



UNIVERSITY OF CRAIOVA  
FACULTY OF SCIENCES  
DEPARTMENT OF PHYSICS

**Thermally induced functionalization of thin films of  
molecular materials obtained by laser techniques**

**Summary of the PhD thesis**

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## Abstract

Today competing bulk, thin films have garnered an increasing interest as alternative form of solid materials that may exhibit enhanced properties and eventually numerous possibilities of applications that will influence our everyday life, in: medicine, pharmacy, electronics, optics, mechanics (abrasive, hard or impermeable coatings), sensing (for gases or for bio-marking), etc. Characterisation and properties of surfaces, together with the applications at the nano- and micro-scale of such materials have opened a totally different world for the solid state physics. Nanotechnology for optoelectronics is targeting always for recent advancements of producing or functionalizing nanomaterials and thin films with semiconducting, conducting or dielectric properties; novel materials with enhanced stability and functional properties are continuously synthesized, possibilities of handling them and solving hot issues being thus easier to be addressed.

As long as the demand for reduced dimensions and advanced properties of materials is continuously increasing, the thin film deposition methods are still in the spotlight and undergo unceasing improvement. Of those, physical techniques are more appropriate to fulfil such demands; therefore they were widely used, especially as laser-based ones.

In the thesis entitled: „Thermally induced functionalization of thin films of molecular materials obtained by laser techniques / Funcționizarea indusă termică a filmelor subțiri de materiale moleculare obținute prin tehnici laser”, the study regarding the thin film deposition by matrix-assisted pulsed laser evaporation (MAPLE) technique was carried out for the three distinct main categories of soft molecular materials: inorganic complexes (zinc benzoate, precursor for ZnO), organics materials (azoic derivatives with liquid crystalline properties), and polymers for optoelectronics (PVC, PAA and PANi). MAPLE regularly, it is possible to observe the high degree of comprehensiveness this technique encompasses: it is one of the most straightforward and flexible way to obtain reproducible and high quality thin films of molecular materials of large interest for various applications. In order to determine the stability domains of matter, and the limits of use for the technological processing of materials which contains it – that may happen at high temperatures, thermoanalytical studies are primarily requested; knowing the kinetic parameters governing their transformations represent a very important tool for understanding their dynamic structure-behaviour relation, the interactions within components and their applicability domains, for predicting the appropriate temperature regimes needed in the technological processes, and may be a strong indication when deciding if to use of a certain material or another in diverse applications.

The interconnection between the results of the thermal and kinetic studies, with those obtained for the thin films fabricated by MAPLE are evident; the present study accomplishes the proposed objectives and brings significant contribution to the usefulness of the thin films obtained by MAPLE technique.



## Published and disseminated results

### *Articles published by the author in ISI ranked journals:*

1. Matrix assisted pulsed laser evaporation of zinc benzoate for ZnO thin films and non-isothermal decomposition kinetics; **Andrei Rotaru**, Catalin Constantinescu, Anca Mândruleanu, Petre Rotaru, Antoniu Moldovan, Katarina Győryová, Maria Dinescu, Vladimir Balek; *Thermochimica Acta*, 498, 1-2, 81-91, 2010, IF=1.938. Citations ISI: 18.

2. Thermal decomposition kinetics of some aromatic azomonoethers. Part II. Non-isothermal study of three liquid crystals in dynamic air atmosphere; **Andrei Rotaru**, Anna Kropidłowska, Anca Moanță, Petre Rotaru, Eugen Segal; *Journal of Thermal Analysis and Calorimetry*, 92, 1, 233-238, 2008, IF=1.630. Citations ISI: 27.

3. Thermal analysis and thin films deposition by matrix assisted pulsed laser evaporation of a 4CN type azomonoether; **Andrei Rotaru**, Catalin Constantinescu, Petre Rotaru, Anca Moanță, Marius Dumitru, Margareta Socaciu, Maria Dinescu, Eugen Segal; *Journal of Thermal Analysis and Calorimetry*, 92, 1, 279-284, 2008, IF=1.630. Citations ISI: 12.

4. Thermal behaviour of CODA azoic dye liquid crystal and nanostructuring by drop cast and spin coating techniques; **Andrei Rotaru**, Marius Dumitru; *Journal of Thermal Analysis and Calorimetry*, DOI:10.1007/s10973-016-5599-z, 2016, IF=1.781

5. Thermokinetic study of CODA azoic liquid crystal and thin films deposition by matrix-assisted pulsed laser evaporation; **Andrei Rotaru**, Anca Moanță, Cătălin Constantinescu, Marius Dumitru, Horia Octavian Manolea, Andreea Andrei, Maria Dinescu; *Journal of Thermal Analysis and Calorimetry*, DOI:10.1007/s10973-016-5599-z, 2016, IF=1.781

6. Thermal behaviour and thin film deposition by MAPLE technique of functional polymeric materials with potential use in optoelectronics; Catalin Constantinescu, **Andrei Rotaru**, Anca Nedelcea, Maria Dinescu; *Materials Science in Semiconductor Processing*, 30, 242-249, 2015, IF=2.264. Citations ISI: 10.

### *Works presented by the author at international conferences as plenary lectures or at universities abroad as invited lectures:*

1. Advanced incremental linear kinetic methods to the study of thermally-induced processes in complex materials. **Andrei Rotaru**. Plenary lecture at the "14<sup>th</sup> Conference on Thermal Analysis and Calorimetry in Russia", 27 September 2013, Sankt Petersburg, Russian Federation.

2. Utility of kinetic study for different thermal decompositions of azoic dyes. **Andrei Rotaru**. Invited lecture at the Gdansk University of Technology. Chemical Faculty, 17 May 2007, Gdansk, Poland.

3. Matrix assisted pulsed laser evaporation of soft functional metal-organic materials, precursors and liquid crystals. Thermal and kinetic studies for enhancing processing conditions and properties of thin films. **Andrei Rotaru**. Invited lecture at the Vilnius University. Institute of Biotechnology, 9 March 2011, Vilnius, Lithuania.

***Regular works presented by the author at international conferences:***

1. Thermal stability and thin films deposition of some polymeric materials with use in optoelectronic and sensor devices. Cătălin Constantinescu, **Andrei Rotaru**, Anca Nedelcea, Petre Rotaru, Maria Dinescu. E-MRS 2012 SPRING MEETING, 14-18 May 2012, Strasbourg, France.

