**UNIVERSITY OF CRAIOVA**

**FACULTY OF PHYSICS**

# ABSTRACT OF PhD THESIS

## *OBTAINING AND CHARACTERIZATION OF ADVANCED MATERIALS THIN FILMS*

***Scientific Coordinator:***

***Professor Dr. Maria Dinescu***

***PhD Student:***

***Morîntale Emilian***

**Craiova**

**- 2010 -**

## ABSTRACT (Thesis)

# *INTRODUCTION*

Dielectric and ferroelectric materials have attracted great interest in recent decades, both in the form of bulk materials as well as in the form of thin films. These materials have many attractive properties for applications in microelectronics, i.e.: capacitors, waveguides, infrared detectors, semiconductor memory circuits (non-volatile memory used as ROM and RAM volatile memories), etc.

The technology of ferroelectric RAM or FRAM memory circuits has penetrated the memory circuits market. FRAM memories use the ferroelectric effect to store information. The ferroelectric effect describes the ability of a material to store an electric polarization in the absence of an applied electric field. Using the ferroelectric effect allows the use of low voltages both for reading as well as for writing data, these devices being used in applications such as mobile communications, to acquire and store data in the absence, for a certain period of time, of the voltage. These devices have been integrated in the metering systems, in computers, appliances or industrial automation.

Developing such type of devices requires both obtaining materials with high dielectric constant, for applications in integrated circuits, memory chips and materials with high thermal stability and low dielectric loss for the realization of filters with applications to mobile and satellite communications. Prestigious laboratories in Europe, USA, Japan, etc.., numerous universities and research institutes, investigate the scientific and practical aspects of ferroelectrics and dielectrics for their use in developing new electronic devices and high-frequency electronics. A widely used class of materials are the perovskite materials: the perovskite structure has $ABO_3$ composition, where A is a mono-, bi-or trivalent element, and B, is an penta-, tetra-or trivalent element. In this category of perovskitive materials we can mention as interesting compositions $BaTiO_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and Ba $(Zn_{1/3}Ta_{2/3})O_3$ (BZT). They have attractive properties and due to the high dielectric constant both in ferroelectric state as well as in paraelectric state, but aslo due to the relatively small losses.

(Ba, Sr) $TiO_3$, for example, has high values of electrical permittivity and shows a nonlinear behavior in the vicinity of its transition temperature. This variation of electric permittivity in the presence of an electric field ("tunability" - acordability) has allowed the fabrication of performant microwave devices.

Current research is focused towards obtaining materials which are structurally complex, with multiple applications, with controlled mechanical, electrical, optical and magnetic properties; the development of such materials and components is a priority for all developed countries.

## *CONTENT*

In this Thesis are presented the results regarding the compounds with complex properties, namely: i) dielectric and ferroelectric materials in the form of thin films obtained by pulsed laser deposition technique (PLD) and ii) organo metallic compounds, in bulk or as thin films, obtained by MAPLE (matrix assisted pulsed laser evaporation). In Chapter 1 (which folows the introduction) is presented a brief description of dielectric and ferroelectric materials and also of the current trends regarding the use of these materials. Therea are also presented the general aspects of the ferroelectricity phenomenon, the ferroelectric properties of the materials and, general aspects of organo metallic compounds.

In Chapter 2 is described the technology for obtaining thin films by pulsed laser deposition method, the PLD experimental system, with emphasis on the advantages and disadvantages of laser ablation, setting of the deposition conditions and the thin film growth mechanisms. Chapter 3 presents the main experimental techniques used for the characterization of the thin films, namely atomic force microscopy (AFM), electron microscopy (EM), X-ray diffraction (XRD), spectroscopic ellipsometry (SE) and thermal analysis (TA). Chapters 4-7 present the original results on obtaining thin films and their structural and morphological characterization. Chapter 4 presents the optical and structural properties of the $Ba(Mg_{1/3}Ta_{2/3})O_3$ thin films obtained by RF plasma assisted pulsed laser deposition. Chapter 5 includes impedance spectroscopic studies of PLZT thin films obtained by PLD and RF-PLD. Chapter 6 investigates the thermal stability of barium and strontium titanate, BST over a wide temperature range. Chapter 7 deals with Cu (II) 2,2 '- dihydroxy azobenzene organometallic compounds, including their thermal and structural analysis as well as the characterization of the thin films deposited by MAPLE technique.

