CONTRACTOR

National Institute for Laser, Plasma and Radiation Physics

Program:	**TE**
Project type:	**Research projects to stimulate the establishment of young independent research teams**
Contract	**TE 14/2013**

Stage name: Stage I with two objectives:

1. Determination of deposition parameters

2. Optimization of deposition process for thein films of BZT- xBCT in order to integrate them in piezoelectric applications

In the frame of this stage the main aim has been related to the preparation of the targets and necessary support for subsequent experiments, aswell as to the adaptation of PLD and RF-PLD deposition systems for preparation of thin films and/or heterostructures of (Ba1_xCax)(Ti1-yZry)O3 (BCTZ). The fabrication of BCTZ targets with diffferent stoichiometries has played a very important role in this stage, based on the fact that the success of scientific objectives proposed in the project depends on the quality of the prepared targets (relative density, precise stoichiometry, physical dimensions). Preliminary experiments of thin film deposition starting from these targets have been performed. Also, there has been a lot of documentation and bibliographic research related to the last literature results on properties of thin films of BCTZ and testing devices based on pulsed laser deposition, and the realization of the web page dedicated to the project.

Objective I. Determination of deposition parameters

Activity 1.1. Target preparation; adaptation of the experimental set-up-ului and materials acquisition

In the last decades, based on the insight of phenomena happening during the diffusion and densification processes, ceramics technology emerged and covered a large area of applications. Because of its low production cost, conventional technology is, by far, the most used method for preparation of ceramic materials. The process of preparation of the samples involves the following main stages:

- preparation of powder mixture;
- formation of semi-finished material by compaction of powder mixture in dedicated matrice;
- sintering;
- finishing.

Solid sollutions of the binary system Ba(Ti0,8Zr0,2)TiO3 – (Ba0,7Ca0,3)TiO3 have been prepared by conventional ceramic technology in order to use them as targets in the growth of piezoelectric thin films by pulsed laser deposition. Specific tests and analyses as granulometry, differential scanning calorimetry (DSC), X-ray diffraction (XRD), densification tests, etc have been carried out. For this activity, the following types of powder have been acquired: barium carbonate, calcium carbonate, titanium oxide, zirconium oxide as shown in the attached financial documents.

Piezoelectric materials of Ba1-0,3xSr0,3xTi0,2(4+x)Zr0,2(1-x)O3 (BCTZO) type have been prepared by solid phase reaction. Samples of BCTZO45, BCTZO50 and BCTZO55 corresponding to composition with x = 0,45; 0,50 and 0,55 have been prepared from high purity powders (BaCO3, CaCO3, ZrO2 and TiO2) with about 1 μm granulation. The homogenization of the powders has been achieved in ethyl alcohol during 10 hours using a moara planatera cu vase si de bile de agat. In order to determine the calcination temperature, thermal analysis of homogene powders has been carried out by DSC, after the drying of the materials. Thus, after XRD validation, the powders calcinated in air at 1350 oC /5h have been ground again for 5 h in ethyl alcohol. After drying, granulation, sieving and uniaxial pressing in cylindrical matrices, samples with raw density of more than 50 % have been obtained, subsequently sintered in air between 1450 oC and 1525 ^{o}C for 4 hours. Ceramic targets of BCTZO45, BCTZO50 and BCTZO55 with densification bigger than 90% have been selected through XRD from these

samples sintered at 1500 ^{o}C / 4h, These targets have been polished in order to remove the superficial layers and to obtain an adequate geometry.

From preliminary XRD analisys, the calcinate powder at 1350^{0} C temperature was regrounded for 5 h in etilic alcohool. Samples with a preliminary density higher than 50% was obtained after driyng, granular, sieving and uniaxial presured in cilindrical matrice. Those samples was sinterized in air for 4 hours in temperatures range 1450 ^{o}C and 1525 ^{o}C. Ceramics targets BCTZO45, BCTZO50 si BCTZO55 with a density higher than 90% has been selected for XRD analisys. In order to remove the superficial layer and to achieve a adecvate deometry the samples sinterized at 1500^{0} C/ 4 h was carefully polished.

Activity 1.2. Structural and chemical and investigation for BZT-xBCT targets.

XRD difractograms for ceramics target show a perovskitic structure. For those systems, at room temperature can coexist few distinct crystallographic phases and for easy comparations the xrd results were Miller indexed in a pseudo cubic symmetry (Pm-3m) Fig 1. In order to avoid spliting effect superinposition $K_{\alpha 2}$ symetri was extracted.

