



# **Investigation of metal-ferroelectric interfaces at micro and nanometric level (Investigarea interfețelor metal-feroelectric la nivel micro și nanometric)**

IFA-CEA cooperation program

Presenting: Dr. Cristina Chirila

Project responsible from the Romanian part

Dr. Lucian Pintilie

## Scope of the project

The main objective of the project will be to study the construction of the metal-ferroelectric interface and the dynamic of charge compensation in relation to polarization switching. The results will be compared to the results of the macroscopic electric measurements performed on standard metal-ferroelectric-metal (MFM) capacitors. Also, the metal-ferroelectric interface will be compared with the results reported for the free surface.

## Important milestones

***End of the 1<sup>st</sup> year***-deposition and characterization of epitaxial PZT films; conclusions regarding the charge compensation on the free surface

***End of the 2<sup>nd</sup> year***-formation of metal-PZT interface and characterization through surface/interface investigation techniques; charge compensation at the interface

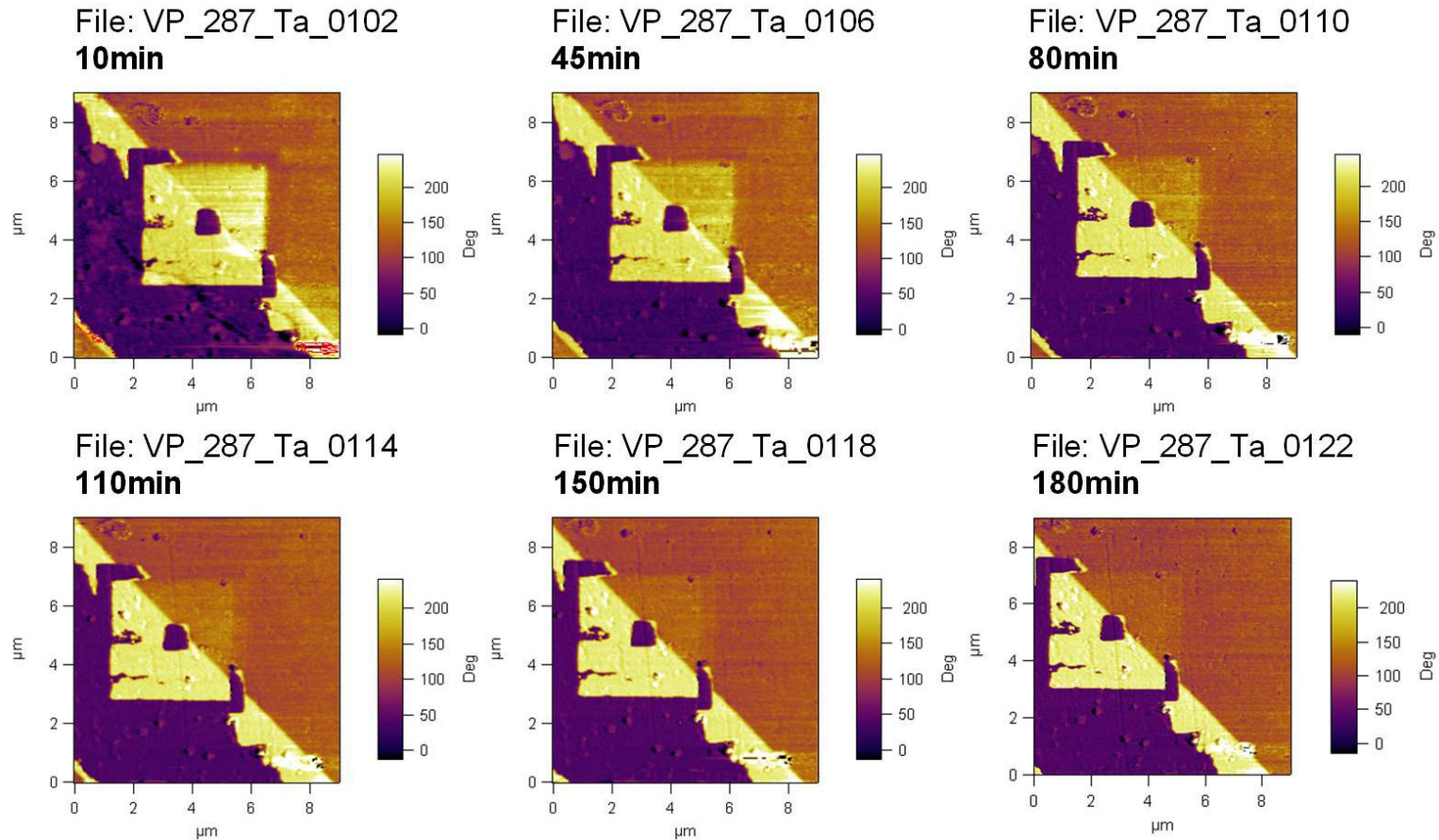
***End of the 3<sup>rd</sup> year***-macroscopic-microscopic correlation

