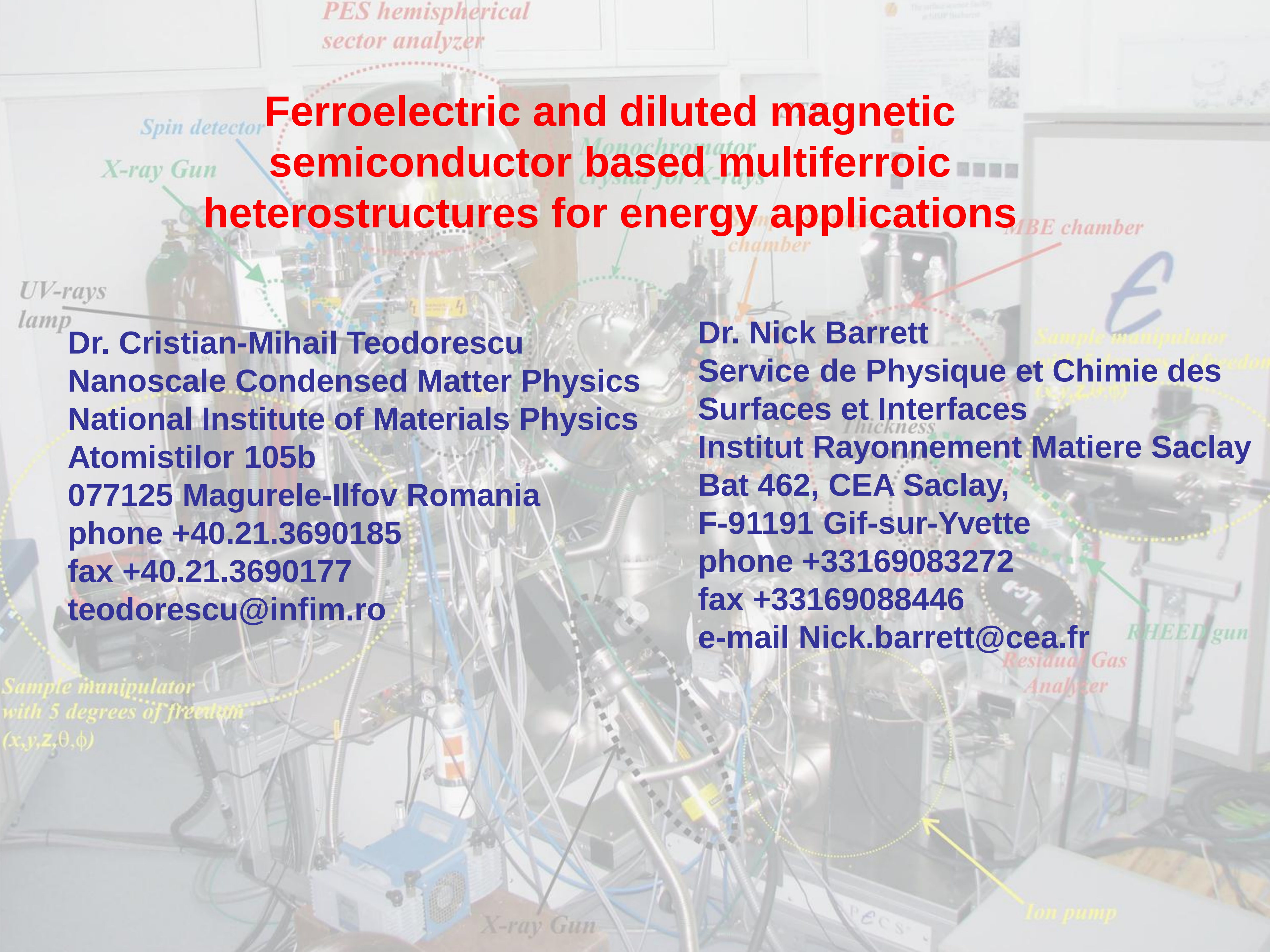
Ferroelectric and diluted magnetic semiconductor based multiferroic heterostructures for energy applications



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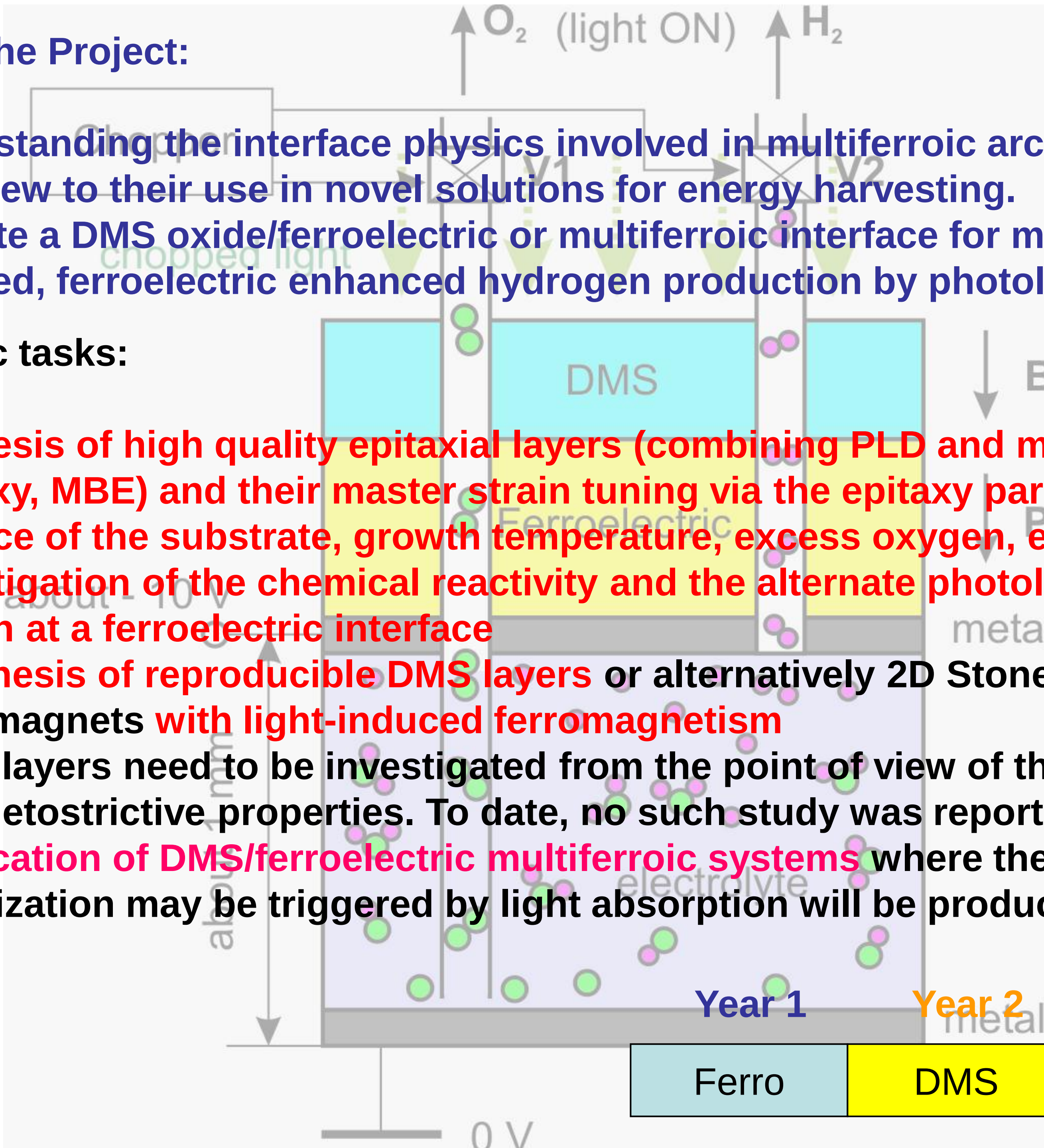
Aim of the Project:

● Understanding the interface physics involved in multiferroic architectures with a view to their use in novel solutions for energy harvesting.
● Validate a DMS oxide/ferroelectric or multiferroic interface for magnetically controlled, ferroelectric enhanced hydrogen production by photolysis.

Scientific tasks:

(i) Synthesis of high quality epitaxial layers (combining PLD and molecular beam epitaxy, MBE) and their master strain tuning via the epitaxy parameters (choice of the substrate, growth temperature, excess oxygen, etc.)
(ii) Investigation of the chemical reactivity and the alternate photolysis route driven at a ferroelectric interface
(iii) Synthesis of reproducible DMS layers or alternatively 2D Stoner ferromagnets with light-induced ferromagnetism
(iv) DMS layers need to be investigated from the point of view of their magnetostrictive properties. To date, no such study was reported.
(v) Fabrication of DMS/ferroelectric multiferroic systems where the electrical polarization may be triggered by light absorption will be produced.