XRD analysis show a slow gradual transition for tetragonal symmetry when proportions is changed from 45 to 55 and is cleary indicate in fig 2 on 42-48° domain.

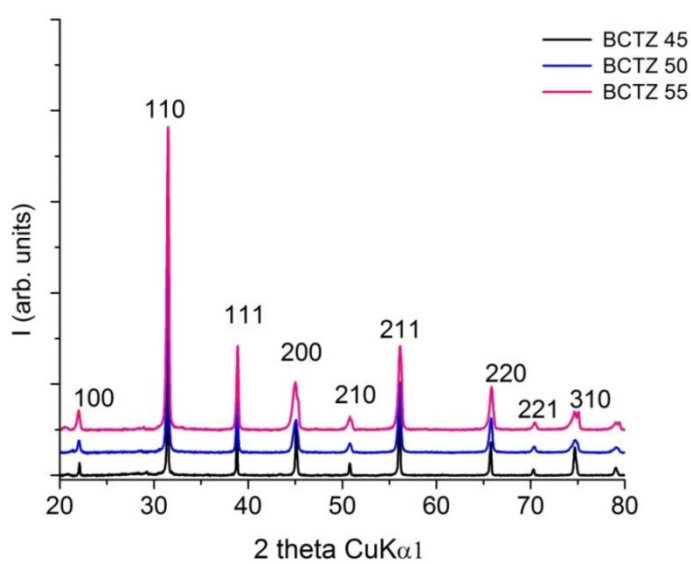

Figure 1 XRD difractogram for BZT-xBCT targets.

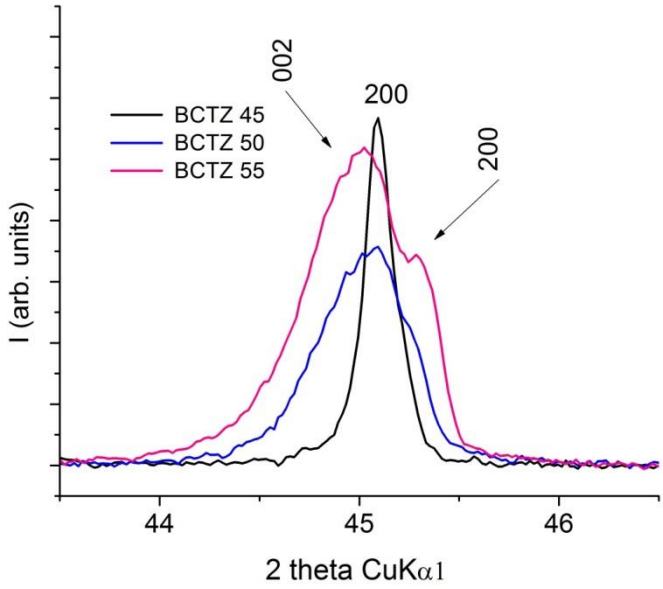

Figure 2 X-ray diffractogram of the three ceramic targets in the angular 42-48o

Objective II: The optimization process of BZT-xBCT thin films deposition for (the integration in) piezoelectric applications.

Activity 2.1. Deposition of BZT-xBCT thin films by PLD

The (Ba1_xCax)(Ti1-yZry)O3 thin films , also known as BCTZ , were deposited by laser ablation on a platinum coted silicon substrate (Pt/Si) and also on a strontiu titanate substrate doped with Nb (STON) using (BCZT45% , BCTZ50%) targets described earlier. The laser wavelength used (employd) was 193 nm (ArF) and laser fluence variated between 2.5 and 3 mJ/cm2. The substrate was mounted on an electric heating system, set at temperatures between 6250 and 7000C, maintained at distances of 4 to 5 cm from the target. During the deposition process , the reaction chamber was flooded with oxygen at pressures from 0.1mbar to 0.6 mbar. The number of laser pulses used was 15.000 and 45.000 . These experimental conditions are detailed in the next table. During the PLD deposition process the targets used were rotated and translated , in the same time, thus avoiding damaging them. Heating of the substrates was made at a rate of 500/min and cooling with 100/min in a (reactive) oxigen atmosphere at a pressure of 2.9 mbar.