## Teams and collaboration

There is a common interest in the proposed topic. The responsible of the Romanian part has collaborated with Dr. Gweneal Le Rhun, member of the CEA team, during their workstages at MPI Halle, Germany. Dr. Pintilie was visiting scientists while dr. Le Rhun was a Humboldt fellow. A few common papers resulted from this collaboration (see the list below). The present project will help to develop the collaboration between the two teams to a new level.

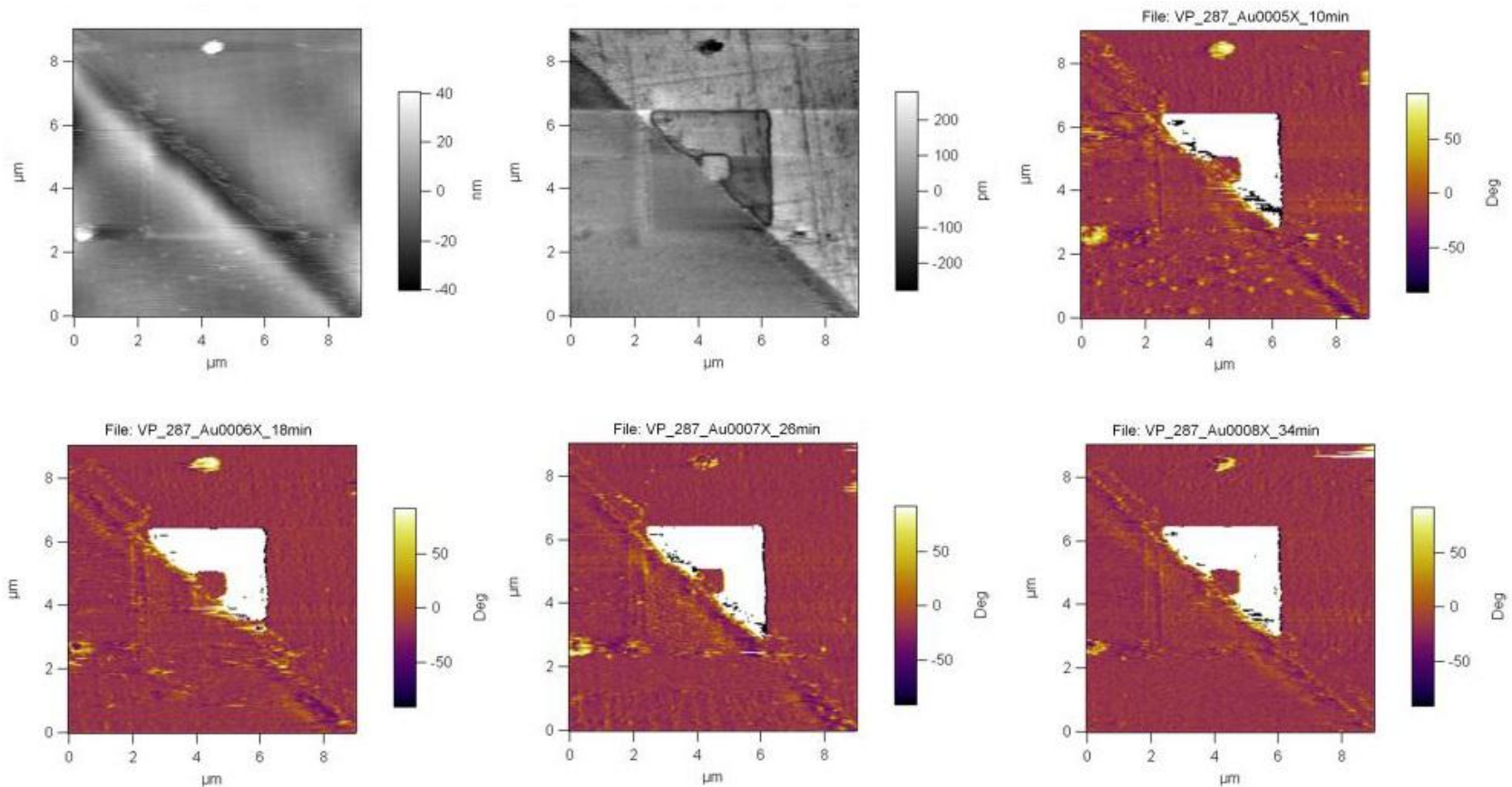
	RO team	CEA team
Project leader (Name)	Dr. Pintilie Lucian	Dr. LE RHUN Gwenaël
<i>Laboratory Institution Address Tel : Fax : e-mail: Head of laboratory</i>	Laboratory Multifunctional Materials and Structures National Institute of Materials Physics Atomistilor 105bis, Magurele 077125, Romania +40-(0)21-3690185 +40-(0)21-3690177 <a href="mailto:pintilie@infim.ro">pintilie@infim.ro</a> Dr. Ionut Enculescu Grown of SRO layer on STO/Si substrates; grown of PZT/SRO on single crystal STO substrates; surface/interface investigation; electrical measurements with temperature; comparison with samples from France	RF Components Laboratory CEA 17 rue des Martyrs, 38054 Grenoble Cedex 9, FRANCE +33-(0)4-38784042 +40-(0)4-38782434 <a href="mailto:gwenael.le-rhun@cea.fr">gwenael.le-rhun@cea.fr</a> AID Marc Grown of STO on Si substrate, and of PZT on SRO/STO/Si; preliminary electrical characterization
	RO team	CEA team
	<b>Dr. Lucian Pintilie</b> <b>Dr. Stancu Viorica (young researcher)</b> <b>Dr. Ioana Pintilie</b> <b>Dr. Cristian Mihail Teodorescu</b> <b>Drd. Cristina Dragoi (young researcher)</b> <b>Drd. Marius Husanu (young researcher)</b> <b>Drd. Lucian Trupina</b>	<b>Dr. Gwenaël Le Rhun (young researcher)</b> <b>Dr. Emmanuel Defay</b> <b>Shi YIN (young researcher)</b>

