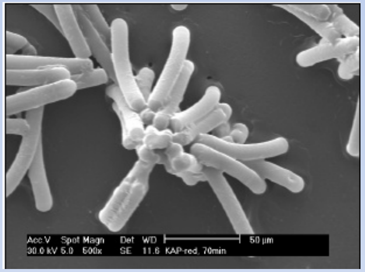
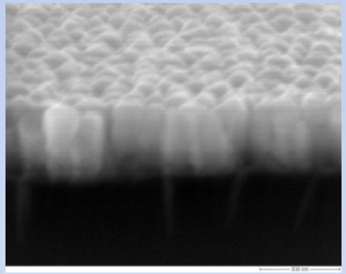
Nanoscience and Nanotechnology at the National Institute of Materials Phy

Lucian Pintilie
General Director of NIMP





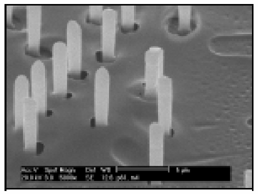


Fig. 4. SEM images of a partially dissolved membrane in which an array of potassium hydrogen phthalate rods was grown.

National Institute of Materials Physics
Atomistilor 105 bis, Magurele, Ilfov county, ROMANIA
http://www.infim.ro; pintilie@infim.ro

Romanian Academy, 3 February 2010

Outlines

- Presentation and strategy
- Resources
- Funding and results
- Some “success stories”
- Conclusions

NIMP Bucharest is devoted to **fundamental and applied research** in the fields of **solid state physics and materials research**.

Priority in the NIMP's strategy for 2006-2010:
- Nanostructured materials and nano-composites: synthesis, characterization and applications

Initiativa NANO

(physical phenomena and the preparation-structure-properties relation in structures below 1 micron, preferably below 100 nm)

-thin films, multilayers and super-lattices

- nanostructured materials, nanocomposites, (even in bulk form at the beginning)

- nanowires, nanorods, nanotubes, nanobelts, nanodots

- quantum structures, clusters

- 2D and 3D interfaces/surfaces

- defect engineering

Laboratories

10. Multifunctional Materials and structures
20. Magnetism and Superconductivity
30. Nanoscale condensed matter physics
40. Optical processes in nanostructured materials
50. Atomic structures and defects in advanced materials

Resources

Human Resources

The institute has presently about **250 workers**, including **177 scientific workers** (**15 PhD supervisors, 94 doctors, 40 PhD students**)

Infrastructure:

About 5 millions EUR invested in research infrastructure, from projects and Core program (XRD powder and thin films; SEM; AFM+PFM; MBE; PLD; RF-sputtering with in-situ structural and compositional analysis; VSM; RES; advanced XPS equipment; STM; SNOM; various characterization equipments for physical properties)

A POS-CCE project of about 10 millions EUR (2009-2011), exclusively for research infrastructure, which will provide:

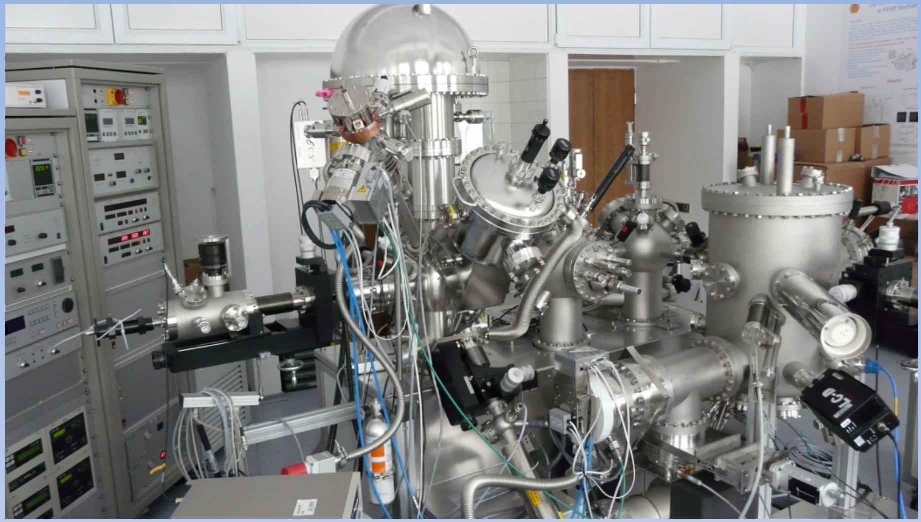
- atomic HR-TEM with state of the art equipment for analysis (STEM, EELS, EDX, etc.)

- clean room with nanolithography facilities (E-beam, FEG-SEM-FIB)

-LEEM+PEEM

-multimode SPM

-PPMS+SQUID



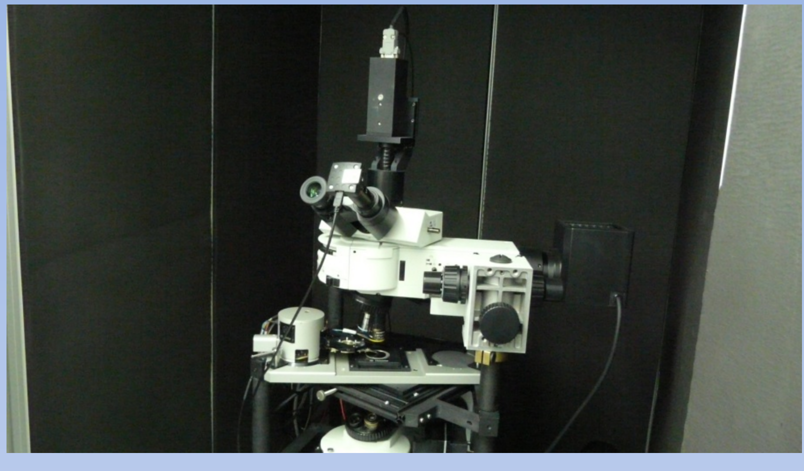
Complex cluster for surface physics: MBE, RHEED, STM, XPS, LEEM

SEM with Cathodoluminiscence

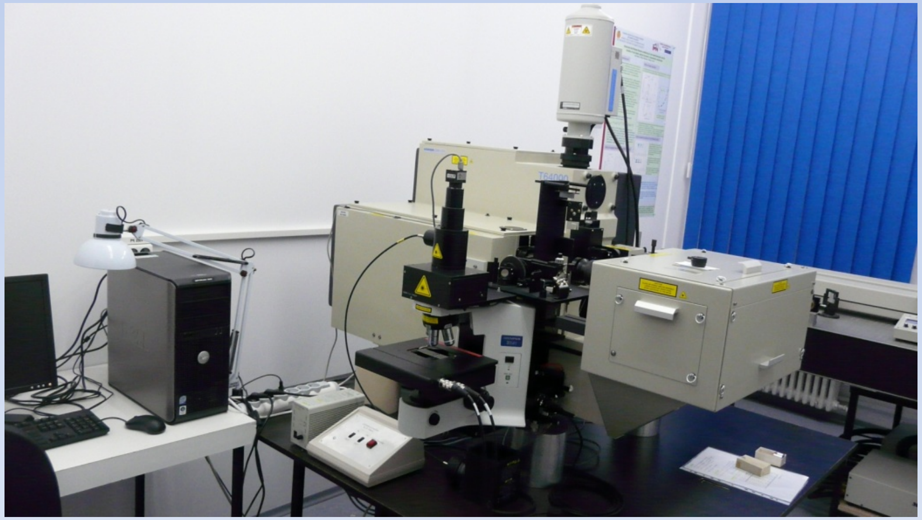
RF-sputtering with in-situ characterization techniques: Auger, ellipsometry

PLD with excimer laser

Scanning near field fluorescence microspectrometer



SNOM+AFM



Raman Microscope

AFM+PFM

Financing 2005-2009:

30 projects containing in the title a word based on NANO

CEEX 2005-11 projects with 13,950,000 lei

CEEX 2006-9 projects with 13,500,000 lei

PN II 2007-5 projects with 10,000,000 lei

PN II 2008-5 projects with 10,000,000 lei

TOTAL: **27,45 millions lei**
(equivalent of about **7 millions EUR**)

International participation (Nano-related projects):

2 network of excellence (FP6-NMP); 1 large collaborative project (FP7-NMP); 4 COST actions; 8 bilateral cooperations; collaboration with over 30 universities and research institutes from all over the world.

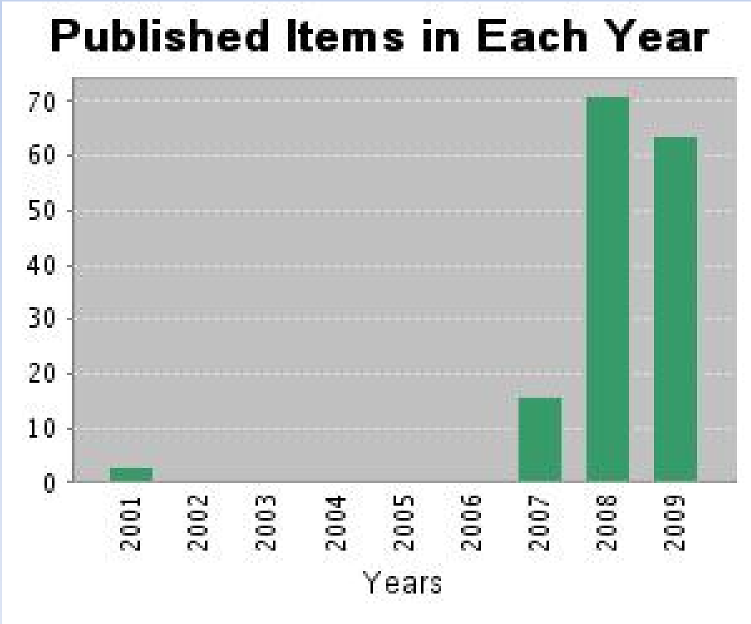
TOTAL: about **500,000 EUR**

Scientific publications:

-An average of about 140 articles/year in ISI ranked journals

Web of Science-Romania-2005-2009
Key words related to nanoscience and nanotechnology