Proba	Target	Collector	N_{Pulse}	Spot Area (mm^2)	Φ_{laser} ($J\backslash cm^2$)	λ (nm)
172	BCTZ 50%	Pt	15000	0.95	3	193
173	BCTZ 50%	Pt	15000	0.95	3	193
174	BCTZ 50%	Pt	15000	0.95	3	193
175	BCTZ 50%	Pt	15000	0.95	2.5	193
176	BCTZ 50%	Pt	15000	0.95	2.5	193
177	BCTZ 45%	Pt	15000	0.95	3	193
178	BCTZ 45%	Pt	45000	0.95	3	193
179	BCTZ 45%	Pt	45000	0.95	2.5	193
180	BCTZ 45%	STON	15000	0.95	3	193

The investigations carried aut after the deposition process included: surface topography performed using atomic force microscopy (AFM – made by Park XE-100), electron microscopy (SEM), structural analysis using X-ray diffraction (XRD – made by PANalytical Xpert MPB), chemical composition analysis through secondary ion mass spectroscopy (SIMSHiden Analytical), spectro-ellipsometry measurements (SE brand Woollam), ielectric constant at low frequencies with an impedance analyzer Agilent 4294 mark; PFM using an atomic force microscope Park XE-100 and a lock-in amplifier.

Activity 2.2. Deposition of BZT-xBCT thin films by RF-PLD

Thin films were deposited using pulsed laser deposition technique assisted by a radiofrequency discharge in oxygen-RF-PLD under the same conditions as those obtained by PLD, for comparison. The deposition conditions are listed in the table below.

Proba	Target	Collector	N_{Pulse}	Spot Area (mm^2)	Φ_{laser} ($J\backslash cm^2$)	λ (nm)	RF Power (w)
172 n	BCTZ 50%	Pt	15000	0.95	3	193	100
173n	BCTZ 50%	Pt	15000	0.95	3	193	200
174n	BCTZ 50%	Pt	15000	0.95	3	193	50
175n	BCTZ 50%	Pt	15000	0.95	2.5	193	100
176n	BCTZ 50%	Pt	15000	0.95	2.5	193	200
177n	BCTZ 45%	Pt	15000	0.95	3	193	100
178n	BCTZ 45%	Pt	45000	0.95	3	193	200
179n	BCTZ 45%	Pt	45000	0.95	2.5	193	100
180n	BCTZ 45%	STON	15000	0.95	3	193	100

Activity 2.3. Morphological Analysis AFM, SEM. XRD Structural Analysis. Chemical and Optical Analysis. Dielectric and Piezoelectric (PFM) Analysis.

In this stage were investigated BCTZ thin layers obtained both by PLD and RF-PLD. In the case of thin layers obtained by RF-PLD cracks were found on the surface of the thin layers, in the case of thin films deposited at high temperatures they even started to peel. This requires further investigation in order to determine the cause of BCTZ thin layers growth problems.

In the case of BCTZ thin films, atomic force microscopy images, scanned over an area of 20x20 μm2, presented in figures 3 and 4 shows a clean surface, without major defects like cracks, drops or strange formations, with a roughness in the order of nanometers.