## Results: Romanian team



The stability in time of the polarization measured on free surface and thru the Ta electrode

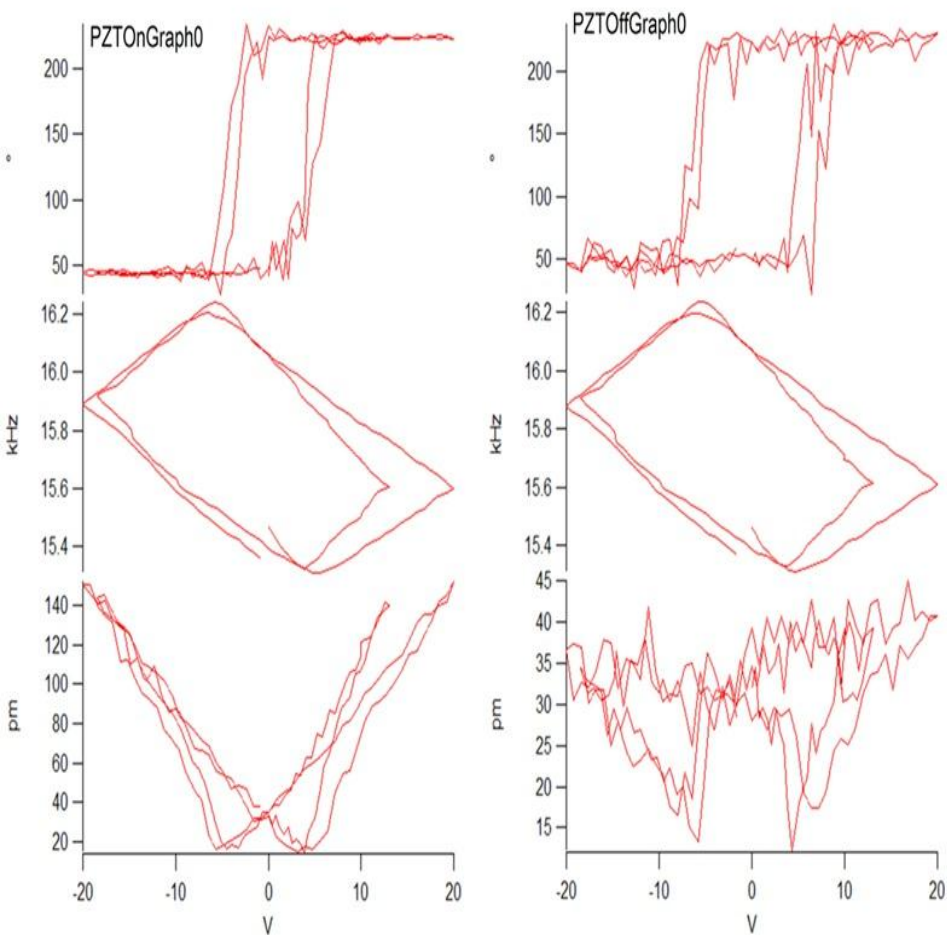
On the free surface the polarization remains stable while on the metallic contact polarization is not stable over the time and reverses in the opposite direction. This results is in accordance with the observation that Ta form a quasi-ohmic contact on PZT



