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Scientific report

Project 269/5.10.2011, Nr. CNCSIS PN-II-ID-PCE-2011-3-0650, period January – October 2014

Title: **Study of polymer-laser interaction in controlled atmosphere. Thin film deposition by laser ablation. Applications**

General objectives:
- Study of PLD deposited thin films. Influence of laser pulse duration
- Study of laser micro-ablation

Considering the proposed objective, the following research activities were envisaged:

A. The dynamics of laser induced plasma of several metallic targets, chalcogenides, ferrite materials or polymers was analyzed through space- and time-resolved optical emission spectroscopy and electric diagnosis
B. We studied the influence of laser pulse duration on the laser induced plasma of a wide range of materials used as target materials for thin film deposition. The deposited thin films with complex chemical composition were analyzed by AFM, XRD, Raman spectroscopy etc. In order to obtain thin films with interesting properties (uniformity, with no large droplets, stoichiometry, optic parameters) we also studied the influence of other experimental parameters and plume dynamics.

During this project stage, various methods, analyzing technique and deposition processes were developed and the obtained results were publishes in ISI indexed journals and presented at several international and national conferences:

Participations at international conferences

1. Georgiana DASCALU, Silviu GURLUI, Petr NEMEC, Oana POMPILIAN, Cristian FOCSA, Nano-, Pico- and Femto-second Laser Ablation of Pure and Rare-earth-doped Gallium Lanthanum Sulphide: A Comparative Study by Space- and Time-resolved Optical Emission Spectroscopy, International Conference on Laser Induced Breakdown Spectroscopy (LIBS 2014), 2014, Beijing, China;
2. G. Dascalu, O. G. Pompilian, I. Mihaila, S. Gurlui, P. Hawlova, P. Nemec, V. Nazabal, C. Focsa, Pure and Rare-Earth Doped Gallium Lanthanum Sulphide Amorphous Thin Films Grown

by Pulsed Laser Deposition in Various Temporal Regimes, European Materials Research Society (E-MRS) Spring Meeting, E-MRS 2014, Lille, France;
3. R. Boidin, S. Gurlui, G. Dascalu, P. Nemec, V. Nazabal, C. Focsa, Pulsed Laser Deposition of Ge-Sb-Se glasses: A plasma plume dynamics study, European Materials Research Society Spring Meeting, E-MRS 2014, Lille, France;
4. G. Bulai, O. Caltun, S. Gurlui, M. Feder, B. Chazallon, C. Focsa, Structural and magnetic properties of rare earth doped cobalt ferrite thin films grown by pulsed laser deposition, International Conference on Thin Films, 2014, Dubrovnik, Croatia;
5. Rémi Boidin, Jean-Marc Kfoury, Silviu Gurlui, Georgiana Dascalu, Petr Nemec, Virginie Nazabal, Cristian Focsa, Space- and Time-Resolved Optical Emission Spectroscopy of Plasma Plume Dynamics in Laser Ablation of Ge-Sb-Se Chalcogenide Glasses, International Conference on Laser Induced Breakdown Spectroscopy (LIBS 2014), 2014, Beijing, China;
6. G. Bulai, O. Pompilian , V. Nazabal, P. Nemec , B. Chazallon, S. Gurlui, C. Focsa, Influence of ablation conditions on the structural and optical properties of Ge-Sb-Te based thin films deposited by PLD, Electroceramics Conference, 2014, Bucharest, Romania;
7. G. Dascalu, O. Pompilian, S. Gurlui, P. Nemec, C. Focsa, Space- and time-resolved optical emission spectroscopy of transient plasma generated by ns and fs laser ablation of Pr- and Er-doped GaLaS, European Materials Research Society Spring Meeting, E-MRS 2014, Lille, France;
8. G. Dascalu, O. Pompilian, N. Cimpoesu, V. Nazabal, P. Nemec, P. Hawlova, B. Chazallon, S. Gurlui, C. Focsa, Improved surface structure and chemical composition of Ge-Sb-Te thin films grown by femtosecond and picosecond PLD, European Materials Research Society Spring Meeting, E-MRS 2014, Lille, France;

Published or submitted papers in ISI indexed journals:

1. P. Nica, S. Gurlui, M. Osiac, M. Agop, C. Focsa, Electrical Characterization of Femtosecond Laser-Produced Plasma from Various Metallic Targets, submitted to EPL-EUROPHYS LETT
2. S. Gurlui, E. Buriana, Photo-responsive behavior of novel polyurethane coumarins, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