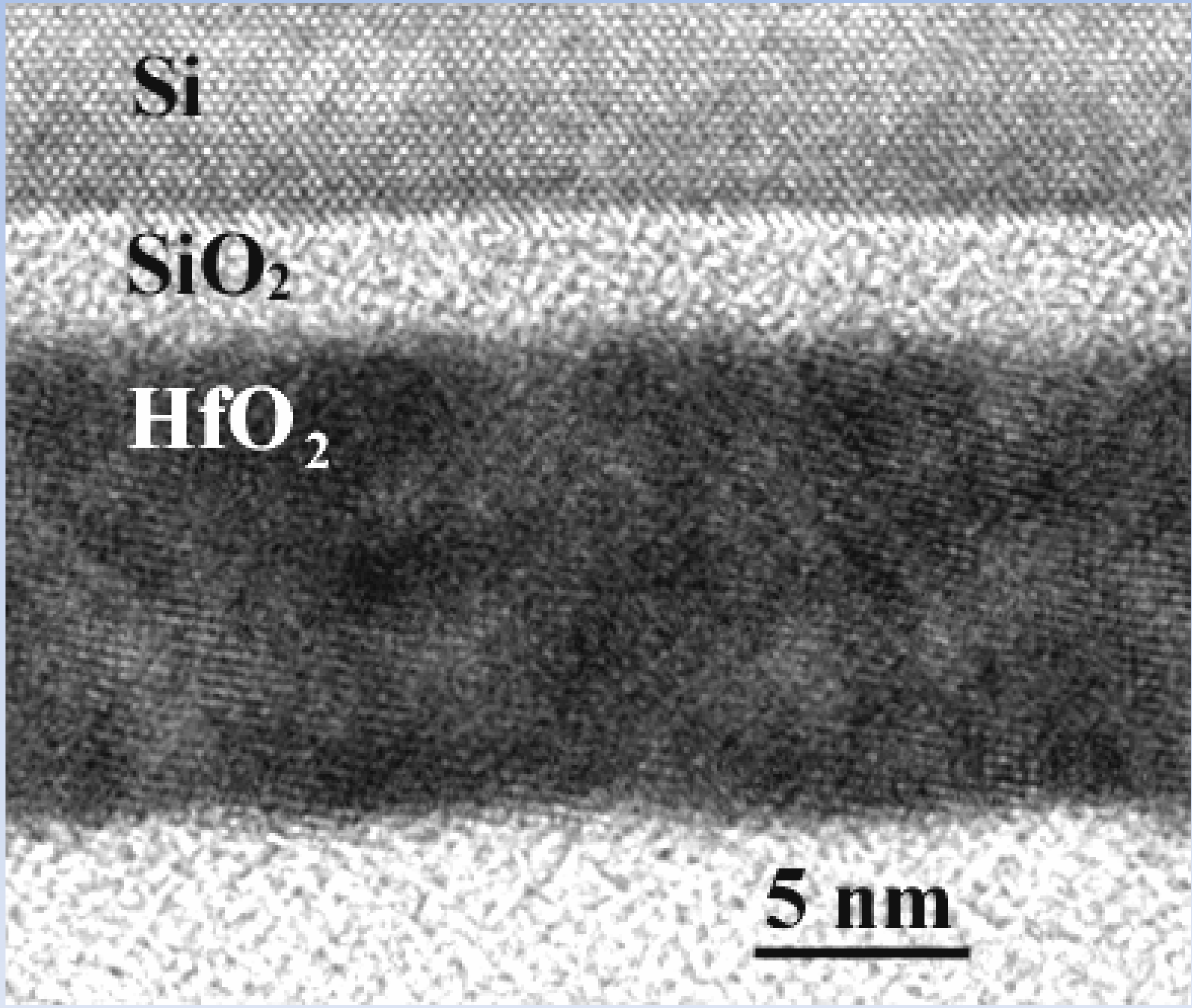
NATL INST MAT PHYS (154)
UNIV BUCHAREST (83)
NATL INST LASERS PLASMA & RADIAT PHYS (68) UNIV
POLITEHN BUCURESTI (68)
ALEXANDRU IOAN CUZA UNIV (55)



Some “success stories”

Fabrication and structural study of sol-gel HfO_2 thin films

Laser processing of nanostructured oxide thin films for transparent and conventional electronics PROLAF project PN2 nr 11061/2007



XTEM image (cross section) of a HfO_2 sol-gel thin film with 12nm thickness, obtained by dip-coating on Si[100] wafer substrate, using an etoxide precursor, densified and crystallized by conventional thermal treatment of 30 minutes at 500°C. The interfacial SiO_2 layer is about 3nm thick.

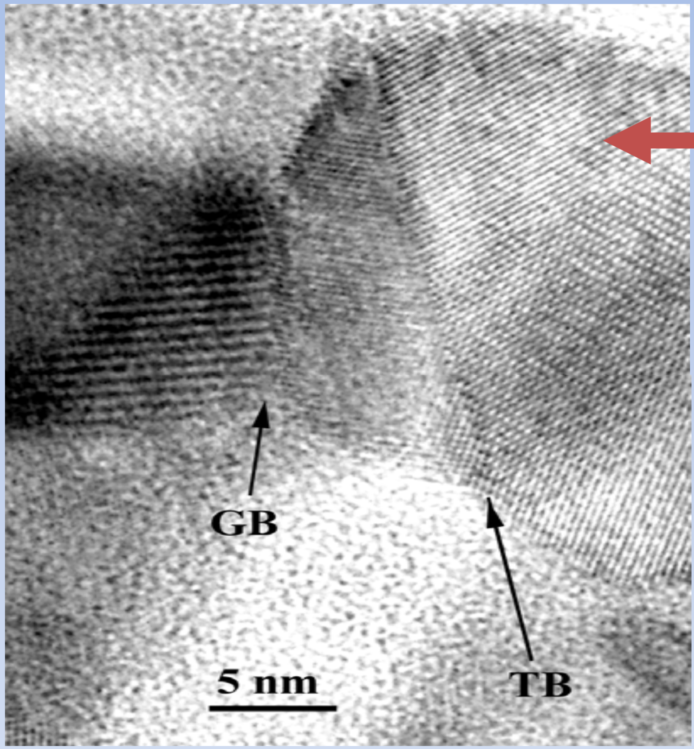
References

Teodorescu VS, Blanchin MG, ***Microscopy and Microanalysis,*** 15, (2009), 15-19

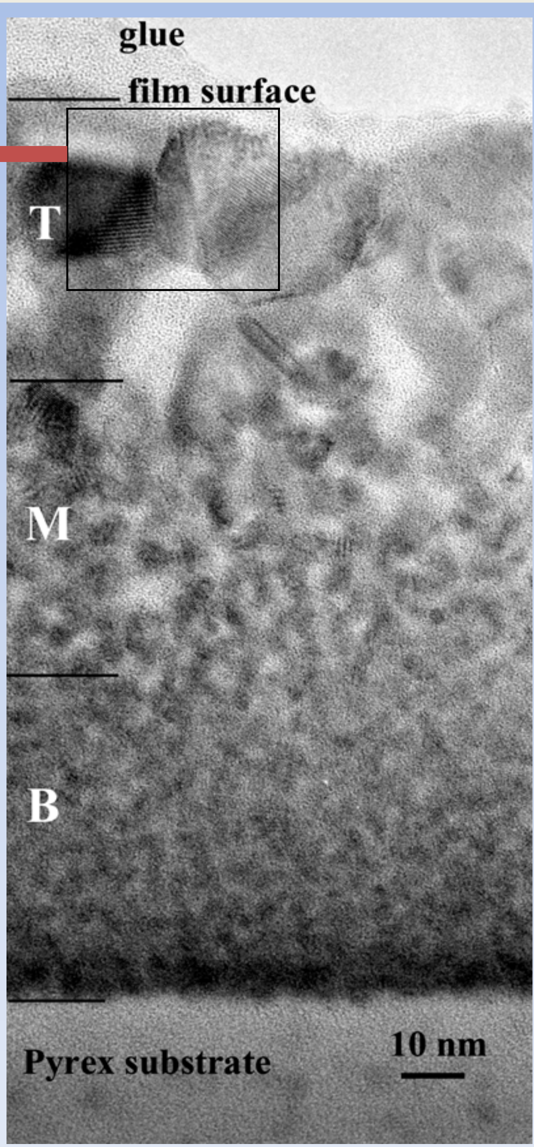
M-G. Blanchin, B.Canut, Y.Lambert, V.S.Teodorescu, A.Barau, M.Zaharescu, ***Journal of Sol-Gel Science and Technology,*** 47, (2008), 165-172

M.Zaharescu, V.S.Teodorescu, M.Gartner, M-G.Blanchin, A.Barau, M.Anastasescu, ***Journal of Non-Crystalline Solids,*** 354 (2008), 409-415

Laser proccesing of sol-gel transparent conducting oxide thin films: ATO, ITO, project CEEX nr:104/2003, Romanian- French collaboration INCDFM-Univ Lyon-DPM



TB – twin boundary ; GB – grain boundary



XTEM image of a ATO film irradiated with 10 laser pulses (193 nm) of 36 mJ/cm^2

layer B, In this area the film nanostructure is not modified, practically is idendical with nanostructure of the nonirradiated film.

Layer M, median area, some structural modifications are present, due to the crystallization proces induced by the heat diffusion in the film thickness

Layer T , top surfaceis crystallized by the direct laser pulse heating showing in fact the absorption depth of the laser radiation, of

REFERENCES

V. S. Teodorescu, C. Ghica, C. S. Sandu , A. V. Maraloiu, M-G. Blanchin, B. Canut, J. A. Roger, **Digest Journal of Nanomaterials and Biostructures** ,1, (2006), 61 - 69

CS Sandu, VS Teodorescu, C Ghica, B Canut, MG Blanchin, JA Roger, A Brioude, T Bret, P Hoffmann, C Garapon , **Applied Surface Science**, 208, 382-387, 2003

CS Sandu, VS Teodorescu, C Ghica, P Hoffmann, T Bret, A Brioude, MG Blanchin, JA Roger, B Canut, M Croitoru , **Journal of Sol-Gel Science and Technology** , 28, 227-234, 2003

STRUCTURAL INVESTIGATIONS OF Ge NANODOTS EMBEDDED IN SiO_2

Project No. 471/2009 (ID 918/2008), Ideas Program

Applications

- LEDs based on quantum confinement effects
- Photovoltaic cells (the 4-th generation) based on quantum confinement effects
- Non-volatile memories (due to strong memory effect)
- Single Electron Devices
- Integrated opto-couplers in microsystems for biotechnology

Output:

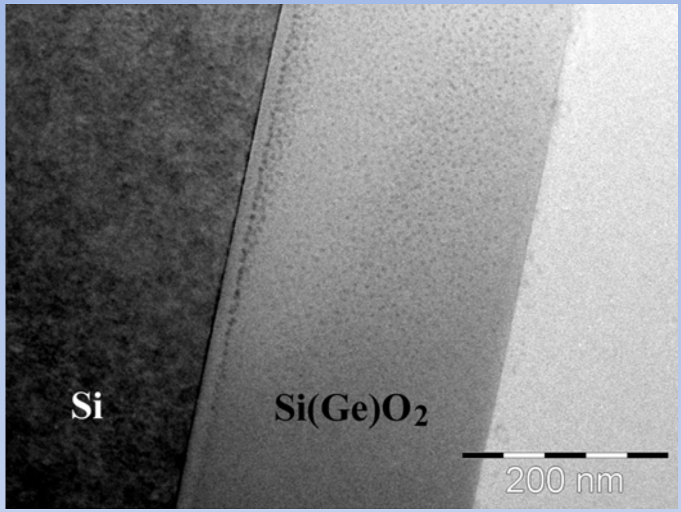
- I. Stavarache, A.-M. Lepadatu, N. G. Gheorghe, M. A. Husanu, G. Stan, D. Marcov, A. Slav, G. Iordache, T. F. Stoica, V. Iancu, V. S. Teodorescu, C. M. Teodorescu, and M. L Ciurea, **STRUCTURAL INVESTIGATIONS OF Ge NANODOTS EMBEDDED IN SiO_2**, *J. Nanopart. Res.* (submitted)

- I. Stavarache, A.-M. Lepadatu, T. F. Stoica, G. Stan, D. Marcov, A. Slav, V. S. Teodorescu, C. M. Teodorescu, A. M. Vlaicu, I. Pasuk, S. Lazanu, G. Iordache and M. L. Ciurea, **STRUCTURAL INVESTIGATIONS OF Ge DOTS EMBEDDED IN SiO_2**, *ROMANIAN CONFERENCE ON ADVANCED MATERIALS: ROCAM 2009*

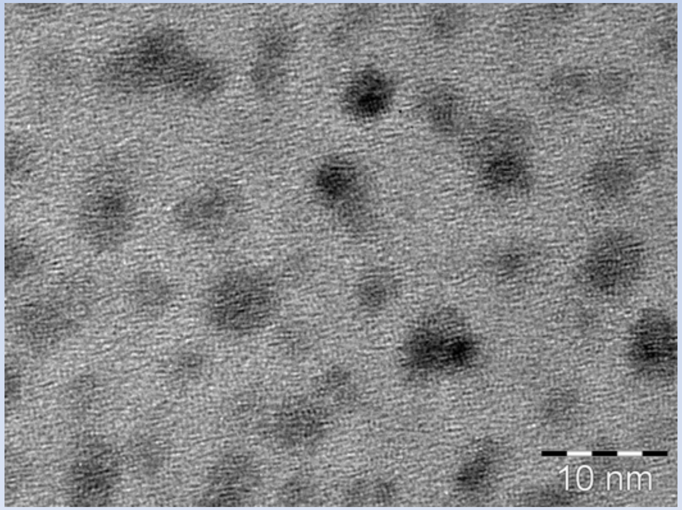
Work team:

Drd. I. Stavarache, Drd. A.-M. Lepadatu, Drd. A. Slav, N. G. Gheorghe, Drd. M. A. Husanu, Drd. G. Stan, Drd. D. Marcov, Dr. G. Iordache, Dr. T. F. Stoica, Dr. V. S. Teodorescu, Dr. C. M. Teodorescu, and Dr. M. L. Ciurea

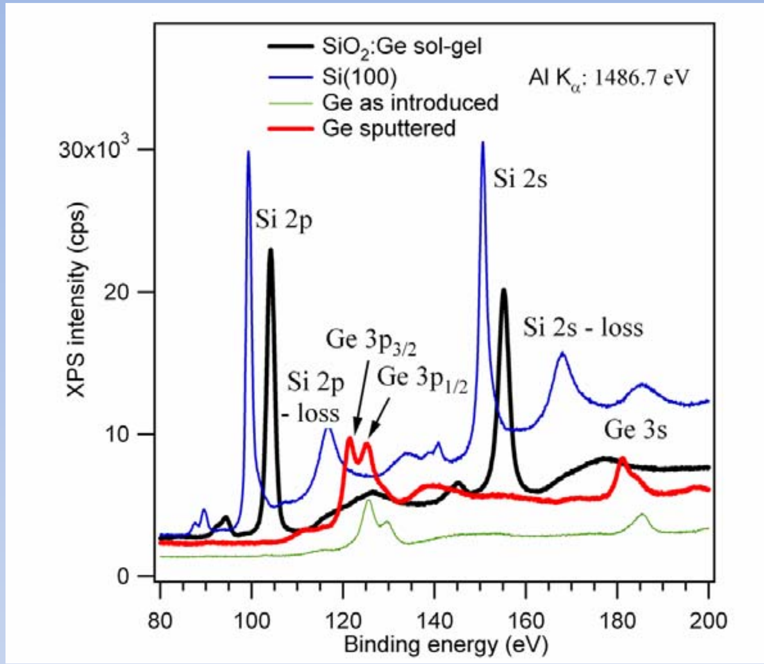
Sol-gel films



XTEM image: 10 nm clear SiO_2 layer at Si interface, followed by Ge rich region and $Si(3\%Ge)O_2$



XTEM image: globular amorphous Ge nanodots in $Si(12\%Ge)O_2$



XPS image: Si 2p-2s and Ge 3p-3s region; surface Ge oxidized

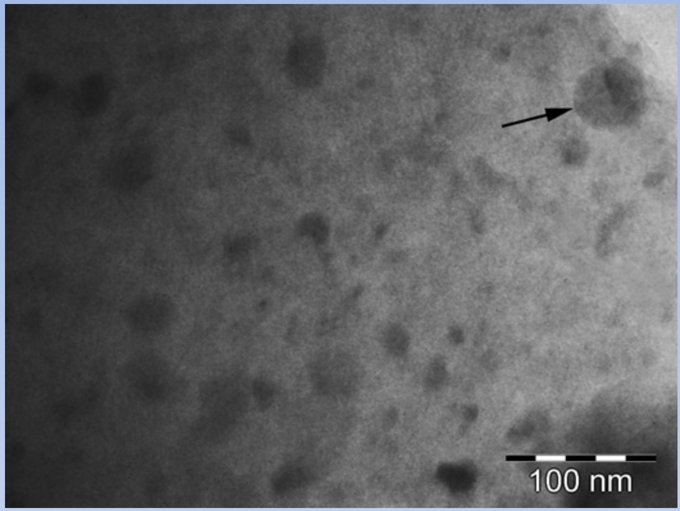
Sol-gel films: amorphous Ge nanodots in amorphous SiO_2 matrix.

❖ *Left up*: the clear SiO_2 band is formed by the oxidation of the Si wafer during the annealing.

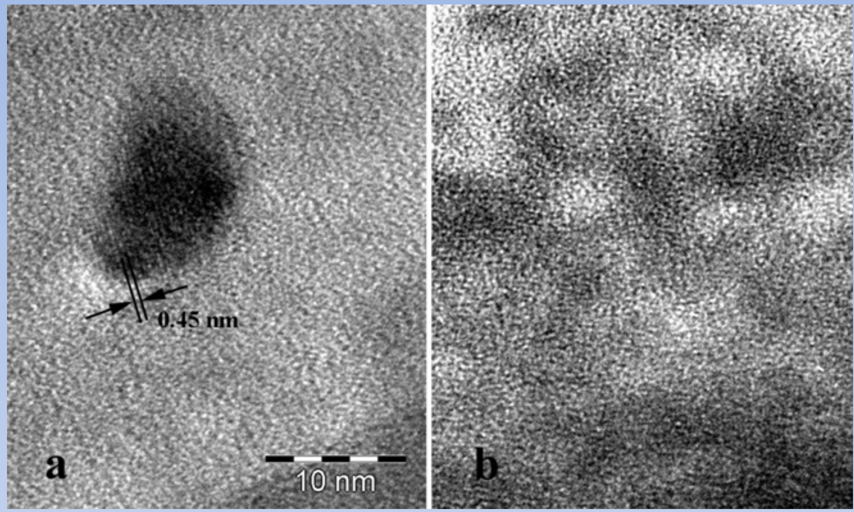
❖ *Left down*: the mean size of nanodots increases from 3.8 nm (3% Ge) to 4.3 nm (12% Ge).

❖ *Right up*: the film surface is formed by a mixture of GeO_2 and SiO_2.

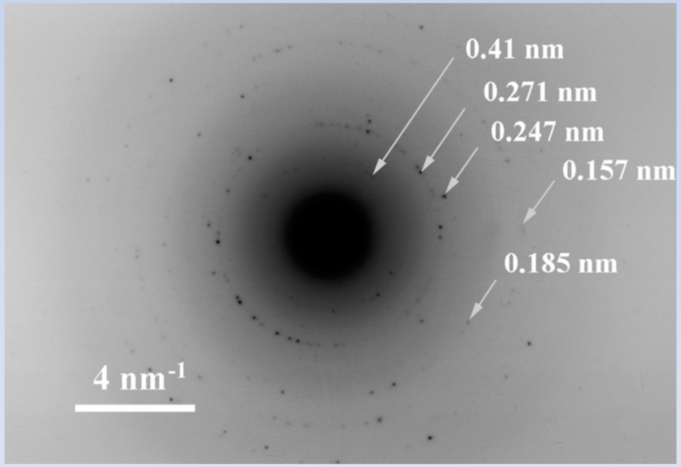
Magnetron sputtered films $Si(40\%Ge)O_2$



TEM image: Ge nanodots; arrow: 50 nm nanodot



HRTEM image: (a) lattice fringes contrast for Ge **tetragonal phase**; (b) amorphous network nanostructure



SAED pattern: **tetragonal phase** for Ge nanodots

Magnetron sputtered films: mixture of **tetragonal Ge nanodots** (specific for **high pressure**) and amorphous ones in amorphous SiO_2 matrix.

❖ *Left up*: mean size of nanodots is 20 nm.

❖ *Left down*: main diffraction data originate from crystalline nanodots larger than 50 nm.

❖ *Right up*: (a) lattice interfringe 0.45 nm, specific to **tetragonal Ge phase**; (b) amorphous network consists of a mixture of Ge and Si oxides.

Smart –cut process:

Quantitative HRTEM: atomic scale measurement of strain field around extended defects

References

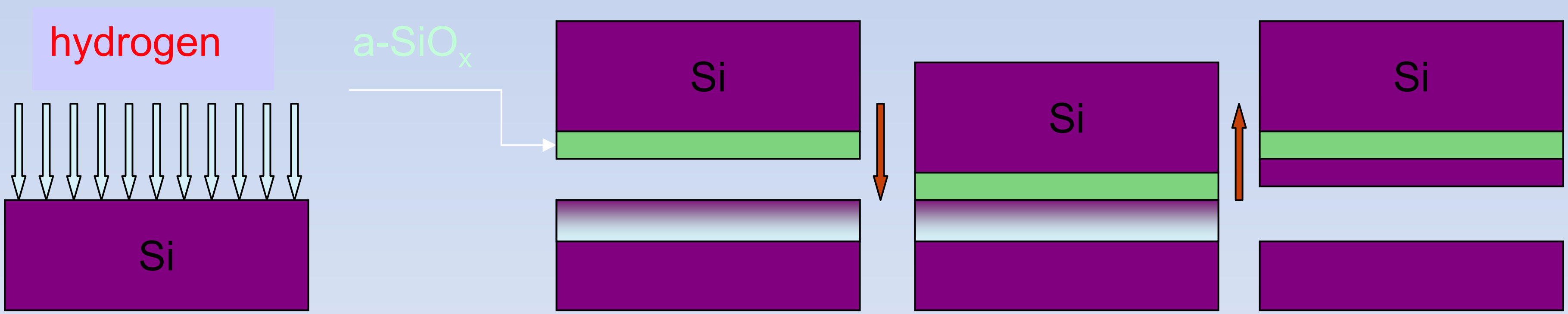
1. C. Ghica, L. C. Nistor, H. Bender, O. Richard, G. Van Tendeloo, A. Ulyashin, ***Philosophical Magazine*** **86**, 5137-5151 (2006).

2. C. Ghica, L. C. Nistor, H. Bender, O. Richard, G. Van Tendeloo, A. Ulyashin, ***Journal of Physics D: Applied Physics*** **40**, 395-400 (2007).

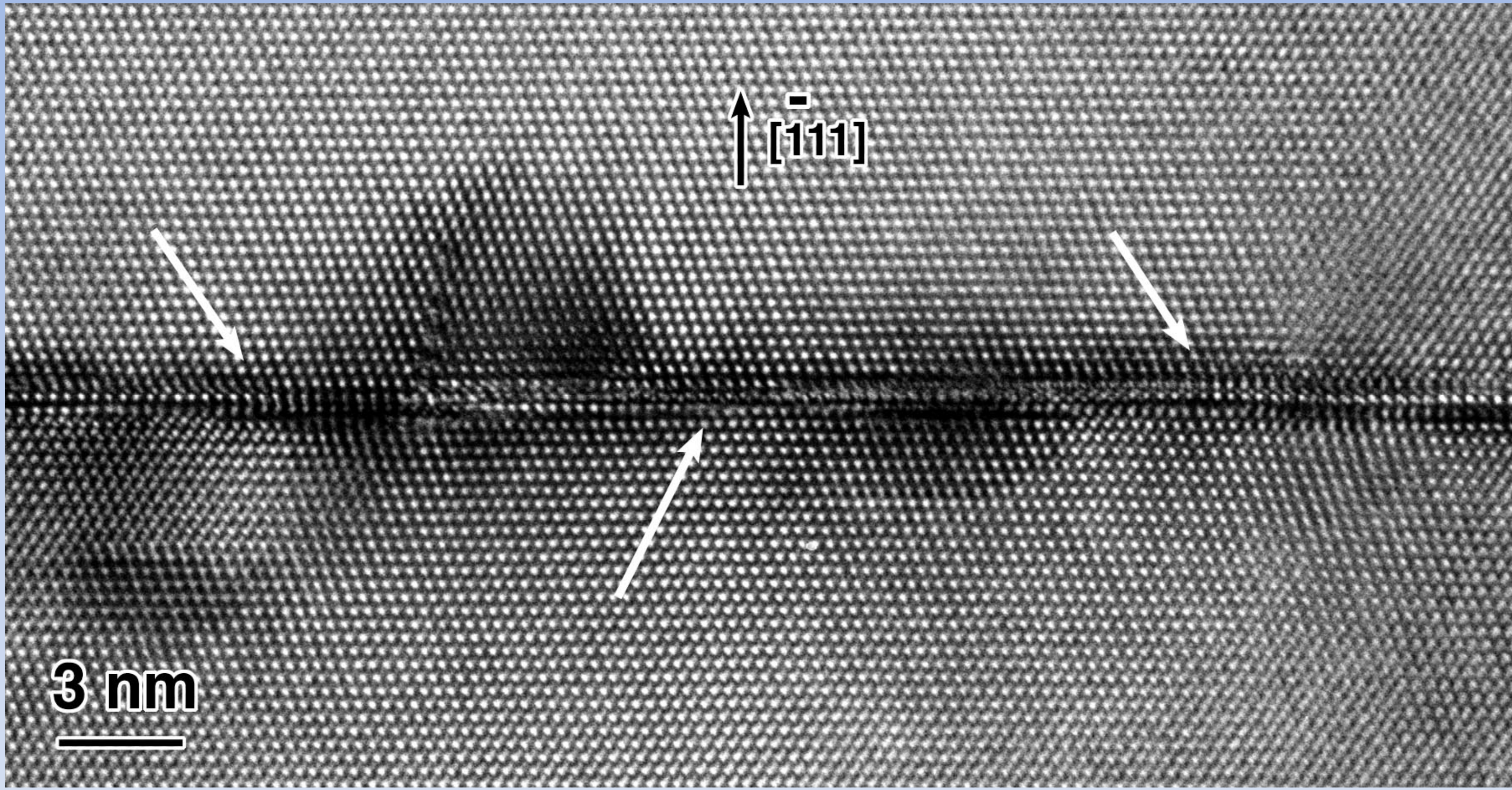
3. C. Ghica, L. C. Nistor, M. Stefan, D. Ghica, B. Mironov, S. Vizireanu, A. Moldovan, M. Dinescu
Applied Physics A *DOI 10.1007/s00339-009-5527-1*