2. Thermal analysis of some aromatic azomonoethers. Non-isothermal decomposition kinetic study of 1-(3-chloro-4-(4-chlorobenzoyloxy)phenyl)-2-(4-chlorophenyl)diazene in air flow. **Andrei Rotaru**, Catalin Constantinescu, Anca Moanță, Petre Rotaru, Maria Dinescu, Eugen Segal. 9<sup>th</sup> Mediterranean Conference on Calorimetry and Thermal Analysis, pag. 8815-18 June 2009, Marseille, France.

3. Thermal and kinetic analysis of some azononoetheric liquid crystals and thin films by MAPLE technique. **Andrei Rotaru**, Anca Moanță, Marius Dumitru, Cătălin Constantinescu, Horia Octavian Manolea, Andreea Andrei, Maria Dinescu. 3<sup>rd</sup> Central and Eastern European Conference on Thermal Analysis and Calorimetry CEEC-TAC3, pag. 426, 25-28 August 2015, Ljubljana, Slovenia.

***Other articles of same thematic, published by the author in ISI ranked journals, and which are not part of the present thesis:***

1. CdS thin films obtained by thermal treatment of cadmium (II) complex precursor deposited by MAPLE technique; **Andrei Rotaru**, Anna Mielarek-Kropidłowska, Catalin Constantinescu, Nicu Scărișoreanu, Marius Dumitru, Michal Strankowski, Petre Rotaru, Valentin Ion, Cristina Vasiliu, Barbara Becker, Maria Dinescu; *Applied Surface Science*, 255, 6786-6789, 2009, IF=1.616. Citations ISI: 21.

2. Multifunctional thin films of lactoferrin for biochemical use deposited by MAPLE technique; Catalin Constantinescu, Alexandra Palla-Papavlu, **Andrei Rotaru**, Paula Florian, Florica Chelu, Madalina Icriverzi, Anca Nedelcea, Valentina Dincă, Anca Roșeanu, Maria Dinescu; *Applied Surface Science*, 255, 5491-5495, 2009, IF=1.616. Citations ISI: 15.

# Chapter 1

## Introduction and background

The thesis entitled: „*Thermally induced functionalization of thin films of molecular materials obtained by laser techniques / Funcționizarea indusă termic a filmelor subțiri de materiale moleculare obținute prin tehnici laser*”, has been elaborated at the Department of Physics within the University of Craiova, for obtaining the title of Doctor (PhD) in the field of „Physics”. Significant experimental research contained in the present thesis was carried out also at INFLPR-National Institute for Laser, Plasma and Radiation Physics.

### 1.1 General overview regarding thin films processing

Today competing bulk, thin films have garnered an increasing interest as alternative form of solid materials that may exhibit enhanced properties and eventually numerous possibilities of applications that will influence our everyday life [1,2], in: medicine, pharmacy, electronics, optics, mechanics (abrasive, hard or impermeable coatings), sensing (for gases or for bio-marking), etc. Characterisation and properties of surfaces, together with the applications at the nano- and micro-scale of such materials have opened a totally different world for the solid state physics. Nanotechnology for optoelectronics is targeting always for recent advancements of producing or functionalizing nanomaterials and thin films [3,4] with semiconducting, conducting or dielectric properties; novel materials with enhanced stability and functional properties are continuously synthesized, possibilities of handling them and solving hot issues being thus easier to be addressed.

### 1.5 Motivation for the current project, the main proposed objectives, and the present study

In the context when the pulsed laser deposition technique is not adequate for obtaining thin films of soft molecular compounds (as mentioned in subchapter 1.2), it is however wise to benefit from its remaining advantages (to be presented in Chapter 2), and therefore the use of its modified version MAPLE (matrix-assisted pulsed laser evaporation) brings novelty and enhancement to the methodology and quality of obtaining thin films of such materials. Before functionalizing in the form of soft molecular thin films, it is impetuous to characterize these materials by thermal analysis and kinetic methods, in order to be able to know their stability, to establish the eventual

thermal processing conditions, to understand the complexity of their transformations with temperature, and to determine the ranges of temperature where they may be employed.

**Main proposed objectives:** *i) finding the appropriate experimental parameters for the laser-based depositions; ii) successful employment of the matrix-assisted pulsed laser evaporation (MAPLE) for the fabrication of thin films of soft molecular materials; iii) obtaining reproducible and high quality thin films of inorganic, organic and polymeric soft materials of large interest for various applications; iv) characterisation of the thermal stability and understanding of the thermal properties of the soft materials employed; v) rigorous kinetic study and understanding the complexity of the transformations taking place through the entire temperature range; vi) determining the thermal processing conditions of some materials and of temperature ranges where they will be further employed.*

The interconnection between the results of the thermal and kinetic studies, with those obtained for the thin films fabricated by MAPLE are evident; the present study accomplishes the proposed objectives and brings significant contribution to the usefulness of the thin films obtained by MAPLE technique.

## **1.6 The structure of the thesis and the brief description of the content of each chapter**

The thesis is structured in *six chapters*: five chapters describing the thematic under the present context, the premises, the performed experiments, the chosen methodology and technology, the implementation of some calculus procedures, the physical-chemical characterisation of thin film materials, the results and discussions, plus a sixth chapter containing the conclusions and the further work proposed.

Actually, the manuscript is divided into *three main parts*. The first part, formed of the first two chapters, represents a literature survey and a personal view upon: the thin films obtaining, the thermal processes and their kinetic modelling, and ultimately the thermal processing of materials. The second part of the manuscript, composed of the following three chapters, is entirely original and comprises the study for reaching and solving the proposed objectives. The third part contains the conclusions and further work proposed by the author.

The present Doctoral/PhD Thesis, elaborated for the purpose of obtaining the title of Doctor (PhD) in the field of "Physics", is an original work and contains herein data published by the author in 6 (six) articles from ISI ranked journals, of which 5 (five) as first author. Also, 3 (three) works have been presented as plenary (1) and invited (2) lectures at international conferences and at universities abroad, while other 3 (three) regular works have been presented at international conferences.

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## Chapter 2

### Theoretical aspects and experimental methods

#### 2.2.3.1 Features of MAPLE deposition technique

Matrix-assisted pulsed laser evaporation (MAPLE) technique [21-23], based on the early work of Nelson *et al.* [36] that transferred intact DNA molecules from a frozen aqueous-DNA target by using pulsed laser energy, actually started as an alternative to spray coating of thin films for chemical vapour sensors [37].

