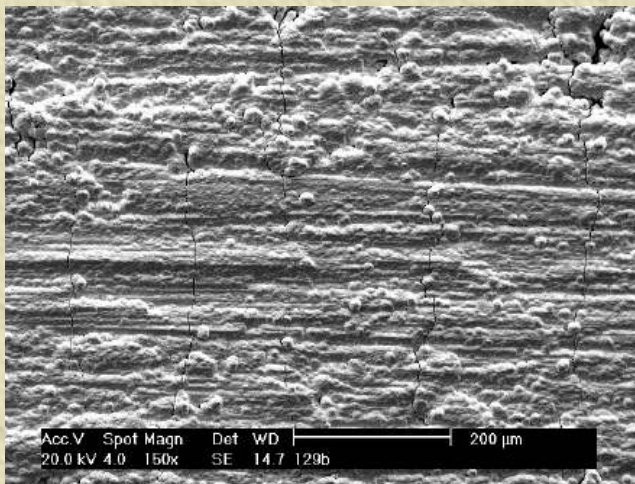


SEM micrograph, high magnification

After High Heat Flux tests ($T \sim 2,000\text{ }^{\circ}\text{C}$)

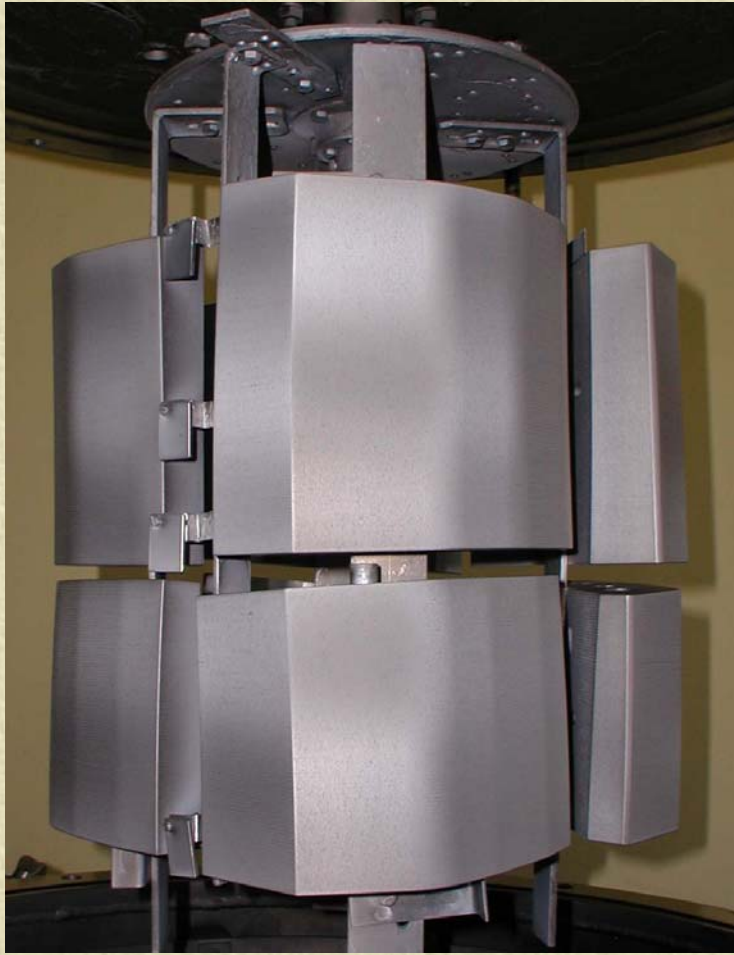


Coatings deposited by conventional PVD or CVD techniques



Nano-structured coatings deposited by CMSII technology (there is no detachment of the coating from the substrate)

W coated CFC tiles for JET (Joint European Torus)



