FINAL STIENTIFIC REPORT.

Title of the project: CONTROL OF ELECTRONIC PROPERTIES IN FERROELECTRIC PEROVSKITE HETEROSTRUCTURES: FROM THEORY TO APPLICATIONS

Final Scientific Report (max. 25 pag.) for the entire period of the project, which has to contain the following aspects (pentru întreaga perioadă de implementare a proiectului şi trebuie să cuprindă următoarele aspect):

Proposed and realized Objectives (Obiectivele prevăzute/realizate):

1. Objectives proposed in the project proposal:

O1. Accurate control of doping of ferroelectric thin films, with clearly demonstrated *n* and *p* type conduction and fabrication of a truly ferroelectric *p-n* homojunction.

This was the most ambitious objective of the project. Doping ferroelectrics is not an easy task, especially in perovskite ferroelectrics with ABO_3 formula. The system has the tendency to generate other defects (e.g. vacancies) to compensate the extra-charges introduced by the doping element. However, the project team has managed to show that n and p type doping in perovskite ferroelectrics of $Pb(Zr,Ti)O_3$ (PZT) type is possible and with clear effects on the macroscopic electrical properties. The study was performed on epitaxial films, to reduce at minimum the structural defects that can smear or even hidden the effect of doping. A composition with Zr/Ti ratio of 20/80 was preferred due to high value of polarization. All the samples were grown by pulsed laser deposition (PLD), on single crystal $SrTiO_3$ (STO) substrates, with top and bottom electrodes of $SrRuO_3$ (SRO) electrodes. The first step in the study was to analyse the impact of the target purity on the electrical properties of epitaxial films. Films were grown from a commercial target with 99.9 % purity and from an in-house made target fabricated from raw materials with 99.99 % purity.

It was found that this small difference in the purity of the target has a significant effect on the electrical properties, especially on the magnitude of the leakage current, which is lower with about one order of magnitude in the films grown from the target with 99.99 % purity. This results suggests that in the targets are impurities acting as donor or acceptors, with direct impact on the density of the free carriers and on the magnitude of the leakage current. The detailed results were published in an article found at position 16 in the publication list.

Next step was to dope the high purity targets with Nb, replacing Ti or Zr in the PZT formula and acting as donors, and with Fe, replacing Ti or Zr and acting as acceptor. The doping was about 1 %, representing about 10^{20} cm^{-3} free carriers. However, the doping in the grown films may be slightly lower, even it is known that PLD growth replicates well the stoichiometry of the target. The obtained results were surprising, in the sens that clear differences could be observed on the electrical properties of the n-type and p-type doped films. The detailed results were published in the article found at position 22 in the publications list. Here a summary of the results will be presented, as in the following table:

Table 1*: Values of remnant polarization (P_r), coercive field (E_C), internal electric field (E_{int}), static dielectric constant (ε_s), potential barrier (Φ_0), and effective density of charge carriers (N_{eff}) for the un-doped PZT, PZT-Fe and PZT-Nb films. The errors in estimating the values of P_r, E_C, E_{int} and ε_s are are between 1 and 3 %, the errors for potential barriers are given in the table (see details in SM).*

Sample	P_r(µC/cm^2)	E_C(kV/cm)	E_{int}(kV/cm)	ε_S	Φ_0 (eV)	N_{eff} (10^{18} cm^{-3})
PZT	67	247	11.8	175	0.15±0.0025	(5-7)
PZT-Fe	51	130	23.5	225	0.11±0.009	(6-8)
PZT-Nb	76	338	26.5	207	0.32±0.02	(3-5)

The higher potential barrier at electrodes and the lower density of free carriers influences the magnitude of the leakage current in the Nb-doped PZT, which is with about two orders of magnitude lower than in Fe-doped PZT, while the capacitance is larger in the doped films (similar thicknesses and areas of the top contacts) and the magnitude of the polarization varies slightly with doping type (see Fig. 1).

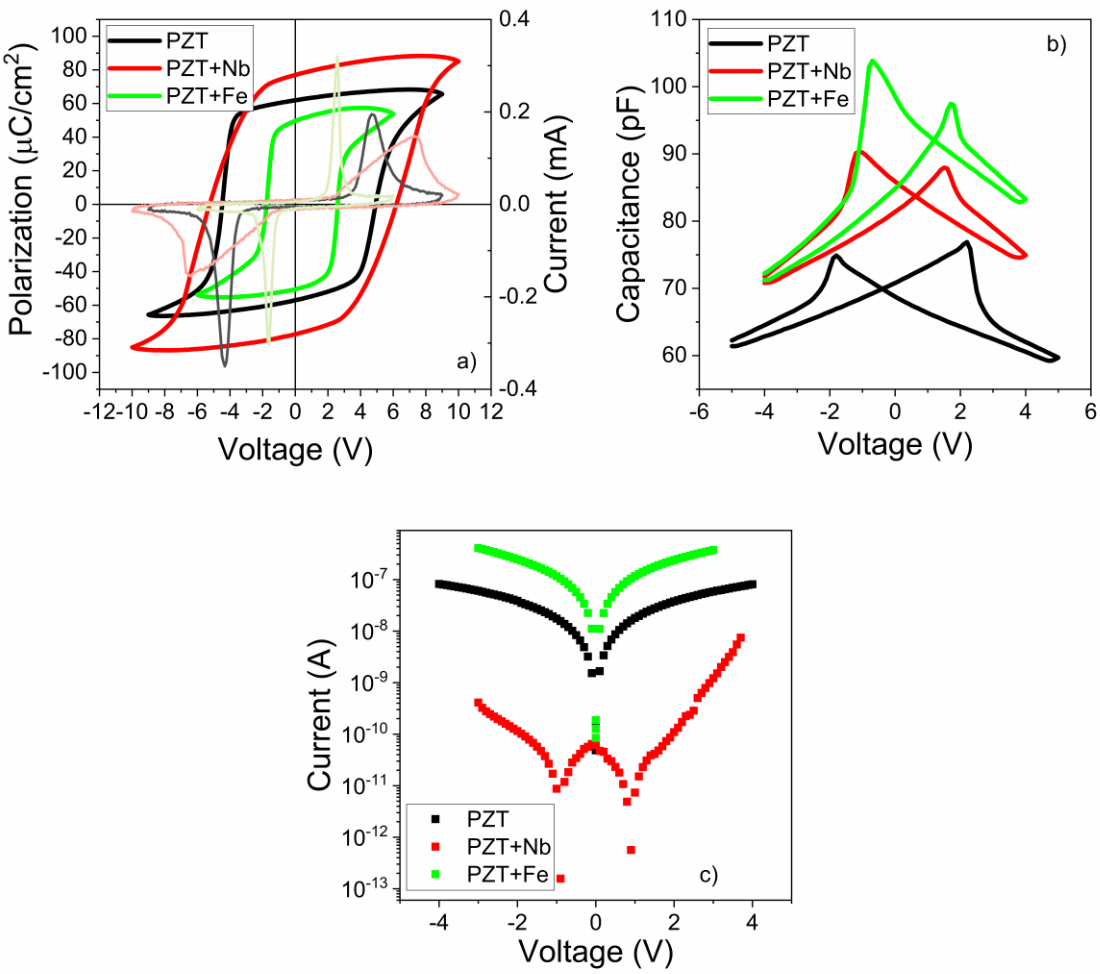

Figure 1 a) The hysteresis P-V and I-V characteristics recorded at RT for 1 kHz frequency of high amplitude pulse; b) The capacitance-voltage characteristics recorded at RT with 0.2 V a.c. signal and at 100 kHz frequency. c) The current-voltage characteristics recorded for totally saturated polarization at RT.

The most surprising result is that the polarization orientation in the as grown doped films depends on the doping type. The polarization is oriented up-wards (towards the surface) in the n-type doped PZT films, while the polarization is orientated down-wards (towards the bottom SRO electrode) in the p-type doped PZT films (see Fig. 2).

One can see that in Fig. 2b (n-type PZT) the colour of the inner square (polarization up-ward) is the same with the colour of outer, not poled, the surface. In fig. 2c the colour if the inner square is opposite (still up-ward) compared to the outer, not poled, surface, suggesting that this has down-ward orientated polarization. This is confirmed by the fact that the rectangular frame of the inner square, which is poled down-ward, has the same colour as the outer surface. In the Fig. 2d is presented an un-doped film, which behaves as n-type PZT due to oxygen vacancies.

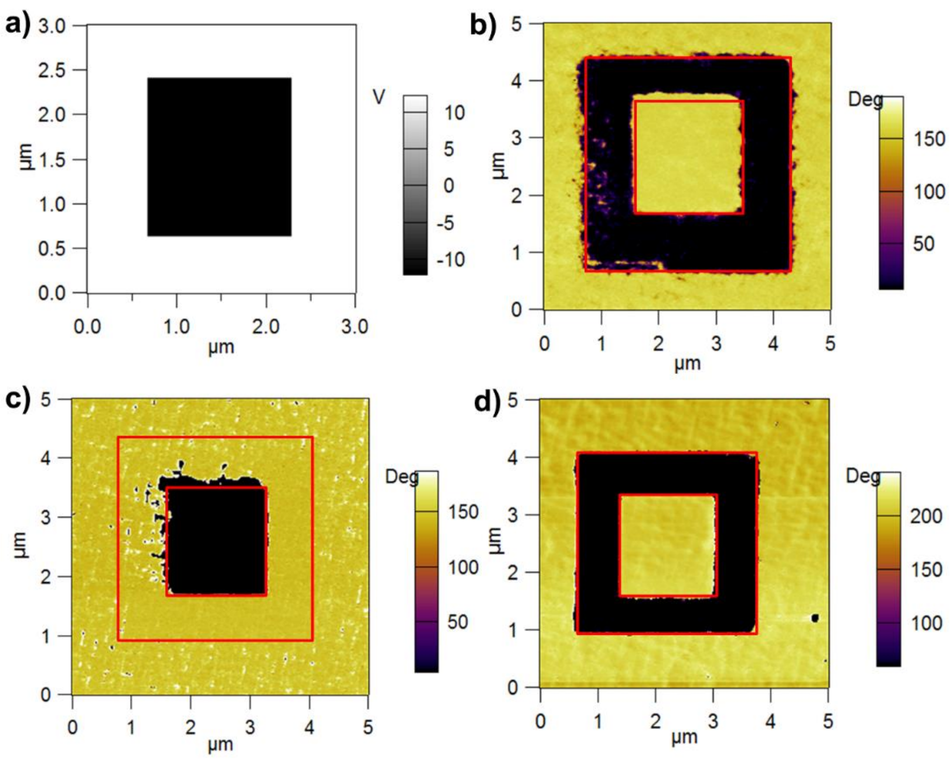

Figure 2 a) Poling map applied for polarization switching; Piezoresponse phase images after domain writing according to the poling map on: b) PZT-Nb; c) PZT-Fe; d) un-doped PZT thin films.

This results suggest that one can estimate the doping type of epitaxial PZT films by analysing the results of PFM investigation performed with same poling map on films known to be not doped. If the results are similar then the doping is n-type, if the colours are opposite then the doping is, most probably, p-type.

In the next step p-n ferroelectric homojunctions were grown by successive deposition of n-type and p-type PZT layers, or vice-versa. The layers have at first equal thicknesses, of 100 nm each, but similar results were obtained for 50 nm thickness for each layer. The goal was to obtain a ferroelectric p-n diode, which for one direction of polarization is closed and for the other is open, thus acting as simple memory cell with non-destructive readout (high current for one orientation and low for the opposite, see Fig. 3, taken from the proposal).

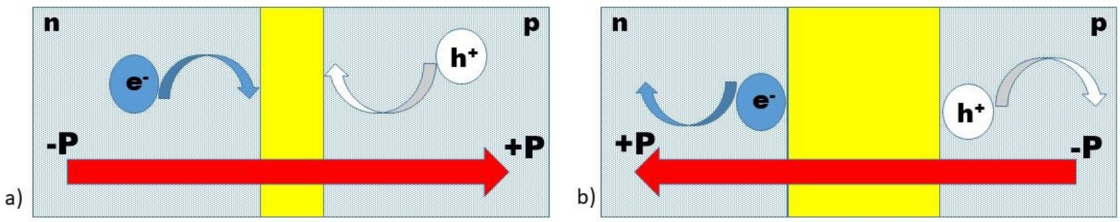

Figure 3 Notations: *n* and *p* stand for conduction type in the two regions; +P and –P stand for the sheets of polarization charges located near the electrodes; e^- and h^+ stand for electrons and holes, respectively. *a)*-polarization is oriented such that electrons and holes are pushed towards the depleted region, leading to a small thickness of it (high capacitance, low resistance, high current). *b)*-polarization is oriented such that electrons and holes are pushed away from the depleted region, leading to a high thickness of it (low capacitance, high resistance, low current).