MAPLE technique [21-23] is similar to the PLD technique; the only difference consists in diluting the material in a volatile non-interacting solvent further to be frozen, or mixing it with another solid which represents this time the matrix. By irradiating the prepared target with a pulsed laser beam, only the solvent/matrix absorbs the laser wavelength and thus the system is evaporated. The solute material is collected on a substrate placed in front of the target, while the solvent is pumped out or the solid matrix is pyrolysed. When applying MAPLE technique, one must be confident that the compound does not absorb the selected laser radiation; therefore, in the case of molecular compounds deposition by MAPLE, the laser wavelengths chosen have to be in the range where the functional compound does not have absorption maxima, respectively in the UV or UV-Vis range, and preferably not in the Vis or IR range. On the contrary, the chosen matrix has to absorb the laser wavelength; therefore this has to be verified by checking the matrixes spectra before performing any deposition experiment. Moreover, during the laser interaction with the target, the matrix and the compound to be deposited shall not photochemically or photothermally interact. It results that only the molecules of the appropriate material are collected on the substrate (Figure 2.1).

Such a non-destructive technique accurately solves the deposition problem of complex chemical structures (organic and bio-organic molecules, inorganic coordination compounds, bio/polymers, cells, etc.) [21-23,38-60]. MAPLE technique provides a gentle mechanism of transferring small and large

molecular weight species or compounds possessing weak bonds (coordination complexes) from a condensed phase into the vapour phase.

Zhigilei and co-workers carried out parametric investigations, both experimental and simulated MAPLE depositions [61-68]. They have simulated the mechanism of laser ablation and molecular dynamics [61-64] in MAPLE depositions and also experimentally investigated them in a group of papers [65-68]. A surface clustering mechanism of a polymer-matrix system was proposed, with the solvent escaping the film while the polymer inflates [65] – rearrangement of the thin film after deposition.

### **2.2.3.3 Perspectives of MAPLE deposition technique**

In the paper entitled “The Matrix-Assisted Pulsed Laser Evaporation (MAPLE) process: origins and future directions”, A. Pique describes the numerous advantages MAPLE technique has produced when used for the deposition of thin films of polymeric, organic and biomaterials for various applications [37]. Besides, another great advantage of MAPLE technique over PLD is the versatile tailoring of nanostructures. For example, instead employing complicated procedures to produce ZnO pixels using PLD and nano-patterning, by MAPLE technique it is possible to deposit Zn(II) complex and further to locally photodecompose it with a laser beam in order to obtain the ZnO directly on the thin film, while the remained Zn(II) complex may be washed out with solvent.

Several new variations of MAPLE technique were proposed in the last years, especially for nano-functionalization and nano-patterning of advanced materials, this highly versatile and successful vapour deposition technique receiving increased attention, and its future as top research area being placed in the spotlight [37].

## **2.3 Thermal analysis and calorimetry techniques of interest and the standard procedure for heterogeneous kinetics**

The thermal analysis techniques belong to the group of experimental techniques that allow for the study and characterisation of samples (a single compound or composed of a mixture of compounds), by measuring a physical-chemical quantity as a function of temperature [69]. Some of the measured quantities may be: the difference between the sample temperature and the one of the reference material (the differential thermal analysis – DTA), luminescence radiation intensity (the thermoluminescent analysis - TLA), volume or thermal conductivity of gases (the evolved gas analysis - EGA), the current intensity or the electrical resistance (the conductometric analysis - AC), etc.

Generally, any of the physical-chemical method of analysis may be assimilated in the class of thermal methods of analysis, if the parameter that is usually registered in isothermal conditions will be measured when the



temperature changes in time. Here will be presented briefly the thermal analysis and calorimetry techniques employed in this work.

## 2.5 References to Chapter 2

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## Chapter 3

# Inorganic complex of zinc benzoate, precursor for ZnO: thermokinetic behaviour and thin films obtained by MAPLE technique

## 3.3 Thin films of zinc benzoate obtained by MAPLE technique, its thermal behaviour and the non-isothermal kinetic study

### 3.3.1 Zinc benzoate thin films by MAPLE technique

Thin films of zinc benzoate have been obtained on Si substrates by MAPLE technique, following the procedure described in the previous section 3.2. First, the experiments were carried out for a duration of 33 minutes (20,000 laser pulses). For low laser fluences (*e.g.*  $0.1 \text{ J}\cdot\text{cm}^{-2}$ ) there is no deposition to be found on the substrates, while when increasing laser fluence (Table 3.1, until  $0.5 \text{ J}\cdot\text{cm}^{-2}$  is reached), the Si substrates are not entirely covered, but the peak to valley roughness ( $R_{P-V}$ ) and root mean square roughness ( $R_Q$ ) values continuously decrease. The ablated and thus deposited material increases with increasing the fluence (from  $0.7$  to  $1.3 \text{ J}\cdot\text{cm}^{-2}$ ), therefore thin films' smoothness and continuity decreases (Table 3.1).

The laser fluence of  $1.0 \text{ J}\cdot\text{cm}^{-2}$  proved to transfer more material, but when analysing the obtained thin film, it revealed worse morphology compared to the sample obtained at  $0.7 \text{ J}\cdot\text{cm}^{-2}$ . When selecting the laser fluence of  $1.3 \text{ J}\cdot\text{cm}^{-2}$ , the obtained films look like already burned and with increased roughness and peak to valley values (Table 3.1), therefore this fluence seems to be much too high.

For doubling the deposition duration (40,000 pulses), at 0.5 J·cm<sup>-2</sup> and 0.7 J·cm<sup>-2</sup> laser fluences, it was observed an increasing amount of deposited material. The double deposition timing for the 0.5 J·cm<sup>-2</sup> sample led to a complete coverage of the Si substrates and a fine thin film formation. For 40,000 laser pulses it results smother and more continuous surfaces, which form in the case of 0.7 J·cm<sup>-2</sup> MAPLE deposition when the transferred material starts to fill the empty places and homogenizes the morphology (Figure 3.1a and 3.1b); peak to valley shortens from 927 nm to 660 nm and the roughness improves from 132 nm to 97 nm.