Year 1	Year 2	Year 3
Ferro	DMS	Ferro+DMS

The concept Photolysis: $H_2O \rightarrow O^{2-} + 2H^+$, 2 e^- involved

Charge accumulation in a ferroelectric: 10 $\mu C/cm^2 \approx 0.6 \times 10^{14}$ e^- / cm^2

$\rightarrow 3 \times 10^{13}$ dissociations / (cm^2 x charging process)

Cycling at 1000 Hz: $\rightarrow 3 \times 10^{16}$ dissociations / (cm^2 s)

$\rightarrow$ 0.05 μmol / (cm^2 s) = 0.5 mmol / (m^2 s) = 9 mg / (m^2 s)

$\rightarrow$ (0.5 mmol x 242 KJ/mol) / (m^2 s) = 141 W / m^2

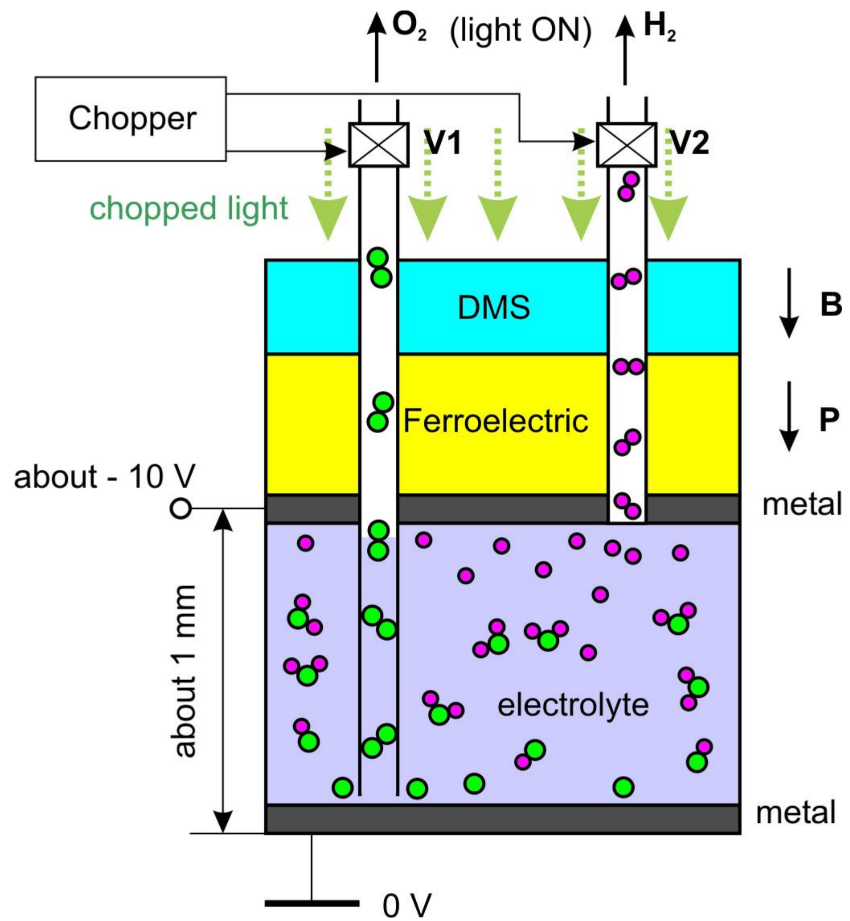
Multiferroics heterostructures

Ferroelectricity ↔ **Feromagnetism**

Photolysis

Diluted magnetic semiconductors (DMS)

Light-induced ferromagnetism



Milestones:

(i) epitaxial ferroelectric layers;
(ii) DMS: rapid magnetic switching;
(iii) DMS: light control of ferromagnetism;
(iv) Coupling DMS with ferroelectrics.

Tasks of the CEA and NIMP teams → available infrastructure

Synthesis:

- **Pulsed laser deposition** — NIMP-NCMP
- **Molecular beam epitaxy** — CEA-SPCSI, NIMP-NCMP

Characterization:

Photoelectron spectroscopy →

- **X-ray photoelectron spectroscopy (XPS)** — NIMP-NCMP
- **High-resolution XPS** — CEA-SPCSI
- **X-ray photoelectron diffraction** — CEA-SPCSI
- **Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS)** — NIMP-NCMP
- **Spin-resolved ARUPS** — NIMP-NCMP

Synchrotron SOLEIL — NIMP-NCMP

EXAFS — NIMP-NCMP

Low-energy and photemission electron microscopy (LEEM-PEEM) — NIMP-NCMP, CEA-SPCSI

XPEEM: Elettra Trieste

Magneto-optical Kerr effect (MOKE) — NIMP-NCMP

Theory — CEA-SPCSI

Scanning probe microscopy — NIMP-NCMP

Common activities 2011-2012:

Published papers:

1. *Reactivity, magnetism and local atomic structure in ferromagnetic Fe layers deposited on Si(001)*, N.G. Gheorghe, M.A. Husanu, G.A. Lungu, R.M. Costescu, D. Macovei, C.M. Teodorescu, **J. Mater. Sci. 47**, p. 1614-1620 (2012).
2. *X-ray photoelectron spectroscopy of pulsed laser deposited* $Pb(Zr,Ti)O_{3-d}$, C. Dragoi, N.G. Gheorghe, G.A. Lungu, L. Trupina, A.G. Ibanescu, C.M. Teodorescu, **Phys. Stat. Solidi A 209**(6), p. 1049-1052 (2012).
3. *Ferromagnetism and reactivity of Fe deposited on GaAs(001) by magnetron sputtering*, V. Vasilache, G.A. Lungu, C. Logofatu, R.V. Medianu, C.M. Teodorescu, **Optoel. Adv. Mater. - Rapid Commun.**, *accepted* (2012), to be published in Nov. 2012.

Manuscripts in final stage of ellaboration:

4. *Room temperature ferromagnetism and local atomic structure in germanium-rich MnGe alloys synthesized on Ge(001)*, G.A. Lungu, N.G. Apostol, D. Macovei, V. Kuncser, D.G. Popescu, M.A. Husanu, C.M. Teodorescu, **Acta Materialia**, *to be submitted*.
5. *X-ray photoelectron diffraction study of relaxation and rumpling of ferroelectric domains in* $BaTiO_3$ *(001)*,
A. Pancoti, J.L. Wang, L. Tortech, C.M. Teodorescu, N. Barrett, **Phys. Rev. B**, *to be submitted*.

PhD theses: Nicoleta G. Apostol (Gheorghe), Dana G. Popescu, to be defended in 2013.

***Common experiments*:**

a) synchrotron radiation experiments at Soleil, Saclay: two sessions between 14-20.2011 and 19-27.11.2011.

b) experiments using the PEEM facility of IRAMIS CEA: one session between 14-18.03.2012.

c) usual way of collaboration: exchange of samples, remote common ellaboration of manuscripts, etc.

***Common projects*:**

a) *HArd X-ray energy filtered PhotoElectron Emission Microscopy* (HAXPEEM), FP7 project - NMP.2011.1.4-3, application on 04.11.2010, unfinanced.

b) *FErroic-ELectrode InTerface electronic structure* (FEEL-IT), ANR-ANCS project, application on 15.04.2011, unfinanced.

c) *Chemical switching of surface ferroelectric topology*, ANR-ANCS project, application on 27.03.2012, results not yet communicated.

d) Three common synchrotron radiation experiments (two accepted at Soleil Saclay, another one at Elettra Trieste, result not yet known).

***Seminars*:**

a) Nick Barrett, *X-ray Photoelectron Emission Microscopy (XPEEM) for materials science*, NIMP Magurele, 15.11.2011

b) Cristian-Mihail Teodorescu, *Molecular polarizability near metal surfaces*, IRAMIS Saclay, 16.03.2012

***Common conferences*:**

a) Nick Barrett, *Full Field Electron Spectromicroscopy of Ferroelectrics*, ROCAM 2012, Brasov 28-31.08.2012 (invited)

b) Cristian-Mihail Teodorescu, *Ferromagnetic Surface Alloys Synthesized by Molecular Beam Epitaxy and Characterized by Inner-shell Spectroscopies*, ROCAM 2012, Brasov 28-31.08.2012 (invited)

c) Nicoleta G. Apostol, George A. Lungu, Laura E. Stoflea, Marius A. Husanu, Cristina Dragoi, Lucian Trupina, Lucian Pintilie, Cristian M. Teodorescu, *Molecular Beam Epitaxy Growth and X-Ray Photoelectron Spectroscopy Analysis of Au/PZT Heterostructures*, ROCAM 2012, Brasov 28-31.08.2012 (oral)

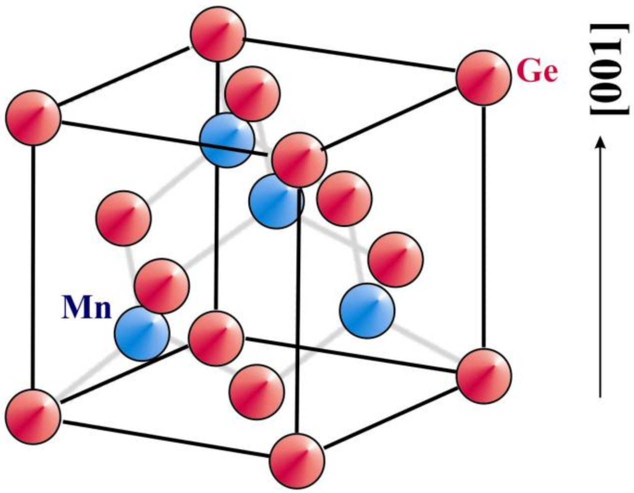
d) Nicoleta Georgiana Apostol, George Adrian Lungu, Ruxandra Maria Costescu, Marius Adrian Husanu, Dana Georgeta Popescu, Laura Elena Stoflea, Cristian-Mihail Teodorescu, *Ferromagnetic compounds stabilized on Ge(001) and Si(001) by molecular beam epitaxy*, ICPAM-9, Iasi 20-23.09.2012 (invited)

e) Nicoleta Georgiana Apostol, Laura Elena Stoflea, George Adrian Lungu, Cristina Dragoi, Lucian Trupina, Lucian Pintilie, Cristian-Mihail Teodorescu, *In situ X-ray photoelectron spectroscopy analysis of Au growth on PZT(001) surfaces*, ICPAM-9, Iasi 20-23.09.2012 (oral)

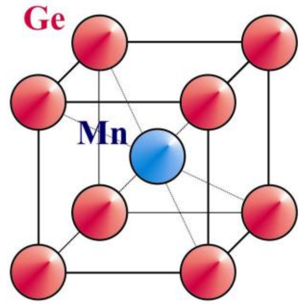
MnGe(001) room temperature surface alloy with light-induced ferromagnetism