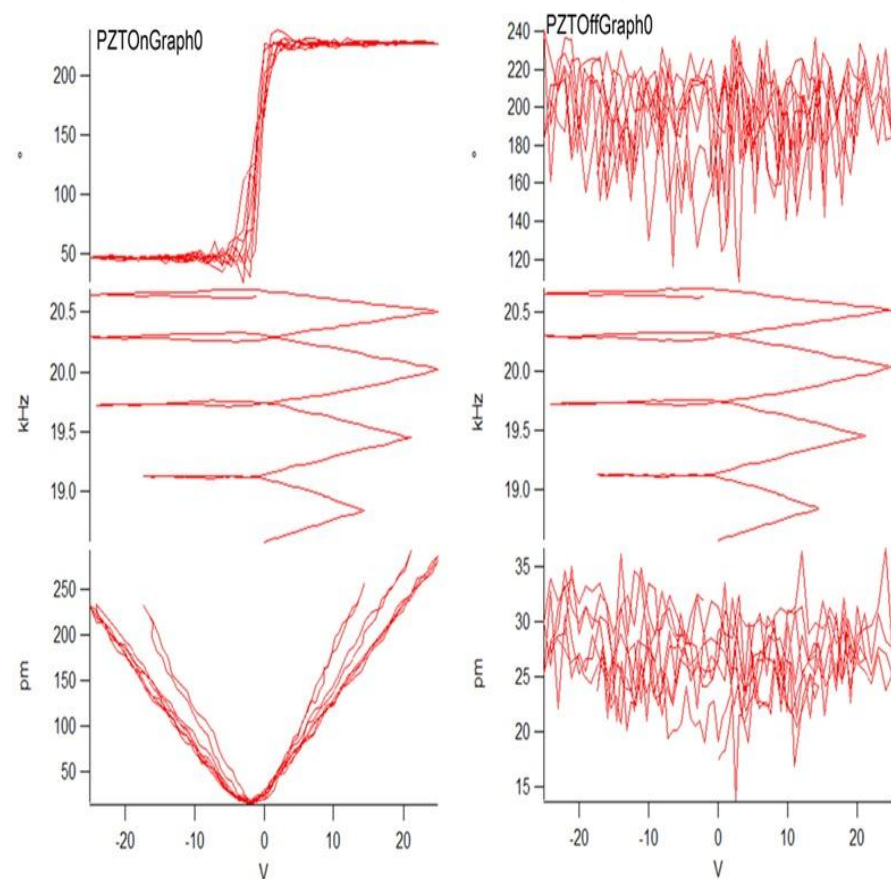
The stability in time of the polarization measured on free surface and thru the Au electrode

In case of the Au electrode no significant changes are present over time. This results is in accordance with the fact that Au form a Schottky barrier type on PZT, apparently the potential barrier keeps charge of opposite sign at the interface necessary to compensation of polarization charge.

VP287\_0018\_OK\_20kHz\_20DC\_3AC on free surface

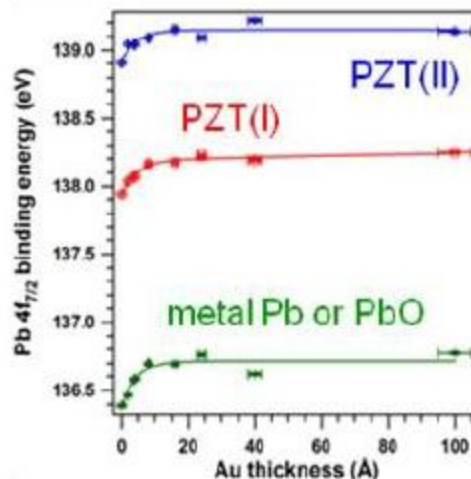
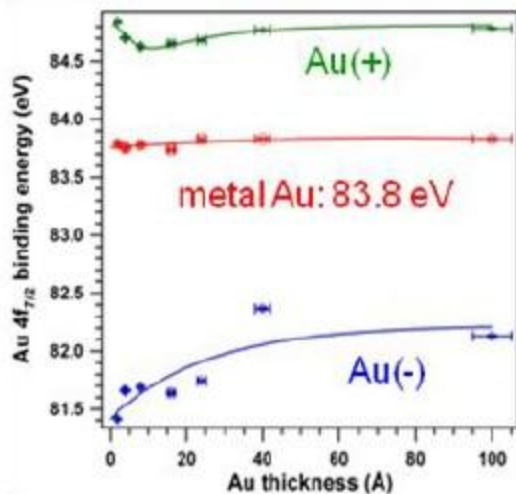