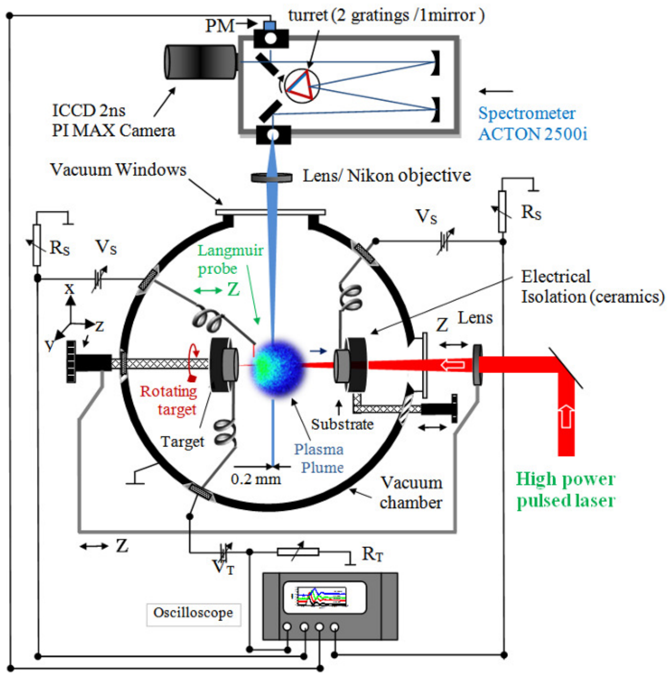
Scientific report

The interaction between the laser radiation and solid material (polymer, magnetic materials, chalcogendes, metals etc.) implies complex processes that are not completely understood and their complexity needs a good understanding of basic physics and chemistry associated with the laser-target interaction and particle-particle interaction in plasma plume. To understand the materials behavior in different irradiation conditions, the implicated physic-chemical mechanism (including shock waves, hydrodynamic instabilities and chemical reactions) and the plasma dynamic in reactive gas is and interesting research subject that needs to be followed. An important aspect is also the laser irradiation with high fluences on the properties of the solid samples. Thus, a systematic study of this phenomenon regarding the plasma formation and then the specific response to different parameters (energy/pulse, wavelength etc.) was necessary. A combined analysis of the induced modifications in the solid material though irradiation and of the gas phase dynamics offered important information for a more complete image on laser ablation of different materials with various applications. These phenomena depend on gas pressure, laser characteristics, and electric properties of the targets.

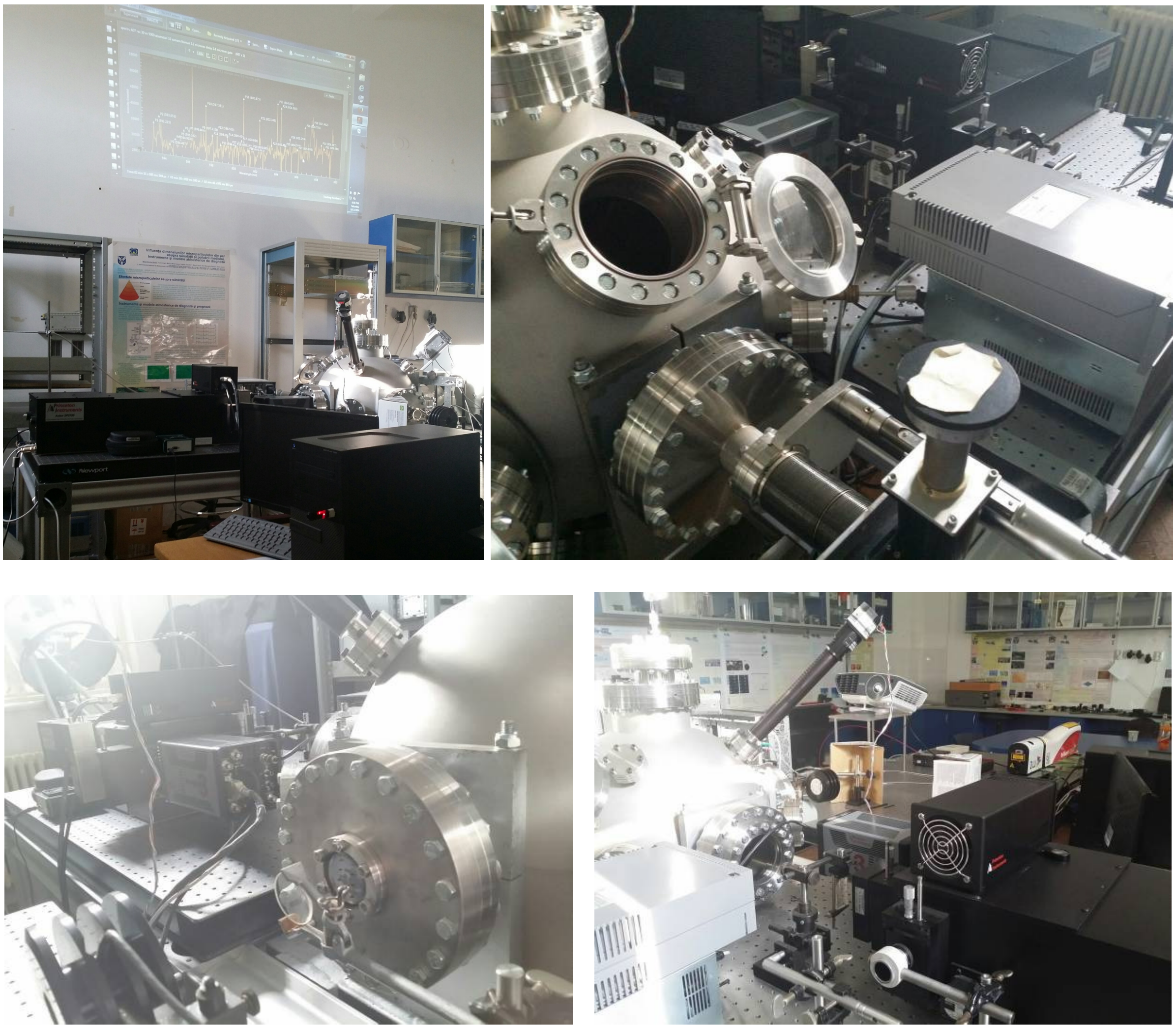
Combined analysis of the induced modifications on the massive material and plasma plume dynamics can give important information on laser ablation mechanism and condensed matter study.