The electrical measurements, especially the I-V characteristics, did not shown the expected non-linear, rectifying characteristic as for semiconductor p-n diodes. Contrary, the characteristics are symmetric and linear, as shown in Fig. 4.

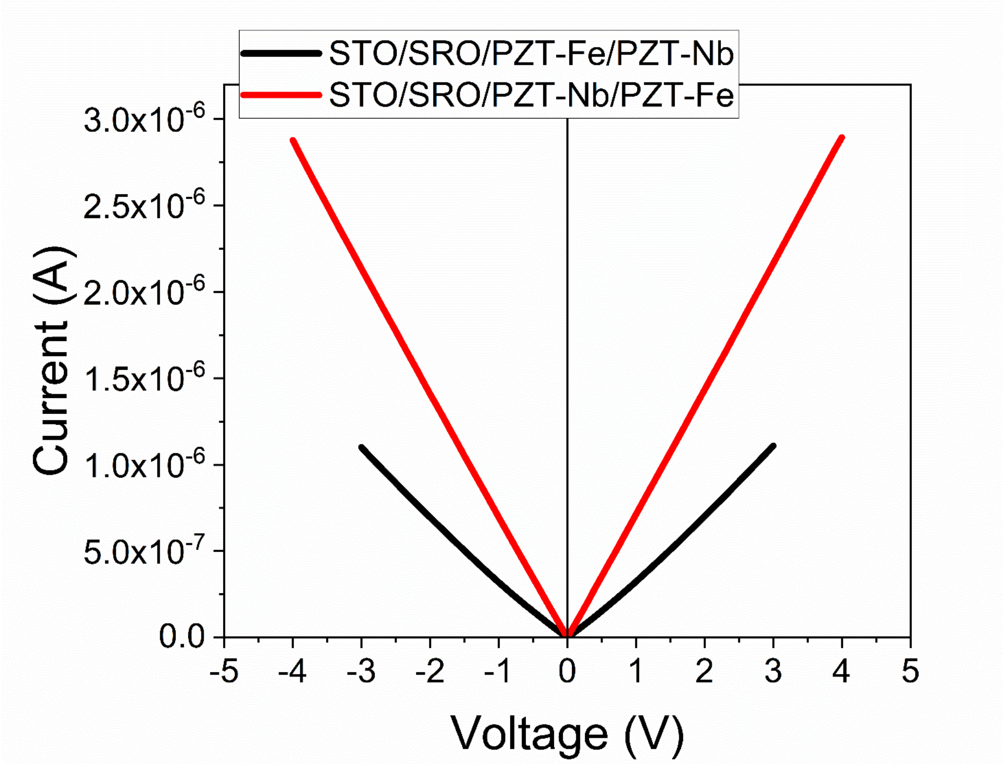

Figure 4 I-V characteristics for the bi-layer structures.

This behaviour was explained by assuming that the total current flowing through the p-n ferroelectric homojunction is the sum of electron and hole currents. The electron currents is given by:

$$J_e = 2\,q\,\left(\frac{2\,\pi\,m_e^*\,k_B\,T}{h^2}\right)^{\frac{3}{2}}\,\mu_e\,E\,exp\left\{-\frac{q}{k_B\,T}\left[\left(\Phi_B^0 - \sqrt{\frac{q\,P}{4\,\pi\,\varepsilon_0^2\,\varepsilon_{op}\,\varepsilon_{st}}}\right) - \sqrt{\frac{q^2\,N_{eff}\,V}{8\,\pi\,\varepsilon_0\,\varepsilon_{op}\,P}}\right]\right\}. \qquad (1)$$

In the above equation, the standard notation was used as follows: m_e^* is the electron effective mass, k_B is the Boltzmann constant, *T* is the temperature, *h* is the Planck constant, μ_e is the electron mobility, *E* is the applied electric field, *q* is the electron charge, Φ_B^0 is the potential barrier at 0 V, *P* is the ferroelectric polarization, ε_0 is the vacuum permittivity, ε_{op} is the optical dielectric constant, ε_{st} is the static dielectric constant. N_{eff} is the effective density of fixed charge in the depleted region and is related to the donor and acceptor concentrations N_D and N_A and finally, *V* is the applied voltage.

A similar formula holds for the hole density current J_h, with appropriate notations for the hole effective mass, hole mobility and effective density of fixed charge in the depleted region. Then the total current density J_{tot} reads:

$$J_{tot} = J_e + J_h. \qquad (2)$$

One can further simplify the field-dependence of the current density by noticing that for *both* types of charge carriers and for a wide range of doping concentrations $\frac{q}{k_B\,T}\sqrt{\frac{q^2\,N_{eff}\,E\,d}{8\,\pi\,\varepsilon_0\,\varepsilon_{op}\,P}} \ll 1$ (this condition holds for concentrations up to $10^{20}\ cm^{-3}$). Then by expanding the corresponding exponential terms in J_e and J_h up to the first order term we identify linear (L) and non-linear (NL) contributions to the electron/hole density currents. For instance, the electron current density acquires the form:

$$J_e \approx \underbrace{2\,q\,\left(\frac{2\,\pi\,m_e^*\,k_B\,T}{h^2}\right)^{\frac{3}{2}}\,\mu_e\,E\,exp\left\{-\frac{q}{k_B\,T}\left[\left(\Phi_B^0 - \sqrt{\frac{q\,P}{4\,\pi\,\varepsilon_0^2\,\varepsilon_{op}\,\varepsilon_{st}}}\right)\right]\right\}}_{J_{e,L}} +$$

$$\underbrace{2\,q\,\left(\frac{2\,\pi\,m_e^*\,k_B\,T}{h^2}\right)^{\frac{3}{2}}\,\mu_e\,E\,\sqrt{\frac{q^2\,N_{eff}\,E\,d}{8\,\pi\,\varepsilon_0\,\varepsilon_{op}\,P}}\,exp\left\{-\frac{q}{k_B\,T}\left[\left(\Phi_B^0 - \sqrt{\frac{q\,P}{4\,\pi\,\varepsilon_0^2\,\varepsilon_{op}\,\varepsilon_{st}}}\right)\right]\right\}}_{J_{e,NL}}, \qquad (3)$$

where, we used $V = E\,d$ and d denotes the sample thickness. One should note that the exponential term includes the effect of the potential barrier reduction induced by the presence of the ferroelectric polarization. Eq. 3 shows that the main contribution to the density current has a linear dependence on the field, whereas the non-linear corrections depend on the doping concentrations. Obviously, the same behaviour is inherited by the total current density J_{tot}. On the other hand, the temperature dependence is controlled by the exponential term in Eq. (3).

Therefore, our model predicts and exponential dependence on temperature, in agreement with the experimental data on the resistance of the *p-n* structure (see Fig. 5), and a linear (or ohmic) dependence on the applied voltage, as observed in the experimental I-V characteristics (see Fig. 4). The non-linearity of the I-V characteristics is a fingerprint of the two correction terms.

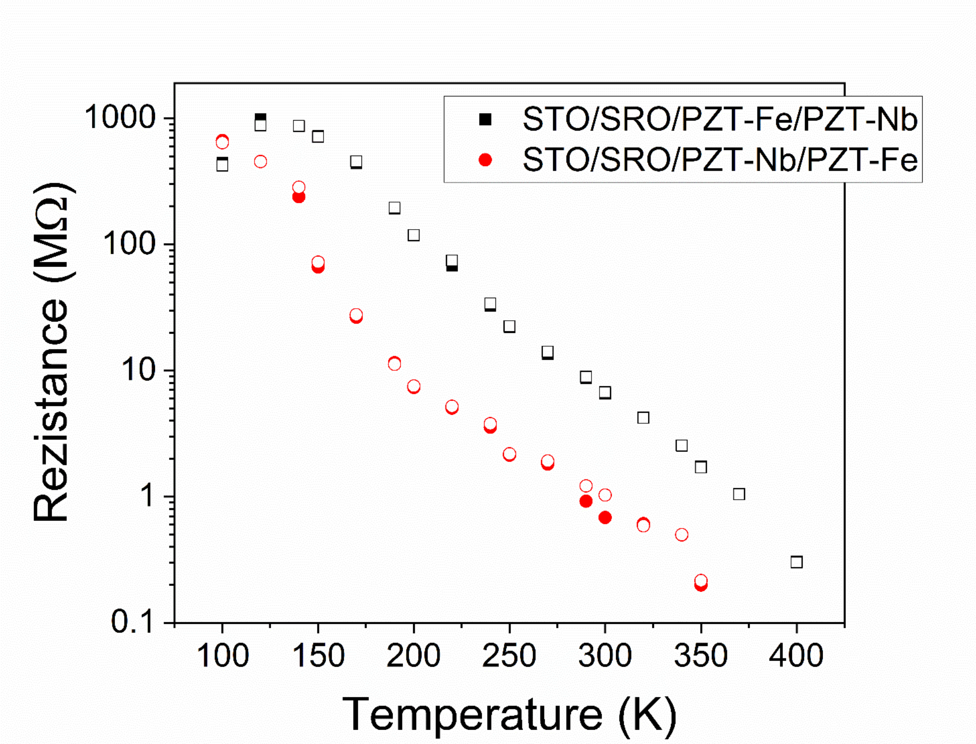

Figure 5 The temperature dependence of the resistance of the two bi-layer p-n structures.

Several other p-n junctions were obtained by changing the thickness of the top layer, 25 nm compared to 100 nm the bottom one. Some asymmetry occurs in this case, with a more pronounced non-linearity in the I-V characteristic. These results were just submitted for publication to ACS Applied Materials and Interfaces (position 30 in the publication list).

A very interesting results was that the capacitance of the ferroelectric p-n junction is higher than the capacitance of the component layers taken separately, for same thickness and top electrode area. This is contrary to what is predicted by the serial model of connecting capacitors (see Fig. 6). According to literature, this is a sign of stabilized negative capacitance (see for example *"Experimental evidence of ferroelectric negative capacitance in nanoscale heterostructures, Asif Islam Khan et. Al, Appl. Phys. Lett. 99, 113501 (2011)* or *„Room temperature negative capacitance in a ferroelectric-dielectric superlatice heterostructure", Weiwei Gao et. Al., Nano Lett. 2014).*

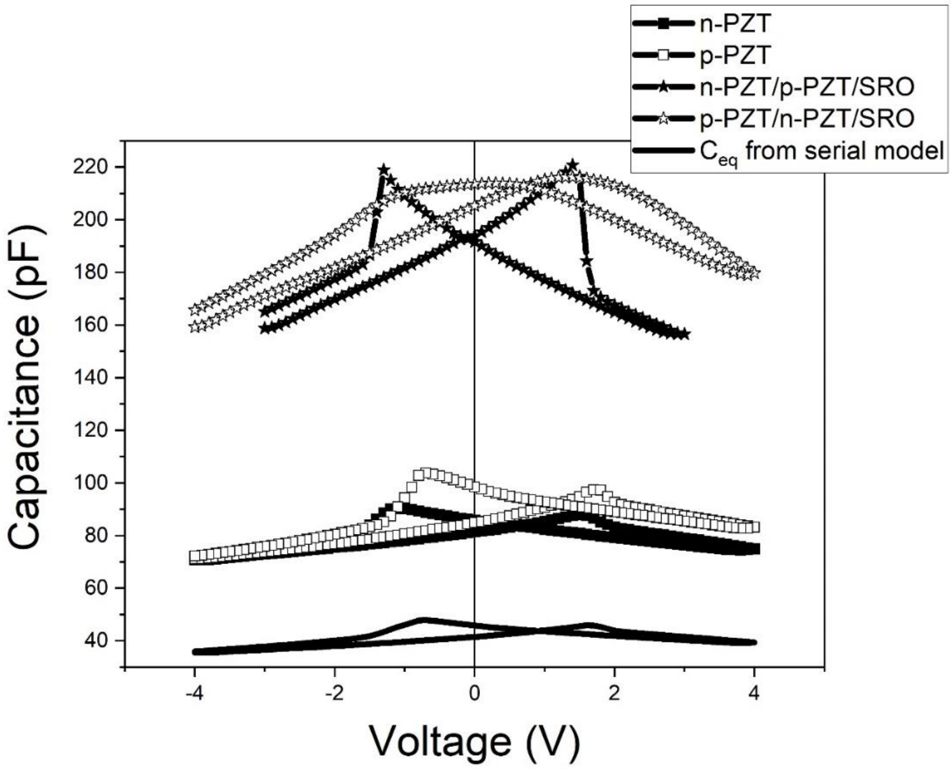

Figure 6 The negative capacitance effect in ferroelectric p-n junctions.