G 1 and G8 divertor tiles coated with 20-25 μm W in series production

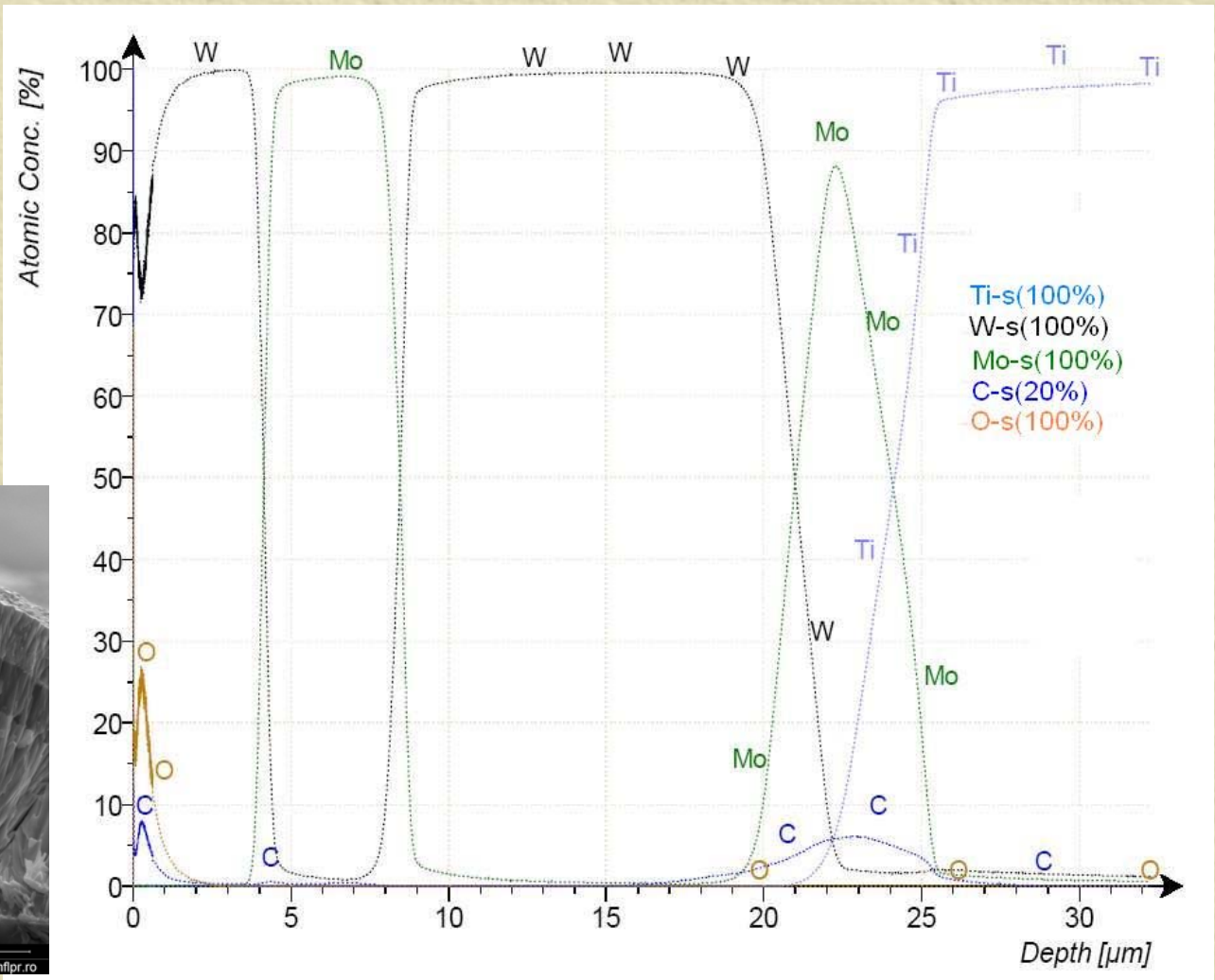
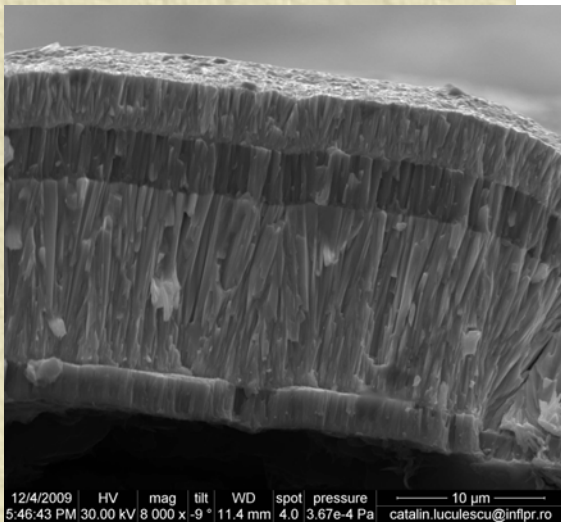