Space and time resolved optical emission spectroscopy was applied to various types of targets and the following information was extracted:

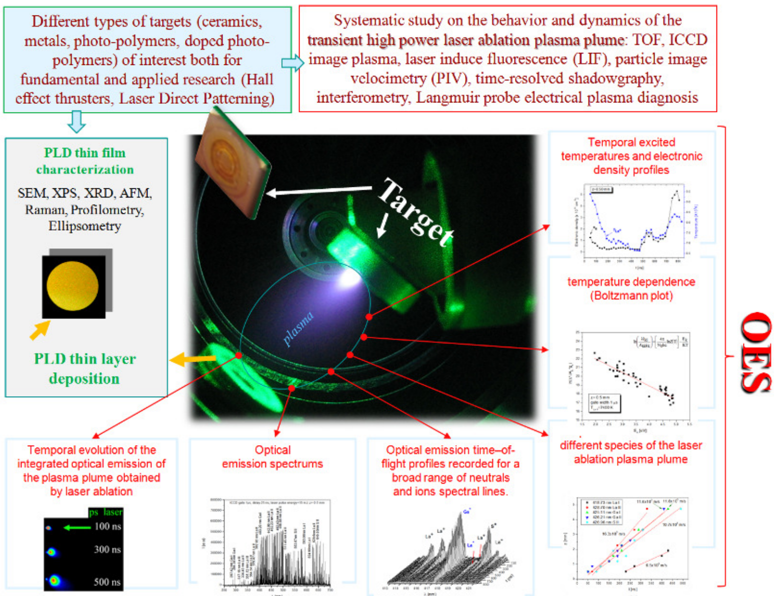
- Space and time profiles of electronic densities and excitation temperatures
- Excitation temperatures of various species found in the plasma using Boltzmann plot
- Velocities of various species
- Determination of individual contributions of the charged and neutral species
- Characterization of the dynamics of some structures fund in the plasma that are influenced by the length of the laser pulse and target type through ICCD imagery
- Plasma plume diagnosis through electrical methods (Langmuir probes, electrostatic analyzer, magnetic field sensors etc.)



Experimental set-up for space and time resolved optical emission spectroscopy of the laser induced plasma using different targets (polymers, metals, ferrite, chalcogenides)



Images of different components of the experimental set-up for thin film deposition and plasma plume analysis by spectroscopic and electric techniques found at LOASL



Schematic representation of different techniques used for plasma characterization and dynamics and thin film deposition and irradiation effect

Effects of laser irradiation on the sample properties were studied taking into account the laser regime (nanosecond, picosecond or femtosecond) and was investigated during and immediately after laser irradiation using metal targets with atomic masses in a large range of values. In the liquid phase, the rate of expansion observed in the lateral direction observed after the laser pulse action is higher for shorter pulse durations and therefore rapid expansion in a short time favors the sideway expansion. Conversely, the size of the ablation plasma in the normal direction to the target surface increases very slowly during irradiation and increases along with the increase of the pulse length. These results are very important for spectroscopic measurements in this timescale because plasma parameters (electron density, atoms and ions, electronic temperature behavior etc.) show a strong dependency to the plasma expansion direction.

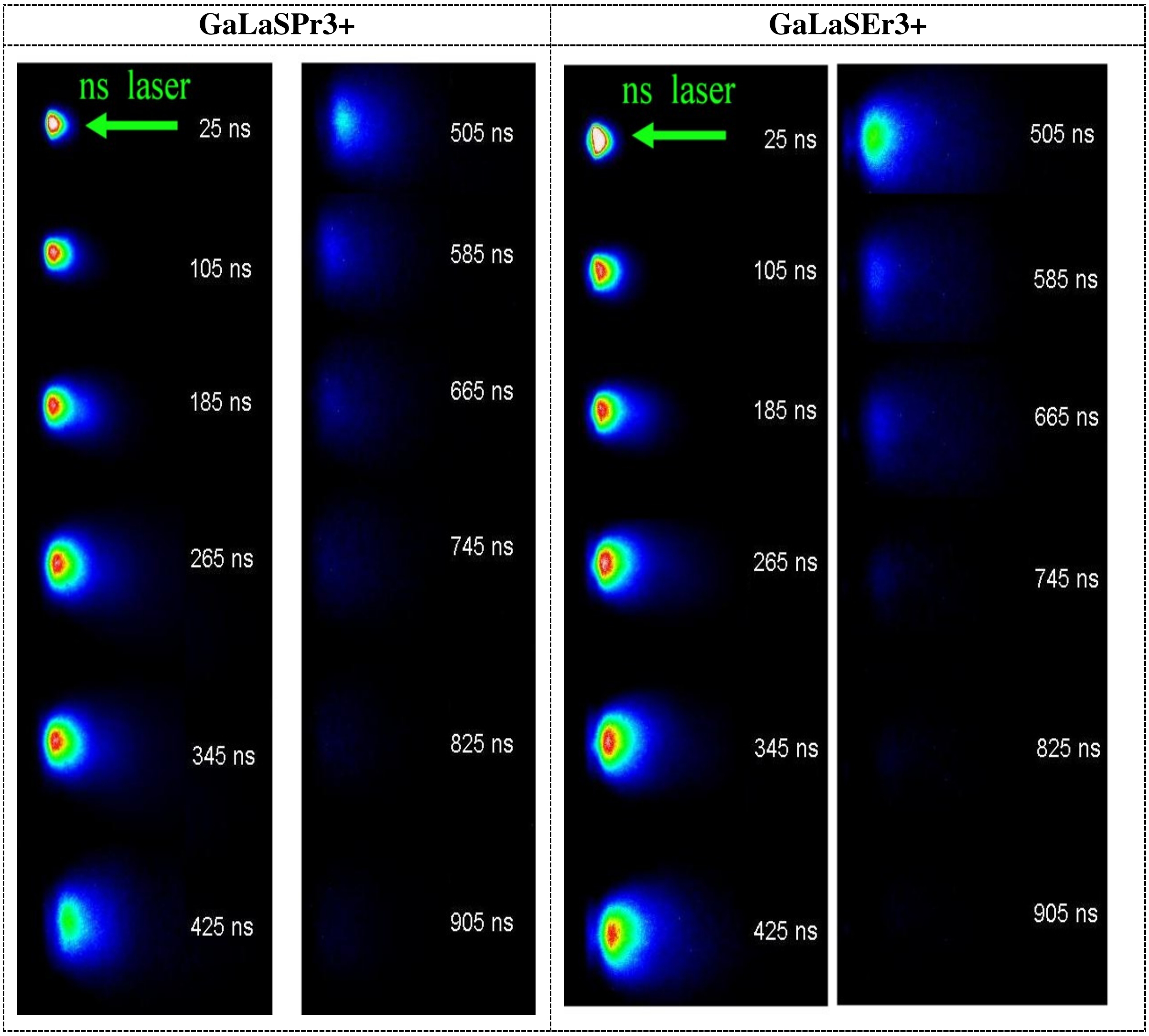
A research stage was focused on series materials of technological interest and with immediate practical applications. Here we mention two categories: ferromagnetic and chalcogenide thin films. We were focused not only on the standard method of obtaining thin layers with a specified thickness but also on those critical parameters which influence the dynamics of laser ablation plume with a subsequent effect on the deposited thin layer quality. A great importance shows: the chemical composition of the target, target-laser coupling, working gas pressure, the geometry of the plume expansion in relation to the direction of the PLD stage, substrate type, substrate temperature etc.