4. **C. Ghica**, Qualitative and quantitative HRTEM characterization of extended defects induced in silicon by H-plasma treatment
Invited lecture at 2nd Croatian Microscopy Congress with International Participation, Topusko, Croatia, May 18-21, 2006.

The schematics of the “Smart cut” process used to produce SOI devices:



HR image of a {111} defect induced in Si by H-plasma treatment.



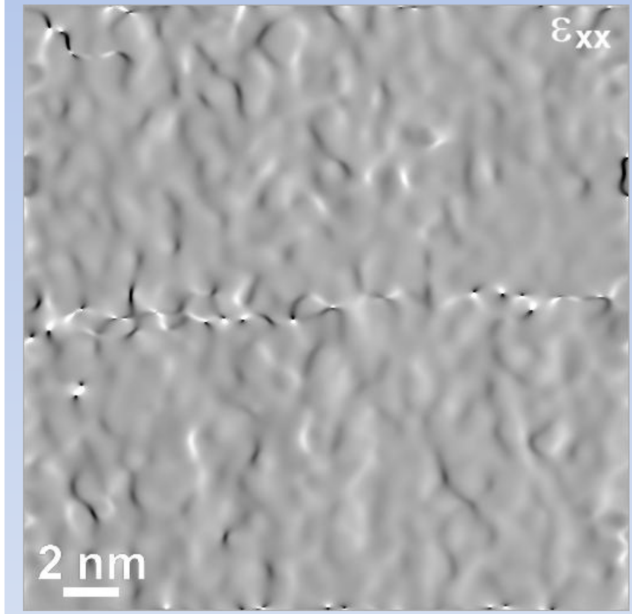
HR pattern of the defect is highly dependent on the recording conditions (thickness, defocus) and position along the defect.

- Frequent common feature: …ABCAABC…-like stacking sequence.

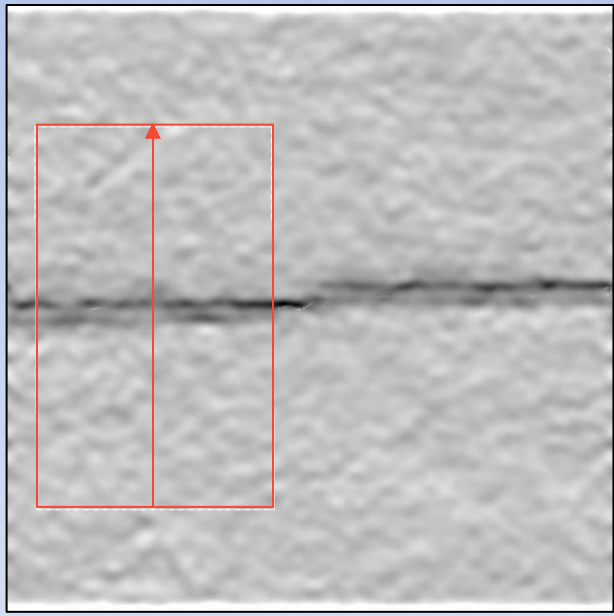
Calculation of the strain field around the defect

$$e = \begin{pmatrix} e_{xx} & e_{xy} \\ e_{yx} & e_{yy} \end{pmatrix} = \begin{pmatrix} \partial u_x / \partial x & \partial u_x / \partial y \\ \partial u_y / \partial x & \partial u_y / \partial y \end{pmatrix}$$

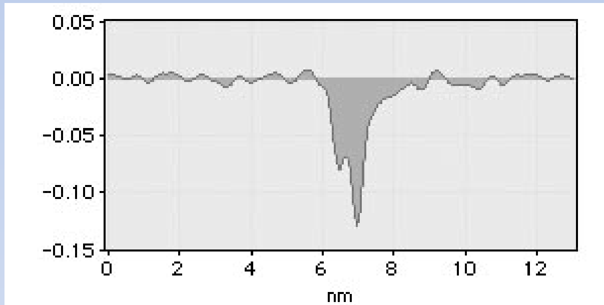
$\varepsilon = 1/2(e + e^T)$
$\omega = 1/2(e - e^T)$



$\varepsilon_{xx} = \partial u_x / \partial x$



$\varepsilon_{yy} = \partial u_y / \partial y$



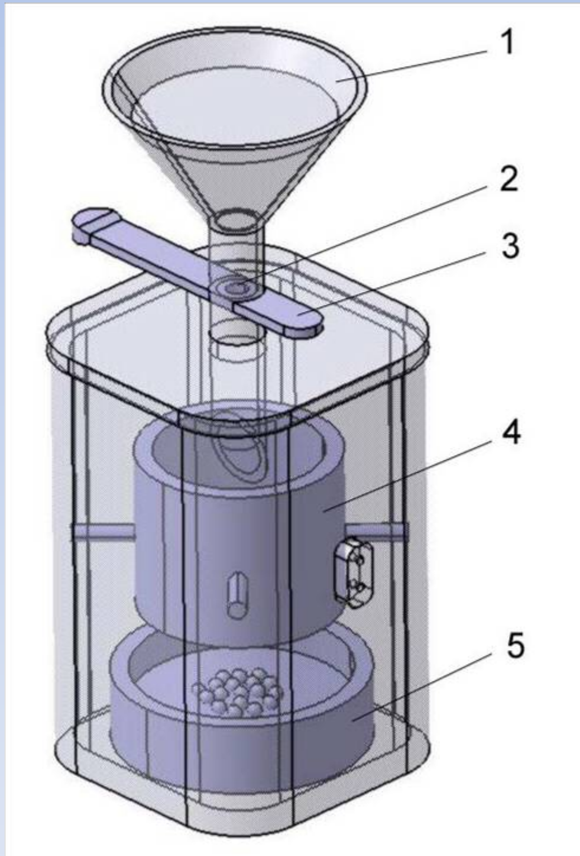
Averaged line profile of ε_{yy}

Micro-lenses for optoelectronic circuits

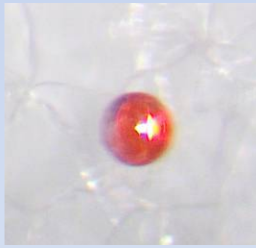
Patent: "Procedeu si Aparat pentru Producerea de Microlentile Calcogenice". Documentul a fost înregistrat la OSIM sub nr. A00243 / 07.04.2006.
Brevet acordat de OSIM (Nr. Hotarare de acordare 6 / 146 / 30.11.2009).

Autori:
M. Popescu, F. Sava, A. Lorinczi / **INCDFM**
S. Micloş, D. Savastru, M. Mustaţa, R. Savastru / **INOE-2000**

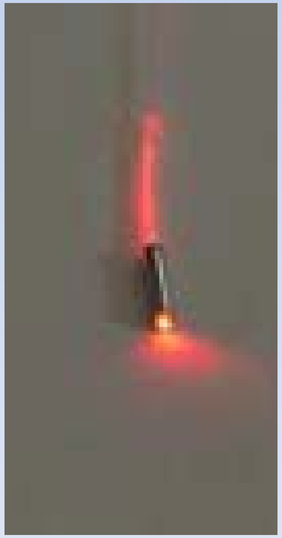
Schematic representation of the apparatus used to produce chalcogenide micro-lenses

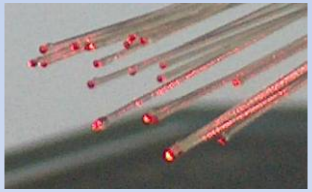


Photograph of a micro-lense

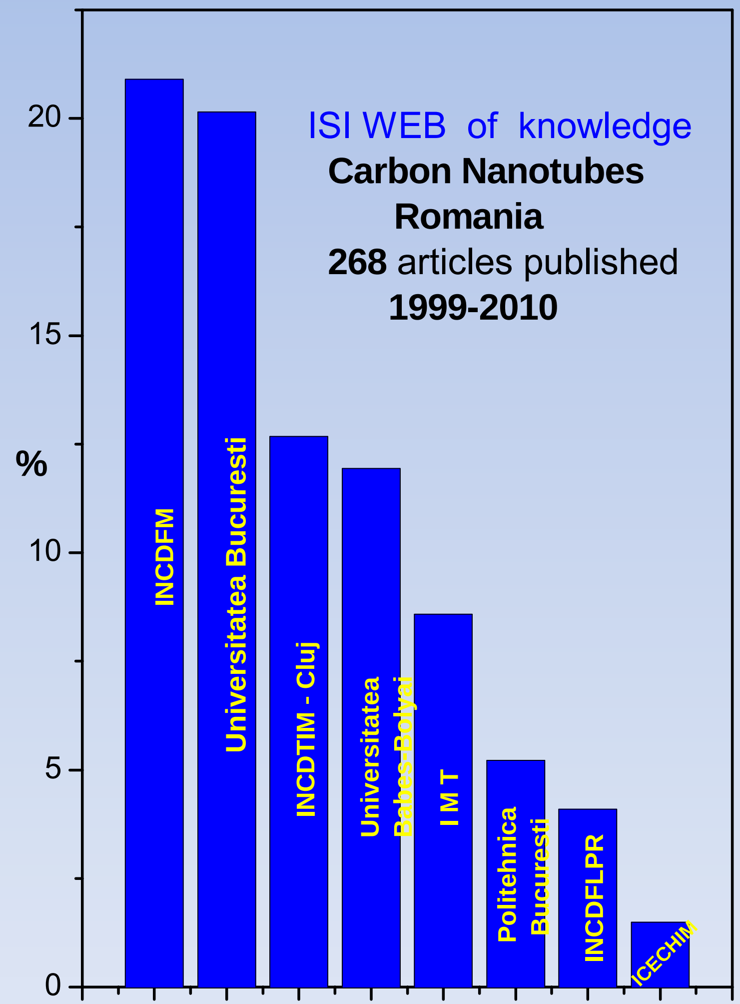


Laser collimator





Nanostructured materials based on carbon nanotubes (CNT)1999-2010



From 22 most cited papers,

7 are from NIMP,

In journals like

***Physical Review B* 65,235401,2002,**

Chemistry of Materials 15, 4149,2003

Carbon 42,3143, 2004

Journal Raman Spectroscopy 36, 676, 2005

Synthetic Metals 100, 13,1999

Synthetic Metals 101, 184,1999

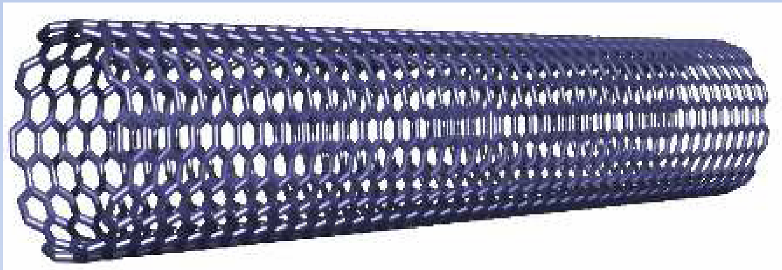
J. Nanoscience&Nanotechnology 6, 289, 2006