G 6 and G7 divertor tiles coated with 20-25 μm W in series production

Approx. 2,000 tiles have to be coated. More than 1,300 tiles were already coated

W/Mo markers for measurement of W erosion in JET divertor

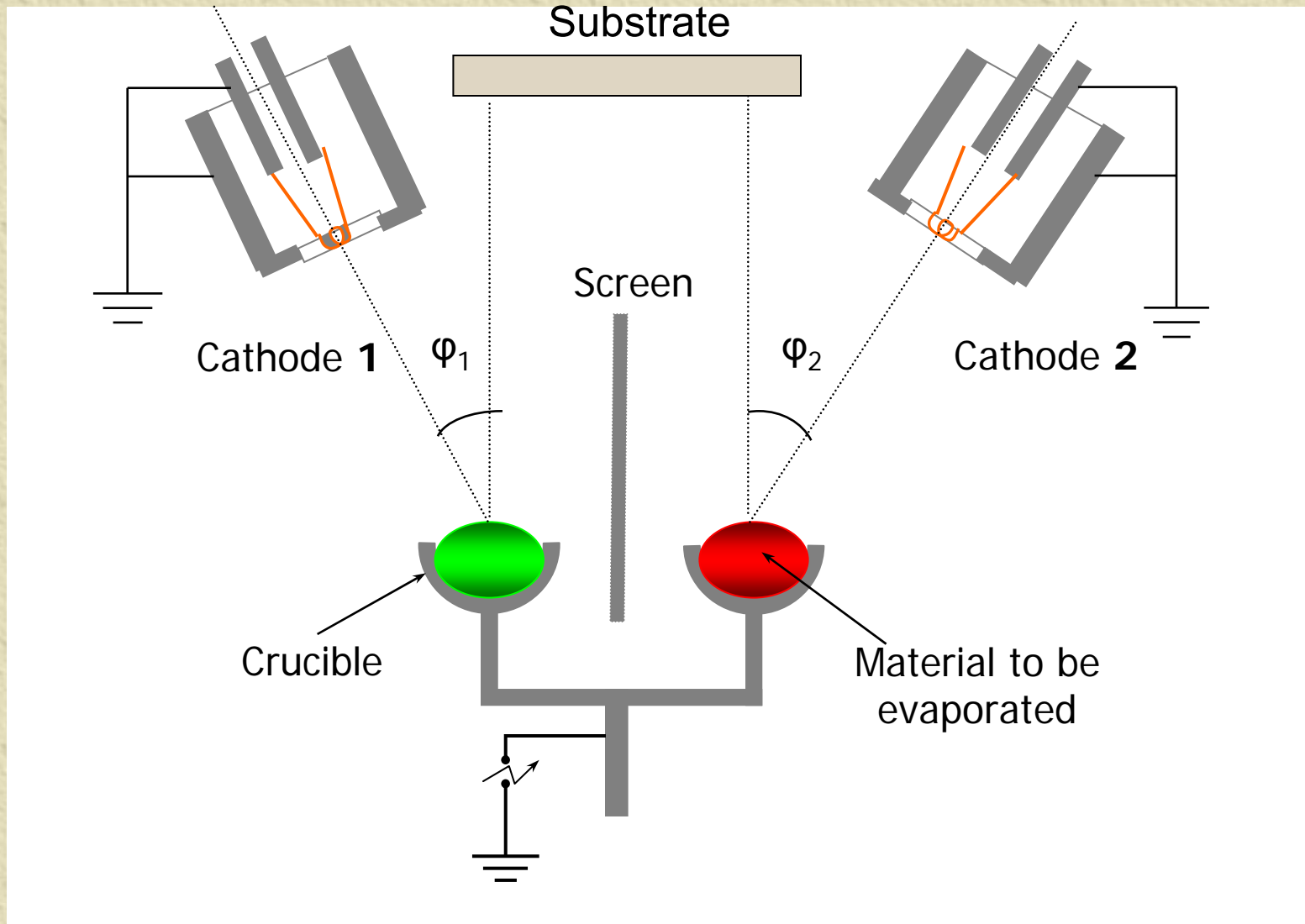
- Structure of markers:
 - 2-3 μm Mo
 - 12-14 μm W
 - 3-4 μm Mo
 - 3-4 μm W
- Applied on particular G6, G7, G1 and G8 tiles