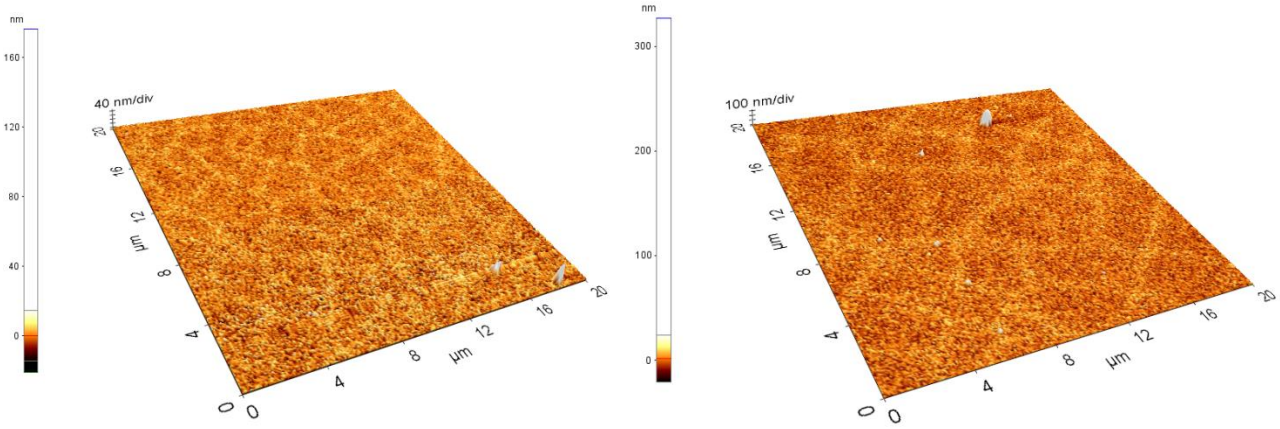

Figure 3.3D images representing the topographies of the BCTZ 50% films surfaces (left) and BCTZ 45% (right) deposited by PLD on Pt / Si substrate, 15.000 pulses, T = 700^0 C

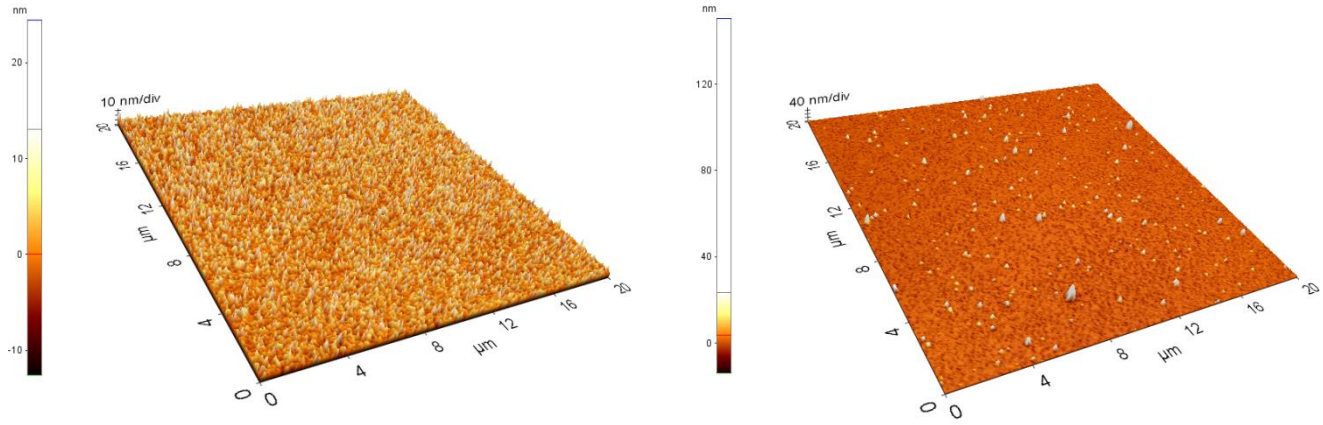

Figure 4. 3D images representing the topographies of the BCTZ 50% films surfaces (left) deposited at Tsub=6250 C on Pt/Si substrate and BCTZ 45%(right) deposited at Tsub=7000 C on STON, 15.000 pulses

Investigating the status of BCTZ thin films surfaces more detailed using scanning electron microscopy (SEM), is observed the occurrence of some well contoured crystallographic formations, with triangular shape. The images was taken in cross section indicate both a columnar growth of the film as well the appearance of some defects in the structure of the film namely some cracks (from place to place) which appear on all the film thickness. These cracks exist the most likely because of the thermal coefficient difference between the constituent materials of the substrate (Pt/Si) and BCTZ, a faster cooling lead to appearance some of tensions in the film structure. This aspect of the films growth can be remedied through a much slower cooling.

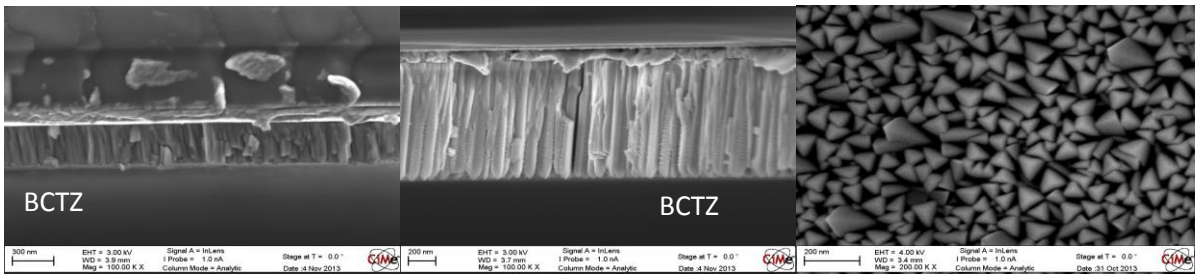

Figure 5 SEM images for BCTZ thin films 45% deposited on the Pt / Si substrate at 15.000 pulses (left) and 45.000 pulses (center, right), Tsub=7000 C