This finding is subject of a patent application at European level (EPO, position 4 in the list of patent requests). Doping on Pb positions was also tested, for example with Bi or La as donors and K as acceptor. Ceramic $BaTiO_3$ (BTO) doped with donor and acceptor atoms were fabricated and the films follow to be grown. The work on doped ferroelectrics and ferroelectric p-n structures will continue, considering the very interesting results obtained until now, some of them not expected. The goal remains the same, to obtain a p-n ferroelectric diode acting as a simple non-volatile memory, with two states read by measuring the current flowing through the diode at a constant applied voltage with magnitude below the coercive voltage. For one orientation the current should be high, for the opposite orientation the current should be low. It is thought that such a device can be realized by playing with the thickness of the component layers and with their doping density. The study will imply continue work on modelling, as performed until now for band structures in doped and not doped PZT, as well for understanding other surface or interface related phenomena observed in ferroelectrics (see articles at positions 2, 3, 4, 5, 6, and 11 in the list of publications).

O2. Design and fabrication of FeRAM memory cells with non-destructive readout.

O3. Design and fabrication of multi-bit FeRAM memory devices.

The work for these two objectives was performed simultaneously because the architectures used are similar, namely ferroelectric-dielectric (or ferroelectric with low polarization value)-ferroelectric. Such structures proved to behave as memcapacitors, thus having multiple memory states and non-destructive capacitive readout. The studies structures were either PZT-$SrTiO_3$ (STO)-PZT or PZT-$BaTiO_3$ (BTO)-PZT. The main results are synthesised in Fig. 7 and published in the article from position 1 in the list of publications.

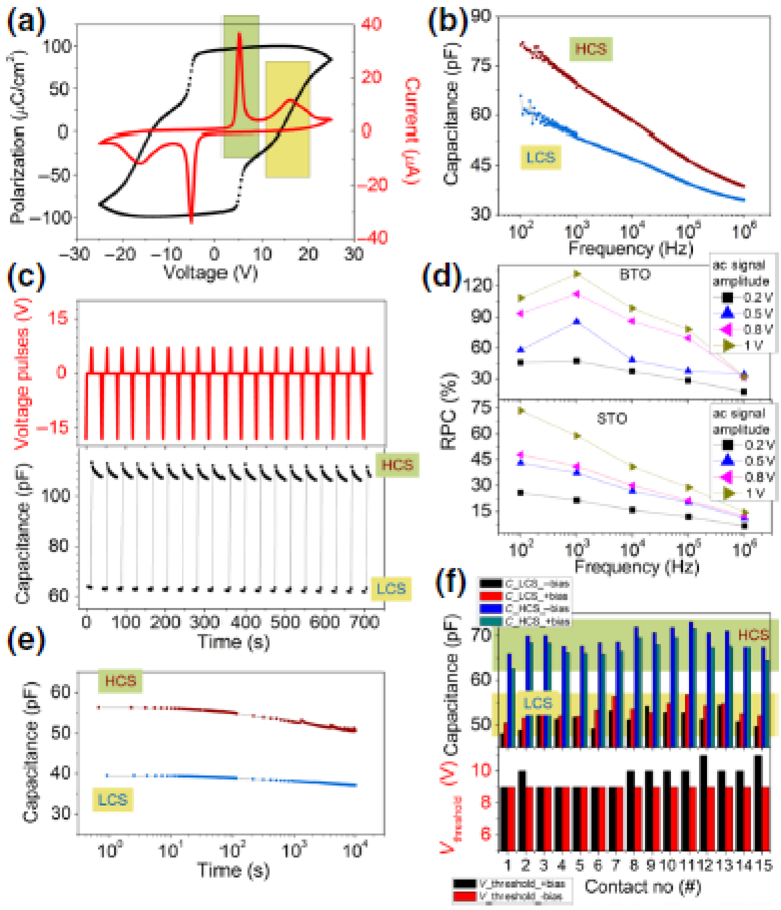

Figure 7 Two different capacitance states. (a) The hysteresis loops obtained for a complete switching cycle for the case of a BTO interlayer exhibiting four switching peaks in current-voltage characteristics accompanied by a step-like increase in the polarization loop; the extreme peaks situated at higher voltages correspond to a totally reversed polarization, where the ferroelectric polarization is either oriented *up*, toward the top interface in both ferroelectric layers, for negative voltages, or *down*, toward the bottom electrode in both ferroelectric layers, for positive voltages; the intermediate peaks are obtained when the applied voltage changes its polarity and indicates a partial reversal of polarization in only one ferroelectric layer, generating either a head-to-head or a tail-to-tail configuration between the polarizations of the two ferroelectric layers. (b) The capacitance vs frequency, using 0.2-V ac signal, measured after setting the high capacitance state (HCS) and the low capacitance state (LCS), respectively. (c) Voltage pulse sequence, combining high-amplitude and low-amplitude pulses with 0.1 s duration, used to repeatedly change the capacitance of the system between LCS and HCS; the capacitance values are measured at 1 kHz frequency and with 0.5-Vac signal. (d) relative variation of capacitance (RPC) ratios for the BTO and STO interlayer cases, respectively, for different frequencies and ac signal amplitudes. (e) evolution of the two distinct capacitance states, during the 10^4 s time period, measured at 1 kHz frequency and 0.2 V amplitude of the ac signal. (f) Distribution of capacitance values for HCS and LCS, measured at 1 kHz and 0.5-V ac signal, and distribution of the voltage threshold defined as the voltage necessary for switching from LCS to HCS for 15 different contacts.

The memcomputing functionality as well as the multiple memory states are demonstrated in the Fig. 8. Efforts were made to test the pyroelectric detection as possible non-destructive readout of non-volatile ferroelectric memories. Pyroelectric properties were tested on several thin film samples (see article found at position 12 in the publication list). It was found that the phase changes with 180 degrees for opposite orientations of polarization, and this finding was exploited through a patent application (first position in the list of patent requests). An example of pyroelectric signals recoded for different orientations of the ferroelectric polarization is presented in Fig. 9. It can be seen that the signals are in anti-phase, and this fact can be exploited for non-destructive reading of the information written in a FeRAM cell.

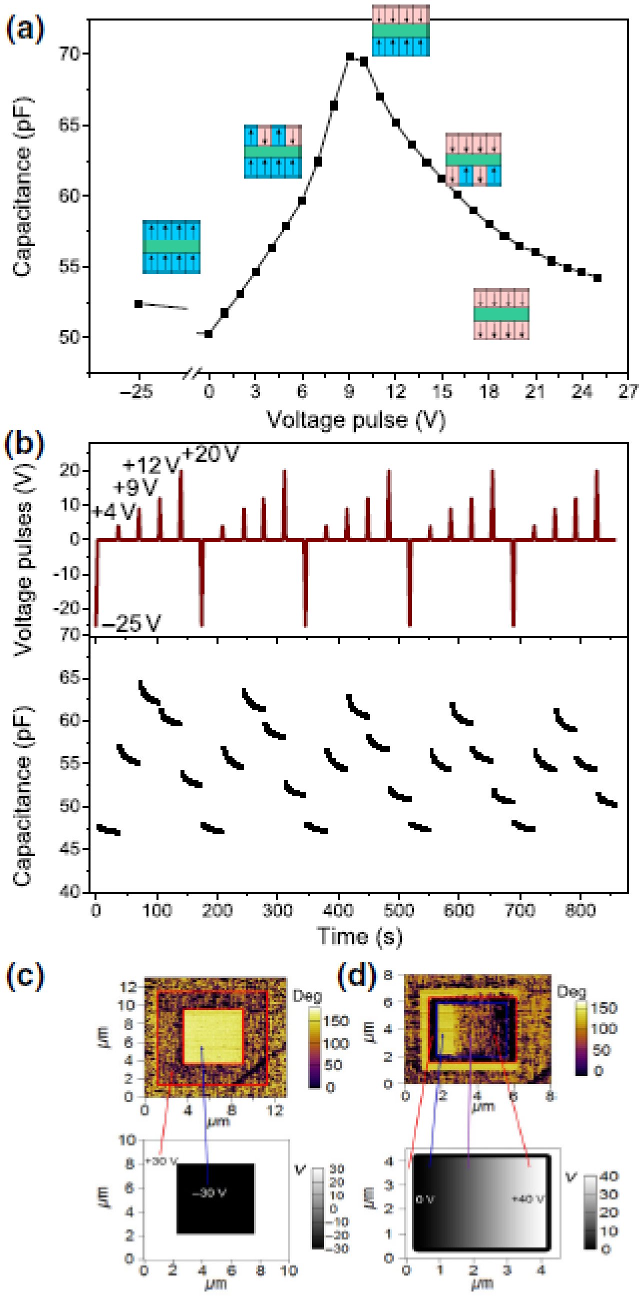

Figure 8 Multiple stable states with continuous capacitive values. (a) A continuous spectrum of capacitance values, with stable intermediate states measured for the STO interlayer case at 1 kHz frequency with 0.5-V ac signal; insets show schematic illustrations of polarization configurations associated with distinct capacitive states. (b) An example of a voltage sequence combining pulses with different amplitudes and polarities used to access different capacitive states. (c) The piezoresponse phase signal obtained using the poling map: the upper PZT layer present totally reverses polarization toward the surface for negative applied bias (bright central rectangular zone) while for positive bias the polarization remains partially reversed, forming with 180◦ domain structure. (d) The piezoresponse phase signal obtained by applying the poling map with a voltage gradient on the totally reversed polarization area from (c): the switching of polarization takes place gradually with increasing the amplitude of voltage; different degrees of partial switching of polarization are obtained in the 8–37 V range.

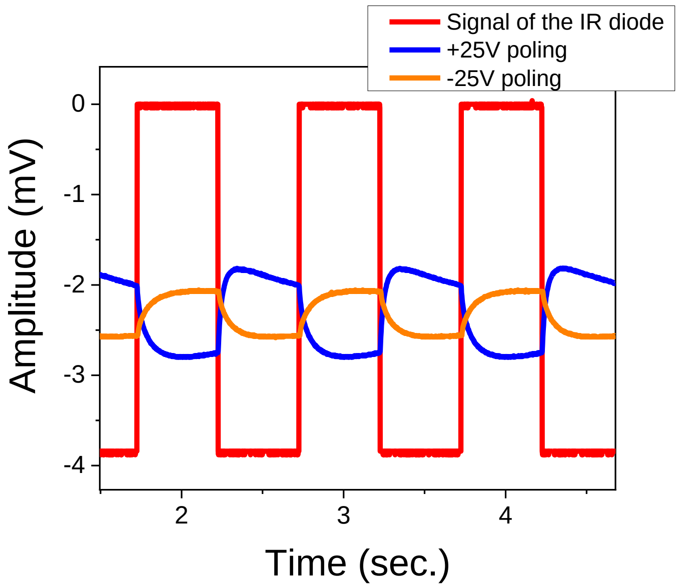

Figure 9 Signal of the IR diode used to illuminate the sample (red rectangular plot), and the pyroelectric signal recorded from the sample after poling for obtaining opposite directions of polarization (blue and orange plots).

O4. Develop new architectures for the next generation photovoltaic solar cells.

Efforts were made in the first part of the project to prepare Bi(Fe,Cr)O_3 targets, with the hope to engineer the band gap for photovoltaic applications. However, the deposited films were very leaky and no short-circuit photocurrent could be measured, as mentioned in the intermediate report. Some effort was then devoted to prepare some hybrid perovskites, including one with Sb ($(CH_3NH_3)_3Sb_2I_9$). This compound has shown a P-V loop that resembles the characteristic hysteresis loop for a ferroelectric (see Fig. 10), but the specific elements supporting the presence of ferroelectricity are not present: polarization saturation; current leaks associated to polarization reversal. More relevant was the fact that the films could not be poled with polarization upward and downward, a fact that points out that the compound is, most probably, not ferroelectric.

