Scientific report

Project name: *ADVANCED RESEARCH ON NBT-BT FERROELECTRIC THIN FILM SYNTHESIS USING RADIOFREQUENCY ASSISTED PULSED LASER DEPOSITION*

Stage name: Stage II/2009 **(**final) having one main objective:

- Structural, morphological, and electrical characterization of NBT-BT thin films with low doping (x=0.06) obtained by PLD.

During this stage the main research activity was especially linked to the morphological, structural and electrical characterization of the (1- x)$Na_{0.5}Bi_{0.5}TiO_3$-x $BaTiO_3$ thin layers with low doping x=0.06 at%, obtained in the previous stage by pulsed laser deposition - PLD. As can be seen in the following paragraphs, in spite of the financial constraints of this project, but also due to existing utilities and consumable materials (Si and Pt/Si substrates, dichroic mirrors for the laser, and a Pt target) already existing in our laboratory, results are promising, with a manuscript being already submitted for publication in Applied Physics A.

As was mentioned in the project proposal, the useful electrical properties of this complicated stoichiometric material can be retrieved in a very narrow doping interval, called morphotropic phase boundary (MPB), namely between $BaTiO_3$ dopings of x=0.06-0.08 at%. Structurally, the coexistence of two crystalline phases, rhomboidal and tetragonal, means that the NBT-BT target is within the region of morphotropic phase transition (MPT) between the structure with rhomboidal symmetry and that with tetragonal symmetry. This aspect brings another element of difficulty in the obtaining of ferroelectric NBT-BT films with properties adequate for industrial applications. But, with the aid of a thorough parametric study one can understand the influence of experimental parameters on the nucleation processes and growth of thin films and, implicitly, on the properties shown by these. In short, besides other parameters (laser fluence, wavelength or repetition rate), the influences of the following are found to be important:

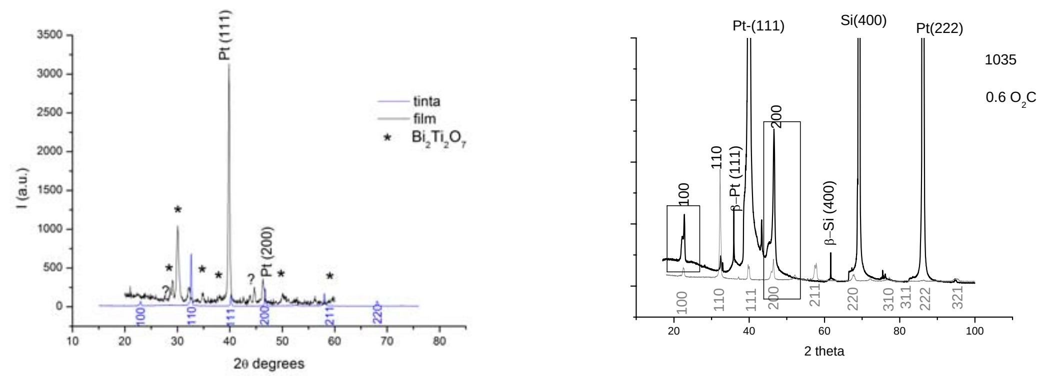
- the used oxygen partial pressure - most of the studies published underline the problem of oxygen vacancies - *Z. H. Zhou et al. (Appl. Phys. Lett. 85, 2004)* underline the role of these vacancies in oxygen-deficient films as being determinant for dielectric losses at low frequencies ($<10^6$ Hz) and for the increase of dc conductivity.
- the substrate temperature - dependency not very often studied in the case of this material, but extremely important.
- the type of the chosen substrate: *Yiping Guo et al. (Thin Solid Films 517, 2974-2978, 2009), Daisuke Akai et al. (Solid State Sciences 10, 928-933, 2008)* - the most utilized substrate is Pt/Si because it is relatively cheap and it can be used for electric measurements.

- Activity 1.1: Morphological characterization of the obtained thin films

1.**The variation of the oxygen partial pressure between 0.1 and 1 mbar O_2** brings important changes to the morphology of the surface, an important fact in the performances of any ferroelectric material. From a morphological point of view, NBT-

BT/PtSi heterostructures were investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). From the atomic force microscopy images, obtained using a Park generation microscope, the aspect of the surface, but also its roughness, are different, but the lack of droplets can be noticed. At higher oxygen pressure rather large crystallites (620 nm) begin to appear, but aspect is irregular and discontinuous. On the other hand, at lower pressures, the size of the crystallites decreases to 400 nm for 0.6 mbar O_2 and 200 nm for 0.1 mbar O_2, the surface of the films having a continuous and relatively smooth aspect.