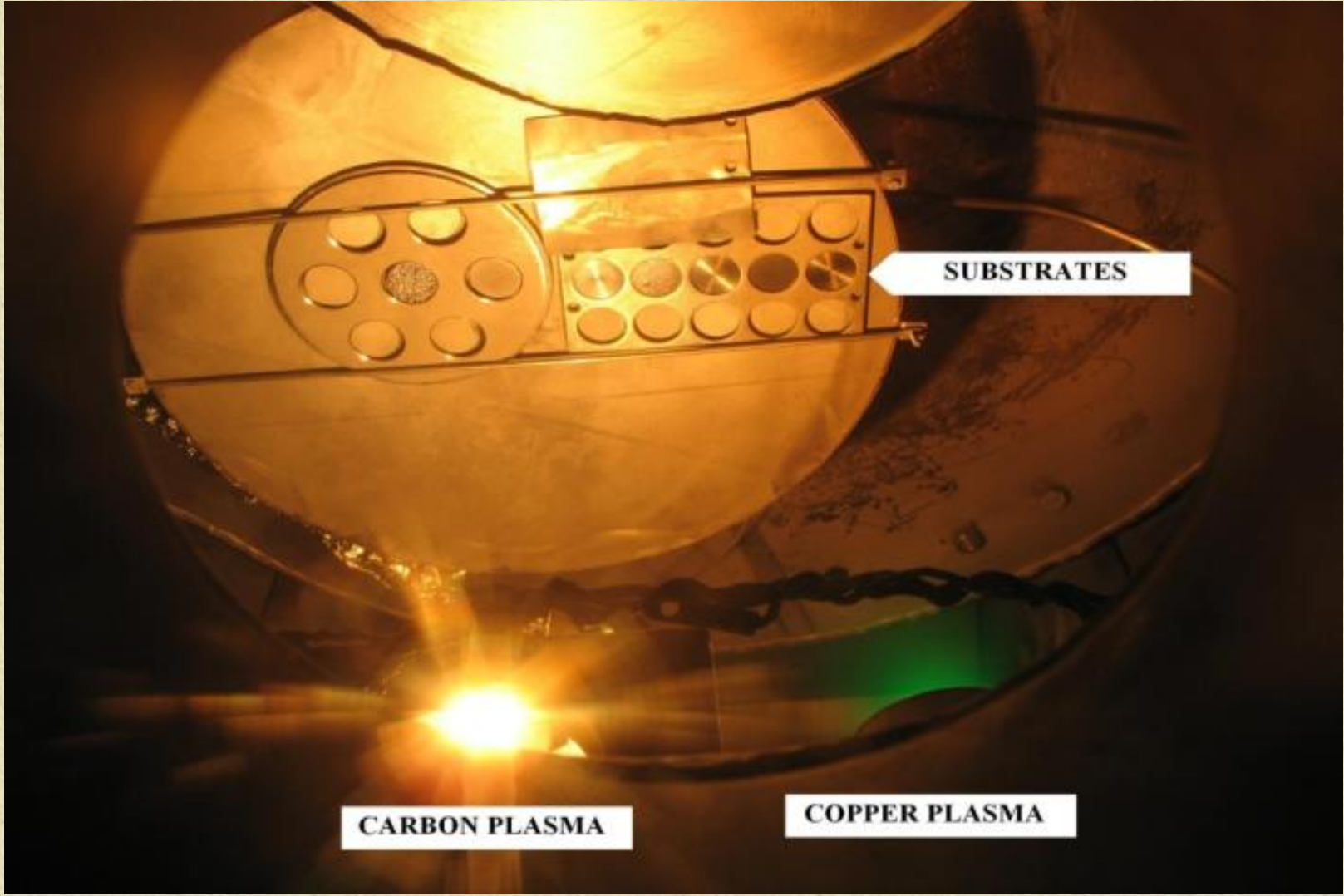
GDOS depth profiles for coating constituents measured on a witness sample