**Table 3.1** Experimental MAPLE deposition parameters and thin films morphology (40 μm x 40 μm) results by AFM imaging

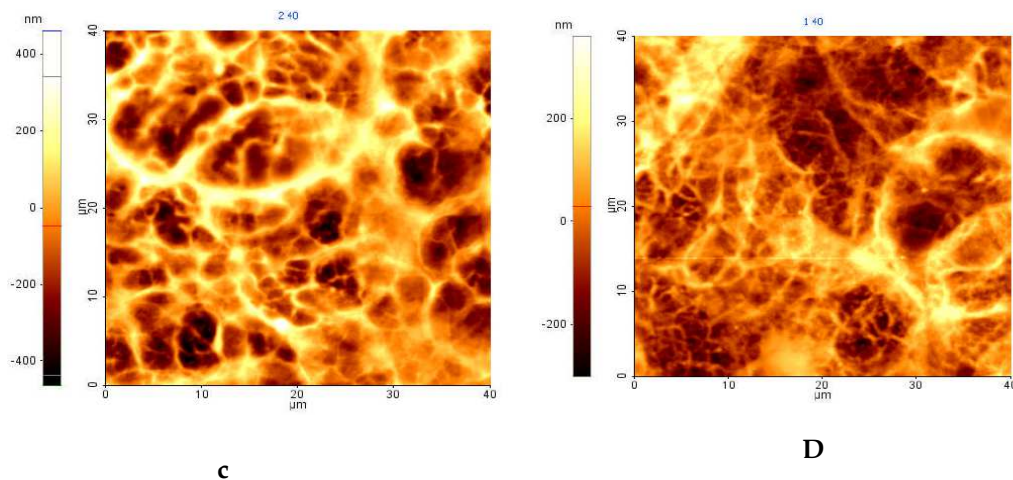
Laser Fluence / J·cm <sup>-2</sup>	Laser Pulses	R <sub>p-v</sub> / nm	R <sub>Q</sub> / nm	Observations
0.1	20,000	-	-	no deposition
0.3	20,000	772	101	disparate droplets deposition
0.4	20,000	283	44	disparate droplets deposition
0.5	20,000	268	13	several circular areas of deposition
0.5	40,000	471	44	uniform circular area deposition
0.7	20,000	927	132	uniform circular area deposition
0.7	40,000	660	97	uniform circular area deposition
1.0	20,000	807	129	high amount of material and irregular deposition
1.3	20,000	1187	202	high amount of material and irregular deposition; burned aspect of the thin film

Since the 20,000 laser pulses MAPLE deposition at 0.7 J·cm<sup>-2</sup> proves to be the best one, doubling the deposition time seems to confirm, and therefore even improve the morphology of the zinc benzoate thin films.

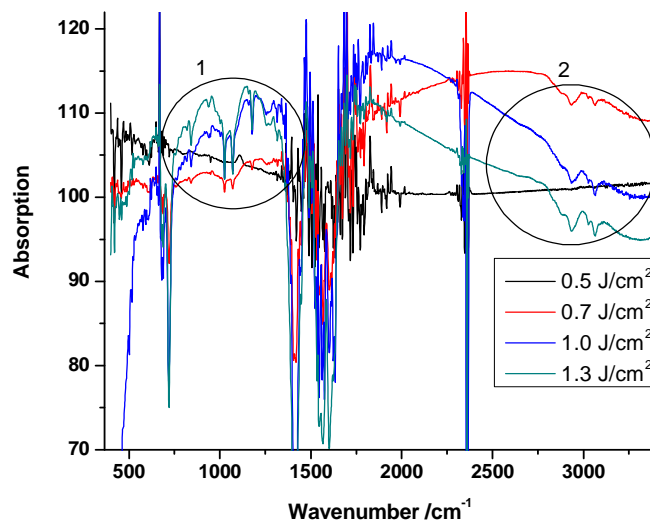
Bi-dimensional images of the morphology of the zinc benzoate thin films obtained by MAPLE technique at 0.7 J·cm<sup>-2</sup> laser fluence for 33 minutes (20,000 laser pulses) exhibit circular drops of around 20-25 μm in diameter, with increased amount of deposited material towards the edge of the circular drops (Figure 3.1c). While increasing the deposition time, the previously obtained circles tend to overlap, and finally (for 40,000 laser pulses) homogenizing the deposited area (Figure 3.1d).

FTIR analysis of the zinc benzoate thin films has been performed. For those laser fluences that were able to transfer significant amount of material (according to the AFM images), the plot of absorption *vs.* wavenumber is presented in Figure 3.3. In this work, the FTIR spectra were recorded only to check the preservation of chemical composition after the laser induced transfer. It may be noticed that for the laser fluence of 0.5 J·cm<sup>-2</sup>, the deposited quantity of material is too low, therefore the absorption signals are too weak to be registered; while for increasing the laser fluences to 0.7-1.3 J·cm<sup>-2</sup>, the amplitude

of peaks increases (regions 1 and 2 in Figure 3.3). The FTIR absorption peaks respect the position acquired in the spectrum for the bulk zinc benzoate, and also those that have been previously reported [10,11].



**Figure 3.1** 3D AFM images of zinc benzoate thin films by MAPLE ( $40 \times 40 \mu\text{m}^2$ ), obtained at  $0.7 \text{ J}\cdot\text{cm}^{-2}$  laser fluence for a) 20,000 pulses; b) 40,000 pulses and 2D AFM images of zinc benzoate thin films by MAPLE, obtained at  $0.7 \text{ J}\cdot\text{cm}^{-2}$  laser fluence for c) 20,000 pulses; d) 40,000 pulses



**Figure 3.3** FTIR spectra of zinc benzoate thin films for fluences ( $0.5\text{-}1.3 \text{ J}\cdot\text{cm}^{-2}$ ) that transferred significant amount of material

### 3.3.2 Thermal analysis and kinetic decomposition studies of zinc benzoate dihydrate $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2\cdot 2\text{H}_2\text{O}$