X-ray diffractograms indicate an increases on various crystallographic directions, thus for the films deposited under the same temperature conditions, oxygen pressure, substrate-target distance, number of pulses but on different substrates namely on platinizat silicon and strontium and barium titanate doped with niobium, the films grow oriented differently. For BCTZ/Pt these grow preponderant oriented (020) and for BCTZ crystallites are preponderant oriented (111). In both cases is observed an increase on other directions but these are still smaller for BCTZ/STON.

In the case of the BCTZ 50% target deposited as films on Pt / Si substrate was aimed the effect of substrate temperature. XRD Diffractograms (fig.6) indicate the formation of some preferentially oriented films (110) and (111) with a better crystallinity in the case of sample deposited at higher temperature.

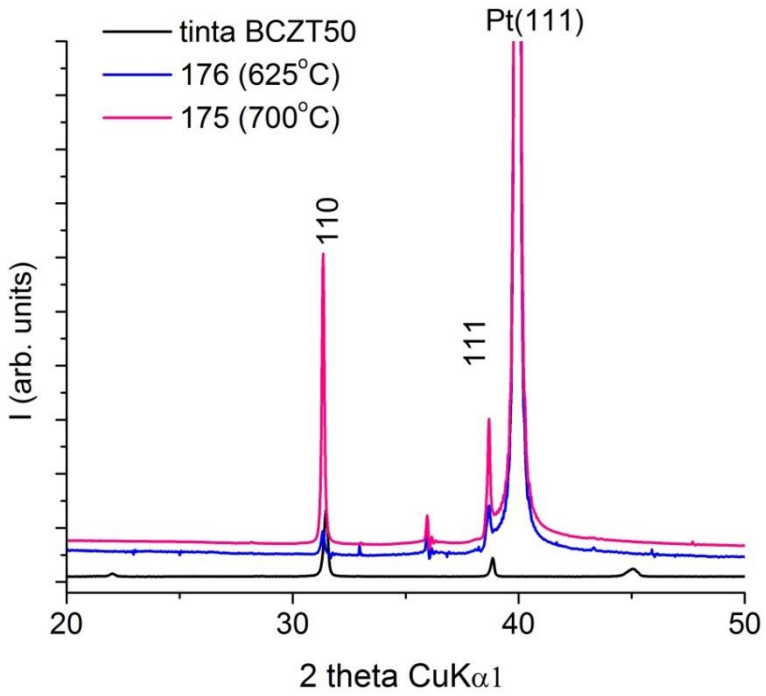

Figure 6: X-ray diffractogram of the target BCZT50 and films obtained from this on substrates Pt / Si deposited at 625 ° C and 700 ° C

In the case of deposition of BCZT50% was studied the nature of the effect of the substrate used and the thickness of the film controlled from the number of pulses. The substrate Pt/Si induces a preferential increase (110) and (111). Is noticed the differences in intensity in the case of the thicker film.

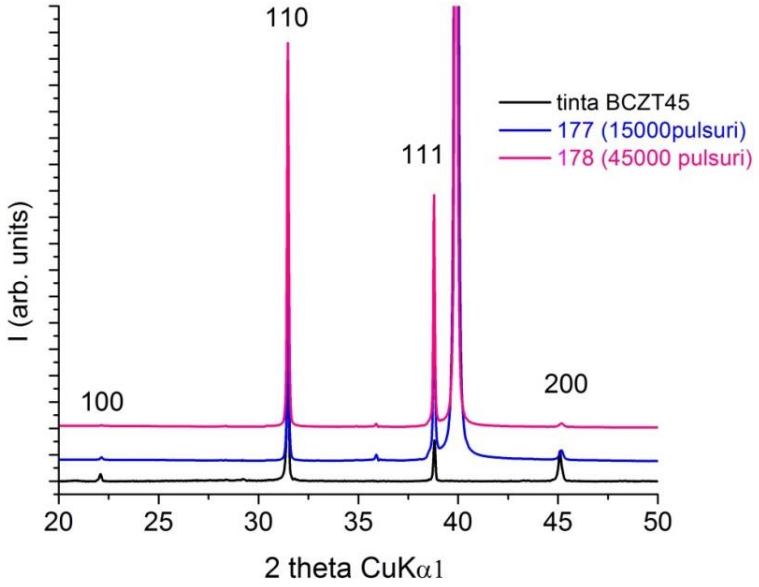

Figura 7: Difractograma de raza X a tintei de BCZT45 si a filmelor obtinute din la 15.000 de pulsuri si 45.000 de pulsuri