Preliminary results showed a tightly coupling between these parameters with significant changes of physico-chemical properties, optical parameters (n, K) etc.

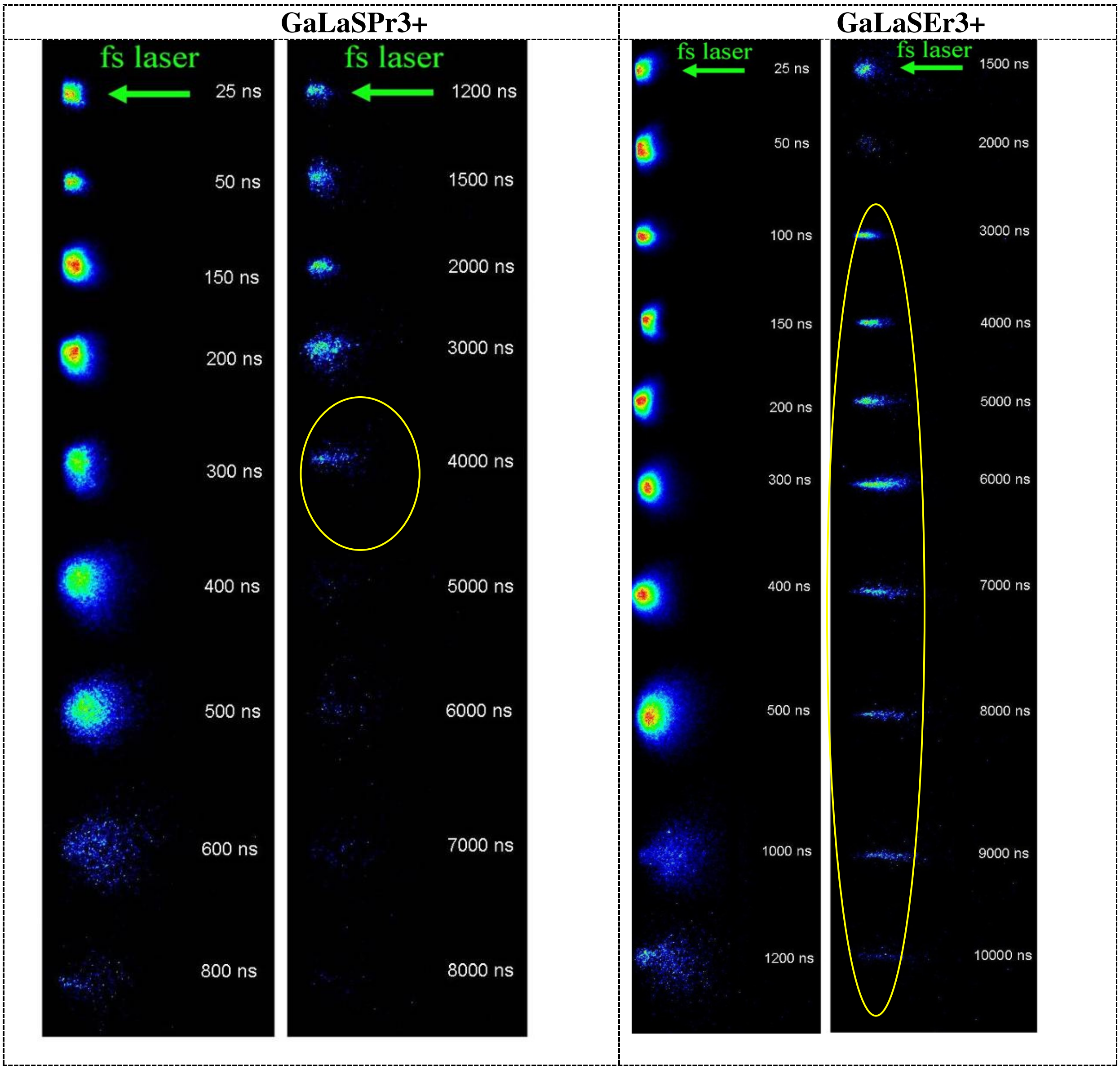
Thus, for a special class of chalcogenides "Pure and rare-earth doped (Erbium or Praseodymium) gallium lanthanum sulphide (GLS)" we highlighted the importance of laser regime (laser pulse duration) and laser fluency on the dynamics of laser induced plume (densities, excitation temperatures, expansion speed etc.) and on the plume geometry. Different laser regimens were used as follows:

In the nanosecond regime we used an Nd-YAG laser with a wavelength of 532 nm, pulse duration of 10 ns, repetition rate 10 Hz and fluence of 4 J / cm2. In picosecond regime we used a Ti-Sa laser with a wavelength of 800 nm, pulse duration 2 ps, repetition rate of 100 Hz and fluence of 1 J/cm2. For femtosecond laser irradiation the laser pulse duration was 120 fs with the other characteristics similar to picosecond regime.

Preliminary results showed significant changes from one regime to another (reflected by ICCD imaging measurements as well as by spatial and temporal resolved optical emission spectroscopy measurements.



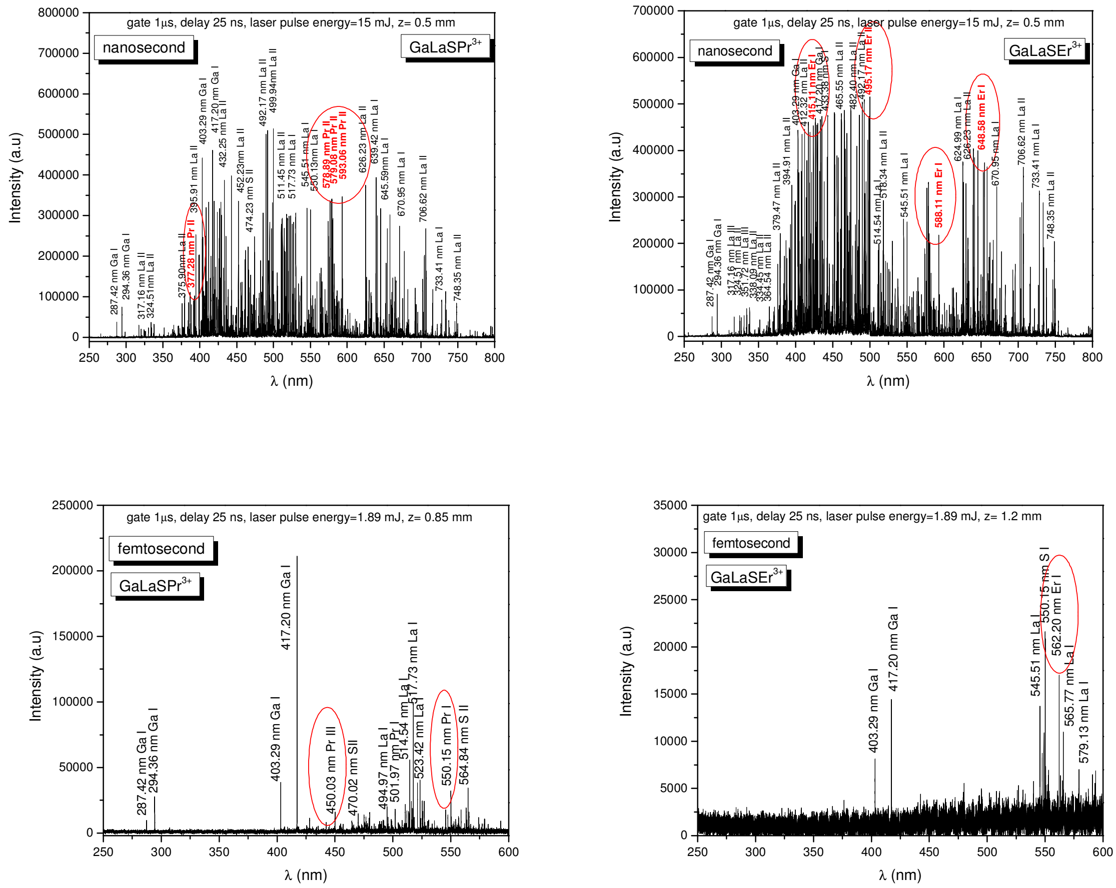
Spatial-temporal evolution of the doped GaLaS plasma in nanosecond regime



Spatial-temporal evolution of the doped GaLaS plasma in femtosecond regime

For an individual characterization of the chemical species present in the plasma, specific spectral measurements were performed. Thus, depending on the laser regime, optical emission spectra of a 0.2 mm thick plasma slices were recorded at different distances from the target surface. From the spatial and temporal profiles, excitation temperatures of different species and temporal evolution of the electron density were studied.

Preliminary results showed a laser ablation plume structure in which the chemical composition as well as laser irradiation regime plays an important role. Preliminary measurements also show the existence of the acceleration region of laser ablation plume. This phenomenon has been the subject of some articles and it is assumed that the origin of this acceleration is based on the "plasma double layer" formed by separating electrical charges during expansion.