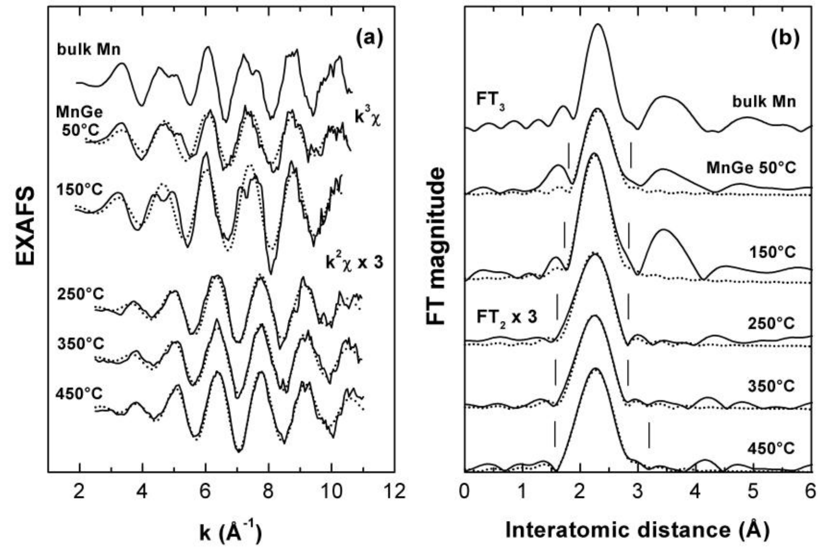
Structures resulted from EXAFS refined data analysis:

ZnS-like

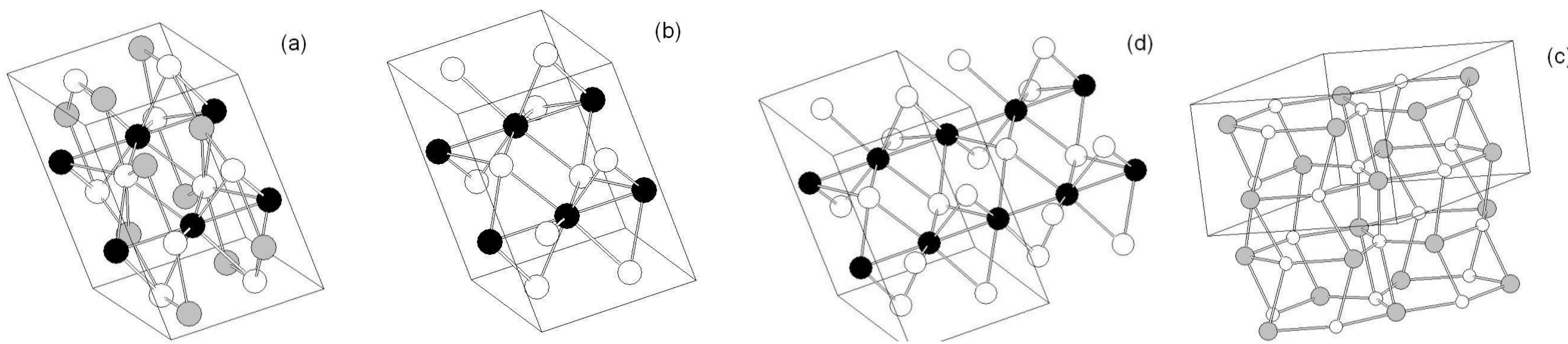


CsCl-like



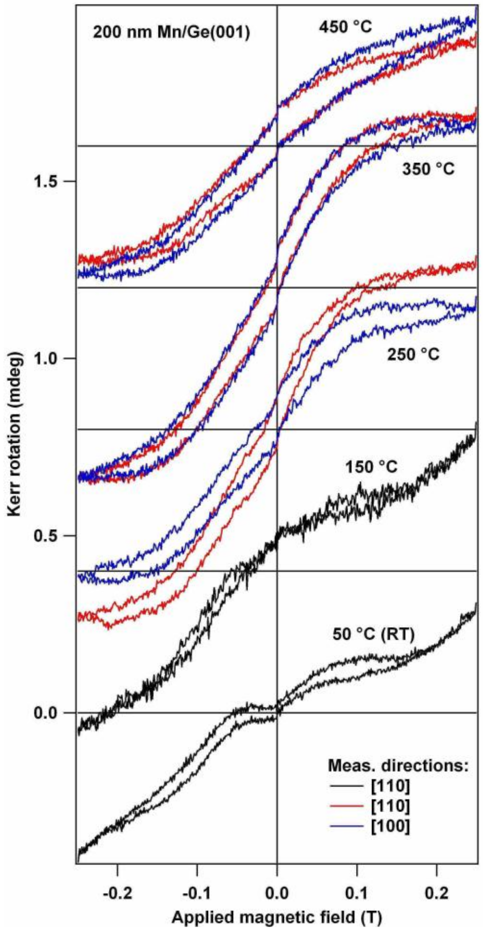


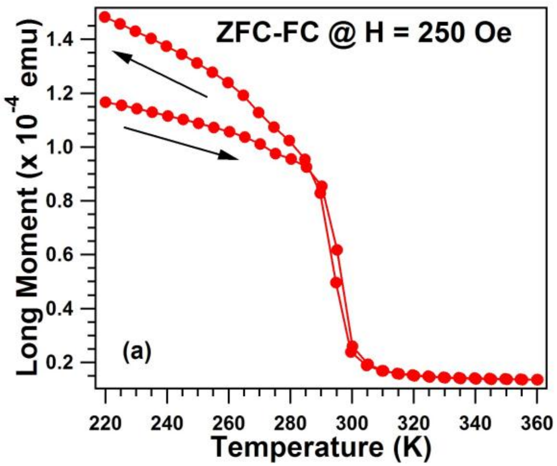
Mn_5Ge_3 clusters

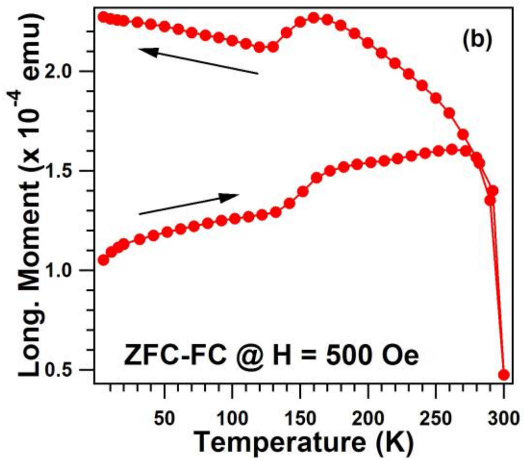


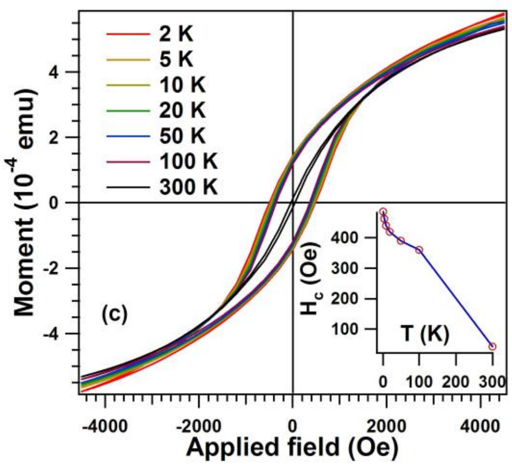
MOKE

in the meantime: **SQUID**

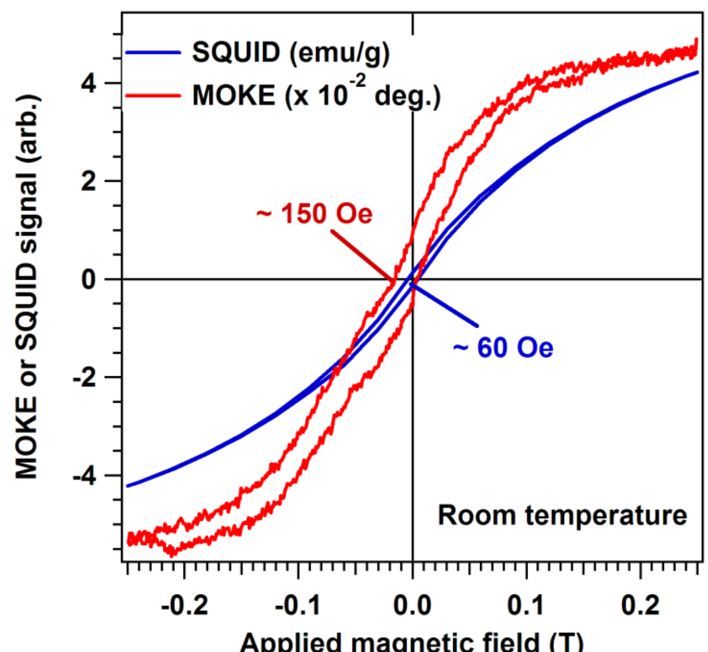




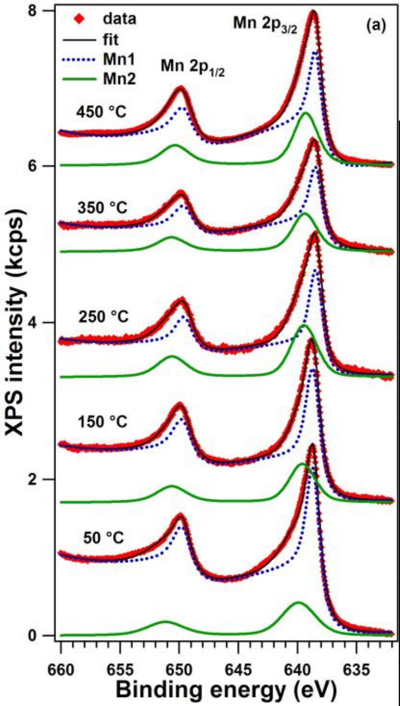




Light-induced ferromagnetism

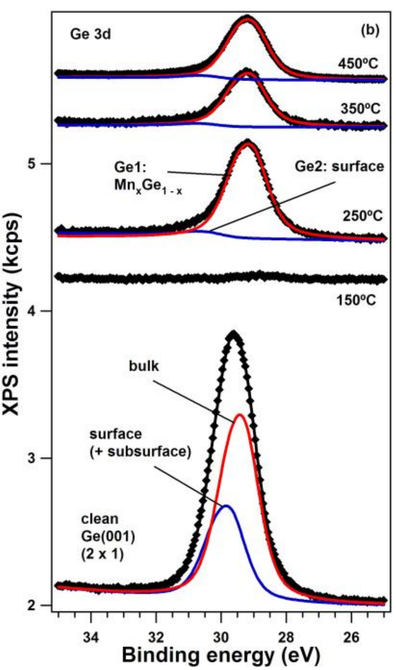


+ setup of a light-induced ferromagnetism tester (exp. operation Nov. 2012)