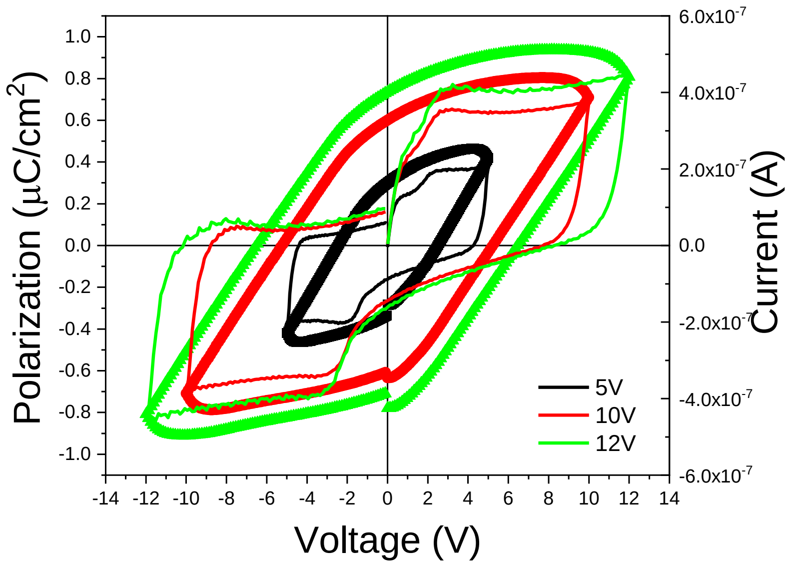

Figure 10 Charge („polarization”) and current hysteresis loops recorded at 1 kHz for a thin film of $(CH_3NH_3)_3Sb_2I_9$.

The work performed on the possible photovoltaic applications of the ferroelectric thin films revealed the fact that it is probably unlikely to have in the near future ferroelectric photovoltaic solar cells due to several facts: low short-circuit current generated by the ferroelectrics; relatively large band gap, that can be theoretically engineered to lower values, but the predicted compunds are hard to synthesise; the hybrid perovskites do not show clear and controlable ferroelectricity, this might be present at microscale but is not evident on large contacts. Despite these not favourable results, the possible use of ferroelectrics in energy related applications was not completely abandoned. Being aware that ferroelectrics cannot be used in generating energy with the same efficiency as the semiconductor or perovskite solar cells, some effort was dedicated to application of ferroelectrics in storing energy as dielectric super-capacitors. Some work as performed in collaboration with groups from abroad (see article found at position 10 in the list of publications).

<u>Other topics studied during the project.</u>

The main effort was dedicated to obtain doped ferroelectric films and to the use of ferroelectrics in non-volatile memories with multiple states and/or non-destructive readout. One has to consider that the initial project proposal was submitted in 2016, the contract was signed towards the end of 2018, and the ending of the project is in 2022. Several other hot topics have drawn the attention to the Project Director and project team members, such as:

- Ferroelectricity in other materials, especially doped HfO_2, but also some organic compounds (e.g. cytosine)-possible applications for non-volatile memories (O1, O2 and O3 in the project).

The teams from NIMP were involved in very lucrative collaborations with teams from France, Greece, Portugal, Germany working in the field of doped HfO_2 for microelectronic applications (non-volatile memories either in 1C-1T architecture, or a s simple 1T ferroelectric field effect transistors). The team of Project Director was involved in the advanced electric characterization to obtain more information on the electronic properties at interfaces, while the second team from NIMP was involved in advanced structural characterisation of HfO_2 based structures. A number of common publications resulted from these collaborations, positions 10, 14, 23, 25 and 29 in the publication list.

The main result obtained to NIMP was to show that the interface properties of metal-HZO-Ge MFS structures depends on the doping type of Ge. Therefore, HZO very thin films were deposited on n-type and p-type Ge substrates (deposition performed by the Greek partner), and the samples were then subject to detailed structural investigation and temperature dependent electrical measurements at NIMP. Using impedance spectroscopy, two interface electrically active defects have been identified in the Ge energy gap. In p-Ge, a shallow donor level is located at only 60 meV from the valence band (VB) and in n-Ge, an acceptor level is located 200–250 meV from the VB. It is characteristic that the donor level in p-Ge is active only at positive gate bias when the MFS is in
depletion, whereas the acceptor level in n-Ge is always active for either positive or negative gate bias. These observations indicate that a pair of acceptor and donor levels, closely spaced in energy, is both located near the top of the VB, consistent with previous observations that the CNL in Ge is close to the VB. In p-Ge, the Fermi level at the interface is close to the CNL leaving the interface neutral, thus the influence of interface defects (traps) on the ferroelectric hysteresis and the C–V is minimum. In contrast, in n-type Ge, the Fermi level at the interface is located well above the acceptor level, thus filling the traps with electrons, is negatively charging the interface. This has important consequences mainly on the C–V characteristics at low temperatures. More specific, the C–V in n-Ge shows a clockwise hysteresis which is an indication that negative charge trapped at the interface masks the ferroelectric behavior which should normally yield a counterclockwise C–V hysteresis. Moreover, as the temperature is lowered, the accumulation capacitance of n-Ge MFS at positive gate bias drops to very low values, almost equal to the depletion capacitance. This is an indication that the negatively charged acceptors prevent free electrons from accumulating at the interface, or in other words, prevents accumulation and keeps the MFS in depletion adding a low depletion

capacitance in series with the HZO oxide capacitance. Despite the detrimental effects of negatively charged acceptors on the C–V characteristics of n-Ge MFS, the ferroelectric hysteresis (polarization–voltage [P–V]) is not affected, especially at high temperatures, mainly because minority carriers easily excited in the low gap Ge are sufficient to screen the polarization charges, keeping depolarization fields in the ferroelectric negligibly small in n-Ge MFS. In contrast, p-Ge MFSs are affected the least by the surface defects showing nearly ideal P–V hysteresis and C–V characteristics, so they are considered as suitable candidates for MFS and FeFET device fabrication (see also Fig. 11).

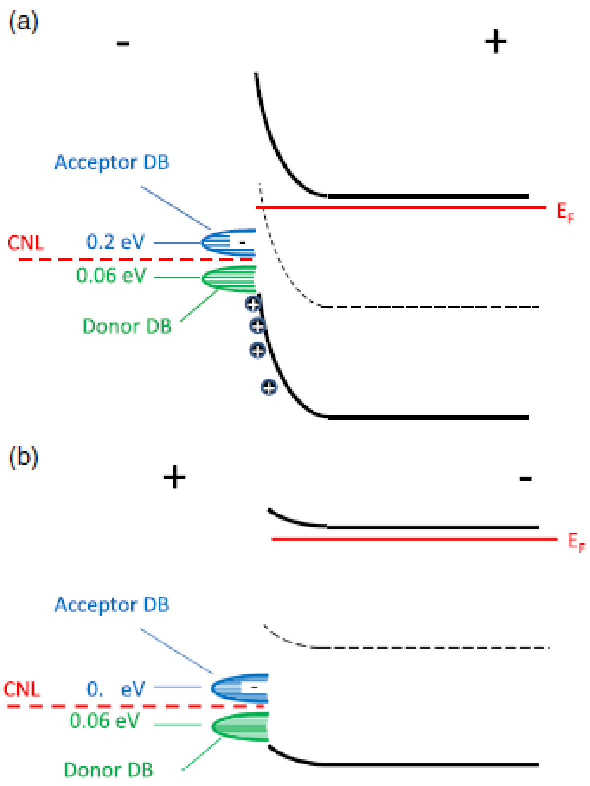

Figure 11. a) Negative bias on the gate: the surface is easily inverted to p-type since there is an upward band bending so that the CNL lines up with the Fermi level to neutralize the surface. Alternatively, in addition to the external negative bias, there is a negative surface charge from the occupied acceptor DBs which attracts mobile minority holes at the surface leading to inversion. b) Positive bias on the gate: the positive charges on the gate are screened by the negative charges occupying the acceptor DBs. As a result, the surface does not easily reach accumulation as it should normally be expected for a positive bias on the gate. Therefore, the surface remains in depletion rather than accumulation for positive values of the gate bias.

- Negative capacitance effect, fundamental aspects.

Another hot topic is the negative capacitance (NC) observed in some ferroelectric structures and the exploitation of this effect to reduce the power consumption in field effect devices (so called negative capacitance field effect transistor-NCFET). This is possible by reducing the swing factor from OFF to ON state (the slope of the drain current-gate voltage characteristic) below the value of 60 mV/decade predicted by the thermodynamic theory (named also Boltzmann's tyranny).

Negative capacitance effect (NC) was evidenced in simple PZT capacitors by deriving the hysteresis loops recorded at different amplitudes of the applied triangular voltage. NC appears to be a transitory effect strictly related to polarization switching and is due to the redistribution of the charges involved in the compensation of the depolarization field, charges that are moving from one interface to the other. This flow of charges during switching leads to an apparent decrease of sample resistance, estimated to about two orders of magnitude (see Fig. 12). It was also found that, in high quality epitaxial PZT layers, the switching is very fast (estimated to about 100 ns or below), with apparently no formation of ferroelectric domains (the polarization just suddenly switch its orientation from UP to DOWN or vice-versa, results published in the article found at position 8 in the publication list; see also Fig. 13). NC was evidenced in many ferroelectric capacitors, although it appears that its magnitude and time duration are influenced by a multitude of factors such as structural quality, quality of interfaces, density of free carriers, the weight of domains with in-plane polarization, etc.

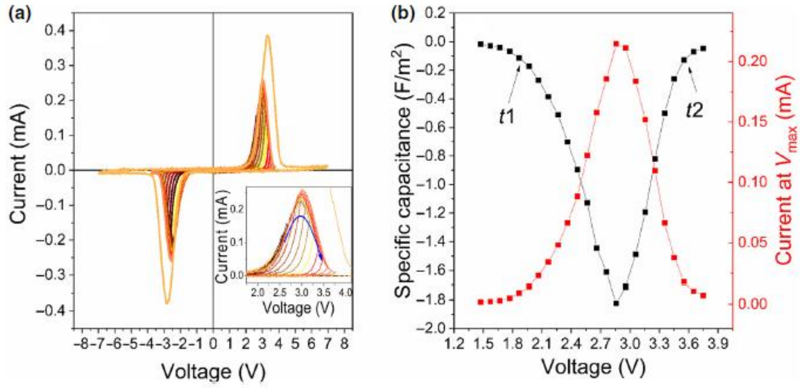

Figure 12 (a) The current hysteresis recorded at different amplitudes of the triangular voltage wave of 1 kHz frequency). (b) The voltage dependence of the maximum value of NC in the positive voltage range, together with the voltage dependence of the current recorded at the maximum applied voltage during the hysteresis measurement.

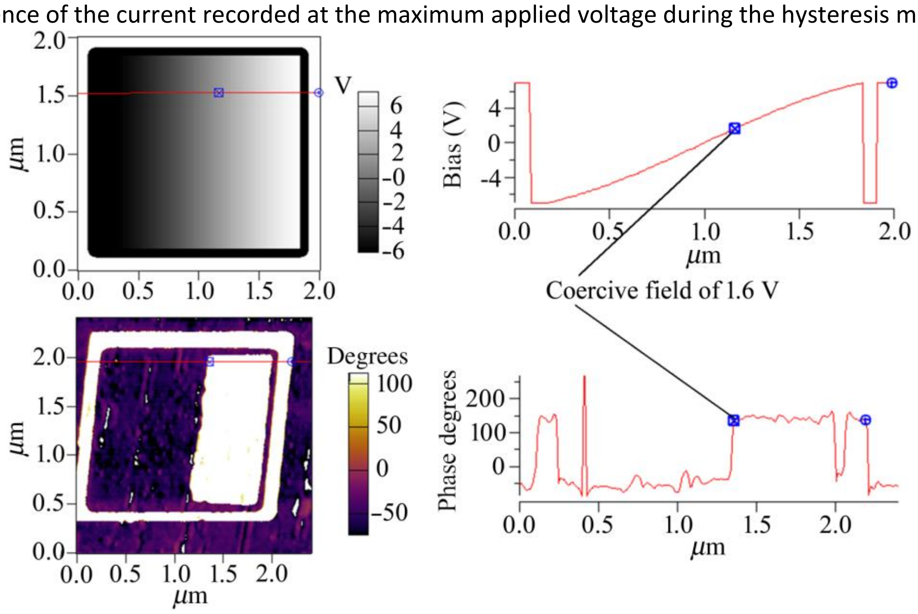

Figure 13 (a) The poling map. (b) The voltage variation while the PFM tip scans the line in (a)—it starts at +5.33 V, then after about 0.1 μm drops to −5.33 V and starts to slowly increase to +5.33 V while the tip is moving on the surface of the sample, after which it drops again to −5.33 V for about 0.1 μm and suddenly changes to +5.33 V for the final 0.1 μm. (c) The phase contrast after applying the poling map from (a). (d) The phase variation while the tip scans the line in (c).