The last part is dedicated to conclusions.

# *CONCLUZII*

1. Using pulsed laser deposition technique (PLD), radio-frequency assisted pulsed laser deposition (RF-PLD) and matrix assisted pulsed laser evaporation techniques (MAPLE), we obtained thin films of Ba $(Mg_{1/3}Ta_{2/3})O_3$ - magnesium and barium tantalate (BMT, a promising dielectric material mainly due to the low dielectric losses and high dielectric constant ($\varepsilon \approx 25$)), thin films $(Pb_{0.67}La_{0.22})$ $(Zr_{0.2}Ti_{0.8})O_3$ - ferrolectric material with important applications in electronic devices and, thin films of Cu (II) 2,2 '- azobenzene dixidroxi, $Cu(DAB)_2$, organo-metallic compound of economic interest with direct applications as thin films for nonlinear optics, optical memory or active membranes in sensor devices.

2. The thin BMT films were morphologically, structurally and optically characterized by using atomic force microscopy (AFM), X-ray diffraction (XRD) and spectroscopic ellipsometry (SE). The structural characterization of the thin films shows that they present a polycrystalline cubic structure with a slightly preferential orientation for the films obtained at a lower temperature of the substrate. The spectroellipsometry investigations reveal that the refractive index varies depending on the deposition parameters. AFM analysis indicates rough surfaces with roughness values of

approximately 35-40 nm for all the samples. Using the transmission spectra and assuming that the band-band transition is a direct transition it was obtained a value of ≈ 4.72 eV of the band gap. The value of 23 of the dielectric constant of the thin film, is close to the large sample value. The dielectric losses are high, but still attractive for applications.

3. Using impedance spectroscopy, we studied the ac conductivity and dielectric properties of $(Pb_{0.67}La_{0.22})(Zr_{0.2}Ti_{0.8})O_3$ (PLZT 22/20/80) thin films obtained by pulsed laser deposition (PLD) and by radiofrequency plasma assisted pulsed laser deposition. Investigations by X-ray diffraction showed the presence of the pure perovskite phase with cubic symmetry. Therefore, were highlighted structural and morphological differences between the films grown by PLD and RF-PLD; the films grown without RF plasma show an amorphous phases and are almost randomly oriented while the films grown by RF-PLD have a pure crystalline perovskitie phase with (100) orientation. The improved crystallinity of the thin films deposited by RF-PLD is due to the RF plasma containing ionized and excited oxygen species. This plasma beam acts in the early stages of the film's growth and in the period between the laser pulses. The ac conductivity measurements of the $Pb_{0.67}La_{0.22}(Zr_{0.2}Ti_{0.8})O_3$ thin films as a function of frequency, amplitude of the alternative field (ac) and the intensity value of the continous field (dc) have shown that radio frequency discharge significantly improves the electrical properties. It was noticed a dependence of the conductivity with the frequency power at high frequencies and/or low amplitude of the field and also a dominant contribution of the dc conductivity at low frequencies and/or high amplitude of the field. The measurements at high dc field (up to 150 kV/cm) indicate that the films grown by RF-PLD have ac conductivity decreased by an order of magnitude compared to the films grown by PLD, most likely due to a smaller number of oxygen voids. This result confirms the advantage of RF-PLD to the classical PLD technique regarding the incorporation of oxygen and minimizing the oxygen vacancies in the film structure.