The deposition on STON induces the growth only on the crystllografic (001) direction. Composition analysis determined/performed using the mass spectroscopy (SIMS), for BCTZ films deposited from different concentrations targets indicates the presence of all necesary chemical elements (Ba, Ca, Ti, Zr), thus proving the transfer of stoichiometry of the composition from the target at substrate. The zirconiu perecentage is higher in the BCTZ45% sample.

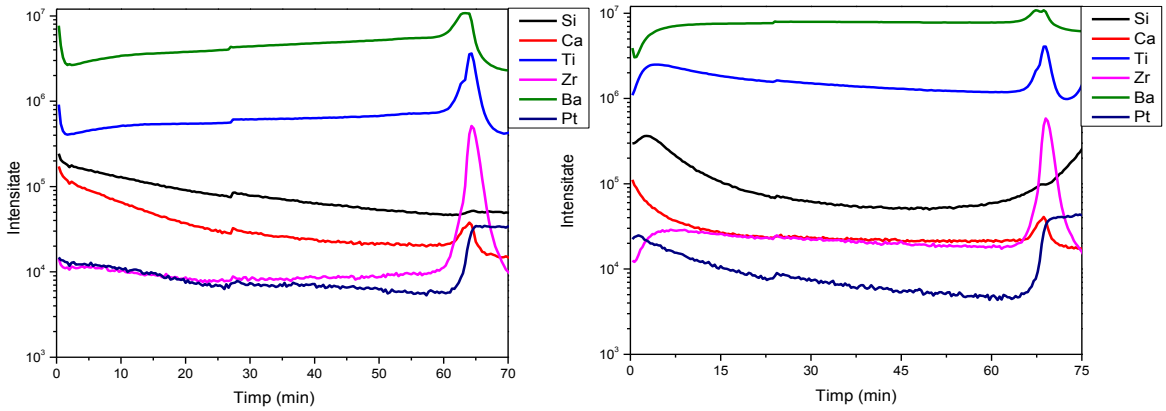

Figure 8: SIMS for thin films of BCTZ 50% (left) and BCTZ 45% (right) deposited on Pt/si in the same conditions.

In terms of optical properties, determined with spectroellipsometry in spectral range of 300-1000nm, it was observed that in (figure 8) the refractive index values are grouped into two different areas , namely the higher values for BCTZ 45%(samples 177-179) and lower values for BCTZ 50% (samples 173-176). The higher refractive index values are obtained for sample 178, with n=2.35 (λ=500 nm). These values are normal for this type of materials, the barium titanate having at the same wavelength n=2.43.

From the point of view of extinction coefficient and implicitly of optical absorption for all the samples where obtained small values k<0.2 (λ=300 nm). At wavelengths greater/higher than 450 nm the thin films are optical transparent.