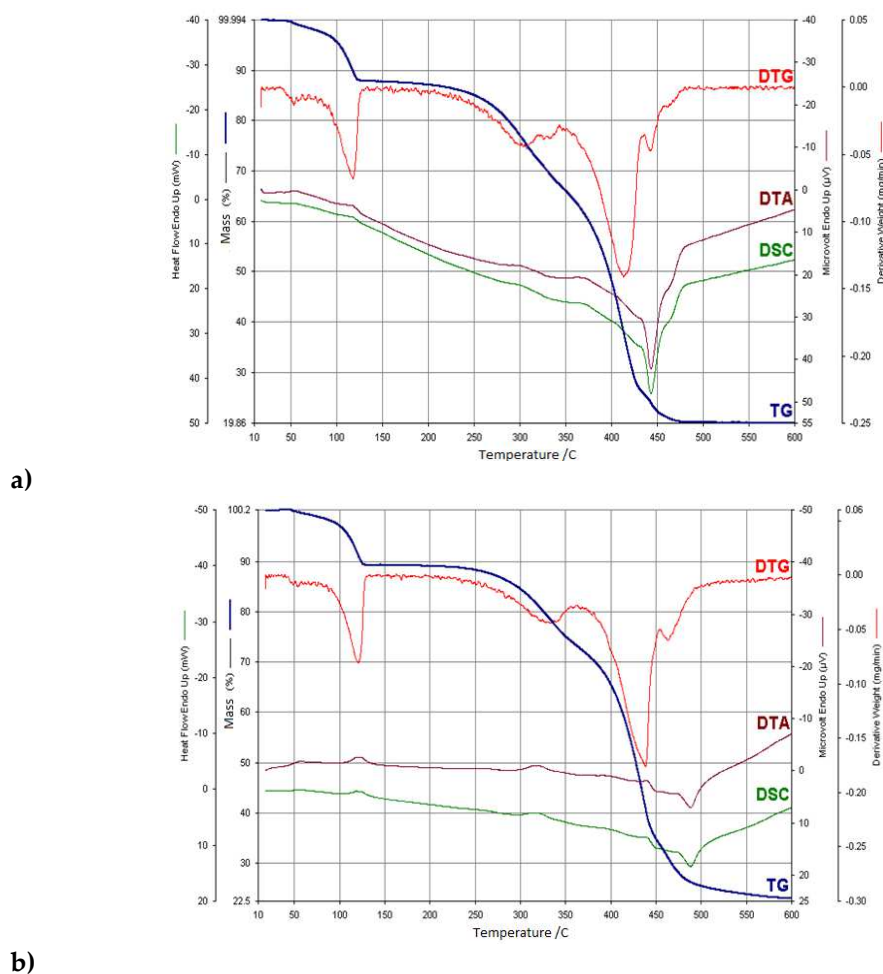
Thermal analysis of  $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2\cdot 2\text{H}_2\text{O}$  crystalline powder was carried out in both air and argon flow. Thermal decomposition studies of zinc complex compounds are important from the scientific point of view, for thermal stability determinations (the case of possible biological applications) and when using

them as precursors, for establishing the thermal and kinetic parameters of the decomposition process and zinc oxide growth. As it is well known from the literature, thermal decomposition and kinetics of such zinc complex crystals are determined by reacting conditions (various gaseous atmospheres) and moreover, very sensitive on the used heating rates, reacting duration and crushing pressures and durations [58-62].

The thermoanalytical curves for the non-isothermal decomposition of  $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , recorded at the heating rate of  $10 \text{ K} \cdot \text{min}^{-1}$  are presented in Figure 3.4a (air flow) and in Figure 3.4b (argon flow).

Two main stages may be noticed in both air and argon flow thermal experiments, similar one to the other; the first stage represents the elimination of two coordinated water molecules (dehydration process), while the more complex second stage represents the loss of organic parts and formation of  $\text{ZnO}$ .

In the following section, 3.3.3, a short description of some non-isothermal kinetic methods, useful for this study, will be presented, since the current kinetic analysis requires a complex stepwise procedure for choosing and further employing them.



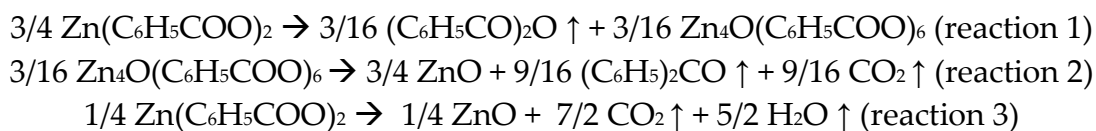
**Figure 3.4** Thermoanalytical curves for the thermal decomposition of  $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 2\text{H}_2\text{O}$  at  $\beta=10 \text{ K} \cdot \text{min}^{-1}$  in a) air flow and b) argon flow

### 3.3.3 Non-isothermal kinetics of heterogeneous processes

#### 3.3.5 Decomposition of $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$ and formation of $\text{ZnO}$

The thermal decomposition of zinc benzoate is a complex process in argon flow, and even more complex in air flow (Figure 3.4). While in argon the decomposition occurs in three steps (Figure 3.4b) – first two endothermic and the third exothermic, in air flow the first and the third step are initiated by gaseous oxygen and continued by the oxygen from inside the organic molecules (Figure 3.4a), when the system becomes activated and releases the intramolecular oxygen. The DSC and DTA curves in air flow identify the same first two endothermic reactions and split the third reaction into two exothermic steps.

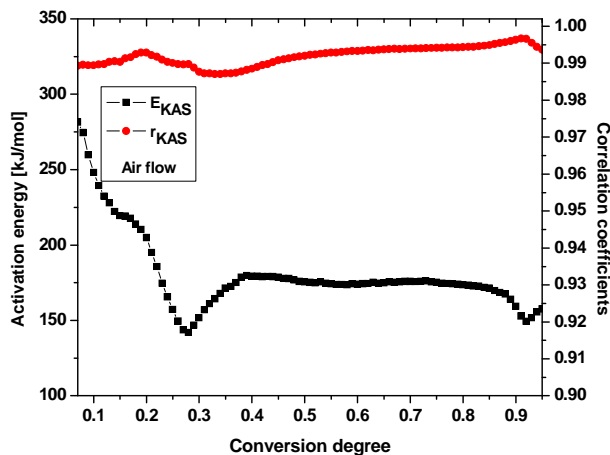
The three proposed decomposition reactions are similar to those proposed by several authors [59-62] for the thermal decomposition in inert dynamic atmosphere of zinc acetate:



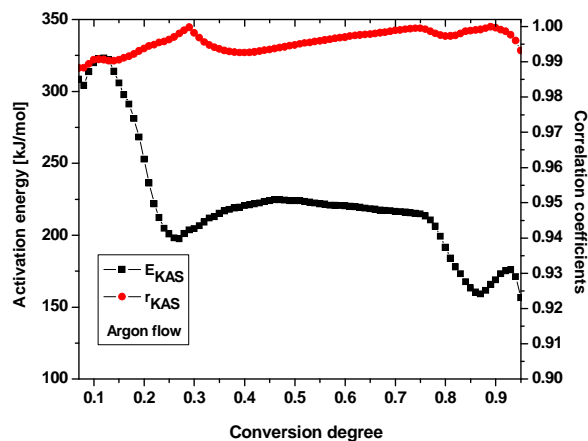
The first reaction represents the loss of  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$  (15% mass loss) and the formation of  $\text{Zn}_4\text{O}(\text{C}_6\text{H}_5\text{COO})_6$ , stable at those temperatures. This reaction represents only  $\frac{3}{4}$  of the decomposition of zinc benzoate, while the second reaction (42% mass loss) represents the decomposition of solid  $\text{Zn}_4\text{O}(\text{C}_6\text{H}_5\text{COO})_6$  to the more stable  $\text{ZnO}$  and happens in a narrow temperature range. The rest of  $\frac{1}{4}$   $\text{ZnO}$  forms at the end of the third reaction, when the high temperatures led to the combustion of organic gases to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . A residue of 22% representing  $\text{ZnO}$  is found for the argon flow case, while in the case of air flow only 20% remain.