ELEMENTARY PROCESSES IN PLASMA AND APPLICATIONS

Mixed layer formation







SUBSTRATES

CARBON PLASMA

COPPER PLASMA



LASER SPECTROSCOPY GROUP

MICRO/NANODROPLETS BEHAVIOUR WHEN EXPOSED TO LASER RADIATION FIELD

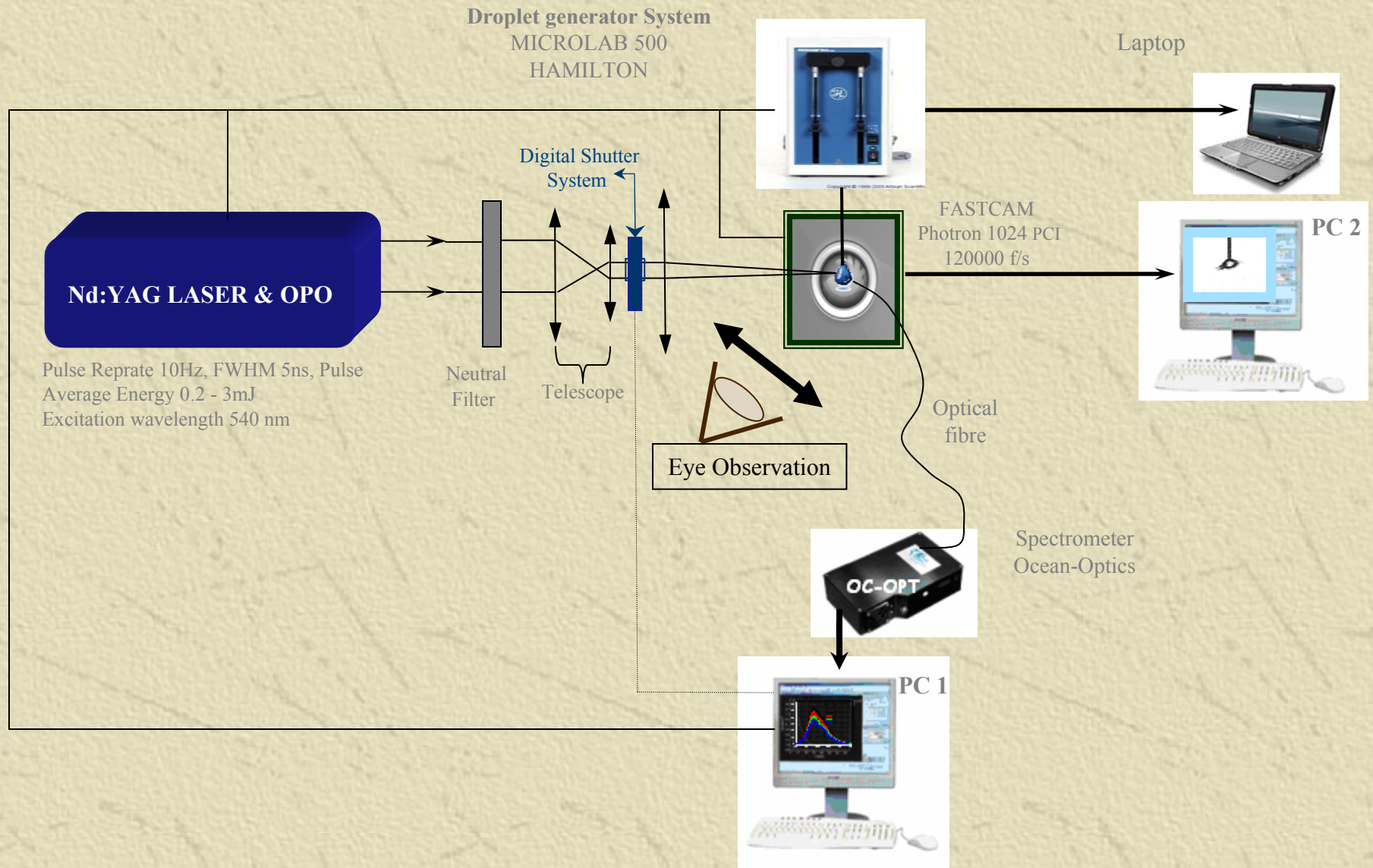
MAIN OBJECTIVES

DEVELOP A MEAN TO TRANSPORT THE MEDICINES TO THE TARGETS WITHOUT DESTROYING THEM DURING TRANSPORT

- Generate micro/nano-droplets which contain different substances: ultrapure water, modified medicines (antibiotics, cytostatics) to better fight Multidrug Resistance to treatment, laser dyes.**
- Characterize the micro/nano-droplets: superficial tension, contact angles, spectral properties.**
- Interaction of microdroplets with laser beams.**