Research directions

Physical properties investigated by optical methods
Chem.Phys.Lett. 406,222,2005

Chemical properties: p type doping, functionalization
Carbon 40,2201, 2002

Electrochemical properties: n type doping, functionalization with organic compounds and polymers
Carbon 47, 1389,2009



Polymer/CNT composites
Polymer48,5279,2007

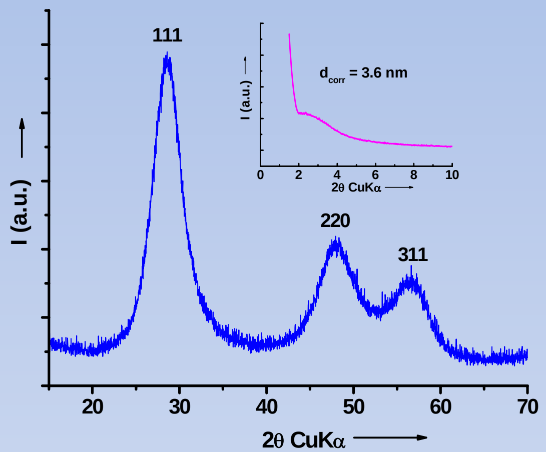
Semiconductor/CNT composites
J.Phys. Cond. Mat. 21,445801, 2009

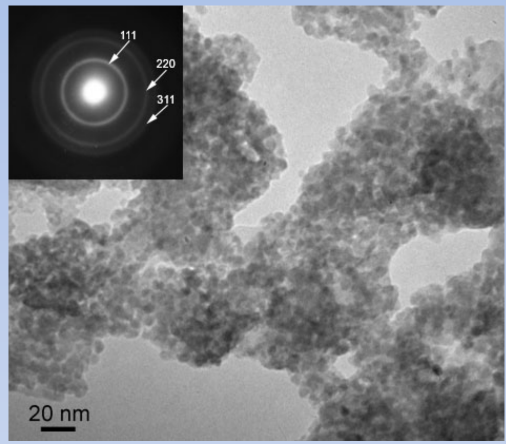
Applications

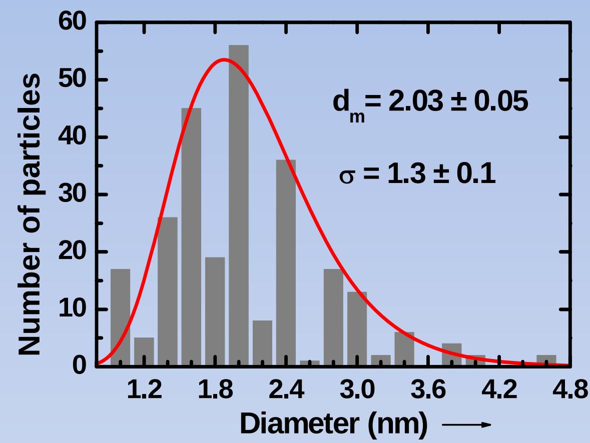
Energy storage
Small 2,1075, 2006

Non-linear optics
Phys. Rev. B72, 245402, 2005

Synthesis of luminescent, cubic ZnS:Mn nanocrystals.



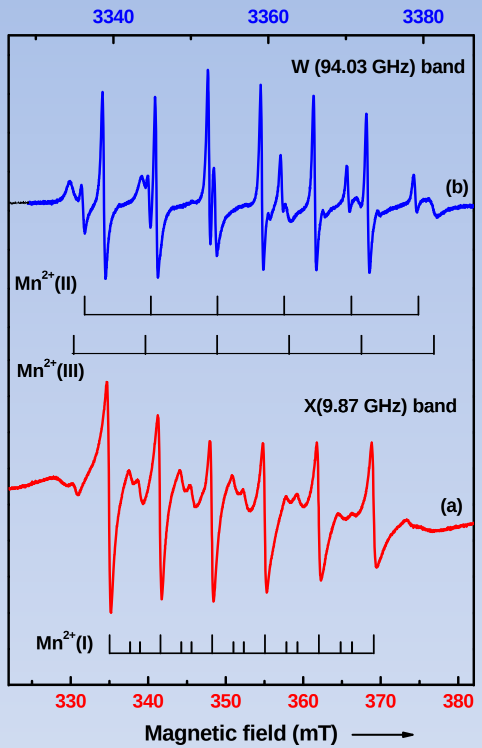




- **Luminescent ZnS cubic nanocrystals, doped with Mn^{2+}ions, were prepared by wet synthesis in the presence of a non-toxic surfactant.**
- **Self assembling results in a mesoporous structure, with a high crystallinity and narrow size distribution centered on d_m= 2nm.**

L. C. Nistor, C. D. Mateescu, R. Birjega and S. V. Nistor, Appl. Phys. A 92, 295 (2008)

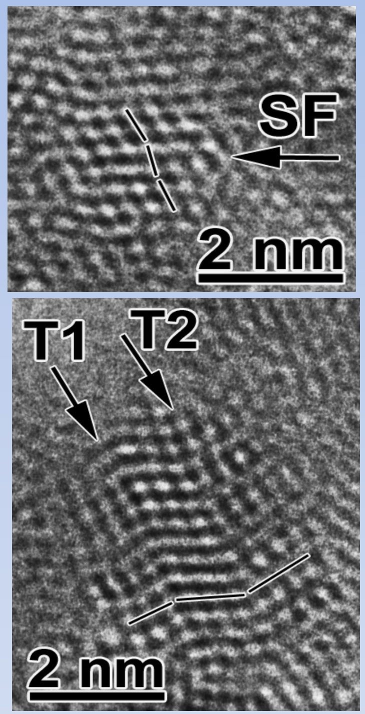
S. V. Nistor, L. C. Nistor, M. Stefan et al., Superlattices & Microstructures 46, 306 (2009)



EPR spectra (multi-frequency) ⇐ indicate: substitutional Mn^{2+} ions, (Mn(I) center) + surface centers Mn(II) si Mn (III).

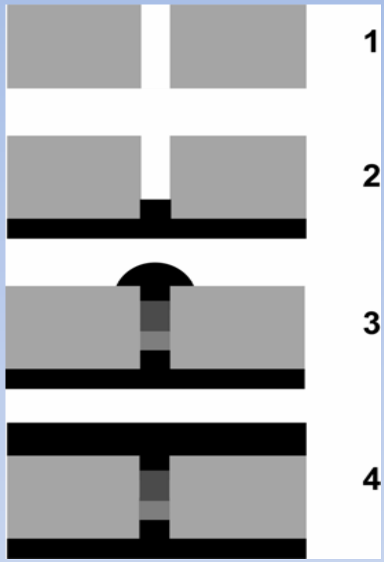
- Mn^{2+} ions are substitutions in Zn^{2+} nods next to extended defects as twins (T) or stacking faults (SF).

HRTEM images ⇒ Showing the presence of defects.



S. V. Nistor, M. Stefan, L. C. Nistor, E. Goovaerts and G. Van Tendeloo, Physical Review B 81 (3) 035336 (2010)

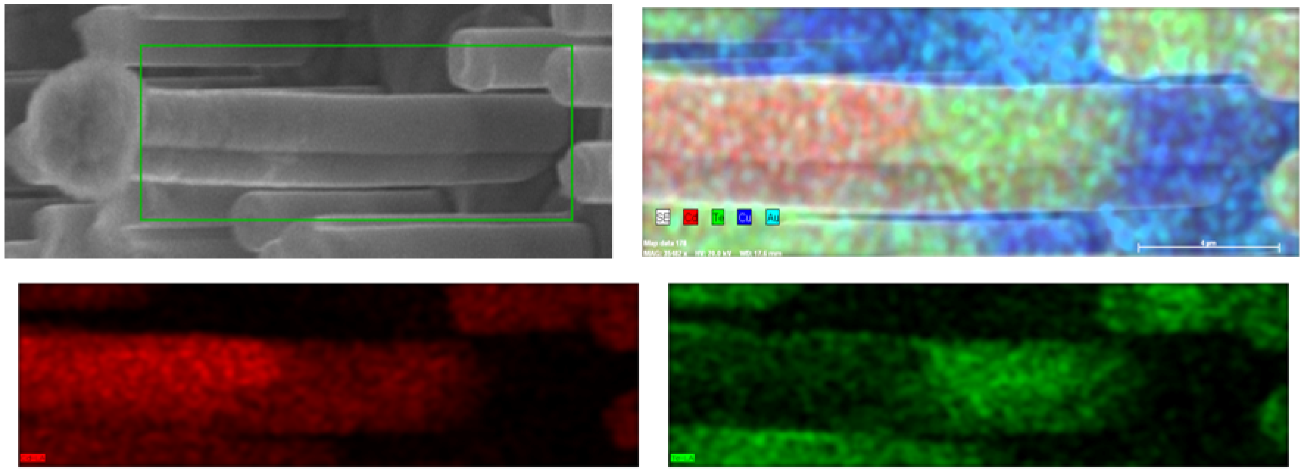
Multi-segment nanowires based photodetectors



Template method

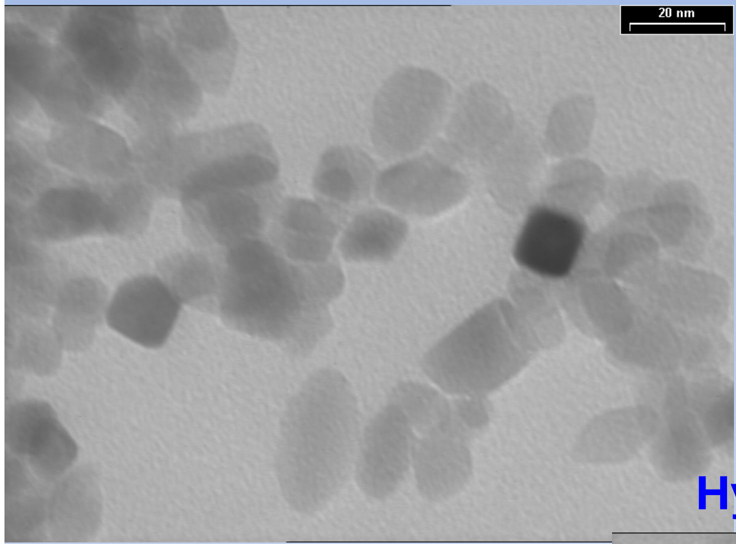
Nanoporous membranes+electrochemical deposition