4. By MAPLE technique we obtained thin films of Cu (II) 2,2 '- azobenzene dixidroxi, further called Cu(DAB)$_2$. To investigate the compound in massive state we used Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), UV-VIS spectroscopy, and, optical microscopy with polarized light. The thin films were analyzed by atomic force microscopy (AFM) and Spectroelipsometry. Cu(DAB)$_2$ material was investigated by thermal analysis in the form of both bulk and thin film form. The results indicate a conservation of the original structure of the compound in the form of thin film, for the samples deposited by MAPLE technique, at 266 nm wavelength against the 355 nm wavelenght. The thermal analysis of the compound in bulk state indicates a high thermal stability in nitrogen atmosphere as compared to air and shows a different behavior for the second stage of decomposition. Also, because the adhesion of the complex compound to the substrate strengthens the bonds, the thermal stability of Cu(DAB)$_2$ increases when it is deposited on silicon substrate. AFM images reveals smooth surfaces and continuous thin films deposited on silicon substrate. The samples have a roughness (RMS) in the 20 nm-26 nm range and do not present droplets. SEM analysis of the Cu(DAB)$_2$ powder shows an acicular crystals microstructure, arranged in a compact array, which is typical for such compounds.

The crystals are between 8-11 μm in length and between 1.5-3 μm in thickness. The spectroelipsometry measurements indicate thickness of the films in the 100 nm - 310 nm range, depending on the deposition conditions, and a refractive index of 2.11 at the wavelength of 550 nm. SEM studies on thin films deposited by MAPLE reveal similar characteristics with the AFM images: the thin layers appear smooth with a few small droplets. In cross section, the thin films were evaluated to have a thickness between 100 and 300 nm depending on the number of laser pulses, with no significant thickness differences between the samples deposited at 266 nm and 355 nm respectively. For 30 000 laser pulses at 266 nm, the thickness of the thin film was ~ 137 nm. The diffraction spectra of "bulk" 2,2 '-dihydroxy azobenzene (DAB) and bulk Cu(DAB)$_2$ samples presents low crystal symmetry and large unit cell, but the bonding of copper in $Cu(DAB)_2$ leads to changes in the structure, such as the consolidation of the unit cell and/or changing the crystal symmetry (displacement of peaks at small angles). Peaks are also broader for the $Cu(DAB)_2$ samples, indicating smaller crystallite sizes. The characteristics of the cell unit and its dimensions for $Cu(DAB)_2$ were determined to be (P21/c); a = 6.8347(6), b = 23.857(2) and c = 9.1596(8) Å; α = 90°, β = 108.9° and γ = 90° (the crystal system is monoclinic). The calculated density is 1.4 $g \cdot cm^{-3}$. Similar diffraction spectra were recorded for the thin films on both types of samples, deposited on silicon and quartz. A good correlation between thermal analysis and SE data was obtained in terms of chemical structure, revealing a good preservation of the initial structure of the compound deposited in the form of thin film by MAPLE technique at a wavelength of 266 nm, as compared to the samples deposited at 355 nm. Micrometer pixels of the compound were transferred on glass plates by LIFT technique (Laser-Induced Forward Transfer), with the purpose of being used as active membranes in the construction of chemoselective sensor devices.

### *Selective references:*


[1] Constantinescu C, Emandi A, Vasiliu C, Negrila C, Logofatu C, Cotarlan C, Lazarescu M. Thin films of Cu(II)-o,o'-dihydroxy azobenzene nanoparticle-embedded polyacrylic acid (PAA) for nonlinear optical applications developed by matrix assisted pulsed laser evaporation (MAPLE). Appl Surf Sci 2009;255: 5480–5

[2] C. Constantinescu, A. Emandi, C. Vasiliu, C. Negrila, C. Logofatu, C. Cotarlan, M. Lazarescu, Applied Surface Science 255 (2009) 5480–5485

[3] Eason RW. Pulsed Laser Deposition of Thin Films. John Wiley & Sons; 2007

[4] Lippert T, Dickinson J, Chemical and spectroscopic aspects of polymer ablation: Special features and novel directions. Chem Rev 2003;103:453-85

[5] Pique A, McGill RA, Chrisey DB, Leonhardt D, Mlsna TE, Spargo BJ, Callahan JH, Vachet RW, Chung R, Bucaro MA. Growth of organic thin films by the matrix assisted pulsed laser evaporation (MAPLE) technique . Thin Solid Films 1999;355-356:536-41

[6] Houser E, Chrisey D, Bercu M, Scarisoreanu N, Purice A, Colceag D, Constantinescu C, Moldovan A, Dinescu M. Functionalized polysiloxane thin films deposited by MAPLE for advanced chemical sensor applications. Appl Surf Sci 2006;252:4871–6