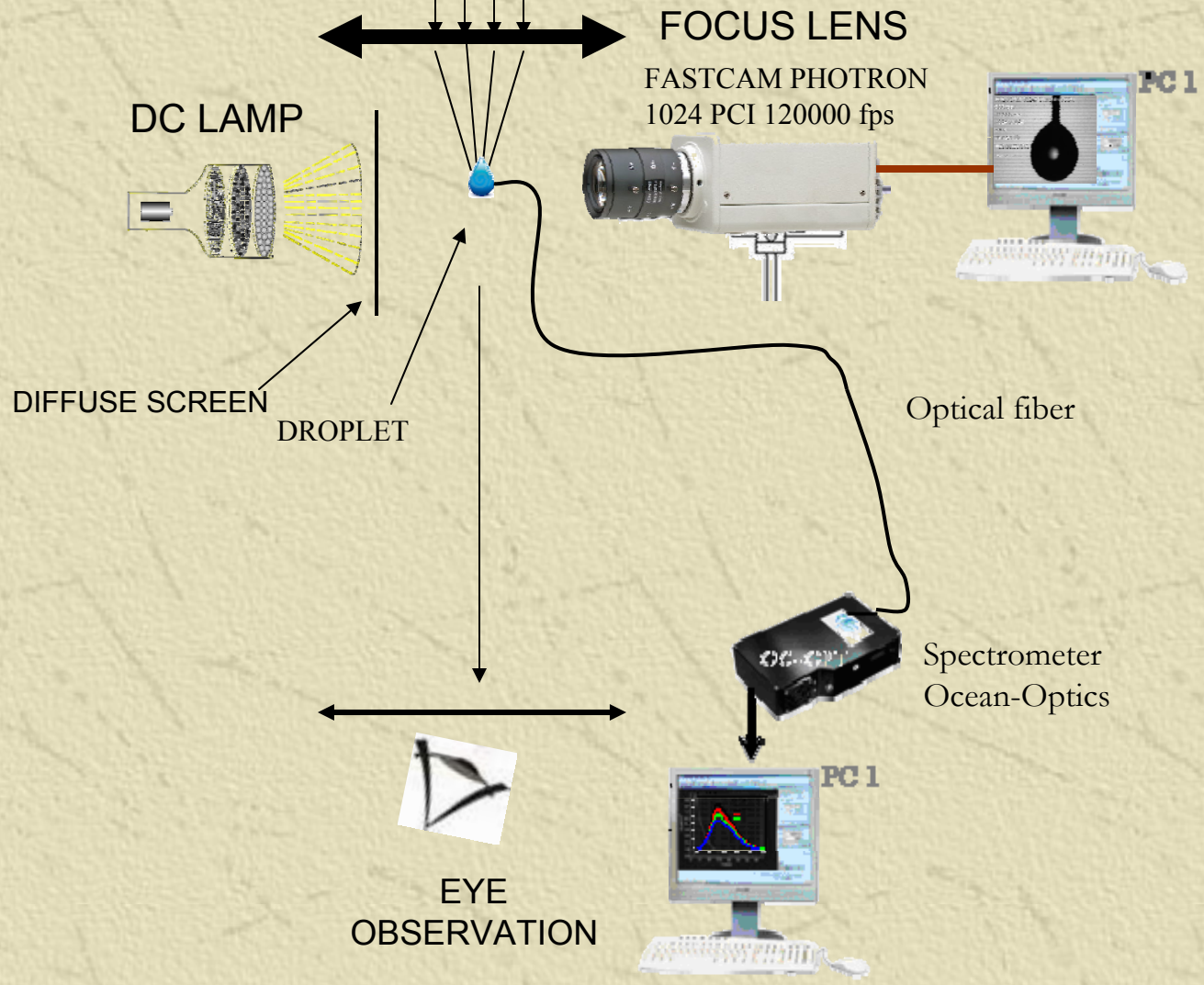
EXPERIMENTAL SET - UP





**Nd-YAG
Laser&OPO**

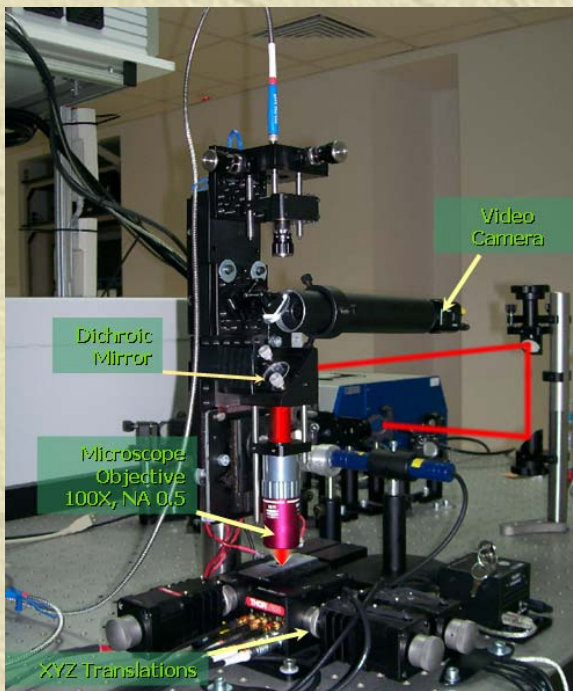
Pulse Repeats 10Hz, FWHM 5ns, Pulse
Average Energy 0.2 - 3mJ
Excitation wavelength 540 nm



SOLID STATE LASERS

Applications connected with Nanosciences and Nanotechnologies

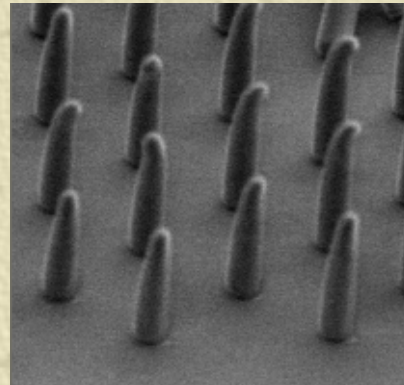
- Direct Laser writing (DLW) with femtosecond pulses for nanopatterning



Workstation for DLW

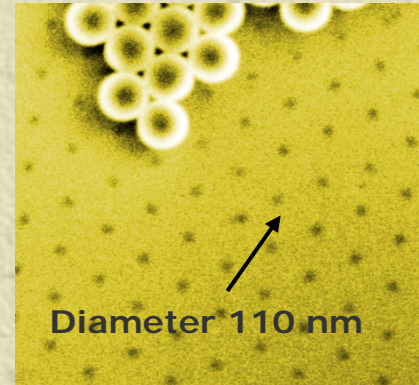
Two-Photon Photopolymerization (TPP)