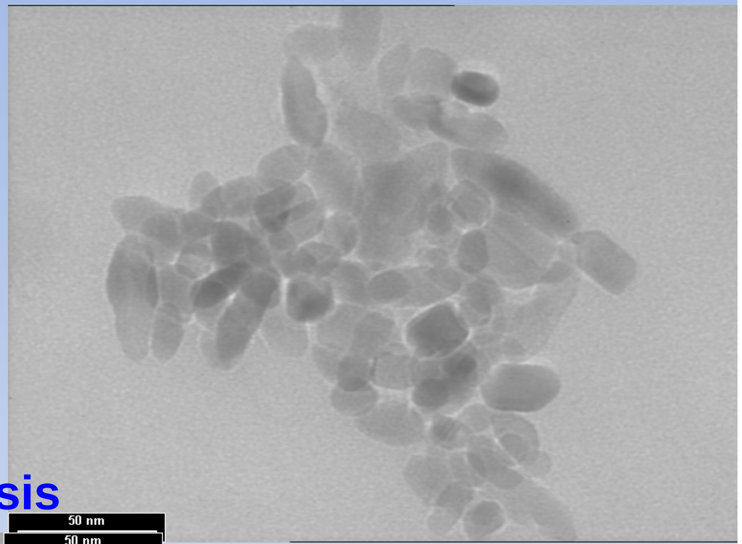
⇒nanowire photodetectors (photoconductors, photodiodes) of up to 80 nm diameter
⇒single bath deposition-easy to transfer to industry



Deposition and properties of CdTe nanowires prepared by template replication
Enculescu I, Sima M, Enculescu M, et al.
PHYSICA STATUS SOLIDI B-BASIC SOLID STATE PHYSICS
244(5),1607-1611 (2007)

TiO_2 NANOCRYSTALS AND NANOSTRUCTURED THIN FILMS FOR PHOTO-CATALYTIC DEGRADATION OF ORGANIC POLLUTANTS

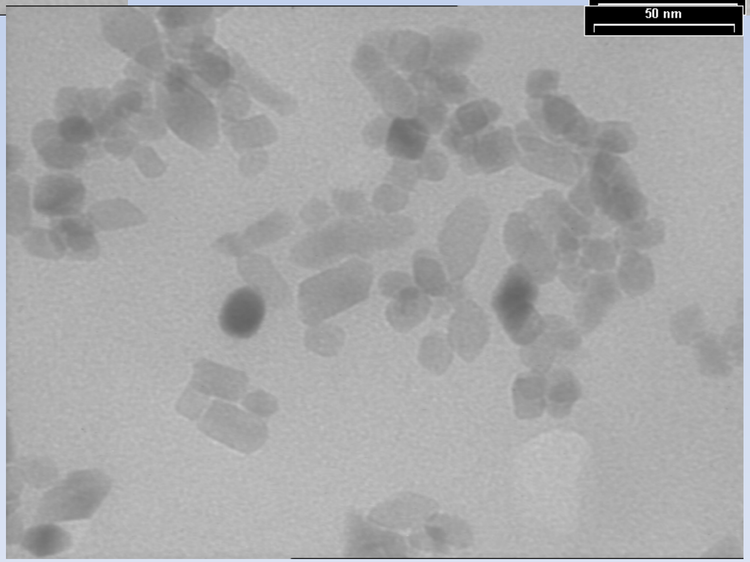




Hydrothermal Synthesis

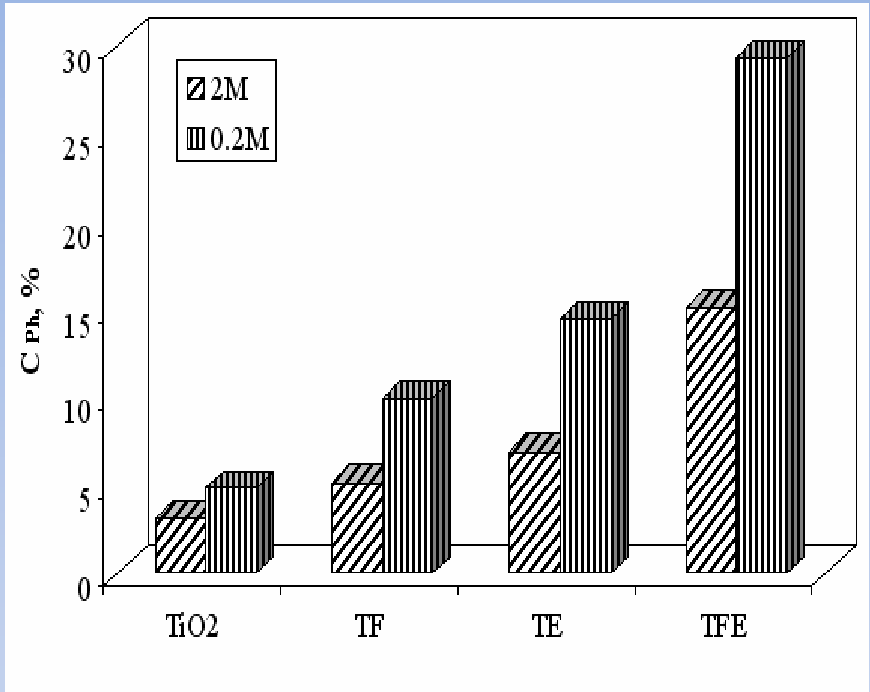
a

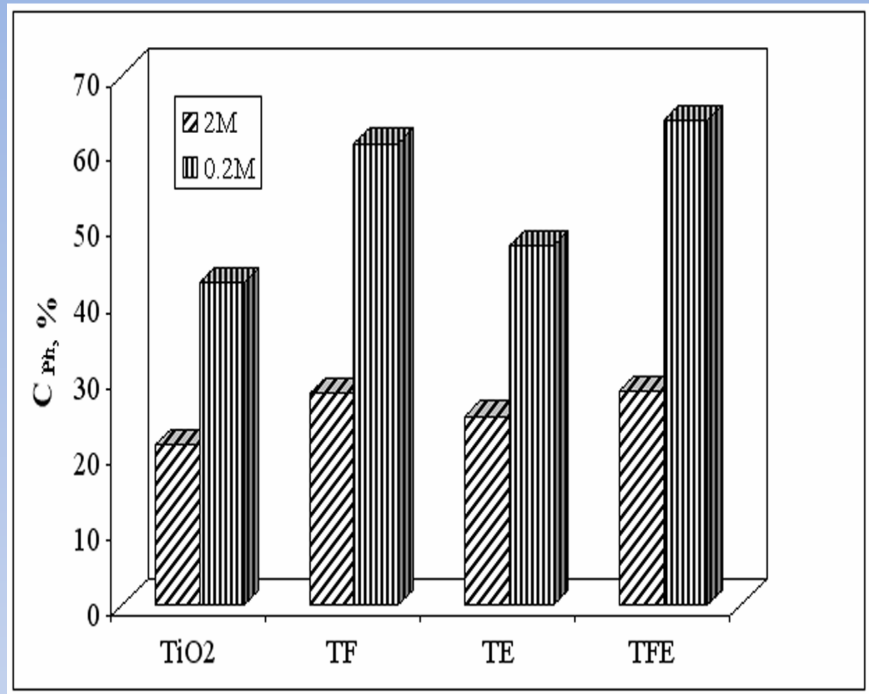
b



c

TEM images of undoped TiO_2 (a), Eu-doped TiO_2 (b) and Fe- and Eu-doped TiO_2 (c).





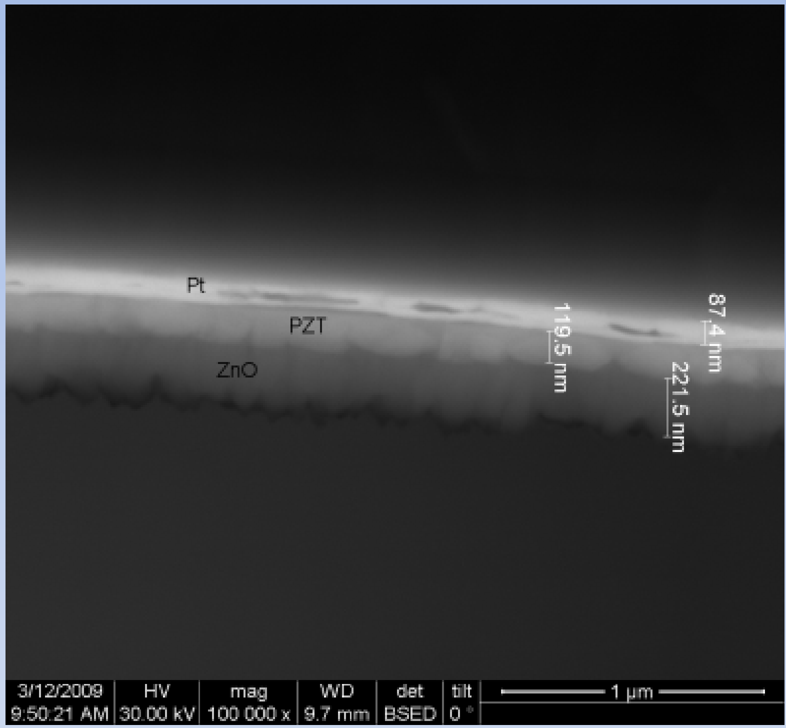
Phenol conversion degree CPh (%) after 5 h of UV illumination (λ = 312 nm) for the hydrotermally synthesized TiO_2 samples; 2M and 0.2 M are the initial Phenol concentrations.

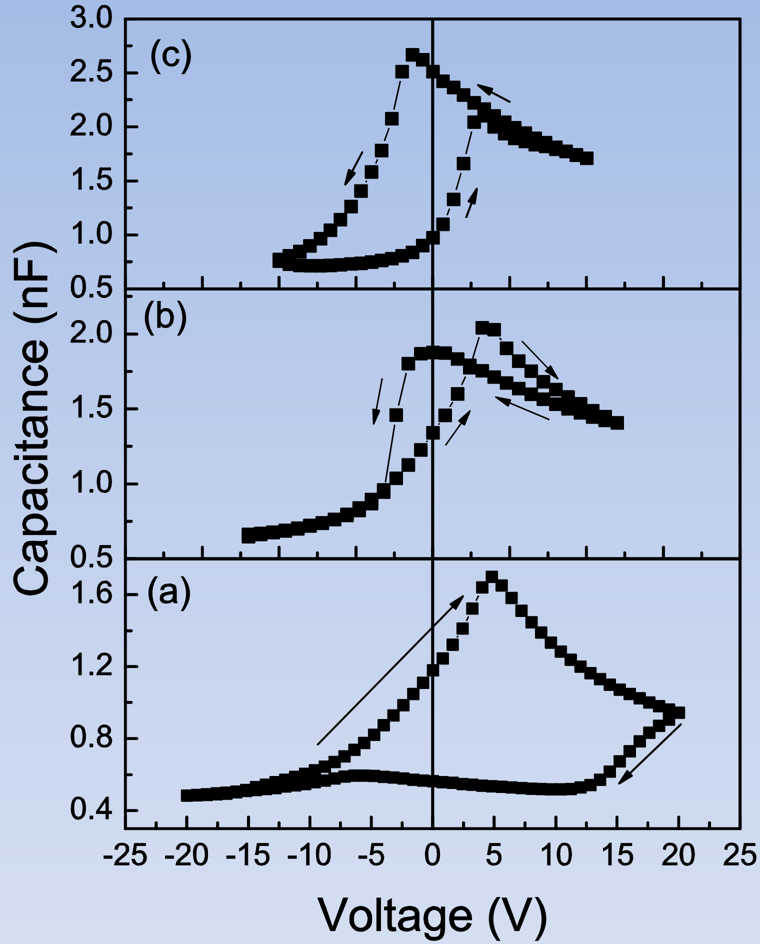
Phenol conversion degree CPh (%) under visible irradiation (λ > 380 nm) catalysed by Fe and Eu doped and codoped TiO_2.

STRUCTURAL AND PHOTOCATALYTIC PROPERTIES OF IRON AND EUROPIUM DOPED TiO_2 NANOPARTICLES OBTAINED UNDER HYDROTHERMAL CONDITIONS

L. Diamandescu, F. Vasiliu, D. Tarabasanu-Mihaila, M. Feder, A. M. Vlaicu, C.M. Teodorescu, D. Macovei, I. Enculescu, V. Parvulescu, E. Vasile (Mat. Chem. Phys.112, 146–153 (2008)).