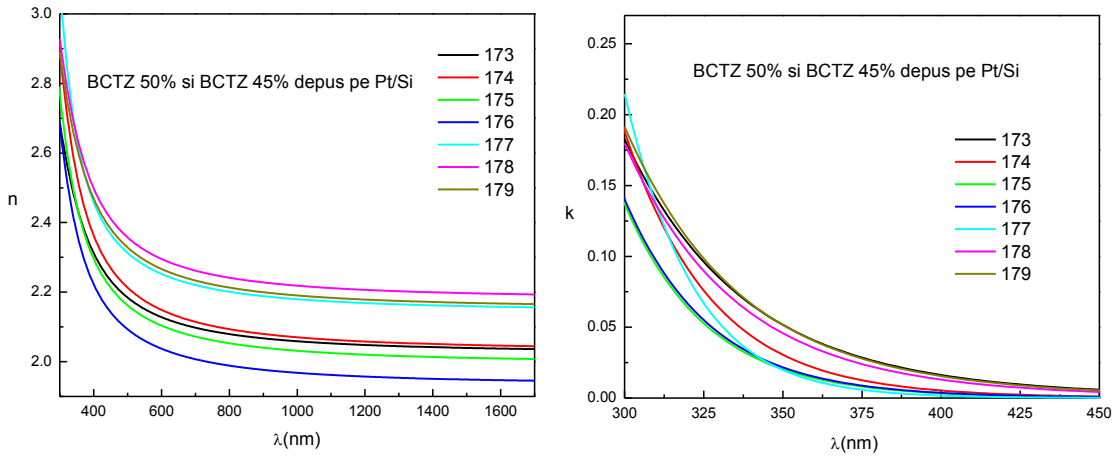

Figure 9: n and k dependencies by wavelength for BCTZ 45% and 50% thin films deposited on Pt/Si substrate

With the help of spectroellipsometry the thicknesses and roughnesses of the BCTZ thin films were calculated, these/which are presented in the table below. Comparing the thicknesses results of BCTZ 45% growth/deposited under the same conditions but at different number of pulses (15- 45 thousand), resulting similar values as those obtained using/with SEM (see figure above). In the case of roughness these are not comparable with the results from Atomic Force Microscopy analyzes, are higher those that result from SE. These differences can be explained in two ways : the areas which are performed on, the experimental measurements are different compared with those two techniques (AFM – μm2, SE – mm2). There is a possibility to exist certain formations on the surface derived from the further contamination or from the sample. A second explanation may come from the fact that the rough layer in ellipsometry is approximate as being composed by 50% material and 50% air, in reality the percentage can be dissimilar/distinct. The small thickness of the films are obtained in the cases where the substrate-target distance was greater(174-176) or in the case of decresing of the laser fluency(175-179).

Proba		Grosime (nm)	Rugozitate (nm)
173	BCTZ 50	335.797±2.61	17.826±1.26
174	BCTZ 50	174.873±1.68	40.310±1.21
175	BCTZ 50	120.477±0.941	34.011±1.01
176	BCTZ 50	106.520±0.508	35.734±0.491
177	BCTZ 45	319.049±1.49	24.808±0.528
178	BCTZ 45	803.831±7.63	50.982±0.87
179	BCTZ 45	498.645±6.09	51.138±0.946

Determination of the dielectric frequency function behavior was determined using an impedance analyzer. More accurate was made capacity,dielectric losses measurements, the relative dielectric constant was calculated with the approximation of the plan capacitor using the determined thicknesses from above.

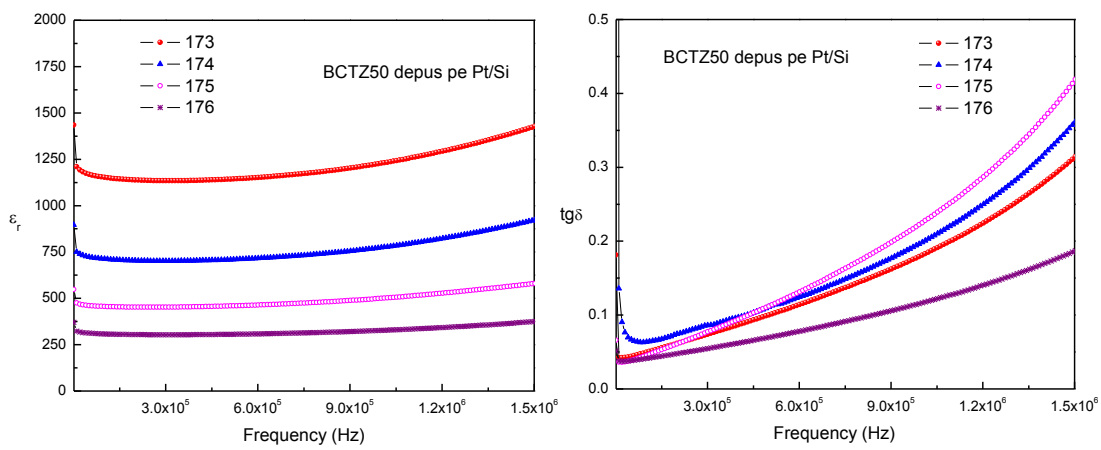

Figure 10 The dependencies of dielectric constant and of frequency losses for BCTZ 50% thin films deposited on Pt/Si.

The highest values of relative dielectric constant (~1500) where obtained for the films deposited from BCTZ 45% target while for BCTZ 50% maximum value was 1250.