[7] Lippert T, Chrisey D, Purice A, Constantinescu C, Filipescu M, Scarisoreanu N, Dinescu M. Laser processing of soft materials. Rom Rep Phys 2007; 59:483-98

[8] C. Constantinescu, **E. Morîntale**, V. Ion, A. Moldovan, C. Luculescu, M. Dinescu, Thermal, morphological and optical investigation of Cu(DAB)2 thin films grown by laser-assisted techniques for sensor development, trimis la Journal of Organometallic Chemistry

[9] Badea M, Olar R, Marinescu D, Segal E, Rotaru A. Thermal stability of some new complexes bearing ligands with polymerizable groups. J Therm Anal Calorim 2007;88:317-21

[10] K. Wakino, Ferroelectrics 91 (1989) 69

[11] N.D. Scarisoreanu, G. Dinescu, R. Birjega, M. Dinescu, D. Pantelica, G. Velisa, N. Scintee, A.C. Galca, Appl. Phys. A—Mater. Sci. Process. 93 (2008) 795

[12] **E.Morîntale**, D. Neacşa, C. Constantinescu, M. Dinescu, P. Rotaru, Thermal behaviour and spectral analysis of the organometallic complex Cu(II) 2,2' – dixydroxy azobenzene, Physics AUC, vol.20 (part1), 37-42 (2010)

[13] **E.Morîntale**, C. Constantinescu, M. Dinescu, Thin films development by pulsed laser-assisted deposition, Physics AUC, vol.20 (part1), 43-56 (2010)

[14] C.Constantinescu, **E. Morîntale**, N. Scărişoreanu, A. Moldovan, M. Dinescu, Nanometric-sized Fe/Pt thin films with perpendicular anisotropy developed by layer-by-layer pulsed laser deposition, Physics AUC, vol.20 (part1), 73-82 (2010)

[15] **E.Morîntale**, N. Scărişoreanu, M. Dinescu, P. Rotaru, Thermal stability of BST in a vast range of temperature, Physics AUC, vol.20 (part1), 83-89 (2010)

[16] C. Constantinescu, **E. Morîntale**, Ana Emandi, Maria Dinescu, P. Rotaru, Thermal and microstructural analysis of Cu(II) 2,2'-dihydroxyazobenzene and thin films deposition by MAPLE technique, J Therm Anal Calorim DOI 10.1007/s10973-010-0971-x

[17] N.D. Scarisoreanu, A.C. Galca, L. Nedelcu, A. Ioachim, M.I. Toacsan, **E. Morintale**, S.D. Stoica, M. Dinescu, Optical and structural studies on $Ba(Mg_{1/3}Ta_{2/3})O_3$ thin films obtained by radiofrequency assisted pulsed plasma deposition, Applied Surface Science, Volume 256, Issue 22, 1 September 2010, Pages 6526-6530

[18] F.Craciun, M.Dinescu, N. D. Scarisoreanu, C.Capiani, C. Galassi, **E Morintale**, Impedance spectroscopy study of relaxor ferroelectric PLZT thin films obtained by PLD and RF-PLD, IOP Conf. Ser.: Mater. Sci. Eng. 8 012003,doi: 10.1088/1757-899X/8/1/012003

[19] C. Constantinescu, A. Rotaru, P. Rotaru, Ana Emandi, **E. Morintale**, V. Ion, A. Moldovan and Maria Dinescu, Thermal analysis and thin film deposition by matrix assisted pulsed laser evaporation of Cu(II) 2,2'-dihydroxy azobenzene, MEDICTA 2009, The 9th Mediterranean Conference on Calorimetry and Thermal Analysis, Marseille

[20] C. Constantinescu, P. Rotaru, **E. Morintale**, V. Ion and Maria Dinescu, Polyacrylic acid: thermal stability and thin films deposition by matrix assisted pulsed laser evaporation (MAPLE), Frontiers in Polymer Science, International Symposium Celebrating the 50th Anniversary of the Journal polymer, 7-9 June 2009, Congress Centrum Mainz, Germany