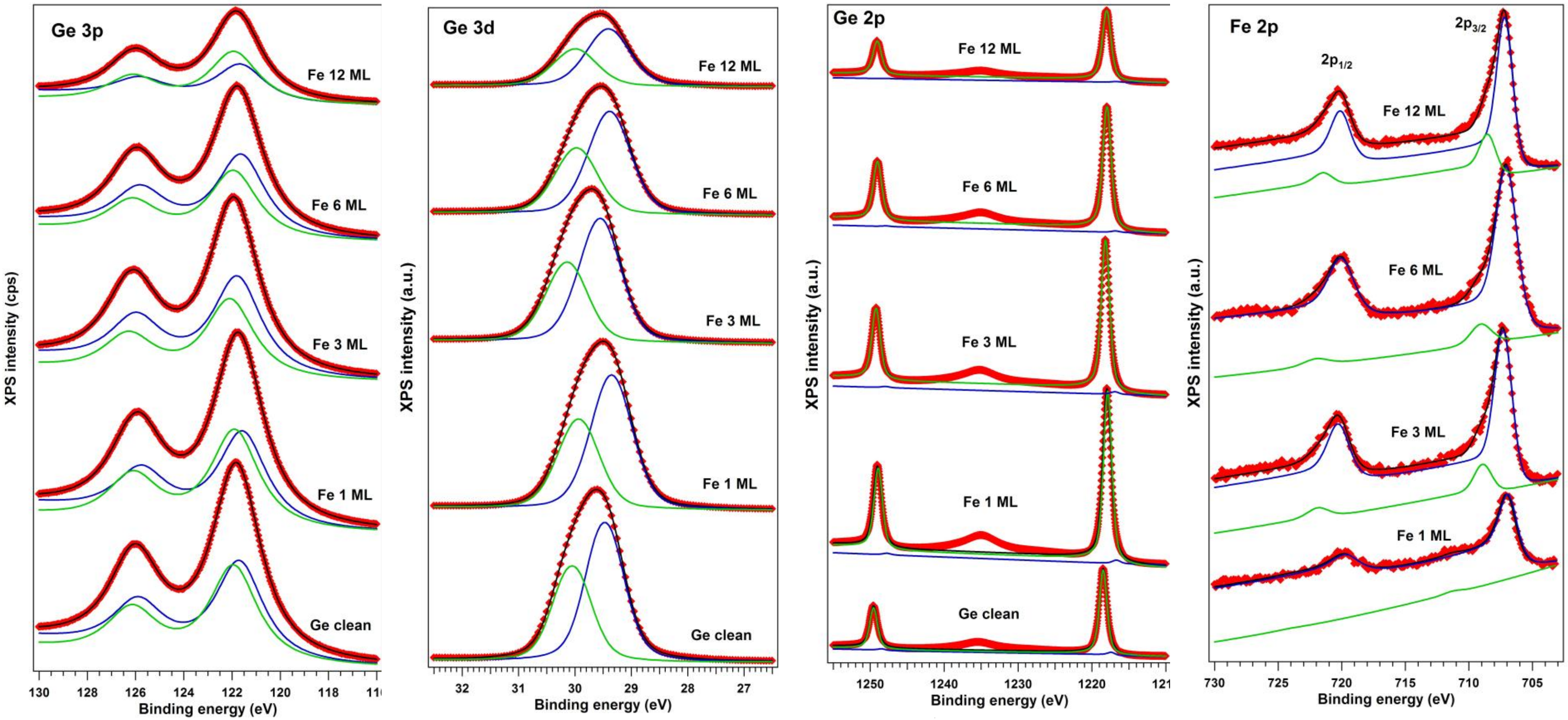


XPS, also new interpretation

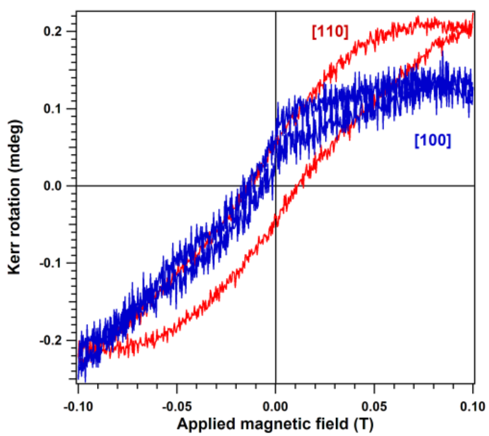
Sample, T_d (°C)	MOKE M_{max} (mdeg)	MOKE M_r (mdeg)	MOKE $\mu_0 H_c$ (T)	XPS components, binding energies (eV): Mn(m) (met.)	Mn(c) (Mn-Ge)	Ge(b) (bulk)	Ge(s) (surf.)	XPS, Mn-Ge composition	EXAFS: N, nature	EXAFS: R (Å)
Ge(001) (2 x 1)	-	-	-	-	-	29.49	29.18	bulk Ge	-	-
Mn/Ge, 50 °C	0.366	0.002	0.007	638.64	639.88	-	-	~ bulk Mn	13 ± 2 Mn	2.67 ± 0.01
Mn/Ge, 150 °C	0.442	0.001	0.007	638.66	639.58	-	-	~ 2.5 % Ge in Mn	13 ± 2 Mn	2.60 ± 0.01
Mn/Ge, 250 °C	0.528	0.063	0.011	638.40	639.43	28.98	30.32	$MnGe_{0.97}$ ~ MnGe	6 ± 1 Ge	2.53 ± 0.01
Mn/Ge, 350 °C	0.532	0.056	**0.027**	638.43	639.38	29.03	30.41	$MnGe_{1.37}$ ~ Mn_4Ge_3	6 ± 1 Ge	2.53 ± 0.01
Mn/Ge, 450 °C	0.334	0.056	0.020	638.44	639.29	28.98	30.34	$MnGe_{1.71}$ ~ **Mn_5Ge_3**	1 ± 0.3 Mn 2.9 ± 0.5 Mn 2.4 ± 0.5 Ge 2.7 ± 0.5 Mn	2.50 ± 0.02 2.50 ± 0.02 2.63 ± 0.04 3.09 ± 0.04
α-Mn	-	-	-	638.78#	638.85#	-	-	bulk Mn	13.1 ± 0.1 Mn	2.638±0.001
Mn_5Ge_3, Mn1 (4*d*)	-	-	0.005 - 0.014$	-	-	B + 0.53	B + 0.94	Mn_5Ge_3	2 Mn1 6 Ge 6 Mn2	2.526 2.538 3.065
Mn_5Ge_3, Mn2 (6*g*)	-	-		-	-				5 Ge 4 Mn1 + 6 Mn2	2.624 3.045



Ge(001):Fe diluted magnetic semiconductor



- **room temperature ferromagnetism;**
- **uniaxial in-plane magnetic anisotropy.**



Fe magnetic moment:
2.5 ± 0.5 mdeg → 1 nm Fe
with 2.2 Bohr / atom
Here $Fe_{0.06}Ge(0.01)$: ~ 0.2 mdeg,
θ = 24 ML = 3.4 nm
→ 0.052 Bohr / atom (Fe + Ge)
→ 0.86 Bohr / Fe atom.

Phys. Status Solidi A **209**, No. 6, 1049–1052 (2012) / **DOI** 10.1002/pssa.201127740

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applications and materials science

X-ray photoelectron spectroscopy of pulsed laser deposited $Pb(Zr,Ti)O_{3-\delta}$

Cristina Dragoi, Nicoleta G. Gheorghe, George A. Lungu, Lucian Trupina, Andra G. Ibanescu, and Cristian M. Teodorescu*