The acquisition for the structural analysis by X-ray diffraction was done using a PANalytical X'Per MRD diffractometer in a Bragg-Brentano geometry. The scanning was continuous with a step of 2 θ=0.02 and an acquisition time per step of 25 s pr 250 s for domains in which an emphasis of structural changes was needed. In the case of NBT-BT thin films deposited at a partial oxygen pressure of 0.1 mbar one can notice the presence of a parasite pyrochlore phase, $Bi_2Ti_2O_7$, which is barium deficient (Fig. 1a). The same behaviour can also be found for samples deposited at higher pressure of 1 mbar O_2. On the other hand, at a pressure of 0.6 mbar O_2 the formation of polycrystalline films with random orientations can be observed, without the presence of parasite phases (Fig. 1b). In these NBT-BT/PtSi a splitting of the (100) and (200) maxima can be observed which suggest the formation of a structure in the boundary region of the rhomboidal-tetragonal morphotropic phase transition in which the two phases coexist. Moreover, the tetragonal maxima are more intense, which indicates a preferential orientation in the (100) direction.

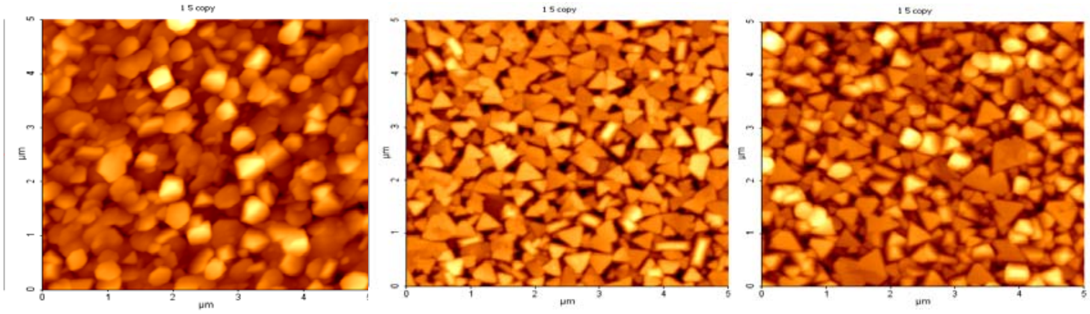


a) 0.1 mbar O_2

b) 0.6 mbar O_2

Figure 1. Diffractograms of the NBT-BT thin films deposited on PtSi substrates at various O_2 pressures.

2. **The temperature variation of the Pt/Si substrate** also leads to significant changes in the morphology of NBT-BT/PtSi films. From the AFM analysis, one can notice that the modification of the substrate temperature (650^0C, 700^0C, 730^0C), also changes the shapes and sizes of the crystallites (Fig. 2).



a) 650^{0}C b) 700^{0}C c) 730^{0}C

Fig. 2. AFM images of NBT-BT/PtSi films obtained at different deposition temperatures.

Figure 3 shows the 3 diffraction spectra compared to the X-ray diffraction spectra of the used target, in the angular ranges 2θ=20-25, and 44-48, respectively. The spectra indicate the formation of polycrystalline films with random orientations, with a phase structure which is strongly dependent on the substrate temperature. For the film deposited at a higher temperature, of 730^{o}C, a single phase can be noticed, namely the rhomboidal one. For the films deposited at lower temperatures a splitting of the (100) and (200) maxima can be noticed, which suggest the formation of a structure in the boundary region of the rhomboidal-tetragonal morphotropic phase transition in which the two phases coexist.

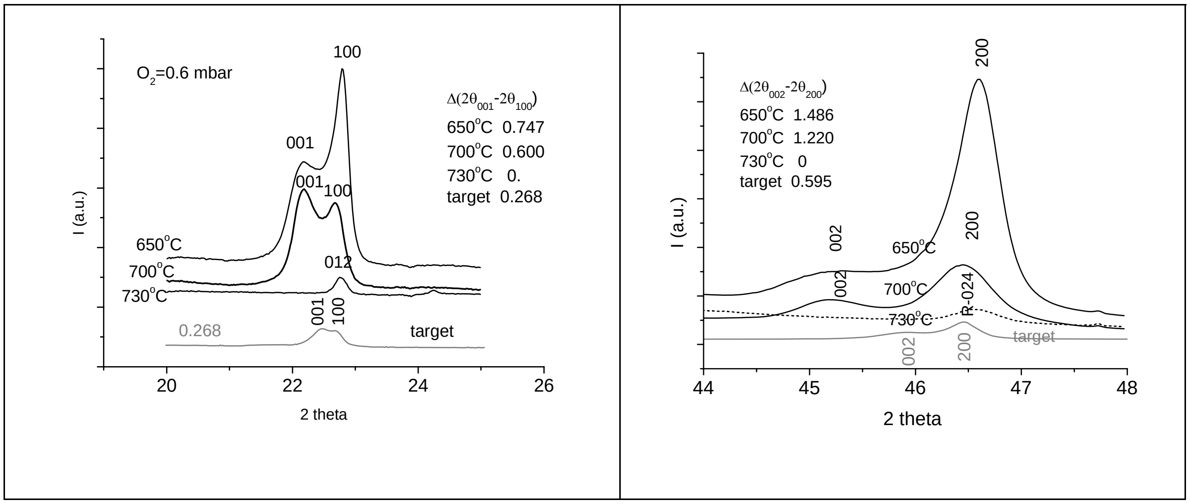


Figure 3. Detailed angular regions 2θ=20-25, and 44-48, respectively, of the X-ray diffraction spectra of films deposited at various substrate temperatures compared with the used target.