A new method was developed to evidence the negative capacitance effect, named dynamic dielectric characterization. As mentioned at objective 1, important results regarding the presence of a stable negative capacitance effect in ferroelectric p-n junctions were obtained.

Several articles were published on this topic, as for examples those mentioned at positions 8 and 13 in the publication lists.

- Fundamental aspects of polarization reversal, domain structure, interface phenomena – can have impact on all objectives of the project

Analysing samples of the same PZT composition, deposited by different methods (PLS, spin-coating) on different type of substrates (single crystal STO, Pt/Si) it was found that the polarization switching critically depends on the structural quality of the samples, as well as the magnitude of the negative capacitance effect. One strongly debated problem in the field of perovskite ferroelectrics is if the polarization switching is homogeneous (is taking place without domain formation) or non-homogeneous (with domain nucleation and growth). Or experimental results support the hypothesis that the switching is homogeneous and that the domains appear when structural defects are present in the sample or when the charge required to compensate the polarization charges is not enough in the structure (or in the film or in the electrodes). It was found that polarization switching is homogeneous in high quality epitaxial samples and turns to non-homogenous in textured or polycrystalline films, as shown in the Fig. 14 and 15.

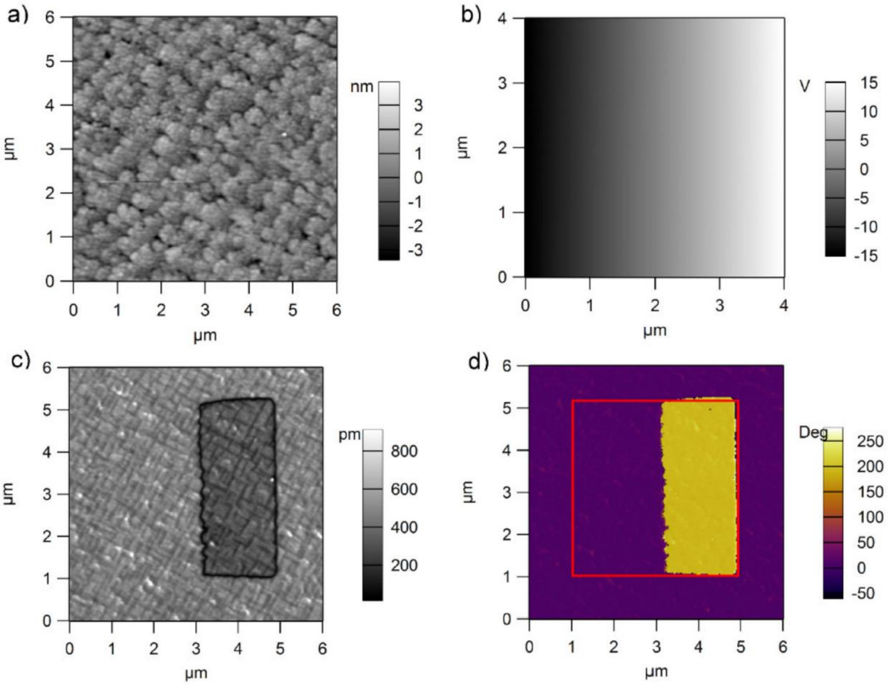

Figure 14. Topography (**a**), poling map (**b**) amplitude (**c**) and phase (**d**) of the PFM signal obtained after poling in the case of the PZT films deposited from commercial targets on a single crystal STO substrate with a bottom SRO electrode. The root mean square on the topography image (RMS) was estimated to about 0.5 nm.

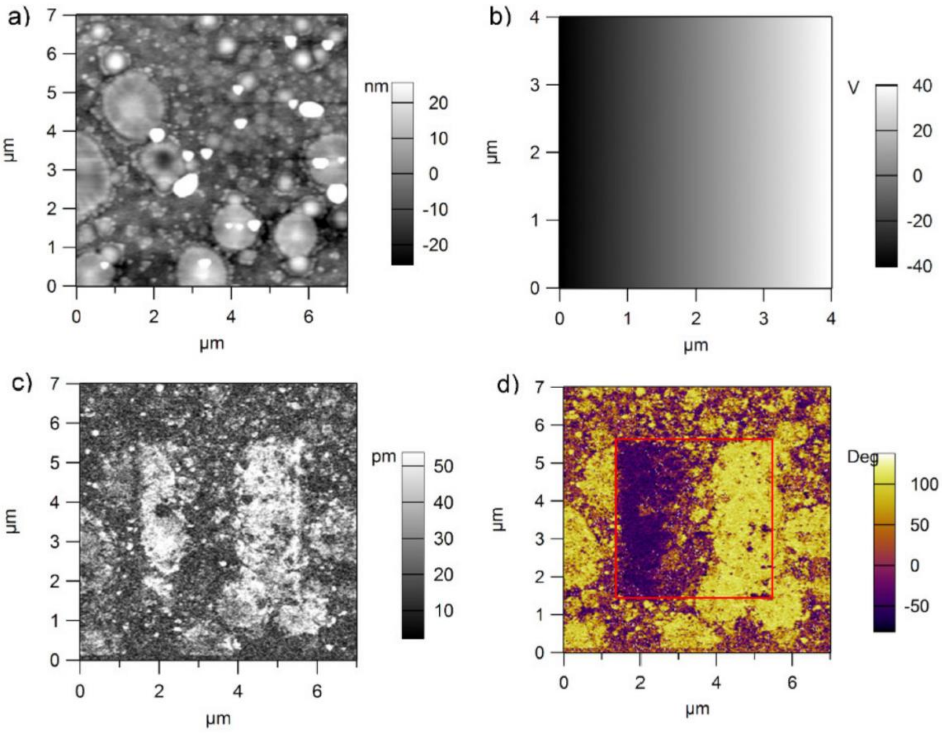

Figure 15. Topography (**a**), poling map (**b**) amplitude (**c**) and phase (**d**) of the PFM signal obtained after poling in the case of the PZT films deposited by sol-gel on an Si substrate with a bottom Pt electrode. The RMS was estimated to about 15 nm.

A deeper analysis of the current hysteresis loops during polarization reversal has led to the observation that the increasing part of the current peak associated to polarization reversal is linear, suggesting a ohmic like dependence of the recorded current on the applied voltage. A new hypothesis was proposed, that the polarization switching is triggered by charge injection to the electrode interfaces, as explained based on Fig. 16.

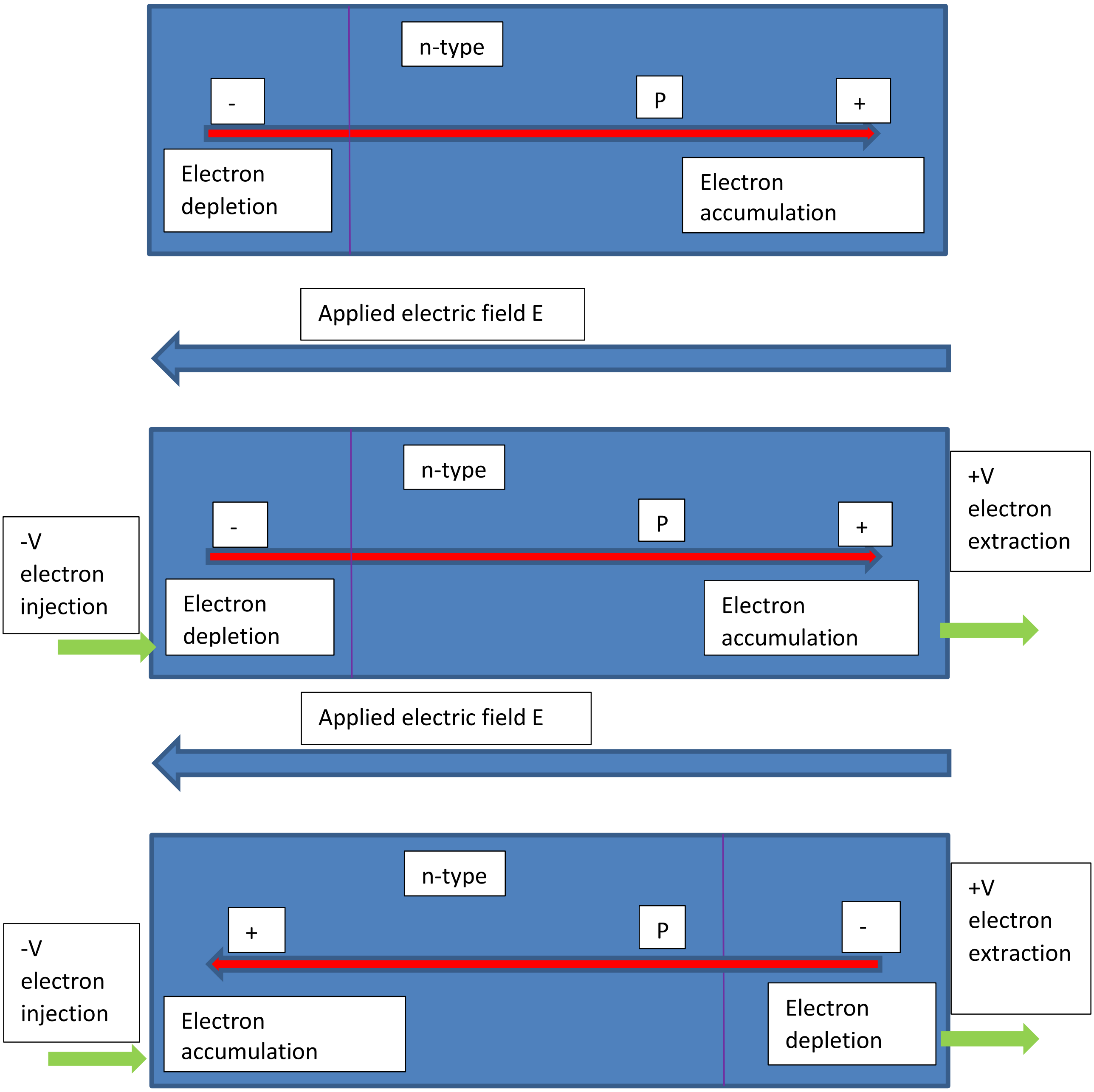

Figure 16. Sketch of the polarization switching triggered by the charge injection at the electrode interfaces.

The assumption is that we start from a mono-domain polarization state, as presented in the sketch shown in Fig. 16 upper line It is assumed that the PZT film has n-type conduction due to oxygen vacancies acting as donors. The polarization state is stabilized by accumulation of electrons at the electrode interface where positive polarization charge is located (right interface) and by positively ionized donors at the electrode interface where the negative polarization charge is located (left interface, where a depletion region is present). When an external electric field E is applied on the sample, as in Fig. 16 middle line, opposite in direction with the existing polarization and of increasing magnitude, then electrons start to be injected at the electrode interface with positive compensation charges and extracted from the interface with negative compensation charges. That means that the depleted region at the left interface will be reduced, while a depletion region starts to develop at the right interface. This injection of charges will gradually destabilize the polarization by annihilating the charges involved in the compensation of the depolarization field. When this charges are totally annihilated, then the depolarization field is no longer compensated and will force the polarization to align to the direction of the external electric field. Notably, the depolarization field in the initial state is having the same orientation as the applied electric field, but after polarization switching the direction of the depolarization field will be opposite to the direction of the external electric field, a situation that it is not favorable for stabilizing the new polarization state. The compensation of the newly established depolarization field requires positive charges at the right interface (electron depletion) and negative charges at the left interface (electron accumulation). It is exactly what the applied electric field does, injecting electrons at the left interface and extracting electrons at the right interface (see Fig 16 lower lien). Such a switching mechanism does not explicitly require domain formation, it is a homogeneous switching without domain formation and at a coercive field significantly lower than the intrinsic one.

A recent result was obtained this year. Multiferroic heterostructures of the colossal magnetoresistance manganite La1-xSrxMnO3 buried under ferroelectric BaTiO3 and PbZrxTi1-xO3 were investigated using soft-X-ray angle-resolved photoemission. The experimental band dispersions from the buried La1-xSrxMnO3 identify coexisting two-dimensional hole and three-dimensional electron charge carriers. The ferroelectric polarization modulates their charge density, affecting the coupling of the 2D holes and 3D electrons with the lattice which forms large Fröhlich polarons inherently reducing mobility of the charge carriers. Our k-resolved results on the orbital occupancy, band filling and electron-lattice interaction in multiferroic oxide heterostructures modulated by the ferroelectric polarization disclose most fundamental physics of these systems needed for further progress of beyond-CMOS ferrofunctional electronics (see Fig. 17 and article at position 28 in the publication list).