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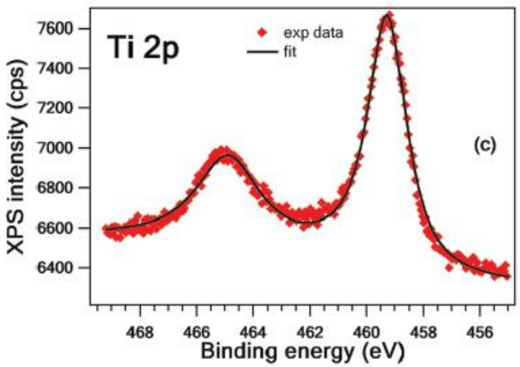
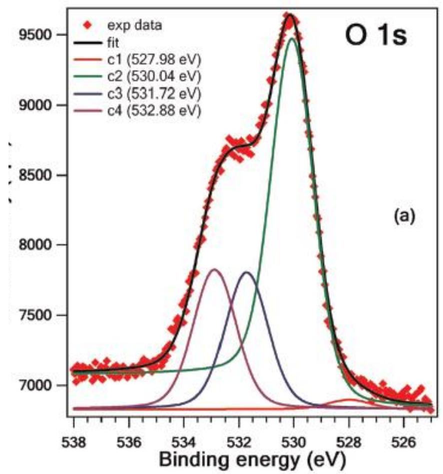
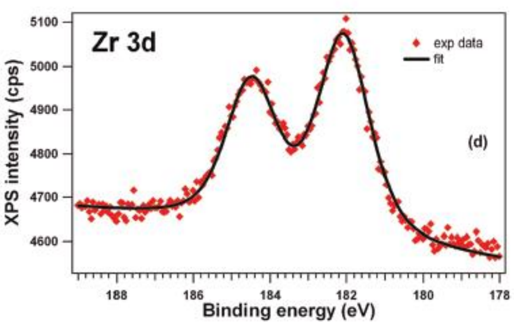
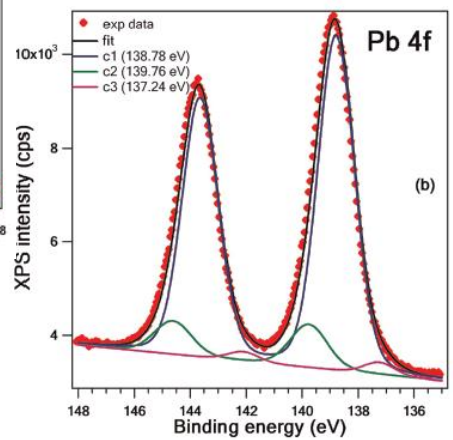
Received 26 September 2011, revised 15 December 2011, accepted 10 January 2012



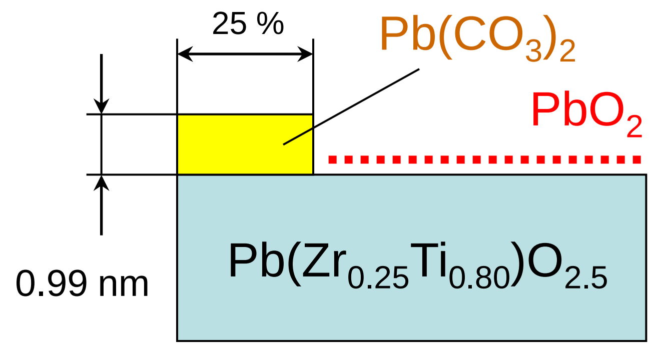






Brownmillerite phase identified

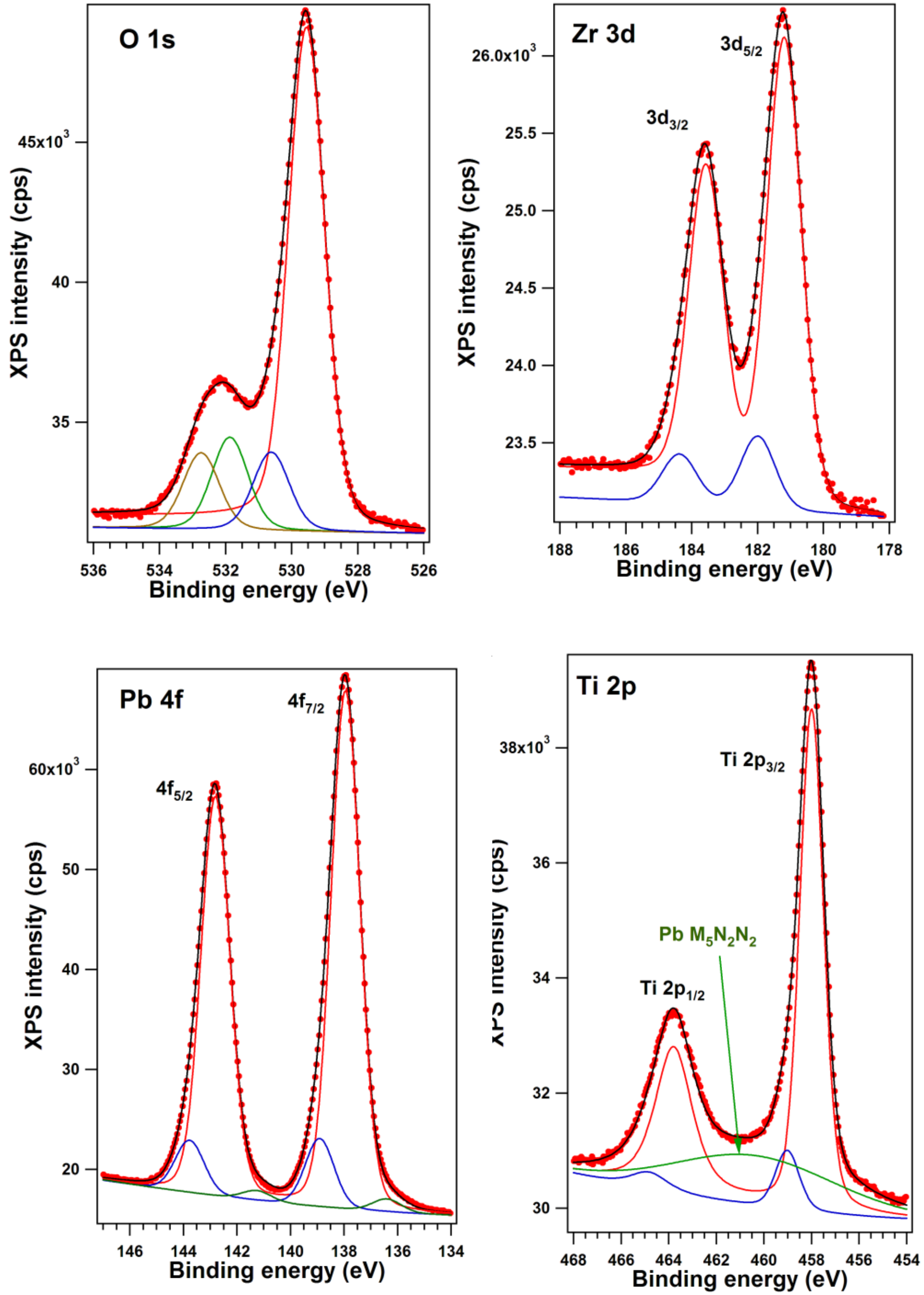
PZT(111)



Atomic level	line	BE (eV)	At. %	Na-ture	Assignment (BE from databases)
O 1s	c1	527.98	1.02	s	surface PbO_2 (529.0 eV)
	c2	530.04	37.01	b	bulk PZT (529.9 eV)
	c3	531.72	14.43	s	$Pb(CO_3)_2$ (532 eV)
	c4	532.88	14.71	s	contamination (532 eV [8])
Ti 2p	-	459.26	11.91	b	bulk PZT (458.6 eV)
Zr 3d	-	182.07	3.68	b	bulk PZT (181.0 eV [6])
Pb 4f	c1	138.78	14.81	b	bulk PZT (137.9 eV [6])
	c2	139.76	1.97	s	$Pb(CO_3)_2$ (138.3 eV)
	c3	137.24	0.46	s	surface PbO_2 (137.4 eV)

Epitaxial PZT(001)

Level	BE (eV)	Ampli (kcps x eV)	Corr. ampli (kcps x eV)	Interpre-tation
O 1s	529.54	26.9	40.8	PZT(1)
	530.62	4.1	6.3	PZT(2)
	531.87	4.2	6.4	cont.(1)
	532.74	5.0	7.6	cont.(2)
Ti 2p	457.99	18.5	10.3	PZT(1)
	459.02	2.2	1.2	PZT(2)
Zr 3d	181.18	7.1	3.4	PZT(1)
	181.99	1.1	0.5	PZT(2)
Pb 4f	137.94	131.7	19.7	PZT(1)
	138.91	17.4	2.6	PZT(2)
	136.39	3.2	0.5	Pb or PbO



manuscript in preparation

PHYSICAL REVIEW B **86**, 094105 (2012)

Polarization dependence of Schottky barrier heights at interfaces of ferroelectrics determined by photoelectron spectroscopy