Ferroelectric-ZnO heterostructures based on nanometric thin films



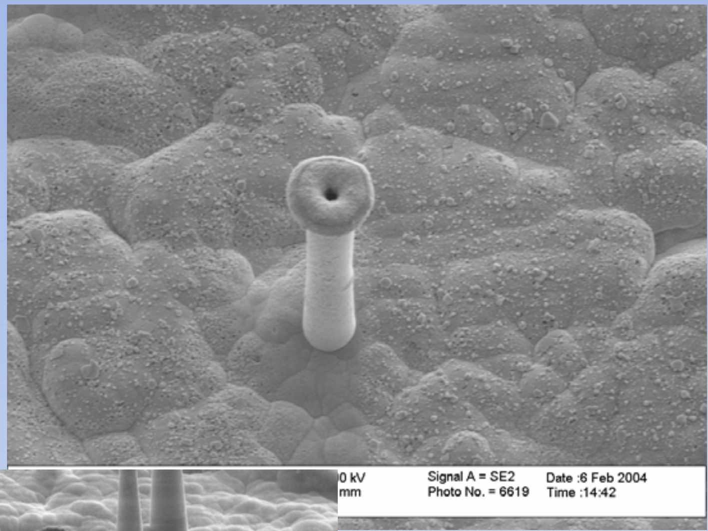


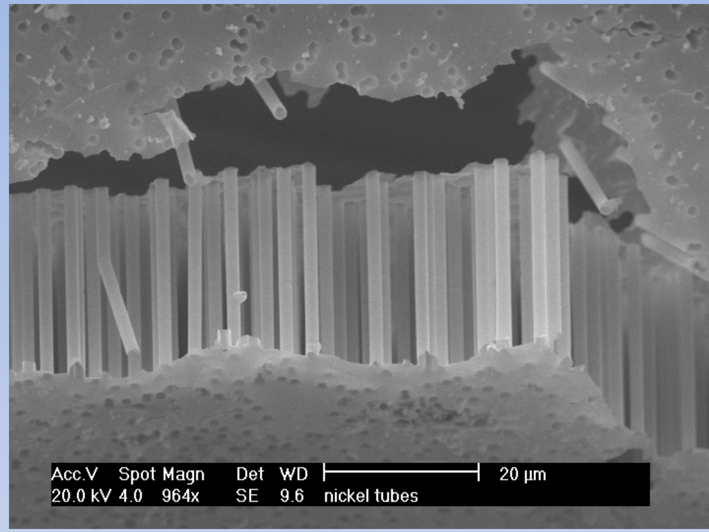
SEM image (left) and C-V characteristics at different temperatures (right)

Application: non-volatile memories

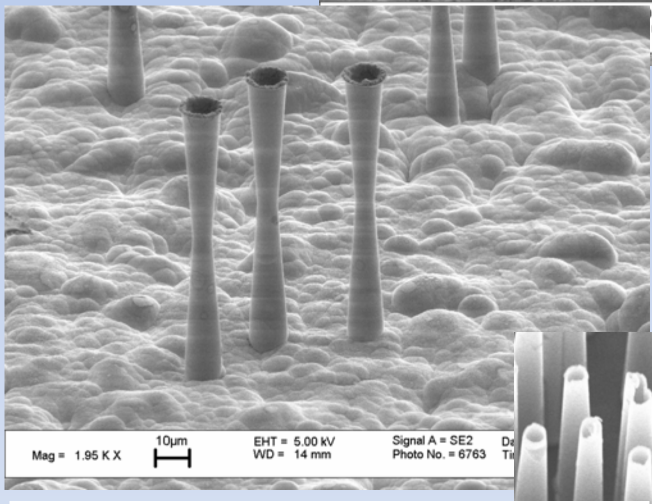
Temperature induced change in the hysteretic behavior of the capacitancevoltage characteristics of Pt–ZnO–Pb„Zr0.2Ti0.8…O3–Pt heterostructures, L. Pintilie, ***C. Dragoi, R. Radu, A. Costinoaia, V. Stancu***, and I. Pintilie, APPLIED PHYSICS LETTERS **96, 012903 (2010)**

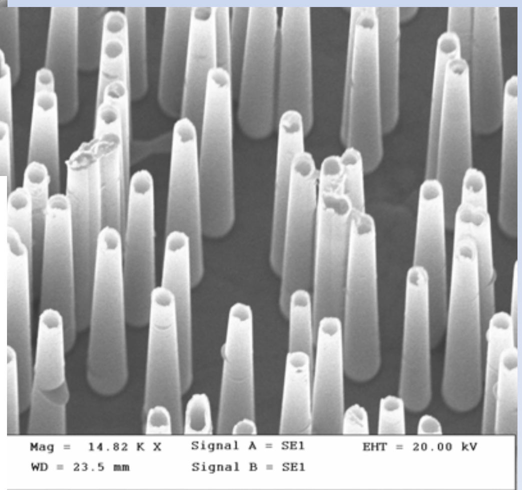
Metallic micro and nanotubes

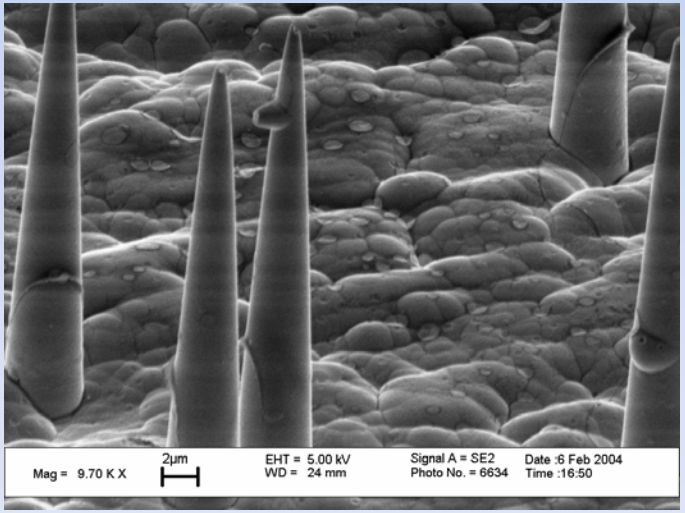




Auto-catalytic deposition using the template method

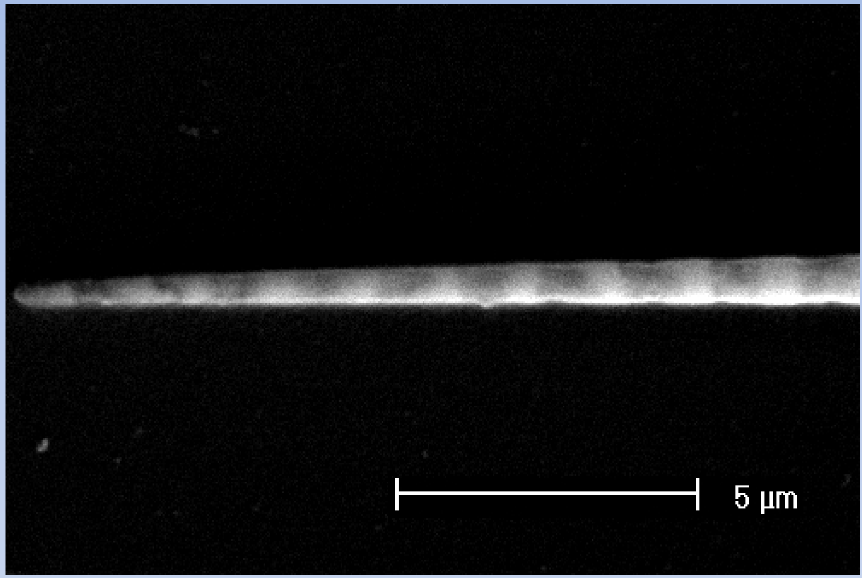


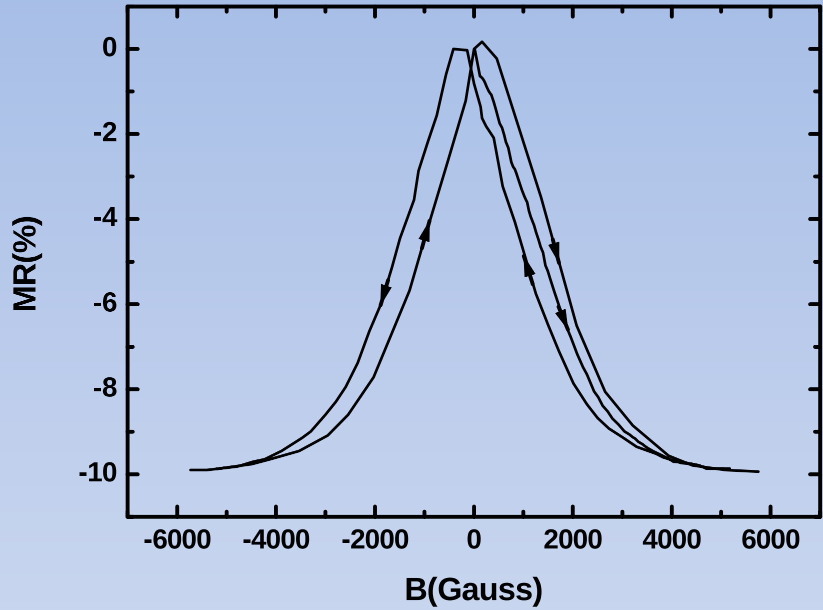


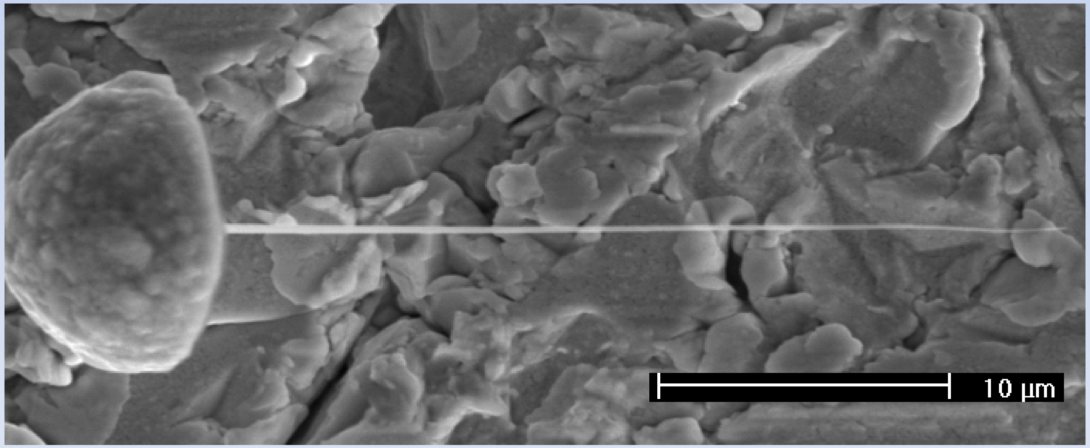


Copper tubes prepared by electroless deposition in ion track templates
B. Bercu, I. Enculescu, R.Spohr
Nuclear Instruments and Methods in Physics B, Vol 225/4 497-502 (2004)

Magnetic field detectors based on giant magnetoresistence of multi-segment nanowires







Current perpendicular to plane single-nanowire GMR sensor

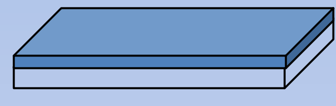
I. Enculescu, M. E. Toimil-Molares, C. Zet, M. Daub,L. Westerberg ,R. Neumann, R. Spohr

APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING 86 (1): 43-47 (2007)

Examples of magnetic nano objects that are of our interest:

- Thin films/multilayers

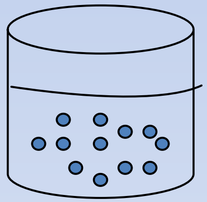
- **exchange coupled bilayers**
(exchange bias, spring-magnets)