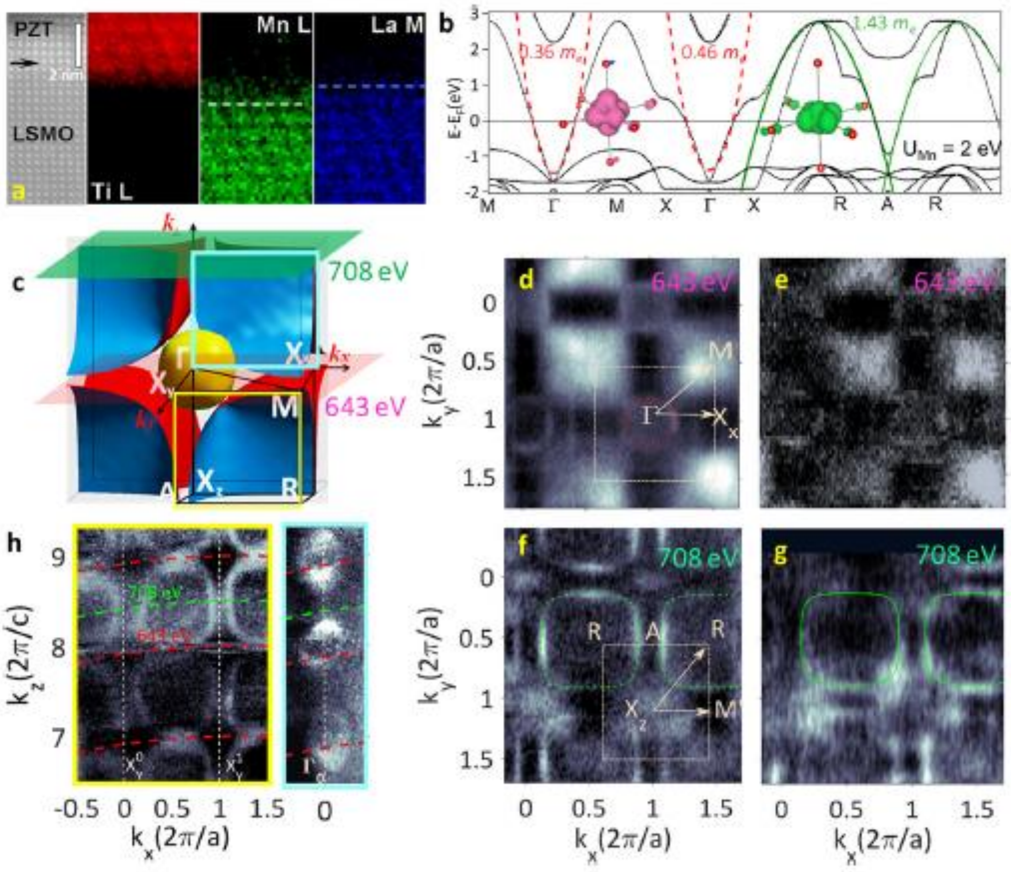

Figure 17 Structural and electronic properties. a High resolution high-angle annular dark-field scanning transmission electron microscopy image at the PbZr0.2Ti0.8O3-La0.7Sr0.3MnO3 (PZT|LSMO) interface, and Ti L, Mn L and La M maps at atomic level. The black arrow indicates the first ferroelectric unit cell (b) Theoretical Hubbard U - corrected density

functional theory band structure for SrTiO3-strained pseudocubic LSMO and (insets) local density of states integrated ± 0.2 eV around the Γ and A bands bottom. (c) Calculated Fermi surface (FS) for strained LSMO. d, e In-plane FS maps for respectively bare LSMO and BaTiO3 (BTO) interface, LSMO|BTO in the ΓMX planes recorded with hv = 643 eV. f, g In-plane FS maps for respectively bare LSMO and BaTiO3 (BTO) interface, BTO|LSMO in the XZAR.plane recorded with hv = 708 eV. h Experimental out-of-plane FS maps for the BTO| LSMO heterostructure in the XYMR and ΓXxXz planes. Colored frames enclosing the out-of-plane FSs encode the probed planes with the corresponding colors from (c).

Several articles were published in relation to this fundamental aspects of ferroelectrics, such as those found at positions 15, 19, 20, 24 in the publication list. Other manuscripts are in preparation and will be submitted in the next months.

2. Presentation of the obtained results, of the realized result indicators; what was not realized compared to estimated results mentioned in the project proposal (if it is the case), with justification (Prezentarea rezultatelor obţinute, a indicatorilor de rezultat realizaţi; a nerealizărilor înregistrate faţă de rezultatele estimate prin cererea de finanţare (dacă este cazul), cu justificarea acestora);

The obtained results were presented above in relation to the initial objectives of the project, and with some hot topics derived from the initial objectives. A synthetic table of realized result indicators is presented below.

Result indicator	**Assumed in the project proposal**	**Realized at the end of the project**	**Observations/Comments**
Published articles or submitted for publications	Minimum 30	**31**	There are a lot of experimental results that were not exploited through publications (e.g. doping on A sites in perovskites; doping of $BaTiO_3$ targets and films; various multilayer structures for multi-bit memory cells or for energy storage)-see **Table 1**
Cumulated impact factor (only for published papers)	Minimum 80	**145.939**	The average impact factor per published article is 5.032-see **Table 1**
Demonstrators	Minimum 2	**3**	n and p doped epitaxial ferroelectric films demonstrating control of polarization orientation by the doping type p-n ferroelectric hmojunction demonstrating resistive like behavior and negative capacitance effect memcapacitor based on tri-layer structure demonstrating multiple memory states
Patent requests	Minimum 2	**4**	See **Table 2**
Conference presentations	12	**26**	See **Table 3**
PhD thesis, finalized or close to finalize	Minimum 3	**8 (3 ended, 5 on-going)**	5 thesis are still on-going (3 at NIMP-CO and P1; 1 at INCDTIM-P2 and 1 at UPB-P3) 3 thesis were finalized during the project-see **Table 4**
Hired young researchers	4	**10**	4 PhD students and 6 post-docs were hired for the project
Workshops	1	**1**	Organized by the Coordinator, 14-16 of September 2021, Magurele, Romania

All the indicators were realized.

Table 1 List of published articles and of manuscript sent for publications

Nr.	Titlu, jurnal, etc.	Autori	IF	AIS
1	**Memcomputing and Nondestructive Reading in Functional Ferroelectric Heterostructures** PHYSICAL REVIEW APPLIED **12,** 024053 (2019)	**Georgia A. Boni, Lucian D. Filip ,* Cristina Chirila, Alin Iuga, Iuliana Pasuk, Luminita Hrib,**	4.532	1.832

	DOI 10.1103/PhysRevApplied.12.024053 WOS:000482588400002 ISSN 2331-7019	**Lucian Trupina, Ioana Pintilie, and Lucian Pintilie**		
2	**Polarization branches and optimization calculation strategy applied to ABO(3) ferroelectrics** MODELLING AND SIMULATION IN MATERIALS SCIENCE AND ENGINEERING **27**(4), 045008 (2019) DOI 10.1088/1361-651X/ab146e WOS:000464723100002 ISSN 0965-0393	**Filip, Lucian D.; Plugaru, Neculai; Pintilie, Lucian**	1.826	0.672
3	**Low value for the static background dielectric constant in epitaxial PZT thin films** SCIENTIFIC REPORTS **9**, 14698 (2019) https://doi.org/10.1038/s41598-019-51312-8 WOS:000489701600034 ISSN 2045-2322	**Georgia Andra Boni, Cristina Florentina Chirila, Luminita Hrib, Raluca Negrea, Lucian Dragos Filip, Ioana Pintilie & Lucian Pintilie**	4.011	1.286
4	**Designing functional ferroelectric interfaces from first-principles: Dipoles and band bending at oxide heterojunctions** NEW J. PHYS. **21**, 113005 (2019) https://doi.org/10.1088/1367-2630/ab4d8b WOS:000494826200005 ISSN 1367-2630	**Rusu, Dorin; Filip, Lucian; Pintilie, L;** Butler, Keith; **Plugaru, Neculai**	3.783	1.489
5	**Impact on Ferroelectricity and Band Alignment of Gradually Grown Au on BaTiO3** PHYSICA STATUS SOLIDI-RAPID RESEARCH LETTERS **13**(7), 1900077 (2019) DOI 10.1002/pssr.201900077 WOS:000477671800008 ISSN 1862-6254	Popescu, Dana Georgeta; **Husanu, Marius Adrian; Chirila, Cristina; Pintilie, Lucian; Teodorescu, Cristian Mihail**	3.729	0.790
6	**The interplay of work function and polarization state at the Schottky barriers height for Cu/BaTiO3 interface** APPLIED SURFACE SCIENCE **502**, 144101 (2020) DOI 10.1016/j.apsusc.2019.144101 WOS:000498639000070 ISSN 0169-4332	D.G. Popescu[1,*], **M.A. Husanu[1], C. Chirila[1], L. Pintilie[1] and C.M. Teodorescu[1]**	5.155	0.671
7	**(Ba,Sr)TiO_3 solid solutions sintered from sol-gel derived powders: An insight into the composition and temperature dependent dielectric behavior** CERAMICS INTERNATIONAL **46**(4), pp. 4180-4190 (2020) DOI 10.1016/j.ceramint.2019.10.136 WOS:000512219600018 ISSN 0272-8842	**Roxana Elena Patru[1],** Constantin Paul Ganea[1], **Catalina-Andreea Stanciu[2], Vasile-Adrian Surdu[2], Roxana Trusca[2], Adelina-Carmen Ianculescu[2*], Ioana Pintilie[1*], Lucian Pintilie[1]**	3.450	0.454
8	**Polarization Switching and Negative Capacitance in Epitaxial PbZr0.2Ti0.8O3 Thin Films** PHYSICAL REVIEW APPLIED **14,** 014080 (2020) DOI 10.1103/PhysRevApplied.14.014080 WOS:000553429500002 ISSN 2331-7019	**Lucian Pintilie, Georgia Andra Boni, Cristina Chirila, Luminita Hrib, Lucian Trupina, Lucian Dragos Filip, and Ioana Pintilie**	4.194	1.649

9	**Resistance hysteresis correlated with synchrotron radiation surface studies in atomic sp2 layers of carbon synthesized on ferroelectric (001) lead zirconate titanate in an ultrahigh vacuum** RSC Adv. **10**, 1522 (2020) DOI 10.1039/c9ra09131a WOS:000507296300035 eISSN 2046-2069	**Nicoleta Georgiana Apostol,** Daniel Lizzit, George Adrian Lungu, Paolo Lacovig, **Cristina Florentina Chiril˘a, Lucian Pintilie,** Silvano Lizzit and **Cristian Mihai Teodorescu**	3.119	0.516
10	**Energy storage performance of ferroelectric ZrO_2 film capacitors: effect of HfO_2:Al_2O_3 dielectric insert layer,** JOURNAL OF MATERIALS CHEMISTRY A **8**, 14171–14177 (2020). DOI: 10.1039/d0ta04984k WOS:000551538000029 ISSN 2050-7488	J. P. B. Silva*, J. M. B. Silva, K. C. Sekhar*, H. Palneedi*, **M. C. Istrate, R. F. Negrea, C. Ghica**, A. Chahboun, M. Pereira and M. J. M. Gomes,	11.301	1.999
11	**Polarization-dependent magnetism of the Ni/$BaTiO_3$ interface,** PHYSICAL REVIEW MATERIALS **4**, 034402 (11 pp.) (2020). DOI: 10.1103/PhysRevMaterials.4.034402 WOS:000517972500002 ISSN 2475-9953	**A. E. Bocirnea**, D. G. Popescu*, **C. Chirila**, R. M. Costescu, V. Kuncser, V. Stancu**, L. Trupina, I. Pasuk**, A. M. Vlaicu, **M. A. Husanu and C. M. Teodorescu**	3.337	1.154
12	**Effect of strain and stoichiometry on the ferroelectric and pyroelectric properties of the epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ films deposited on Si wafers** MATERIALS SCIENCE AND ENGINEERING B-ADVANCED FUNCTIONAL SOLID-STATE MATERIALS **266**, 115042 (2021) https://doi.org/10.1016/j.mseb.2021.115042 WOS:000621174300004 ISSN 0921-5107	**C. Chirila, G. A. Boni, L. D. Filip, M. A. Husanu,** S. Neatu, **C. Istrate**, L. G. Le Rhun, B. Vilquin**, L. Trupina, I. Pasuk**, M. Botea, **I. Pintilie, L. Pintilie**	4.706	0.605
13	**Negative capacitance in epitaxial ferroelectric capacitors evidenced by dynamic dielectric characterization** MATERIALS TODAY COMMUNICATIONS **26**, 102076 (2021) https://doi.org/10.1016/j.mtcomm.2021.102076 WOS:000635374100004 eISSN 2352-4928	**G. A. Boni, C. F. Chirila, L. D. Filip, I. Pintilie, L. Pintilie**	2.678	0
14	**The role of interface defect states in n and p-type Ge Metal-Ferroelectric-Semiconductor structures with $Hf_{0.5}Zr_{0.5}O_2$ ferroelectric** PHYSICA STATUS SOLIDI A: APPLICATIONS AND MATERIALS SCIENCE **218**, 2000500 (2021) https://doi.org/10.1002/pssa.202000500 WOS:000605180400001 ISSN 1862-6300	**Georgia A. Boni, Cosmin M. Istrate**, Christina Zacharaki, Polychronis Tsipas, Stefanos Chaitoglou, Evangelos K. Evangelou, Athanasios Dimoulas, **Ioana Pintilie, Lucian Pintilie**	1.759	0.471
15	**Ferroelectricity in thin films driven by charges accumulated at interfaces** PHYSICAL CHEMISTRY CHEMICAL PHYSIC **23**, 4085-4093 (2021) https://doi.org/10.1039/D0CP05617K WOS:000621595300004 ISSN 1463-9076	**C. M. Teodorescu**	3.430	0.854