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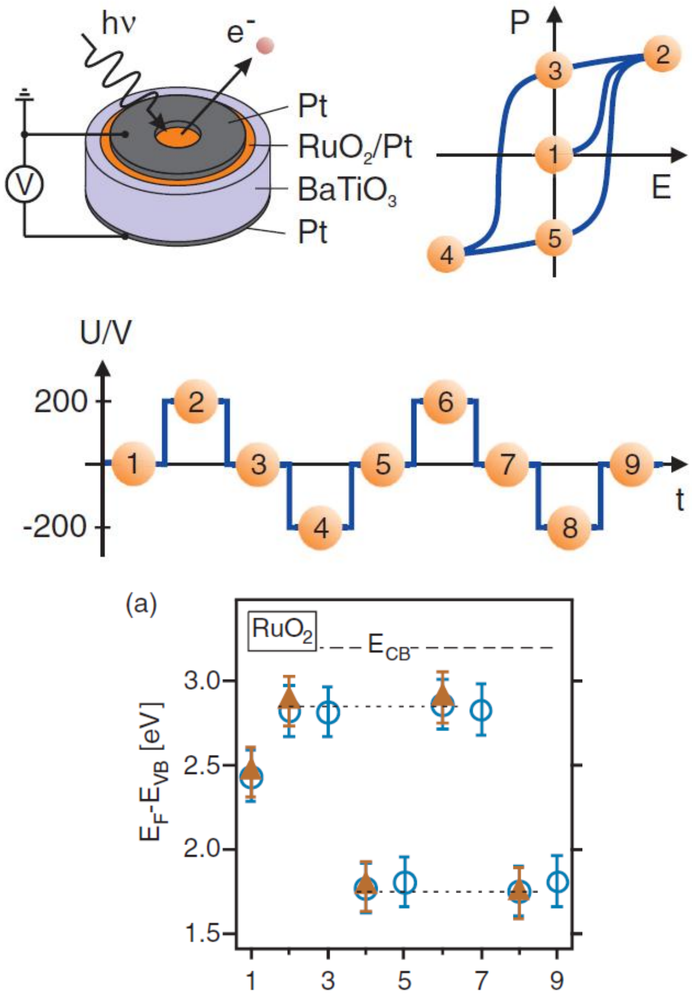
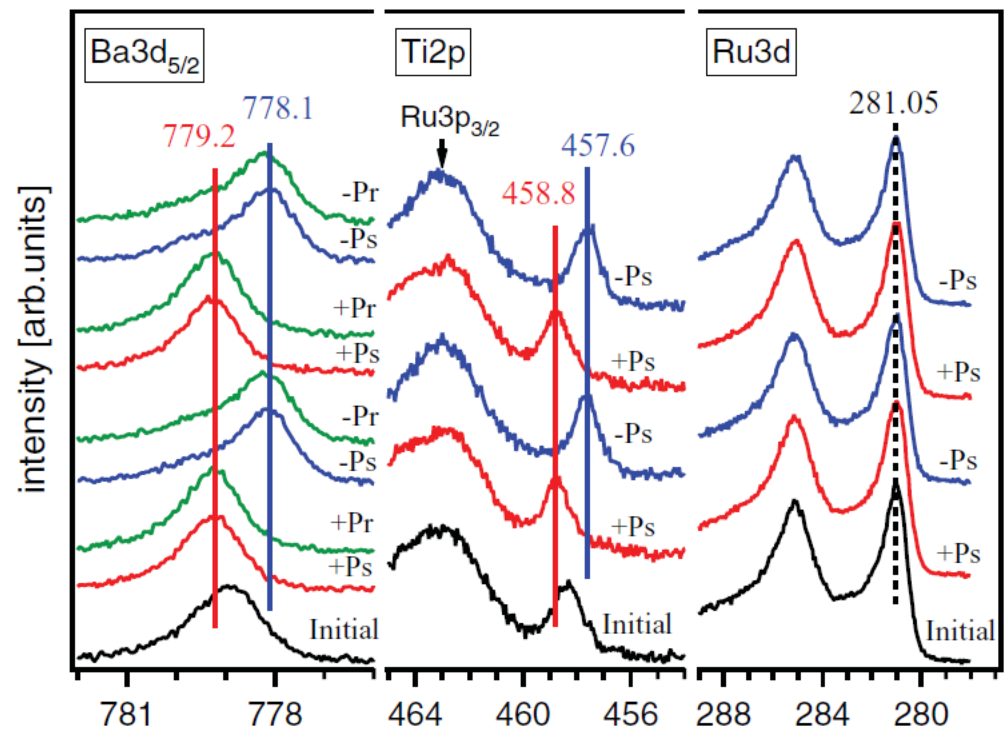
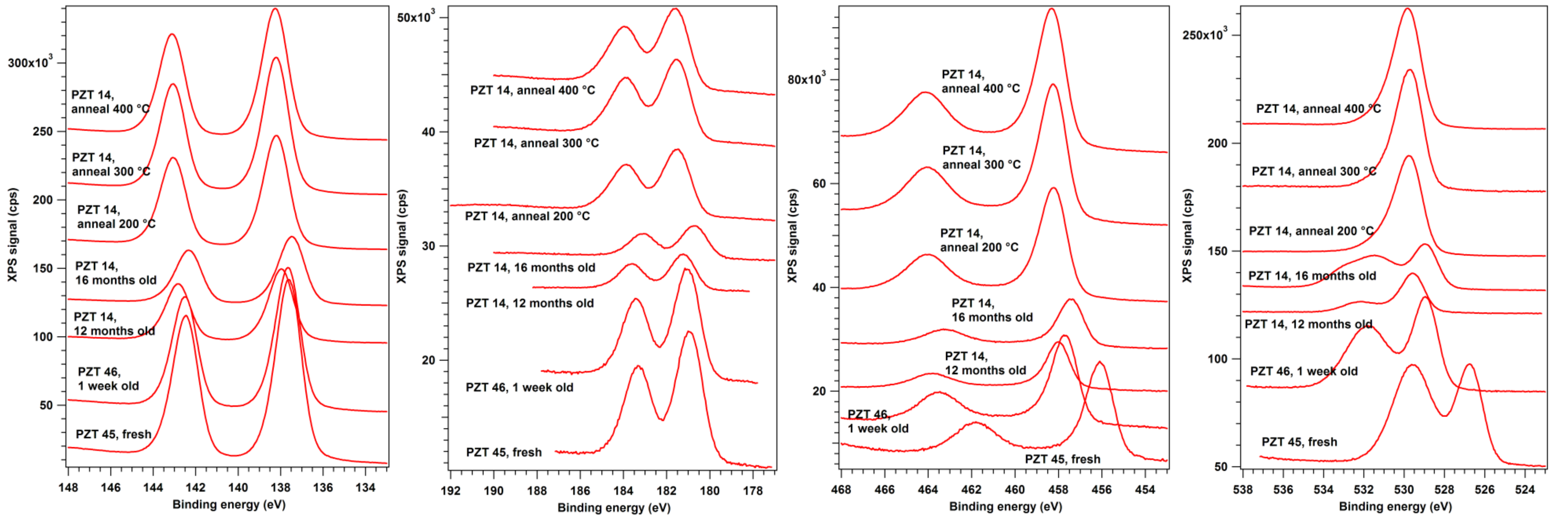
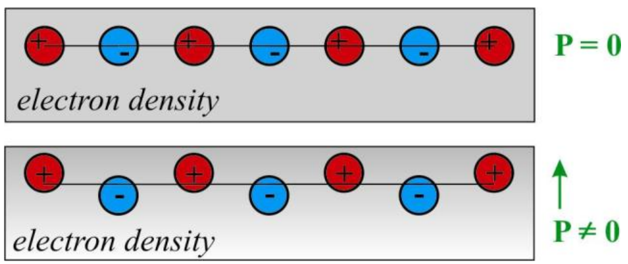
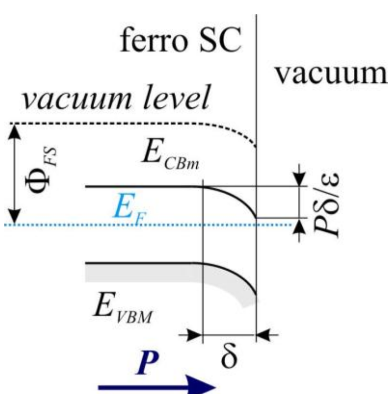


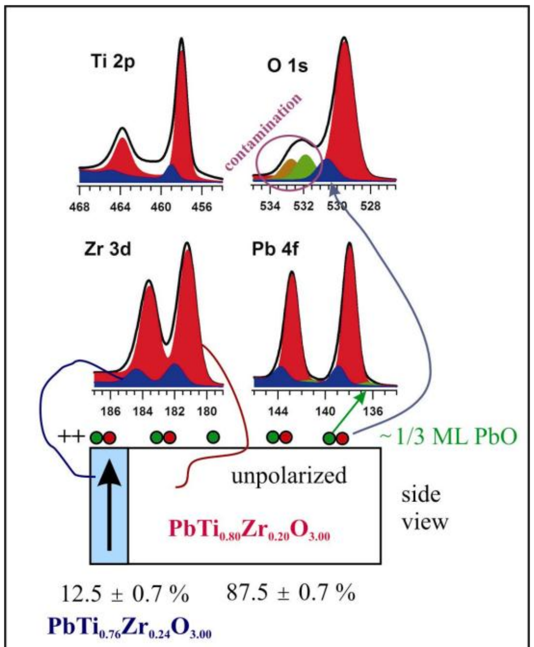


Back to the synthesis and accurate characterization of PZT layers:

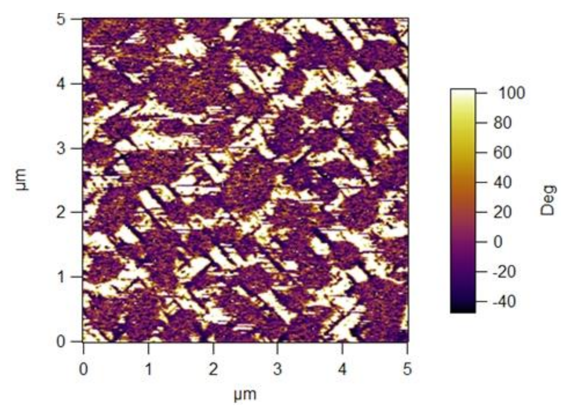






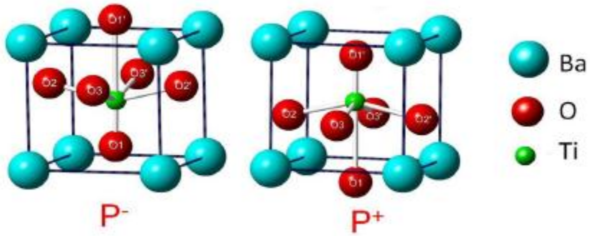


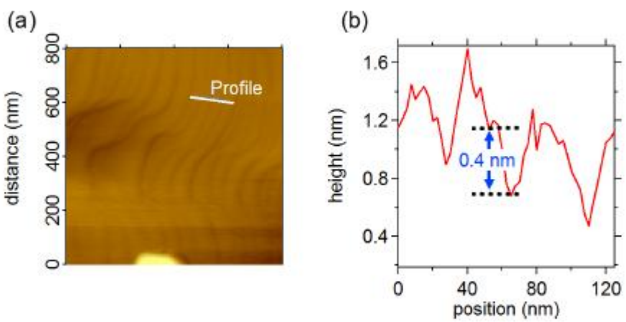
PFM

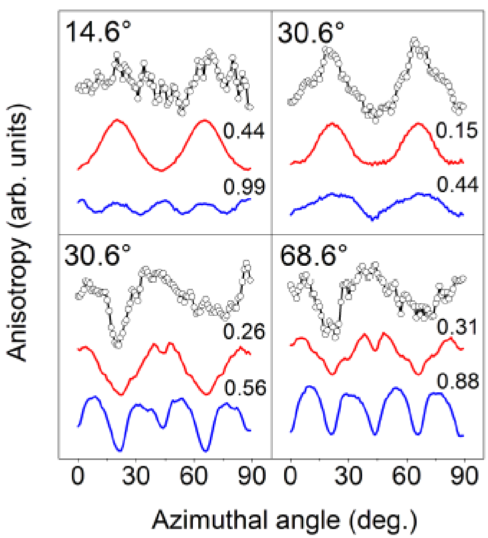


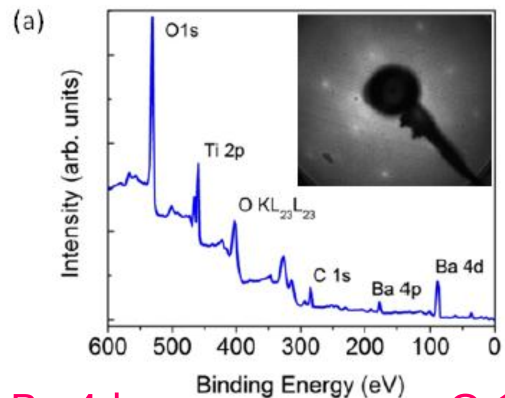
Ferroelectric domains atomic structure and surface rumpling in $BaTiO_3$

XPS





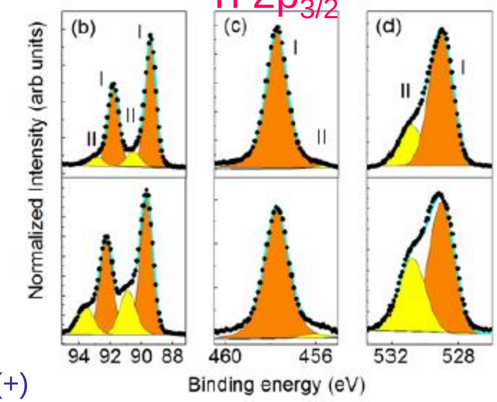




Ba 4d

Ti $2p_{3/2}$

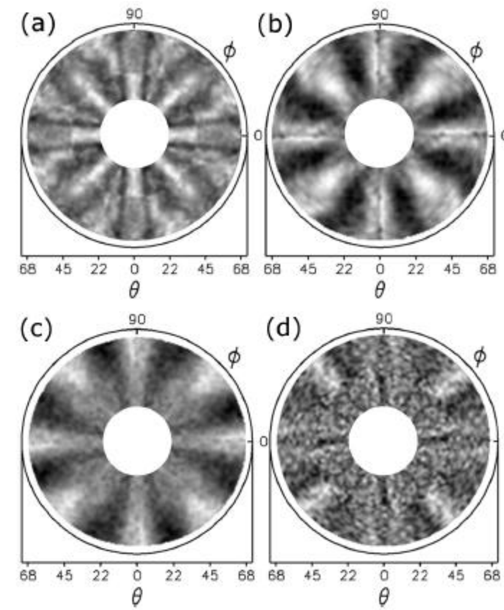
O 1s



XPD

Ba 4d

Ti $2p_{3/2}$

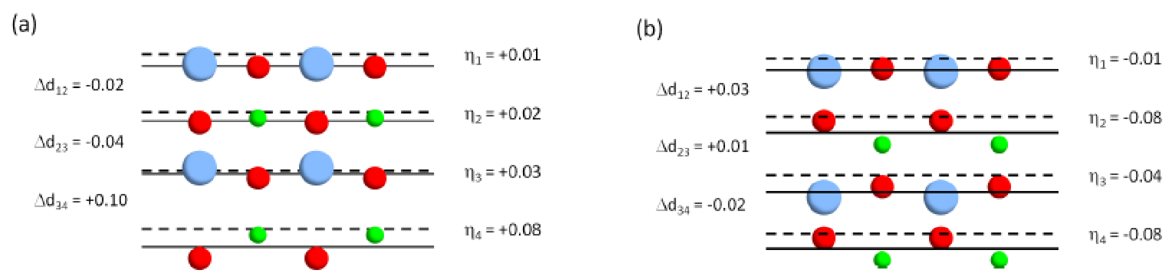


O 1s

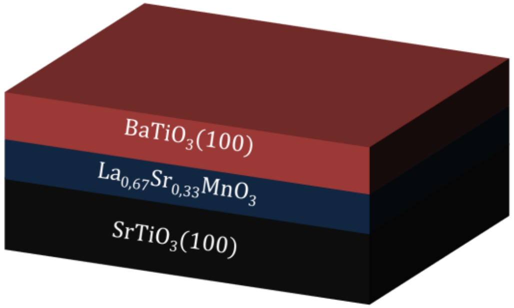
C 1s

$P^{(+)}$

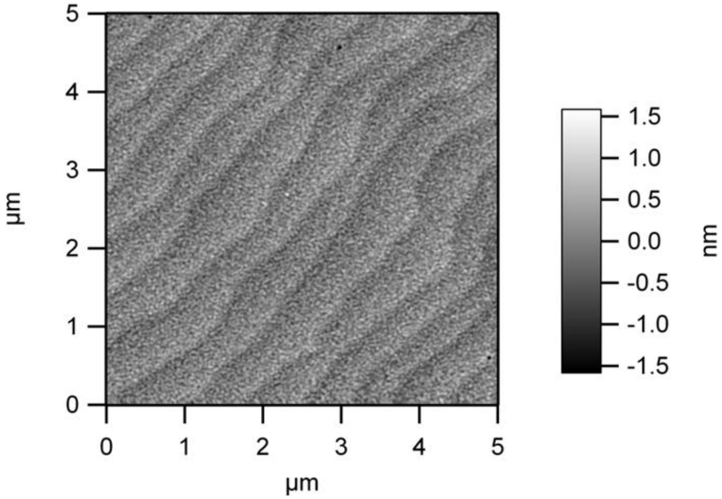
$P^{(-)}$



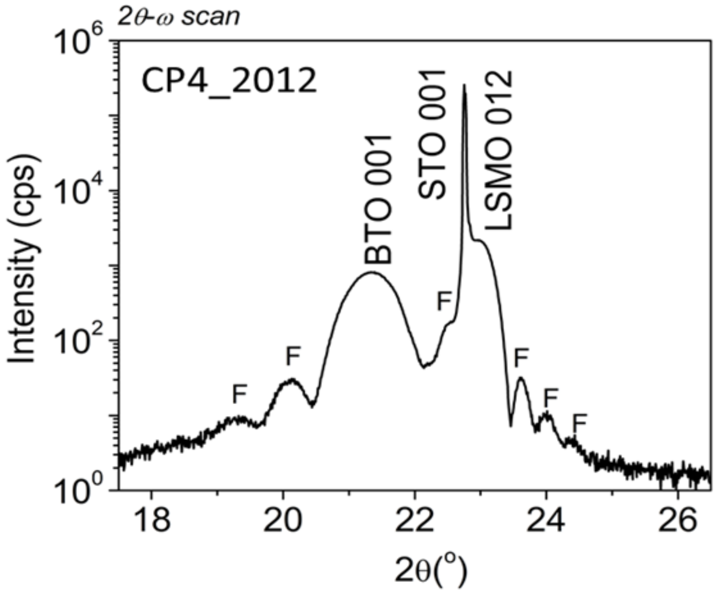
Coupling of magnetic / FE systems



- 11-13 nm BTO
- 20 nm LSMO
- PLD at NIMP, Magurele
- BTO strain 2.3 %

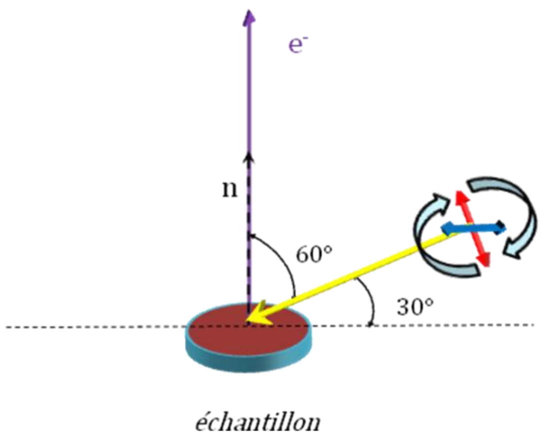


AFM image of surface showing flat terraces with one unit cell step heights

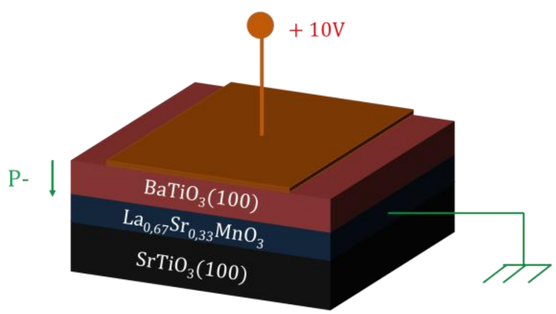


XRD spectra

Experiment with in-situ polarization



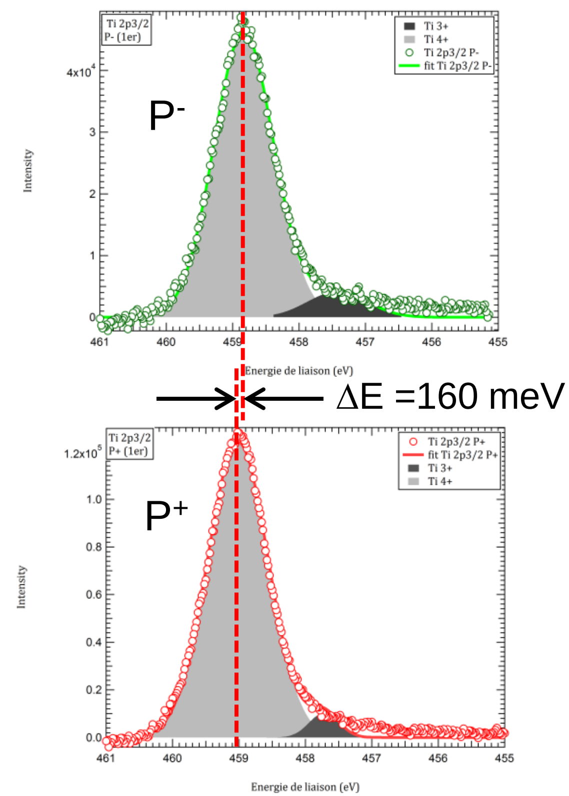
Experimental geometry showing the four possible light polarizations used on the BACH beamline (ELETTRA, Trieste)