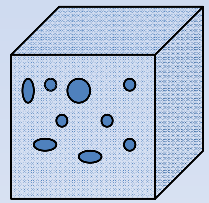


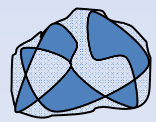
- **spin valves** as multilayers and as nanogranular thin films

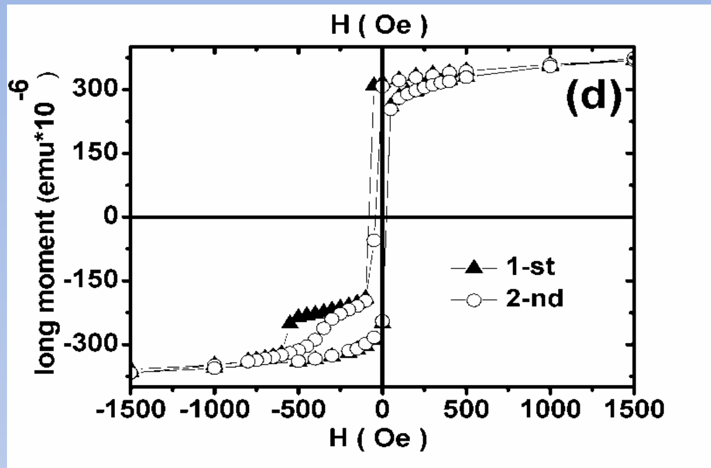
- Magnetic nanophases /nanocomposites:

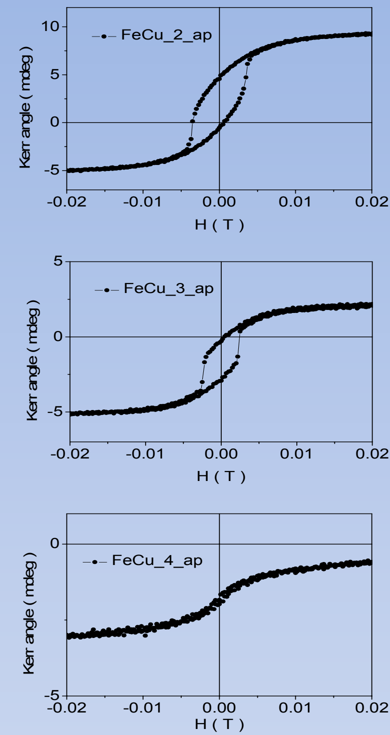
- magnetic nanopowders
- core-shell nanoparticles (colloidal, clusters)
- magnetic nanoparticles in liquids (ferrofluids)
- magnetic nanoparticles in polymers
- magnetic nanophases in solid matrix







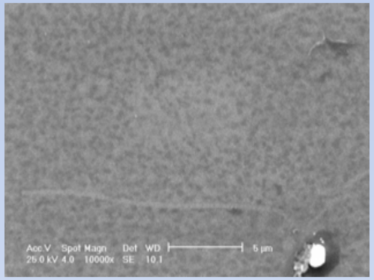


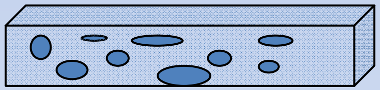


Spin valves:

-multilayers

-nanoglobular t.f.





Studied vs conc./comp. of the ferromagnet by:

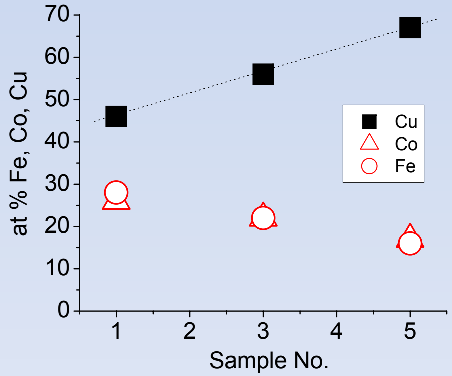
-SEM,EDX,TEM

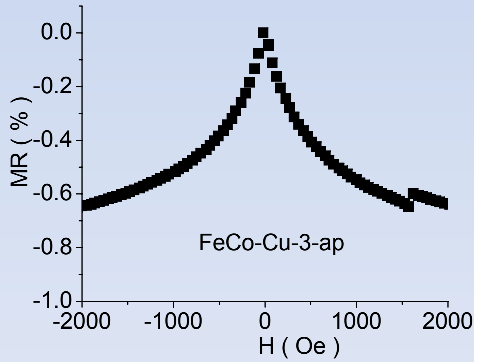
-VSM

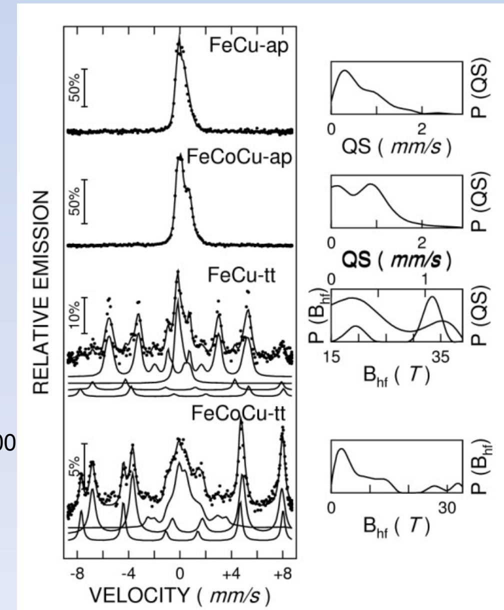
-MOKE

-CEMS

-Magnetoresistance

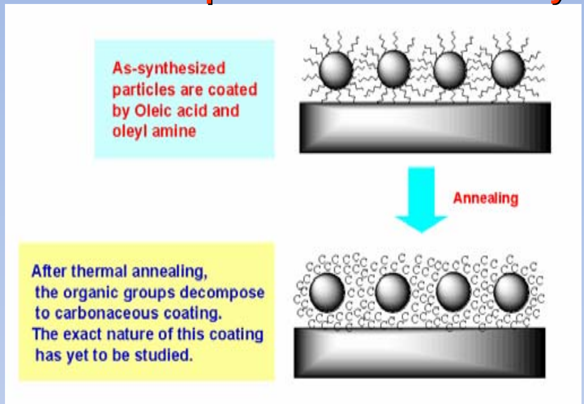






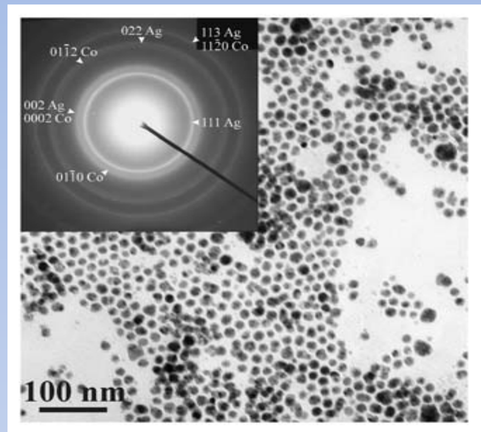
SELF - ASSEMBLED CORE_SHELL COLLOIDAL MAGNETIC NANOPARTICLES

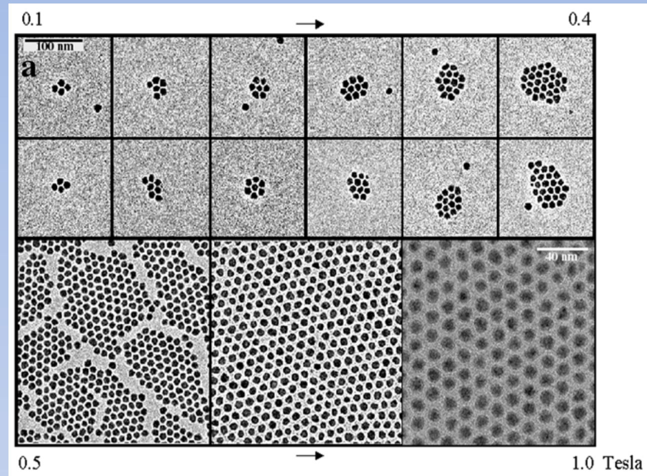
❖ Principle of the self-assembly



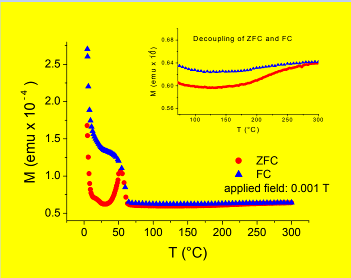
Core-shell Ag-Co nanoparticles

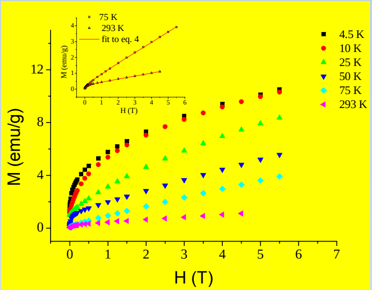
$Co_2(CO)_8 + 2AgClO_4 \rightarrow 2Ag + Co + 8CO + Co(ClO_4)_2$



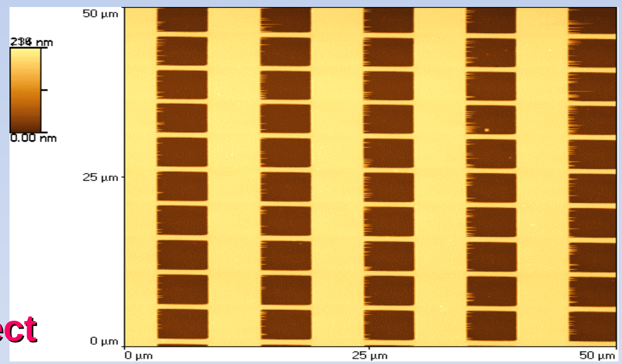


❖ Breakthrough in data storage, biomedicine, catalysis and nanoelectronics





$$M_{tot} = M_{sat}^{SPM} \cdot L\left(\frac{\mu_{SPM} H}{k_B T}\right) + M_{sat}^{FM} \cdot \left(\frac{\mu_{FM} H}{3 k_B T}\right)$$



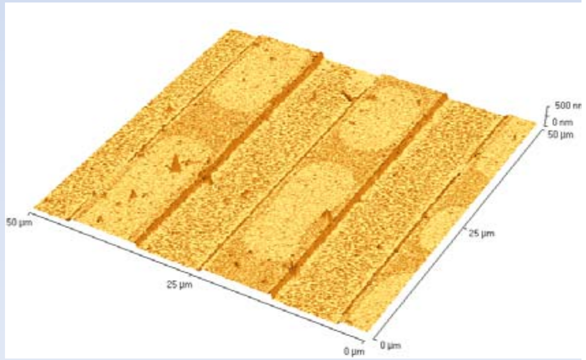
APPLICATIONS

❖ Magnetic-conducting bimetallic nanosystems that exhibit GMR effect

❖ Use of patterned substrates with logic capabilities

❖2D regular arrays of GMR nanosensors on a single chip may be achieved!

PN II 12-129 / 2008 with IMT Bucharest



Scientific output 2005 – 2010 on magnetic nano-materials:

- **Over 70 scientific articles in ISI journals and 100 communications at international conferences**
- **Cumulated ISI Impact Factor: 120**
- **Over 250 citations in ISI journals**

Participation in international projects 2005 – 2010 on nano-materials:

- **15 bilateral cooperations**
- **2 NATO projects & linkage grants**
- **2 EU FP 6 and FP 7 projects**

Technological output 2005 – 2010 on nano-materials:

- **2 national patents**

National projects CEEX and PN II 2005 – 2010 on nano-materials: 14

Conclusions

NIMP has expertise, resources and results in Nanoscience and Nanotechnology

NIMP can be a reliable partner in any collaboration in Nanoscience and Nanotechnology

Thank You!