VP287\_i\_0006\_OK\_20kHz\_25DC\_4AC on the Au electrode



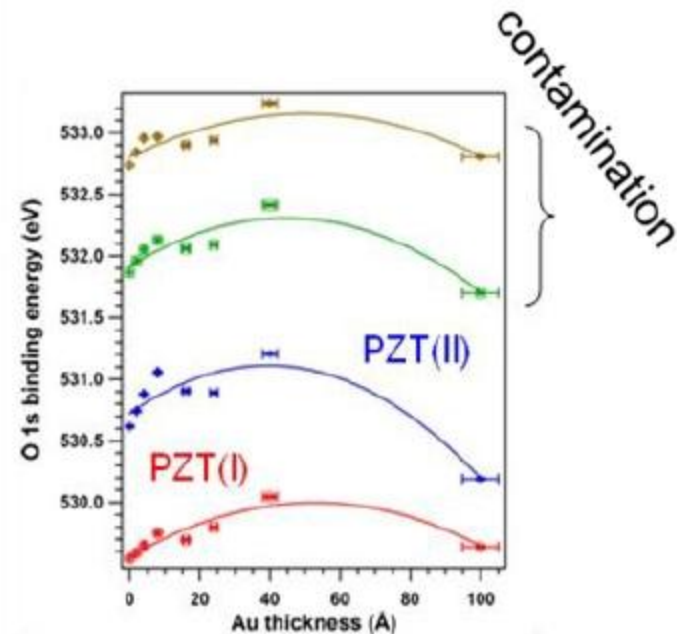
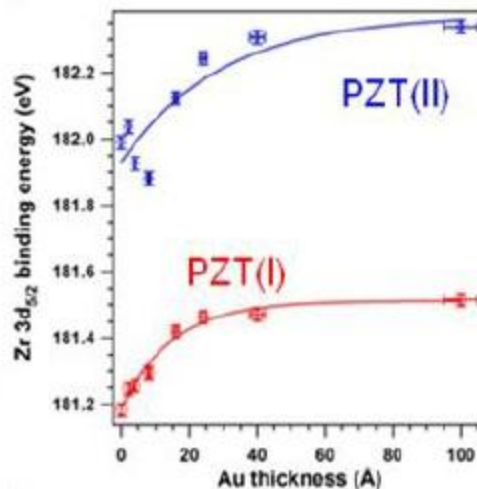
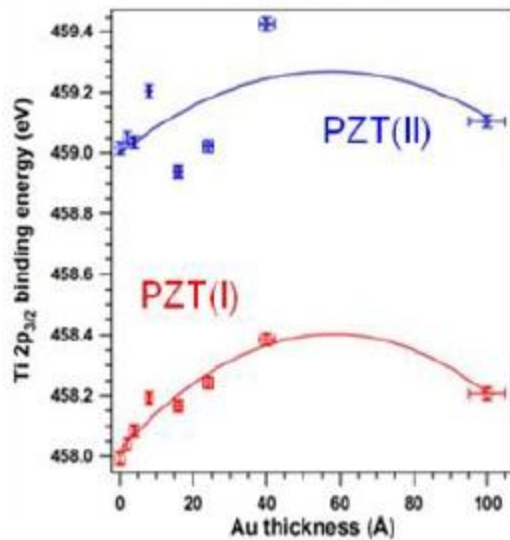
Piezoelectric hysteresis loops recorded on free surface and thru the Au electrode