Figures 3.7 and 3.8 show the variation in activation energy with the conversion degree towards the formation of  $\text{ZnO}$  from the thermal decomposition of zinc benzoate, in air and in argon flow respectively. The evaluation was done using the TKS-SP software [100,104], with  $\alpha$  step of 0.01, while obtaining the activation energy with correlation coefficients greater than 0.98800 for both air and argon studies.

For the argon flow experiments, the first reaction has a decreasing activation energy from  $320 \text{ kJ}\cdot\text{mol}^{-1}$  to  $180 \text{ kJ}\cdot\text{mol}^{-1}$  (at  $\alpha=0.28$ ), followed by a small increase in the activation energy up to  $210 \text{ kJ}\cdot\text{mol}^{-1}$  (at  $\alpha=0.35$ ) – Figure 3.8. In air flow, the reaction initiates with the oxygen from the air, results in the activation energy being lower, this time decreasing from  $270 \text{ kJ}\cdot\text{mol}^{-1}$  to  $135 \text{ kJ}\cdot\text{mol}^{-1}$  (at  $\alpha=0.28$ ), and it is followed by a severe increase to  $170 \text{ kJ}\cdot\text{mol}^{-1}$  (once more at  $\alpha=0.35$ ) standing for the intramolecular oxygen reaction – Figure 3.7.



**Figure 3.7** Isoconversional activation energy for the non-isothermal decomposition process of  $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$  in air flow



**Figure 3.8** Isoconversional activation energy for the non-isothermal decomposition process of  $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$  in argon flow

The beginning of the second reaction at  $\alpha=0.35$  (start of constant activation energy) in both cases indicates that the first reaction offered the same products actually, independent on the source of consumed oxygen. As well, being constant in the range of  $\alpha=0.35-0.85$  (air flow) and between  $\alpha=0.35-0.75$  (argon flow), the activation energy indicates together with the DTG curve a simple process for the second reaction:  $\bar{E}_{\text{KAS}}=175 \text{ kJ}\cdot\text{mol}^{-1}$  (air flow) and  $\bar{E}_{\text{KAS}}=215 \text{ kJ}\cdot\text{mol}^{-1}$  (argon flow). The difference in activation energy of the second reaction may be explained as a supplementary effort the system has to overcome in the absence of the external oxygen (argon flow) in order to complete the reaction. Since the activation energy of the third reaction in argon flow is lower and even decreasing, it begins earlier, at  $\alpha=0.75$ . The shape of the activation energy variation of the third reaction is similar for both air and argon flow cases, indicating the same reaction, regardless of atmosphere; thus independent of implied oxygen. As well, its profile is almost identical to the first reaction one, the trough-like shape being one more indication of zinc benzoate decomposition.



The results of IKP method (Table 3.5) are identical with the average values of isoconversional activation energies by KAS method, although obtained with less confidence.

**Table 3.5** Invariant Kinetic Parameters for ASKM (CR method)

<i>Atmosphere</i>	$E_{inv}$ <i>kJ·mol<sup>-1</sup></i>	$\ln A_{inv}$ <i>A/s<sup>-1</sup></i>	$r_{inv}$
Air flow	174.1	26.414	0.97583
Argon flow	212.2	31.412	0.97612

Due to the complex process (3 chemical reactions), the Master plots method requires the exact knowledge of initial and final conversion degrees and therefore cannot be used in this case. Perez-Maqueda *et al.* criterion can discriminate between conversion functions, even using only parts of the process. Since the complexity of the process is not suitable for kinetic predictions, this criterion is powerful enough to indicate the activation parameters ( $E, A$ ) and can prove their constancy with respect to the heating rates.

**Table 3.6** Perez-Maqueda *et al.* kinetic parameters (CR method)

<i>Atmosphere</i>	<i>Kinetic Model</i>	$E$ <i>kJ·mol<sup>-1</sup></i>	$\ln A$ <i>A/s<sup>-1</sup></i>	$r$
Air flow	P1/3	175.3	24.955	0.99366
Argon flow	P1/3	218.8	31.185	0.99629

Table 3.6 presents the kinetic parameters of the second reaction within the process, obtained with increased accuracy. The activation energies are those expected and the conversion function remains the same for both types of experiments. The obtaining of unchanged conversion function with the employed atmosphere is a great achievement, to be discussed in the followings.

For the third reaction, the evaluation of all kinetic parameters is impossible due to the small amount of zinc benzoate that was left to decompose ( $1/4 \text{ Zn}(\text{C}_6\text{H}_5\text{COO})_2$ ), and which anyway has a variable isoconversional activation energy.