Optical emission spectra of 0.2mm plasma slice using different irradiation conditions

Unlike in the nanosecond regime, in femtosecond regime the plasma presents a completely different dynamics. Doping elements contribute to a substantial increase of time (by an order of magnitude) for which the plume emits in the UV- VIS region.

Also, after ~1000 ns the plume, of both dopants, has a tendency to split and the plume presents a slower expansion. Also, compared with the studies conducted so far, we observed for the first time a filamentary structure beginning with 3000 ns ($GaLaSPr^{3+}$) or 4000 ns ($GaLaSEr^{3+}$). Thus the laser ablation plume profile changed substantially during expansion.

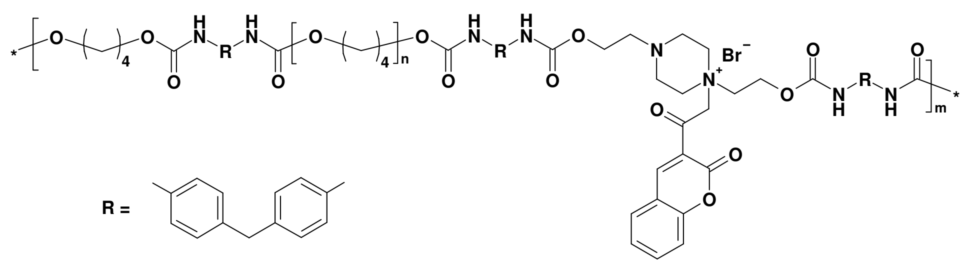
Thus, if in general, the profile of laser ablation plume behaves after a ⟦cos⟧^n (α) low with n = 8 in the « classic » regime, in the case mentioned above the index has much higher values. The laser ablation plasma gets a filamentary geometry starting from distances of 11 mm from the target and could influence the quality of PLD layer.

Another research objective of this stage was to analyze specific types of polymers for the development of polymer-metal multilayered systems.

In this context, it has been observed that some of the organic polymer-based substrates presented several advantages over inorganic ones: they are more flexible, offering a variable rigidity domain and can take different forms following the action of external stimuli. Moreover, the properties of the polymeric material can be adjusted according to specific requirements by chemical modification or by varying the polymerization conditions and/or crosslinking. Micro- and nanostructures obtained on a polymeric support can be extremely useful for a variety of applications, such as development of conducting circuits or substrates for adhesion control, but whatever the nature of their origin, polymeric nanoparticles are considered stable structures, in contrast to other systems. In this context, metallic nanoparticles (Cu, 99.4% purity and Ni, 99.6 % purity) were implemented by ablation of polyimide substrates

The studies that refer to surface structuring of polymer thin films showed that the irradiation conditions have a significant influence (frequencies range and energy values). The international studies on this phenomenon followed the development of materials capable of generating a controllable surface structure, without making a direct connection between the chemical structure and the nano-structuring mechanism. Currently, several theoretical models and mechanisms that try to explain the processes of surface reordering of the polymeric materials are reported and these are based on two types of phenomena: the first group of theories involves a reorganization of the polymer material and its compression under UV radiation and the second group is based on polymeric material displacement (photo-induced flow).

In this context, the novelty degree of this project refers to the fact that the chemical structure of the polymer will essentially influence the type of mechanism which determines the nano-structuring process (compression or flow). To explain these aspects, we studied types of polymers with different architectures with flexible, semi-flexible or rigid base chain and side chain connected with different types of chromophores.

Structure


We obtained polymer thin films on quartz substrate and special glass with transparency in the UV and IR (CaF) region using spin coating deposition method. Synthesized polymers were investigated:

- Polyimide (six polymers)
- Polyurethane coumarin (coumarin chemically linked, pendant polymeric chain in position 3).

We specify that the polymers studied were synthesized at the Institute of Macromolecular Chemistry "P. Poni" from Iasi. Structural and chemical analysis techniques confirmed the chemical structure of the compounds listed above.

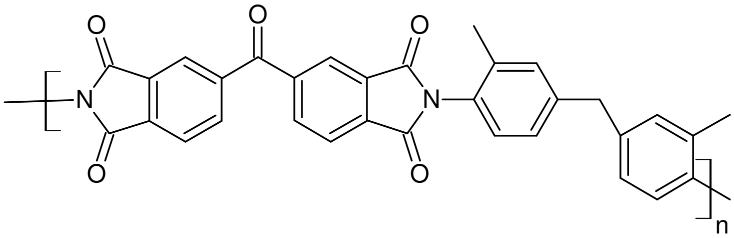
We studied the photochromic effects of laser radiation on thin polymer films and in tetrahydro furan {THF} and dimethylformamide (DMF) solutions. Were highlighted the dynamic processes of photo-dimers. The modifications of the electronic absorption and emission spectra were correlated by taking into account the molecular interactions that may occur in the solid phase and in solutions for molecules found in the ground state and excited electronic states .

On the other hand, the ordered supra-molecular nanostructures that can be generated in block copolymer films were used as matrices for nano-materials development. In the micro-phase separation process, the supra-molecular function between the incompatible phases plays an important role in nanostructure formation such as spheres, cylinders, lamellae. Moreover, the ordering of a single phase domain could lead to a micro-phase separation through complex mechanisms as a result of photoactive groups incorporation in block copolymers structure and of the molecular order transfer to supra-molecular dimensions. Usually, the ordered periodic structures obtained from a series of specific copolymers are in the 5-50 nm region. From this perspective, a study of a photopolymer block copolymer was initiated in which about 4% coumarin was covalently attached. Coumarin and most of coumarin derivatives are strongly fluorescent in solution and presents a extinguishing process in solid state due to the fluorophore crystallization phenomenon.