# XPS data analysis (I): band bending

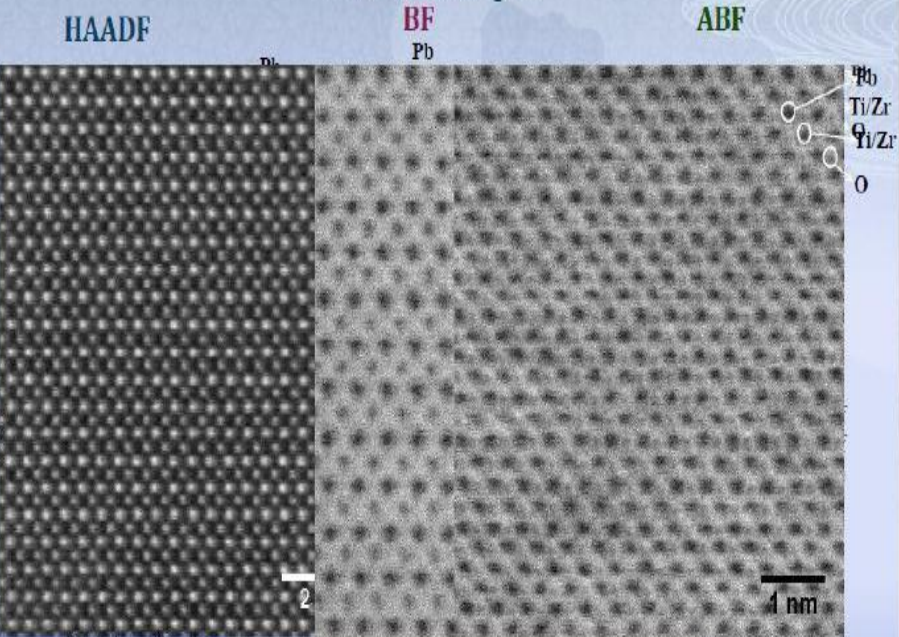


Two phases, with similar band bending:

$$\Phi_{\text{PZT}} - \Phi_{\text{Au}} \sim 0.45 \pm 0.05 \text{ eV}$$

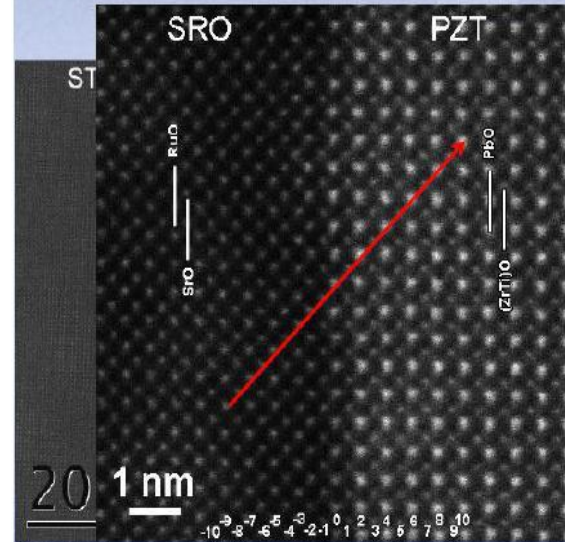


# STEM images



# Z-contrast in STEM-HAADF

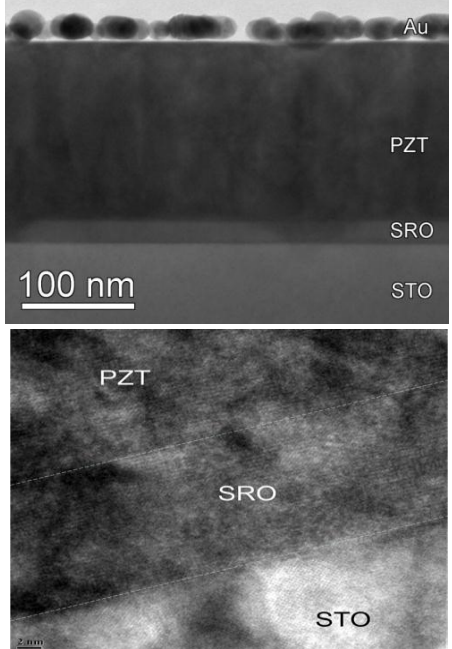
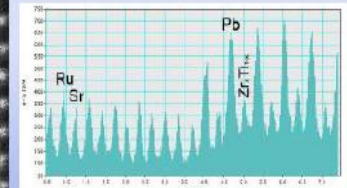
High - Angle Annular Dark Field STEM image of the SRO - PZT interface.



$$\sigma_R(\theta) = \frac{Z^2 \lambda_R^4}{64 \pi^4 a_0^3} \frac{d\Omega}{\left[ \sin^2\left(\frac{\theta}{2}\right) + \frac{\Theta_0^2}{4} \right]^2}$$