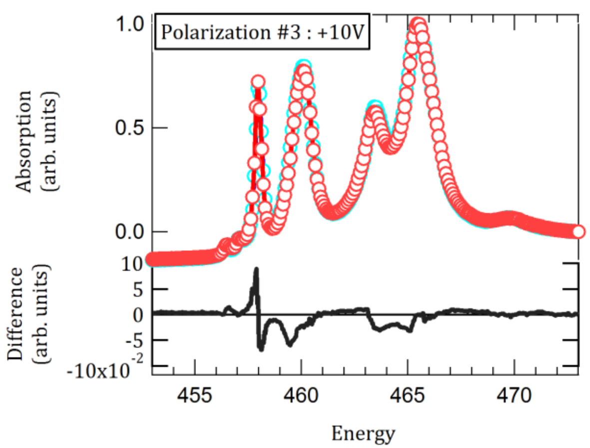
In-situ polarization using Cu plate

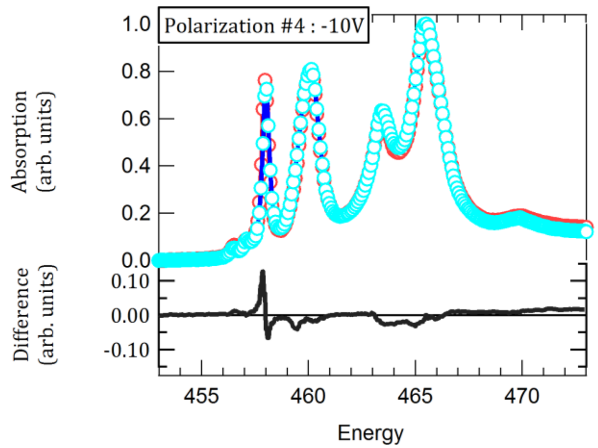
XPS

Higher BE for P^+ polarization
0.8 % V_O as estimated from Ti^{3+}



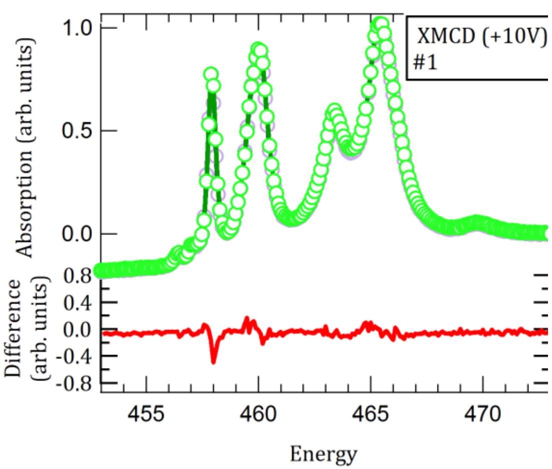
X-ray linear dichroism Ti $L_{2,3}$

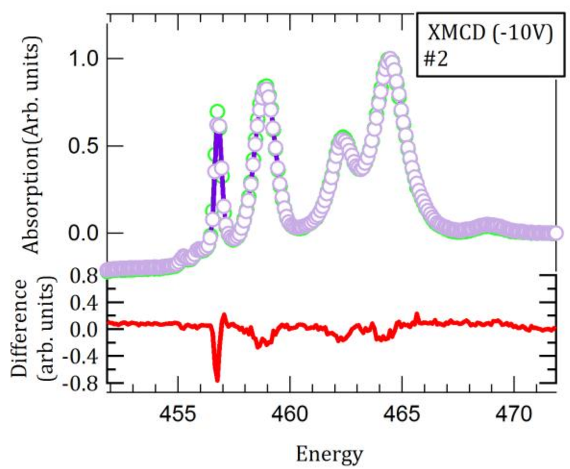




XLD XAS shows that switching is symmetrical, no pinning

X-ray circular dichroism Ti $L_{2,3}$





- ❑ XMCD XAS Ti $L_{2,3}$ shows *magnetic anisotropy*:
- ❑ Ti has a non-zero magnetic moment
- ❑ Hybridization Ti 3d - Mn 3d?
- ❑ Ti 2p XMCD signal is larger for P^+ than for P^- polarization

Benefits and collaboration prospects:

New projects submitted to date: 3 (ANR-ANCS pending)

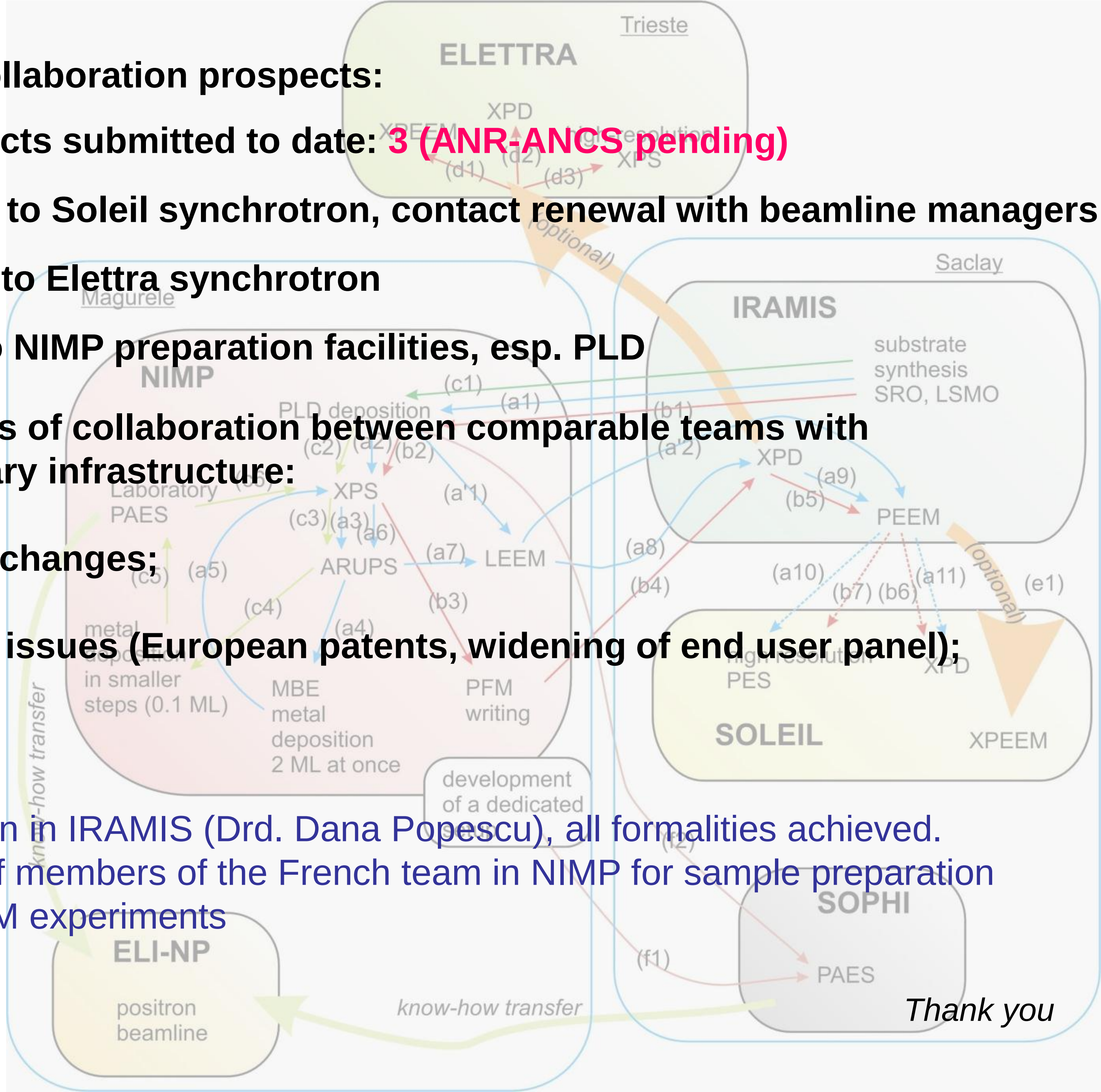
Access of RO team to Soleil synchrotron, contact renewal with beamline managers

Access of RO team to Elettra synchrotron

Access of F team to NIMP preparation facilities, esp. PLD

Usual benefits of collaboration between comparable teams with complementary infrastructure:
- **papers;**
- **scientific exchanges;**
- **manpower;**
- **valorisation issues (European patents, widening of end user panel);**
- **etc.**

One stage foreseen in IRAMIS (Drd. Dana Popescu), all formalities achieved.
Short term stays of members of the French team in NIMP for sample preparation and common LEEM experiments



Thank you