In agreement with literature data, according to which coumarin and its derivatives have excellent fluorescent properties, fluorescence spectrum of the investigate polymer in DMF solution and thin film form were recorded. In this case, the coumarin attached to polyurethane molecule chain emits at 320 nm (λ_{exc}=280 nm) and at 440 nm as a large peak due to aggregate formation. Aggregate formation was confirmed by atomic force microscopy (AFM).

We emphasize that laser ablation can cause physical and chemical processes that can lead to nanoparticles formation of any base material: metal, alloys, semiconductors, different ceramics. Laser ablation differs fundamentally from other methods of nanoparticles synthesis based on chemical and physical interactions. For this purpose, were obtained metal-polyimide layers by modifying the laser pulse energy and ablation time. Surface characteristics analyzed by AFM clearly indicate a strong interaction between Ni nanoparticles and the polyimides atomic chain compared with Cu-polymer nanostructures. Furthermore, Ni-polyimide nano-structures present higher a self-organization degree. Additional structural data will be obtained in the following stages to the project.

The chemical structure of the studied polyimide is the following.

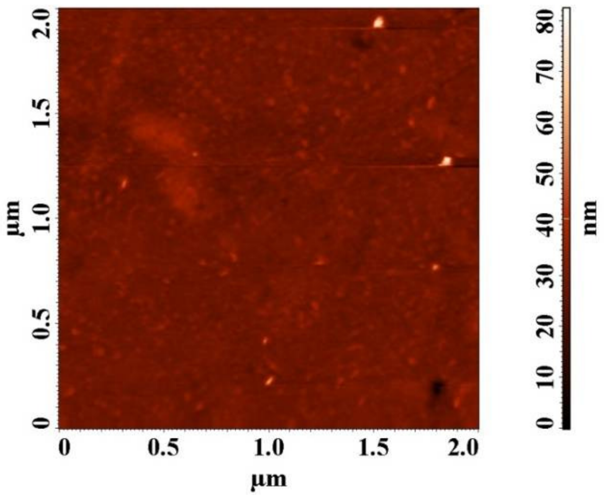


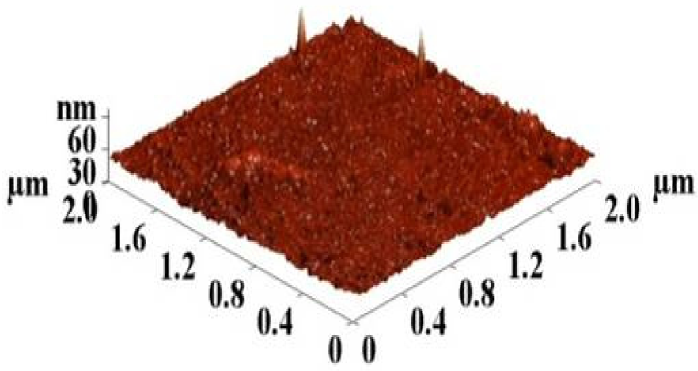
BDTA-MMDA

We present the figures of the polymer-metal films surfaces obtained by atomic force microscopy.

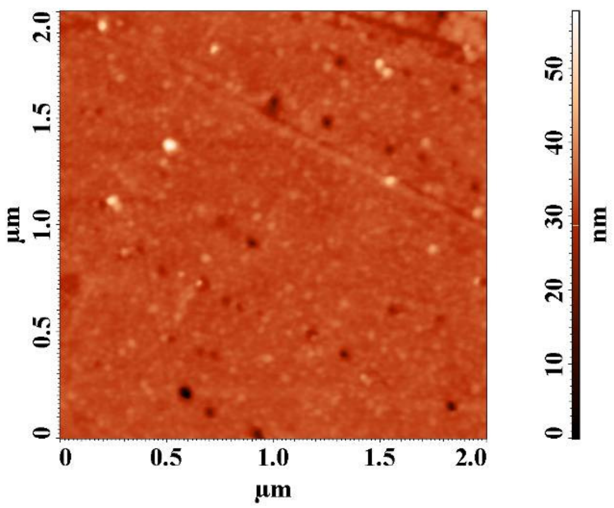
Polymer/metal depositions

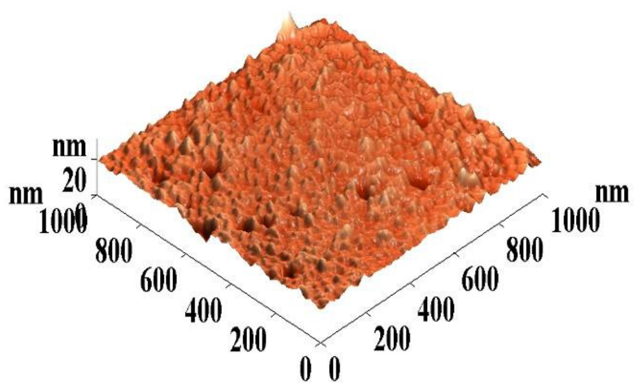
- The sample deposited on the polymer film
- Target: Cu; Substrate: Polymer
- d = 2 cm , p = 10^{-2}Torr , E = 30 mJ
- Open time = 40 sec (400 pulses)