$\lambda_R$  = relativistically corrected  $\lambda$   
 $a_0 = h^2 e_0 / \pi m_0 e^2$  = Bohr radius  
 $\Theta_0$  = screening parameter

SrRuO<sub>3</sub>: <sup>38</sup>Sr, <sup>44</sup>Ru  
 PZT: <sup>22</sup>Ti, <sup>40</sup>Zr, <sup>82</sup>Pb



STEM images revealed a very good interface quality between SRO and PZT

In case of structure deposited by sol-gel the interfaces are not so sharp

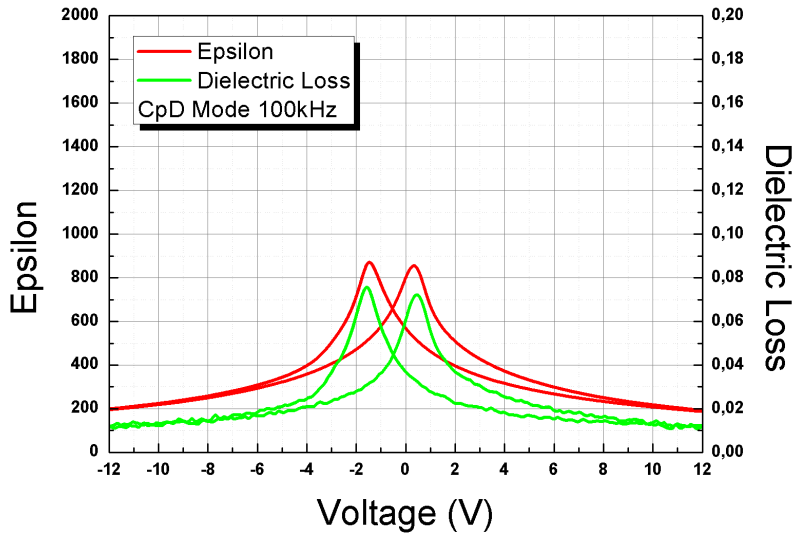
The Au layer tends to agglomerate and to form spherical particles with a diameter of 10 - 20 nm

A gap of about 1 nm is formed between PZT and Au, this result is unexpected but can explain the barrier formation at the PZT/Au interface

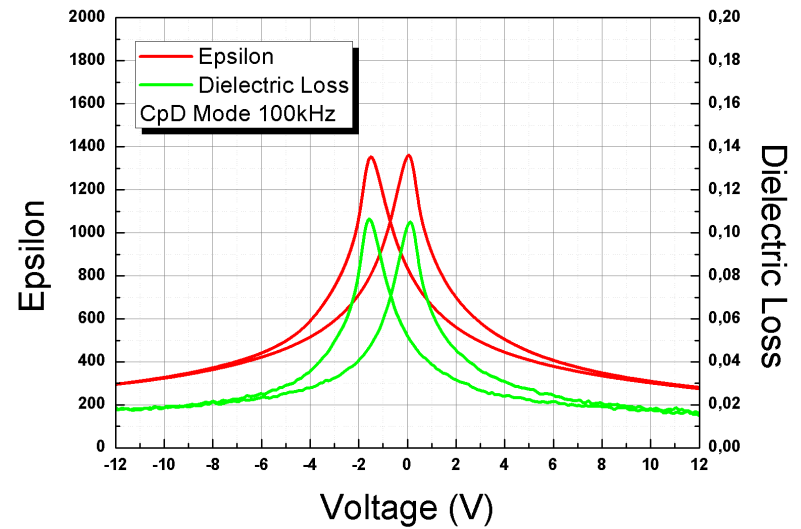
TEM on both PZT structures sol-gel and PLD



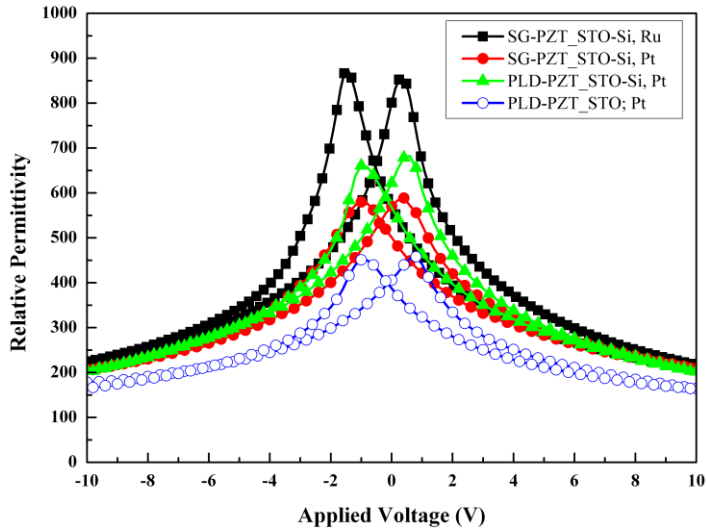
# Results: French team



Good quality STO template-  
Mosaicity(STO-002):  $0.45^\circ$



Less good quality STO template-  
Mosaicity(STO-002):  $1.54^\circ$



❑ Strong effect of top electrode (Ru, Pt) on relative permittivity.