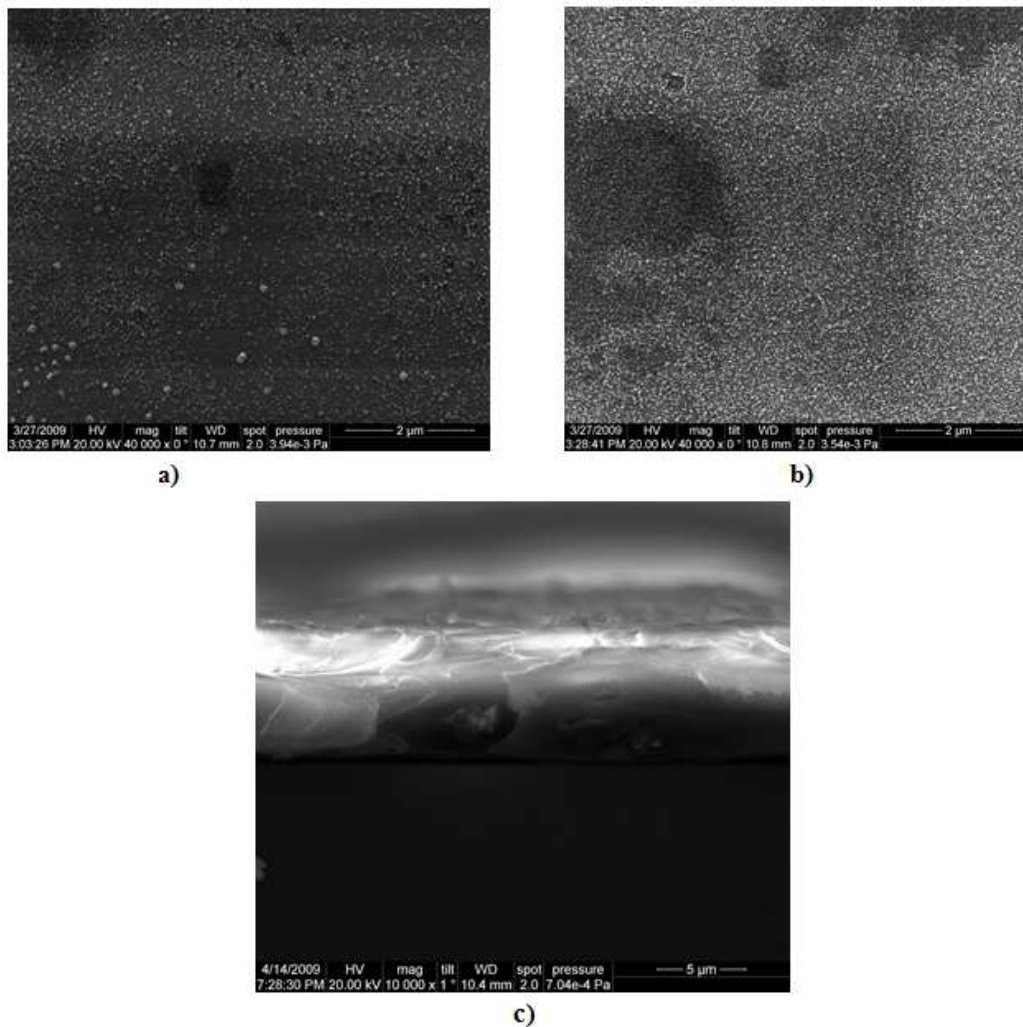
### 3.3.6 Obtaining ZnO by thermal treatment of the zinc benzoate thin films

The thin films of  $\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2$  obtained by MAPLE technique have been thermally treated in static air atmosphere inside a muffle furnace, from room temperature (r.t.) to 650 °C, while heating with the rate of 1 K·min<sup>-1</sup>. After reaching 650 °C, the samples were left in the furnaces to cool down to r.t.

After thermal treatment, the thin films shrink, becoming much smoother – the peak to valley roughness ( $R_{P-V}$ ) reduces 3 times, from 927 to 312 nm, and RMS roughness ( $R_Q$ ) decreases 5.5 times, from 132 to 23 nm (as marked in

Figure 3.11 with black and white pentagonal signs). This result is somehow in accordance with the ~20% ZnO that remain as final product of the thermal decomposition.

In Figure 3.12, the SEM images for the thin films obtained after thermal treatment (processed at  $0.5 \text{ J}\cdot\text{cm}^{-2}$  – Figure 3.12a, and at  $0.7 \text{ J}\cdot\text{cm}^{-2}$  – Figure 3.12b, for 40,000 laser pulses each) are presented. Both thin films are well covered, have a smooth appearance, but the one at  $0.7 \text{ J}\cdot\text{cm}^{-2}$  is more compact [106,107]; this is also confirmed by the SEM image of the cross-section (Figure 3.12c) [107].



**Figure 3.12** SEM images on the calcinated zinc benzoate samples, deposited by MAPLE at a fluence of  $0.5 \text{ J}\cdot\text{cm}^{-2}$  (a), and at  $0.7 \text{ J}\cdot\text{cm}^{-2}$  (b). Both samples were deposited for 40 000 laser pulses. The cross-section image (c) is on a sample deposited at  $0.7 \text{ J}\cdot\text{cm}^{-2}$ .

For the MAPLE deposition conducted at a fluence of  $0.7 \text{ J}\cdot\text{cm}^{-2}$  and 40,000 laser pulses, the thickness of ZnO deposited layer obtained after calcination is approximately  $5.5 \mu\text{m}$  (Figure 3.12c). Since the ZnO thin film in Figure 3.12c is compact and continuous (a similar example in Ref. 106), it is not possible to make any assumption regarding its growth mechanism – during MAPLE deposition of the zinc benzoate precursor, or during the thermal treatment.

### 3.5 References to Chapter 3

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## Chapter 4

### Organic azo-derivative dyes with liquid crystalline properties: thermokinetic behaviour and thin films obtained by MAPLE technique

#### 4.4 Summary of Chapter 4

After the introductory part for the azoic dyes with liquid crystalline properties and possible applications, in this chapter two main parts were discussed: *i*) the first part was dedicated to the compound **4CN** (4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene), and *ii*) the second part was dedicated to the compound **CODA** (4-[(4-chlorobenzyl)oxy]-3,4'-dichloroazobenzene). In the first part, for the **4CN** azoic dye, the thermal analysis of the phase transitions and decompositions (TG-FTIR, DTG, DTA, DSC, HS-OMPL), the kinetics of the thermal decomposition, and the thin films deposition by MAPLE technique and physical-chemical analysis of the surfaces (AFM, SEM, FTIR) were investigated and discussed. The thermal decomposition and respective kinetic study confirmed two chemical reactions – the first one taking place by a complex mechanism, while the second one representing the burning of the

carbonaceous rests formed after the first reaction. The 4CN compound reveals several phase transitions at both heating and cooling which were evidenced during the study, by combining DTA, DSC and optical microscopy. Thin films obtained by MAPLE technique on Si and SiO<sub>2</sub> are structured and exhibit evident differences determined by the substrate and laser fluence; it was shown that they also possess the initial chemical structure of the 4CN material.