16	**Accidental Impurities in Epitaxial Pb(Zr0.2Ti0.8)O-3 Thin Films Grown by Pulsed Laser Deposition and Their Impact on the Macroscopic Electric Properties** NANOMATERIALS **11**, 1177 (2021) DOI 10.3390/nano11051177 WOS:000657014200001 eISSN 2079-4991	**Georgia Andra Boni, Cristina Florentina Chirila, Viorica Stancu,** Luminita Amarande**, Iuliana Pasuk, Lucian Trupina, Cosmin Marian Istrate, Cristian Radu, Andrei Tomulescu,** Stefan Neatu**, Ioana Pintilie, Lucian Pintilie**	4.324	0.671
17	**Electro-active properties of nanostructured films of cytosine and guanine nucleobases** NANOTECHNOLOGY **32**, 415702 (2021) https://doi.org/10.1088/1361-6528/ac10e4 WOS:000675211200001 ISSN 0957-4484	Marcela Socol, **Lucian Trupina, Aurelian-Catalin Galca, Cristina Chirila, George E. Stan,** Aurel-Mihai Vlaicu, Anda Elena Stanciu, **Andra Georgia Boni, Mihaela Botea**, Anca Stanculescu, **Lucian Pintilie**, Bogdana Borca	3.551	0.706
18	**Nd-doped ZnO films grown on c-cut sapphire by pulsed-electron beam deposition under oblique incidence** APPLIED SURFACE SCIENCE **563**, 150287 (8 pp.) (2021). DOI: 10.1016/j.apsusc.2021.150287 WOS: 000691459900003 ISSN 0169-4332	M. Nistor, E. Millon, C. Cachoncinlle, **C. Ghica**, C. Hebert, and J. Perriere	6.707	0.873
19	**Band-order anomaly at the gamma-Al_2O_3/$SrTiO_3$ interface drives the electron-mobility boost** ACS Nano **15**, 4347–4356 (2021). DOI10.1021/acsnano.0c07609 WOS: 000634569100054 ISSN 1936-0851	A. Chikina, D. V. Christensen, V. Borisov, **M. A. Husanu**, Y. Z. Chen, X. Q. Wang, T. Schmitt, M. Radovic, N. Nagaosa, A. S. Mishchenko, R. Valenti, N. Pryds, and V. N. Strocov	15.881	3.681
20	**Homogeneous versus Inhomogeneous Polarization Switching in PZT Thin Films: Impact of the Structural Quality and Correlation to the Negative Capacitance Effect** NANOMATERIALS **11**, 2124 (2021). https://doi.org/10.3390/nano11082124 WOS:000690109600001 eISSN 2079-4991	**Lucian Pintilie, Georgia Andra Boni, Cristina Florentina Chirila, Viorica Stancu, Lucian Trupina, Cosmin Marian Istrate, Cristian Radu and Ioana Pintilie**	5.076	0.756
21	**New solid forms of the diuretic compound 4-Chloro Salicylic Acid-5-Sulfonamide** JOURNAL OF MOLECULAR STRUCTURE **1241**, 130682 (2021). https://doi.org/10.1016/j.molstruc.2021.130682 WOS:000670212600013 ISSN 0022-2860	Turza A., Miclaus O. M, **Zarbo L**., David M., Kacso I., Borodi G.	3.196	0.293
22	**Controlling polarization direction in epitaxial Pb(Zr0.2Ti0.8)O3 films through Nb (n-type) and Fe (p-type) doping** SCIENTIFIC REPORTS **12**, 755 (2022) https://doi.org/10.1038/s41598-022-04802-1 WOS:000804787700053 ISSN 2045-2322	**Cristina Florentina Chirila, Viorica Stancu, Georgia Andra Boni, Iuliana Pasuk, Lucian Trupina, Lucian Dragos Filip, Cristian Radu, Ioana Pintilie, and Lucian Pintilie**	4.380	1.285
23	**Progress and perspective on different strategies to achieve wake-up-free ferroelectric hafnia and zirconia-based thin films** APPLIED MATERIALS TODAY **26**, 101394 (2022)	J.P.B. Silva, K.C. Sekhar, **R.F. Negrea** , J.L. MacManus-Driscoll, **L. Pintilie**	10.41	1.775

	https://doi.org/10.1016/j.apmt.2022.101394 WOS:000820423500003 ISSN 2352-9407			
24	**Electrode dependence of polydomain stability in ferroelectric thin films** SCRIPTA MATERIALIA **213**, 114589 (2022) DOI 10.1016/j.scriptamat.2022.114589 WOS:000791227200005 ISSN 1359-6462	I. B. Misirlioglu and **L. Pintilie**	5.611	1.409
25	**Metastable ferroelectricity driven by depolarization fields in ultrathin $Hf_{0.5}Zr_{0.5}O_2$** COMMUNICATIONS PHYSICS **5**, 178 2022) https://doi.org/10.1038/s42005-022-00951-x WOS:000821604300002 ISSN 2399-3650	N. Siannas, P. Tsipas, C. Zacharaki, S. Chaitoglou, L. Bégon-Lours, **C. Istrate, L. Pintilie**, A. Dimoulas	6.368	2.365
26	**Nanoscopic correlations from curve fitting of photoelectron spectromicroscopy data cubes of lead zirconate titanate films** RESULTS IN PHYSICS **36**, 105436 (9 pp.) (2022). DOI: 10.1016/j.rinp.2022.105436 WOS: 000798982700001 ISSN 2211-3797	**L. E. Abramiuc**, L. C. Tănase, A. Barinov, **C. F. Chirilă, C. M. Teodorescu**	4.565	0.622
27	**Self-consistently derived sample permittivity in stabilization of ferroelectricity due to charge accumulated at interfaces** PHYS. CHEM. CHEM. PHYS.**24**, 5419 (2022) DOI: 10.1039/d1cp05222e WOS:000755898700001 ISSN 1463-9076	**C. M. Teodorescu**	3.676	0.823
28	**Ferroelectricity modulates polaronic coupling at multiferroic interfaces** COMMUNICATIONS PHYSICS **5**, 209 (2022) https://doi.org/10.1038/s42005-022-00983-3 WOS:000840841900001 ISSN 2399-3650	**Marius Adrian Husanu**, Dana Georgeta Popescu, Federico Bisti, **Luminita Mirela Hrib, Lucian Dragos Filip, Iuliana Pasuk, Raluca Negrea, Cosmin Istrate,** Leonid Lev, Thorsten Schmitt, **Lucian Pintilie**, Andrey Mishchenko, **Cristian Mihail Teodorescu** and Vladimir N. Strocov	6.368	2.365
29	**Memory Window Enhancement in Antiferroelectric RAM by Hf Doping in ZrO2** IEEE ELECTRON DEVICE LETTERS **43** (9), pp.1447-1450 (2022) DOI 10.1109/LED.2022.3189159 WOS:000845067200018 ISSN 0741-3106	Lomenzo, Patrick D.; Li, Songrui; **Pintilie, Lucian; Istrate, Cosmin M.**; Mikolajick, Thomas; Schroeder, Uwe	4.816	0.931
	TOTAL published articles	29	145.939	32.997
30	**Resistive-like behaviour in ferroelectric p-n bi-layer structures based on epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films** Submitted to ACS Applied Materials and Interfaces	**G. A. Boni, C. Chirila, L. Trupina, R. Cristian, L. D. Filip,** V. Moldoveanu, **I. Pintilie, L. Pintilie**	10.383	1.608
31	**Structural and electrical charge transport properties in oxygen deficient PbTiO3-δ ceramics**, Submitted to Materials Science & Engineering B.	I. Perhaița1, L. E. Mureșan, **S. Garabagiu, L. P. Zârbo**, G. Borodi, **C. Morari, L.-M. Pioraş-Ţimbolmaş**, A. Nicoara	3.407	0.544
	TOTAL manuscripts submitted or under revision		13.79	2.152

Table 2 List of submitted patent requests

	Nr.propuneri brevete	**Anul înregistrării**	**Autorul/Autorii**	**Numele propunerii de brevet**
OSIM	A00284	14.05.2019	Iuga Alin Romulus, **Boni Andra Georgia, Pintilie Lucian**	Method of nondestructive reading of a ferroelectric memory by pyroelectric detection.
OSIM	A00723	11.11.2019	**Boni Andra-Georgia, Chirila Cristina Florentina, Pintilie Lucian**	Method of characterization of ferroelectric structures in relation with polarization switching.
OSIM	A00226	28.04.2020	**Kuncser Andrei Cristian, Radu Cristian, Stănoiu Adelina,** Simion Cristian Eugen	Method of determination of specific surface by automated processing of electron tomograms.
EPO	EP22465566.2	10.11.22022	**Boni Andra-Georgia, Chirila Cristina Florentina, Pintilie Lucian**	Ferroelectric p-n homojunction with negative capacitance, method of making the same

With bold are members of the project team.

The list of conference presentations is not included because it is too long, only the invited contributions are given in the **Table 3**.

Nr.	Title of the presentation	Details about the conference	Authors
1	Recent results in the field of epitaxial ferroelectrics	IV. International Ceramic, Glass, Porcelain, Enamel, Glaze and Pigment Congress-SERES 2018, Eskisehir, 10-12 Oct., Turkey	**L. Pintilie**
2	Recent results and new functionalities in ferroelectric based structures	Sustainable Industrial Processing Summit & Exhibition, Phafos, Cyprus, 22-27 Oct. 2019	**L. Pintilie, I. Pintilie**
3	Strain driven defects in epitaxial thin films: HRTEM quantification and nanoscale mapping	EMN Epitaxy, Amsterdam, The Netherlands, 17-21 June 2019	**C. Ghica**
4	Recent Results Regarding the Fundamental Properties of Epitaxial PZT Ferroelectrics	Joint conference of the IEEE International Frequency Control Symposium and IEEE International Symposium on Applications of Ferroelectrics, 19-24 July 2020, on-line	**L. Pintilie, G. A. Boni, L. D. Filip, C. Chirila, L. Hrib,** V. Stancu, **R. Negrea, C. Istrate, L. Trupina, I. Pasuk, I. Pintilie**
5	Interplay between surface charge accumulation, conduction band filling and ferroic ordering, 13^{th} International	Conference on Physics of Advanced Materials (ICPAM–13), Sant Feliu de Guixols, September 24–30 2021	**C. M. Teodorescu**
6	BaTiO3-based systems with confined geometries: from synthesis to applications	International Conference CONSILOX, October 1-3 2021, Alba Iulia, Romania	**C. A. Ianculescu**
7	Microscopic model for ferroelectricity and its statistical treatment	IBWAP 2022 – 20th International Physics and Materials Science, Constanța, Romania, July 12–15, 2022	**C. M. Teodorescu**
8	Homogeneous versus non-homogeneous switching in ferroelectrics: can charge injection trigger the switching?	E-MRS Spring Meeting, 30 May-3 June 2022, on-line	**L. Pintilie**

9	Abnormal behaviour in p-n ferroelectric homojunctions	Global Expert Meet on Condensed Mater Physics, Rome, Italy, 15-19 June 2022	**L. Pintilie**
10	Homogeneous Versus Non-homogeneous Switching in Ferroelectrics: Novel Insights.	AMSE, 3rd International Congress on Advanced Materials and Engineering, Opatija, Croatia, 21-25 July 2022	**L. Pintilie**
11	Doping epitaxial Pb(Zr,Ti)O3 thin films	7th International Conference on Advances in Functional Materials Kyushu, Japan, 25-28 July 2022, moved for 9-12 of January 2023 (on-line)	**L. Pintilie**

With bold are members of the project team.