J. Optoe. Adv. Mat. (2009).



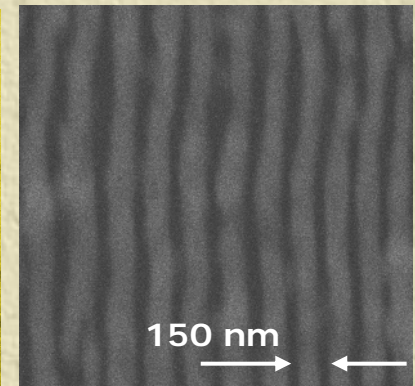
Optical Near-field Enhancement for Laser Ablation

J. App. Phys. (2009).



Laser induced periodical surface structures (LIPSS)

J. Laser Micro/NanoEng. (2009).



Applications:
photonic crystals, metamaterials, plasmonics



PHOTONIC PROCESSING OF ADVANCED MATERIALS

Characterization Equipments

Morphological analysis



AFM



Structural analysis



XRD

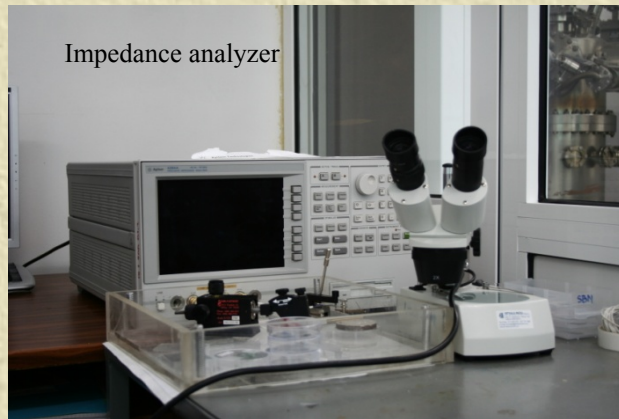
Optical analysis

Spectroellipsometer



Dielectric and ferroelectric analysis

Impedance analyzer



Chemical analysis

SIMS





INTERNATIONAL COOPERATIONS

PROGRAMUL	DENUMIREA PROIECTULUI	SUMA	PERIOADA FINANTARII
PHOREMOST UE	Nanofotonica pentru realizarea de tehnologii la scara moleculara IST-511616	73.619 EUR	2005-2008
FUNMIG UE	Fundamental processes of radionuclide migration 516514/2005	53.300 EUR	2005-2009
FORBEST UE	Increased service lifetime of forging tools by combined surface treatments COOP-CT-2004-508710	58.500 EUR	2005-2007
EMDPA STREP UE	New elemental and molecular depth profiling analysis of advanced materials by modulated radio frequency glow discharge time of mass spectrometry STRP032202	263.498 EUR	2006-2008
3 DEMO UE	Single step 3d depositionb of complex nanopatterned multifunctional oxidex thin films STRP033297	253.000 EUR	2007-2009
BONSAI UE	Bio-imaging with Smart Functional Nanoparticles FP6/LSHB-CT-2006-037639	249.700 EUR	2006-2009
CURARE UE	Computer-aided laser surface treatment and combined nitriding of forging dies with the objective of a lifetime increase Grant No. 222317/2008	150.000 EUR	2008-2010
EURATOM UE	Manufacturing and testing of W-coated CFC tiles for installation in JET for the ITER-like Wall project 1EU-1/2008	804.000 EUR	2007-2010
MagPro2Life	Advanced M agnetic nanoparticles deliver smart P rocesses and P roducts for L ife	235 000 EUR	2009-2012



PROGRAMUL	DENUMIREA PROIECTULUI	SUMA	PERIOADA FINANTARII
FP7 –ICT-2009-4-247868, e-LIFT	Laser printing of organic/inorganic material for the fabrication of electronic devices	195.000	2010-2012
NATO-SfP 982671	Polymers based piezoelectric sensor array for chemical warfare agents detection	243.000	2007 - 2010
FU06-CT-2007-00064	Deposition of Be-C&W films by TVA method and retention study	100.000	2009-2011
WP09-PWI-07-01/PS	Study of the substrate temperature influence during film deposition; formation of the stable alloys Be/C, Be/W	100.000	2009-2011
WP09-PWI-07-02/PS	Study of the ternary system formation Be-C-W using Thermo-ionic Vacuum Arc method; influence of oxygen on the process	100.000	2009-2011