In the second part, for the CODA azoic dye, the thermal analysis of the phase transitions and decompositions, the kinetics of the thermal decompositions, and the nanostructures/thin films deposition by MAPLE technique, including the physical-chemical analysis of the surfaces (OM, AFM and FTIR) were investigated and discussed. The thermoanalytical study was performed in both air and argon flow atmospheres, revealing significant differences. Also, the thermal effects of the phase transitions were evidenced by DTA and DSC; they are in agreement with previous investigations regarding its liquid crystalline properties. The kinetic study of the two decomposition processes that take place in air – formation of heptafulvalene and its burning – are complex processes that may not be described by a unique kinetic model. For the first step, the activation energy generally increases with increasing the conversion degree, indicating parallel reactions; the activation energy trend can be separated into two regions according to the slope of the increase: up to  $\alpha=0.3$  ( $E_{\text{Ortega}}=97\rightarrow 135$  kJ·mol<sup>-1</sup>) that may be related to higher contribution of the thermo-oxidative decomposition of CODA into intermediary compounds, and after  $\alpha=0.3$  ( $E_{\text{Ortega}}=135\rightarrow 160$  kJ·mol<sup>-1</sup>) that may be related to the higher contribution related to the formation of heptafulvalene. For the second step, the activation energy is quasi-constant; the activation energy stability region ( $a=0.2-0.93$ ) may be regarded as an indication of a singular reaction for the global combustion process of heptafulvalene, however the combustion of the product from the thermo-oxidative decomposition of CODA, namely heptafulvalene, seems to take place in a more complicated manner than it was expected: for the Ortega evaluation these values are affected most probably by the inhomogeneity of the material continuously changing composition during the combustion process. The results of applying the Perez-Maqueda *et al.* criterion are matching for the activation energy and the pre-exponential factor determined by IKP method, but are inconsistent for the unicity of the correct conversion function; when applying the Gotor *et al.* master plots method, the conversion function that provides a reasonable match for the experimental curves of the global combustion process of heptafulvalene by the theoretical representation is in this case F0.74, a result contradicting both P1.05 and A3.00 models obtained previously by integral and differential procedures within the Perez-Maqueda *et al.* criterion. In the Gotor *et al.* master plots it was evidenced that the second investigated process is not described just by an unique kinetic model, but is actually composed of at least two main reactions that most probably are almost successive and overlapping to a certain extent and have their own mechanisms. Since the isoconversional activation energy is quasi-constant in the stability region ( $a=0.2-0.93$ ), it is very likely that the reactions

composing the second step take place with fairly similar activation parameters (E and A) – supported by the good linearity in the Perez-Maqueda *et al.* curves.

By employing the MAPLE technique, nanostructures and thin film growth on Si substrates may be controlled by wisely changing the experimental parameters: laser energy, area of the laser spot and deposition time; the growth type is determined by the actual values of the energy and area of the laser spot, while the dimensions are determined by the deposition time. The chemical composition of CODA was preserved after the MAPLE transfer, the FTIR spectra of the deposited materials possessing all characteristic transmittance peaks of the initial material.

## Chapter 5

### **Polymeric materials for optoelectronics: thermal behaviour and thin films obtained by MAPLE technique**

#### **5.4 Summary of Chapter 5**

In this chapter, the thermal behaviour and matrix-assisted pulsed laser evaporation for thin film deposition of polymeric materials PVC (polyvinyl chloride), PAA (polyacrylic acid), PANi (polyaniline) are presented. Thermal analysis investigations led us to the conclusion that for the two dielectric materials, PAA and PVC, the maximal temperature to which they can be considered stable is around 200°C, while for PANi this temperature is smaller, around 150°C. Their thermal behaviour gives an inside glimpse into the way the laser irradiation may influence the thin film morphology during MAPLE: lower thin film roughness is observed when endothermic degradation processes of the compound are predominant. The best thin films of PVC, PAA and PANi obtained by MAPLE processing were reported here for the optimal experimental deposition parameters. Optical microscopy, AFM and SEM images reveal continuous and smooth surface for the thin films, with roughness in the range of 10-15 nm for PVC and for PAA, and ~50 nm for PANi. Spectroscopic ellipsometry analysis indicates thin film thicknesses in the range of 95-125 nm, consistent with AFM measurements. FTIR spectroscopy proves that complete preservation of the initial compound may be obtained when using certain solvents, proving that MAPLE is a suitable technique for polymer thin film growth with homogenous, controlled thickness.

## Chapter 6

### Conclusions and further work

In the last chapter of the present PhD thesis, the review of the most important results obtained and presented in this manuscript is discussed with respect to the accomplishment of the initially proposed objectives. The further work to be carried out by the author in his future research activities related to this broad topic of investigation is also proposed here.

The PhD thesis contains dedicated introduction and background description of the research topic tackled in this study. The theoretical aspects were clearly presented for the understanding required here, while the experimental methods were specified.

A broad category of materials, namely: soft materials containing organic parts (inorganic coordination complexes, linear organic molecules and polymers) was investigated here in an attempt to interconnect the results of the thermal and kinetic studies, with those obtained for the thin film processing by MAPLE (matrix-assisted pulsed laser evaporation) technique.

After discussing the obtained results through the manuscript, with main ones presented here above, it can be concluded that the main proposed objectives:

*i) finding the appropriate experimental parameters for the laser-based depositions;*

*ii) successful employment of the matrix-assisted pulsed laser evaporation (MAPLE) for the fabrication of thin films of soft molecular materials;*

*iii) obtaining reproducible and high quality thin films of inorganic, organic and polymeric soft materials of large interest for various applications;*

*iv) characterisation of the thermal stability and understanding of the thermal properties of the soft materials employed;*

*v) rigorous kinetic study and understanding the complexity of the transformations taking place through the entire temperature range;*

*vi) determining the thermal processing conditions of some materials and of temperature ranges where they will be further employed;*

they were effectively approached and accomplished.

The results of this study, together with several issues that were not approached during this work, have opened a number of possible subjects for future research; emerging from the current study, some of them are presented in the followings:

- Investigation of other zinc coordination complexes from the thermal, kinetic and deposition points of view, in order to obtain thin films of ZnO after thermal treatment;
- Use of pulsed laser deposition (PLD) technique directly for the deposition of ZnO (eventually) from zinc coordination complexes targets;
- Advanced nano-structuring of CODA and 4CN compounds by several deposition techniques and development of direct applications.
- Intercalation of several polymers as thin films obtained by MAPLE when a single target is employed.
- A general MAPLE parametric study for soft materials containing organic parts, where different solvents and different concentrations shall be used during the MAPLE deposition.