- *Activity 1.2: Dielectric and ferroelectric characterization of the obtained thin films.*

On certain samples which have been selected based on their good structural and morphological properties - those obtained at an oxygen pressure of 0.6 mbar O_2, dielectric and ferroelectric spectroscopy studies were performed. In Figure 4 we present the capacity variation (proportional to the dielectric permittivity) during heating and the dielectric losses at various frequencies: 1, 2, 5 and 10 kHz, respectively. The increase of the dielectric permittivity at temperatures above 160^{0}C can be attributed to the phase transformation from ferroelectric relaxor (rhomboidal phase) to antiferroelectric phase (tetragonal phase).

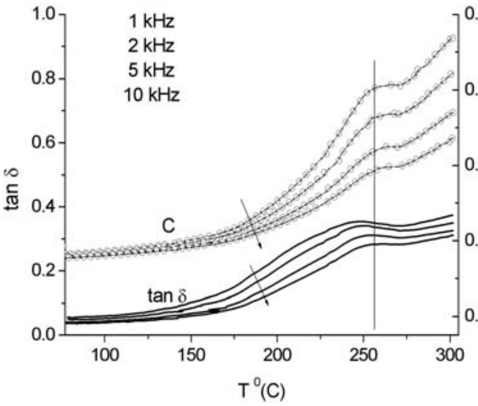


Fig. 4. Dielectric permittivity and relative losses as a function of temperature at different frequencies for the NBT-BT/PtSi films.

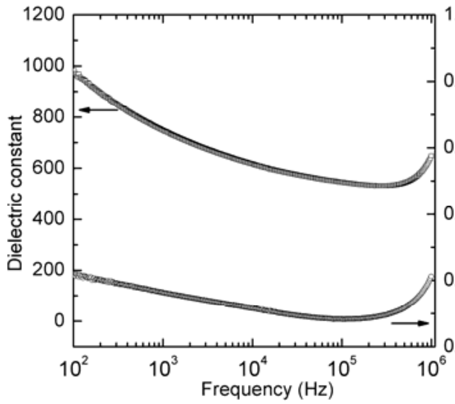


Fig. 5. Dielectric permittivity and relative losses as a function of frequency for the NBT-BT/PtSi films.

In figure 5 we present the behaviour of the dielectric permittivity (dielectric constant) and of the dielectric losses as a function of frequency.

- *Activity 1.3: The study of the influence of experimental parameters (substrate temperature, laser fluence, oxygen pressure) on the properties of NBt-BT films.*

This stage has the role to synthesize the best results obtained in the previous activities and to bring forth the possible activities to follow in order to improve the properties of the NBT-BT films:

1) when discussing the oxygen pressure, it is very clear that the optimal value for the growth of NBT-BT/PtSi thin films is 0.6 mbar O_2. The films obtained at other pressure have a discontinuous aspect or present cracks, which means that the dielectric and ferroelectric behaviour cannot be determined through conventional methods. Another set of samples was produced in order to be able to check the reproducibility of the process and the conclusions are the same.

2) when discussing the substrate temperature, the obtained results are impressive compared to those found in the scientific literature on this topic. The possibility to produce NBT-BT/PtSi thin films that are situated within the morphotropic phase boundary from a compositional and crystallographic structure point of view is a new and innovative fact and will need to be capitalized by publishing in specialized journals with high ISI coefficient or by the realization of a patent. The problem of the high porosity of the films remains to be solved. Choosing an Nb:SrTiO type of substrate which has a lower crystalline lattice mismatch with NBT, of ~ 3%, and using a high laser fluence are good premises to achieve lower porosities, relative deformation and induced defects.

Due to this project, our work was presented at the International Conference on Laser Ablation 2009 in the form of a poster entitled: „**Lead-free ferroelectric thin films obtained by pulsed laser deposition**". Moreover, based on the good results discussed above, this work was awarded the 3rd prize, and the manuscript was sent for publication in APPLIED PHYSICS A.

In conclusion, the results presented in this report prove that the objectives of the second stage of the project were achieved. Moreover, another manuscript remains to be sent for publication in APPLIED PHYSICS LETTERS based on the results obtained in this stage.

Project Director,

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