Table 4 Table of PhD thesis, students and newly hired personnel on the project.

No.	Name	Title of the thesis	Starting date	Expected date for public defence	Hired for the project	Team	Supervisor
Still on-goimg PhD theesis							
1	**Cristian Radu**	**Techniques of electronic microscopy used to study ferroelectric materials**	**Oct. 2019**	**Sept. 2023**	**2019**	**NIMP-CO**	**L. Pintilie (project director)**
2	**Istrate Marian Cosmin**	**Structural and microscopic information in nanostructured materials (chapter dedicated to doped HfO_2)**	**Oct. 2018**	**June 2023**	**2019**	**NIMP-P1**	**V. Teodorescu NIMP-UB**
3	**Pena Adrian Constantin**	**Control of spectral and transport properties of graphene by applying external fields (a chapter will be dedicated to graphene on ferroelectric surfaces).**	**Oct. 2018**	**June 2023**	**2019**	**NIMP-P1**	**C. M. Teodorescu (leader of P1 team)**
4	**Timbolmas Larisa Milena**	**Quantum simulations with QED circuits**	**Oct. 2018**	**May 2023**	**2019**	**INCDTIM-P2**	**V. Chis UBB Cluj**
5	Trusca Roxana	Nanomaterials with different architectures	Oct. 2018	Sept. 2023		UPB-P3	E. Andronescu UPB
PhD Thesis finalized during the project (in the first year when the project was first submitted in 2016)							
1	**Bucur Ioana Cristina**	**Correlation between ferroic order and charge accumulation at ferroelectric surfaces and interfaces.**	**Oct. 2015**	**Dec. 2018**		**NIMP-P1**	**C. M. Teodorescu (leader of P1 team)**
2	**Bocîrnea Amelia Elena**	**Magnetism and Schottky barriers at metal/semiconductor interfaces**	**Oct. 2015**	**Dec. 2018**		**NIMP-P1**	**C. M. Teodorescu (leader of P1 team)**
3	Nicoara Adrian	Materials alkaline activated with intumescent properties	Oct. 2015	Nov. 2019	2019 (as post-doc)	UPB-P3	A.Badanoiu UPB

With bold are PhD thesis related to the project.

Other young researchers hired for the project: NIMP-CO hired 2 post-docs; NIMP-P1 hired 2 post-docs; UPB-P3 hired 1 post-doc.

Information about the workshop organized in 2021 (chair was the project director).

Workshop announcement

IWMP

6th edition of the
INTERNATIONAL WORKSHOP OF MATERIALS PHYSICS

14th -16th of September 2021

The National Institute of Materials Physics (NIMP) announces the organization of the 6th edition of the International Workshop of Materials Physics (IWMP). The topic for the 2021 edition is dedicated to ferroelectric and multiferroic materials, with special emphasis on thin films, multilayers, super-lattices and nano-objects. Aspects related to modeling, fabrication, characterization and potential applications will be presented and discussed.

Similar to the first five editions, the 6th edition of IWMP is organized on invitation only. The aim is to attract well known researchers in the field, the final purpose being to establish new collaborations concretized in common publications, projects and exchange of personnel.

Young researchers willing to present their latest results on topics related to the main topic of the workshop are invited to submit a 2 page abstract (A4, Times New Roman 11, single spacing, 2 cm margins, including figures and references) to the organizers (pintilie@infim.ro). The best abstracts will be selected for oral presentations during the workshop.

The workshop will take place at NIMP premises located in Magurele, Romania.

Register in advance for this meeting:
https://us02web.zoom.us/meeting/register/tZMsc-CpqzksG9TekfNxNad_U0dZjriUBbci

After registering, you will receive a confirmation email containing information about joining the meeting.

Workshop Program
14 of September
9:00 – 9:10 Opening
9:10-9:50: Liliana Mitoseriu: **Scale-dependent properties in $BaTiO_3$ ceramics with structural instability**
9:50-10:30: Antonio Casares (on-line): **Multi-Modal-Correlative Microscopy** (sponsor presentation, Zeiss)
10:30-11:10: Maryline Guilloux-Viry (on-line): **Niobates Ferroelectric Thin Films: i/ Growth and Characterization of Perovskite and TTB Phases in the K-Na-Nb-O System; ii/ Potential of Application in High Frequency Miniature Tunable Devices**
11:10 – 11:30 coffee break
11:30-12:10: Michael Springborg: **Shapes (of) Matter**
12:10-12:50: Ibrahim Burc Misirlioglu (on-line): **Interface limited stability of ferroelectricity in thin film heterostructures: Electrostatic interactions, elasticity effects and phase coexistence**
12:50-13:30: Jorge Iniguez: **Optimizing steady-state negative capacitance**
13:30 – 14:30 lunch
14:30-15:10: Josep Fontcuberta: **Electron transport and plasmonic response of metallic oxides**
15:10-15:50: Valerie Demange: **Oxide nanosheets as seed layers for epitaxial growth of complex oxides**
15:50-16:30: Brian Rodriguez: **AFM tip-induced strain effects in $BiFeO_3$ films: from structural phase changes to polarization switching and nanofabrication**
16:30 – 16:45 coffee break
16:45-17:25: Marty Gregg (on-line): **Conducting Ferroelectric Domain Walls: Fundamentals of Transport and Device Opportunities**
19:15 dinner
15 of September
9:40-10:20: Marin Alexe: **Incommensurate spin crystal phases in ferromagnetic and ferroelectrics**
9:40-10:20: Pintilie Lucian: **Summary of the project results**

10:20-11:00: Gustau Catalán: **Switching dynamics and "giant" electrocooling effect of antiferroelectric PbZrO3.**
11:00 – 11:20 coffee break
11:20-12:00: Vincent Garcia: **Controlling antiferromagnetic textures in $BiFeO_3$ multiferroic thin films**
12:00-12:40: Nathalie Jedrecy (on-line): **Electro- and magneto- resistance in perovskite-based multiferroic junctions**
12:40-13:20: Pavlo Zubko (on-line): **Domains and lattice curvature in ferroelectric superlattices and supercrystals**
13:20 – 14:30 lunch
14:30-15:10 Torsten Granzow: **Anomalous photovoltaic effect in low-leakage solution-deposited $BiFeO_3$ films: Influence of doping and substrate stress**
15:10-15:50: Igor Stolichnov: **Switching in HfO_2-based ferroelectrics: an insight from nanoscopic analysis**
15:50-16:30: Marie-Helen Chambrier (on-line): **Ferroelectric state in a α-Ln2WO6 polymorphes stabilized in thin film**
16:30 – 16:45 coffee break
16:45-17:25: Gregory S. Rohrer (on-line): **High Throughput Studies of Metal Oxide Water Splitting Catalysts for the Development of Structure-Property Relations**
17:25: 18:05: Eric L. Altman (on-line): **Coupling Elastic, Electrostatic and Magnetic Responses in Transition Metal Silicate Monolayers**
19:15 dinner
16 of September
9:00-9:40: Nick Barrett: **Interface chemistry, oxygen vacancies, charge injection and polarization stability in ferroelectric hafnia-based films for non-volatile memories**
9:40-10:20: Uwe Schroeder: **Stabilization of the Ferroelectric Phase in Doped Hafnium Oxide Films: Influence of Dopants and Oxygen Vacancies**
10:20-11:00: Athanasios Dimoulas (on-line): **Scaling of HZO ferroelectric in Ge MFS for low power FTJ**
11:00 – 11:20 coffee break
11:20-12:00: Bertrand Vilquin: **Nanostructuration effect on the wake-up effect of $Hf_{0.5}Zr_{0.5}O_2$ capacitor**
12:00-12:20: Cristian Mihail Teodorescu: **Charge accumulation, conduction band filling and ferroicity**
12:20-12:40: Georgia Boni: **Dynamic dielectric characterization of ferroelectric capacitors- Evidencing negative capacitance**
12:40-13:00: Leontin Padurariu: **Dynamic Finite Element Method for describing complex dielectric properties in ferroelectric-based composites**
13:00-13:20: Marius Husanu: **Ferroelectricity and rhombohedral distortion in the electronic band structure of strained $PbZrTiO_3$**
Underlined are the presentations related to the project.

Analysing the obtained results and the reported result indicators, one can conclude that all the objectives were tackled during the project and all the indicators assumed in the project proposal were achieved. One can appreciate the value of the cumulated impact factor, proving that the vast majority of the articles were published in journals with high impact factors. New collaborations started with groups from Portugal, France, Germany, Greece, Luxembourg, Turkey. Some of these collaborations were concretised in project proposals, some of them funded, as for example:

- Energy Efficient Embedded Non-volatile Memory Logic based on Ferroelectric $Hf(Zr)O_2$ – H2020 project coordinated by CEA-France, with partners from France, Switzerland, Germany, Greece, and Romania, project started in 2018 and ended in 2021
- EIC Pathfinder Open proposal with partners from Luxembourg (coordinator) and Turkey, submitted in 2022 but not funded, will be resubmitted in 2023

Remarks on the cooperation between the 4 teams of the project: the cooperation was good between CO and P2 on the theoretical aspects of the doped ferroelectrics, there are still data to analyse that probably will be valorised in a common publication; very good between CO and P1, concretized in many common articles (e.g. 5, 6, 9, 11, 16, 18, 20, 22, 23, 25, 26, 28, 29 in the list of publications); very good between CO and P3 regarding the preparation of the targets (one common paper, 7 in the list of publications; others are in preparation, especially on doped $BaTiO_3$ targets and films).

3. Estimated impact of the obtained results, underlining the most significant obtained result (Impactul estimat al rezultatelor obţinute, cu sublinierea celui mai semnificativ rezultat obţinut).

One can estimate that the project had a significant impact on several levels:

- Scientific impact: a significant amount of knowledge was acquired during the project, the main results being shared with the international community through the published articles. **In the opinion of the project director the most important result is that successful n and p type doping was demonstrated in epitaxial PZT ferroelectric films and that true ferroelectric p-n junctions could be grown.** It was found that the properties of the junction depend on the order of growth and on the thickness of the component layers. These results were obtained after more than three years of intensive work to prepare various targets, to grown and characterize a vast number of samples, to analyse the experimental data and to develop suitable theoretical models to explain the properties of the doped films and of the p-n junctions. Even so, further work is needed to investigate the optimum doping concentration, the optimum thickness of the films, the p-n junctions obtained by combining films doped om A sites with films doped on B sites. The final goal being to obtain a rectifying ferroelectric p-n junction with low conduction for one direction of polarization and high conduction for the opposite direction.

  Other important scientific results, such as memcapacitive behaviour or stabilized negative capacitance effect, were obtained on tri-layer structures and on p-n bi-layer samples.
- Potential economic impact: some results may represent valuable solutions for some of the problems encountered in the field of applications based on ferroelectric materials, especially in microelectronics, more specifically in non-volatile memories. Here are some advantages of the structures studied in the present project: 1) A p-n ferroelectric homojunction with high and low conduction states depending on the polarization orientation can represent the simplest architecture for a ferroelectric non-volatile memory with non-destructive reading, far simpler than a ferroelectric field transistor (1 T memory, requiring three terminal structures, while a diode is a two terminal device); the results are encouraging but an estimated 4 years of work are necessary to obtain a functional proof of concept; this will be mainly technological work to accurate control of doping, to optimize the doping concentration and layer thicknesses and to build an array of diodes to demonstrate the memory function; potential behaviour as memristor is not excluded, opening applications in analogue computing. 2) optical non-destructive readout, as for example through a pyroelectric effect, can represent also an important step forward in the field of ferroelectric memories, opening the possibility to use ferroelectric layers in devices similar to blue-rays, only that in the IR domain; the problem to solve in this case is to optimize and maximize the pyroelectric reading and to eliminate the possible damaging effect if internal electric fields arising from the strain imposed by the substrate.
- Social impact: several young researchers were hired and trained during the project. This can be considered a gain of the project, most of them deciding to follow a carrier in research.

The updated web page of the project can be found at:
https://infim.ro/en/project/control-of-electronic-properties-in-ferroelectric-perovskite-heterostructures-from-theory-to-applications/

Project Director,

Dr. Lucian Pintilie

(*Nume, Prenume, Semnatura*)