❑ Strong effect of STO substrate quality on dielectric constant of PZT

## Benefits of the collaboration

### *Romanian team:*

- Dr. Chirila (Dragoi) Cristina had opportunity to see how the french team prepare and characterize their materials within the frame of the project ( 2 inch wafers), but also to see all the fabrication process at 200/300 mm wafer level used for projects with industrials.

### *French team:*

- Dr. Gwenael Le Rhun and Shi Yin (PhD student), had to opportunity to visit NIMP and all their facilities
- Shi Yin made some PLD depositions and PFM characterizations together with the romanian team.

Both teams learned that the quallity of STO has a strong influence on dielectric properties of PZT films

## Perspectives for the next years

Foreseen common activities:

- Testing common metals used in microelectronics (Cu, Al) as electrodes and compare the results with Au electrodes from XPS and PFM point of view and to be correlated with electrical measurements (C-V, P-V, I-V)
- Testing Ru and Pt as top electrode on the same structure on both PLD and sol-gel films
- Finalizing the comparison of surface properties and PFM results on sol-gel and PLD deposited PZT52/48 films both on SRO/STO/Si and SRO/STO substrates

Publications:

L. Pintilie, C. Dragoi, and I. Pintilie, “**Interface controlled photovoltaic effect in epitaxial Pb(Zr,Ti)O<sub>3</sub> films with tetragonal structure**”, JOURNAL OF APPLIED PHYSICS 110, 044105 (2011)

Cristina Dragoi, Nicoleta G. Gheorghe, George A. Lungu, Lucian Trupina, Andra G. Ibanescu, and Cristian M. Teodorescu , “**X-ray photoelectron spectroscopy of pulsed laser deposited Pb(Zr,Ti)O<sub>3-d</sub>**”, Phys. Status Solidi A 209, No. 6 (2012)

S. Yin, G. Le Rhun, E. Defay, B. Vilquin, G. Niu, Y. Robach, C. Dragoi, L. Pintilie, “**Pizeoelectric epitaxial sol-gel Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> film on Si(001)**”, submitted to JAP

**Conferences:**

**“ European Crystal Growth Conference (ECCG -4)”**

“Influence of deposition method on structural and electrical properties of PZT thin films growth on Si substrate”, C. Dragoi, Y. Shi, L.Trupina, I. Pasuk, I. Pintilie, G. Le Rhun, L. Pintilie

**“European Conferince on Composite Materials (ECCM 15)”.**

“Multiferroic behavior on symmetric and nonsymmetric heterostructures based on  $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3 - \text{CoFe}_2\text{O}_4$ ”, C. Dragoi, G. Ibanescu, A.Filimon, I. Pintilie and L. Pintilie

**“Electroceramics XIII”**

“Preparation and characterization of double perovskite  $\text{Sr}_2\text{Fe MoO}_6$  by various methods”  
M. Cernea, L.Trinca, G.Ibanescu, A. Iuga, L.Pintilie

**“The 7`th International Conference on Advanced Materials (ROCAM 2012)”.**

“Comparison Between Electrical Properties of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  and  $\text{BaTiO}_3$  Capacitors with Bottom  $\text{SrRuO}_3$  Contact and Different Metals as Top Electrode“, G.Ibanescu, C. Dragoi, I. Pintilie, L. Pintilie

“Structural, Electric and Magnetic Properties of  $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3 - \text{CoFe}_2\text{O}_4$  Heterostructures”  
C.Chirila, G.Ibanescu, L. Hrib, A. Filimon, R. Negrea, I.Pasuk, V. Kuncser, I. Pintilie and L.Pintilie

“Toward Integration of Epitaxial Piezoelectric Thin Films on Silicon Substrate for MEMS Applications ”  
G. Le Rhun, S. Yin, C. Dragoi, L. Trupina, J. Abergel, B. Vilquin, Y. Robach, E. Defay, L. Pintilie