From the point of view dielectric losses, they are of the order of 10-2 at low frequencies and comparable as values for both compositions.

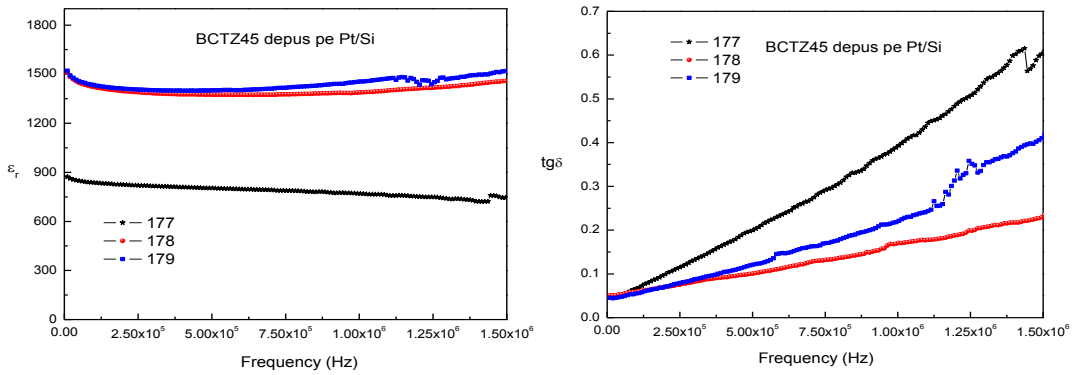

Figure 11: Dependencies of dielectric constant and loss frequency for thin films deposited BCTZ 45% Pt / Si

Piezoeletric response microscopy have been performed using a PARK XE 100 system. The cantilevers used were with platinum tip which were brought into contact with the surface film, then a dc electric field was applied and a ac test field between the lower electrode and the metalalic tip of Pt. The field was generated using a dc voltage amplifier and the ac test with a lock-in amplifier. The same lock-in generator was used to analyze the vertical deflection signal from the PSPD, to extract the amplitude and the phase of the cantilever oscillation due to local deformation induced by the applied dc electric field. Thin layers of BCTZ / Pt / Si shows a piezoelectric hysteresis which confirms the piezoelectric characteristics of these thin films. Piezoelectric coefficient d33 values were of about 150-188 pm/V, a high value for thin film structure as compare with the literature reported values..

Activity 2.4: Management, analysis of results, dissemination, editing

Due to the good results obtained so far in the project compared with existing reports in the literature have been made following dissemination activities in three conferences:

1. INDLAS 2013 - In May 2013, was supported by the oral presentation titled "Pulsed laser deposition of lead-free growth (Ba1-xCax) (ZryTi1-y) O3 Thin Films and Their structural, optical and electrical properties" in which properties of (Ba1-xCax) (ZryTi1-y) O3 films deposited on Pt / SiO2 / Si substrates by pulsed laser deposition were presented. Following the structural and morphological investigations, it was found that the film shows smooth surfaces with pure perovskite phase. They also have moderate dielectric constant (≈ 450) and relatively low dielectric loss (≈ 3.5%).

2. COLA 2013 – In this conference was disseminated a poster entitled "The structural, optical and electrical properties for triple-point composition (Ba1-xCax) (ZryTi1-y) O3 thin films obtained by Pulsed Laser Deposition". Were the results obtained from the deposition of thin films of perovskite unleaded (Ba1-xCax) (ZryTi1-y) O3 applicability in MEMS devices. They present a dielectric constant (≈ 1200) and dielectric losses lower than those previously reported (≈ 1.5%). Piezoelectric measurements on BCTZ films deposited on Pt / Si have shown promising behavior.

3. E-MRS 2013 Spring Meeting - TITLE poster with "Pulsed laser deposition of lead-free growth (Ba1-xCax) (ZryTi1-y) O3 thin films and their structural, optical and electrical properties" was held in this. The structural, optical and electrical properties on BCTZ films on Pt / Si obtained by pulsed laser deposition substrates were disseminated.

It was also made the project web page: http://ppam.inflpr.ro/TE_14_ro.htm.

In conclusion, we can say that the first phase objectives were achieved considering the results presented in the report. Also, activities from stage 2014 are already underway, namely:

- Getting heterostructures based on thin films of BZT-x BCT with high piezoelectric properties.

Project manager,

Dr. Nicu Doinel Scarisoreanu