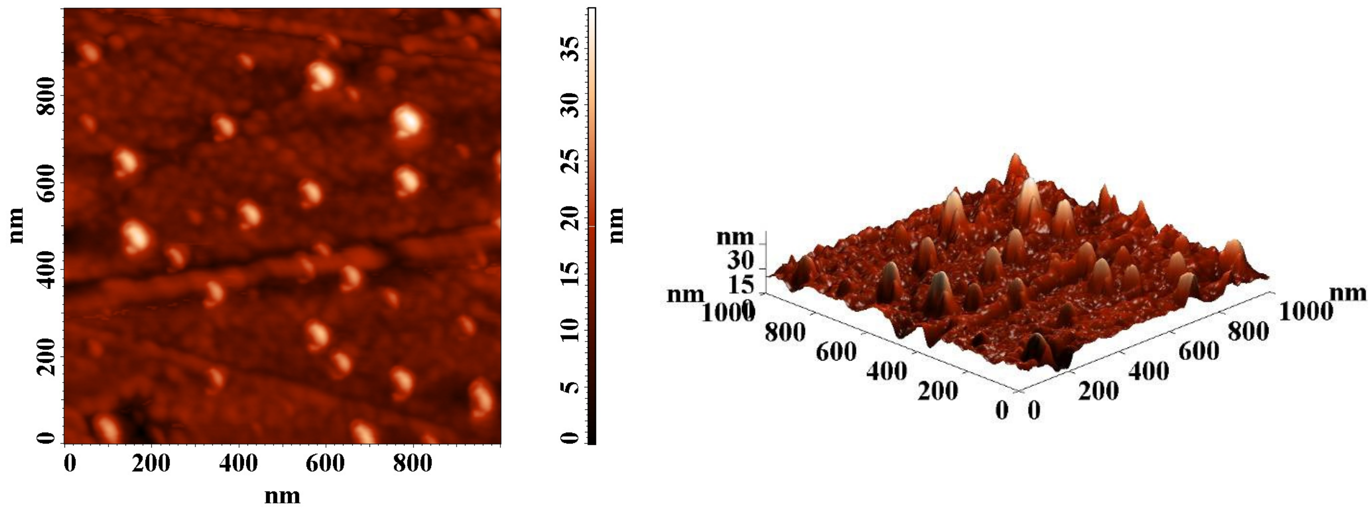


- Cu–polymer sample
- Target: Cu, substrate: polymer
- d= 2cm, p= 10^{-2}Torr, E= 30mJ
- deposition time = 600 sec (6000 pulses)

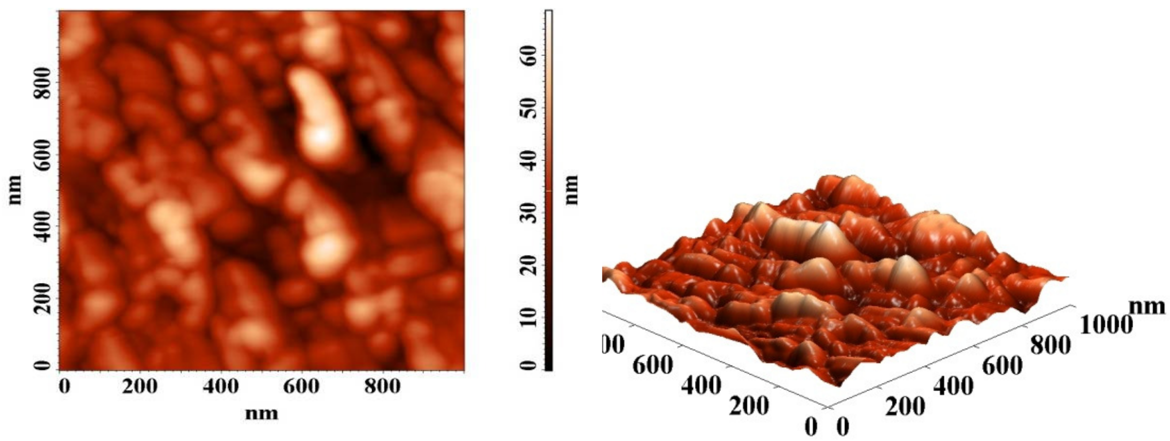




- Ni-polymer sample
- Target: Ni, substrate: polymer
- d= 2cm, p= 10^{-2}Torr, E= 30mJ
- deposition time = 40 sec (400 pulses)



- Ni-polymer sample
- Target: Ni, substrate: polymer
- d= 2cm, p= 10^{-2}Torr, E= 30mJ
- deposition time = 600 sec (6000 pulses)



LOASL together with the group of researchers from the University of Science and Technology of Lille 1 in France (prof. C. Focsa) observed an oscillatory phenomenon in laser ablation plasma. Such phenomenon drew the attention of the international scientific community and has been the subject of several invited papers and ISI publications. To understand the complexity of self-organization and oscillatory phenomena in laser induced plasma, a systematic study based on the nature of the irradiated material, influence of different experimental conditions (working gas, distance of observation, laser fluence, laser treatment etc.) and also mathematical model is required.

The first preliminary results were obtained using nanosecond pulsed laser. Our findings reveal that the oscillatory structure is based on elementary processes found in laser ablation plasma (excitation and ionization collisions, re-combinations) and depends on the electric properties of the target and the structure shows different dynamics during its expansion from the target surface to the substrate on which the thin film is formed. Such self-organization mechanisms in laser induced plasma could induce different properties ranging from stoichiometry and optical properties of the layers deposited by PLD.

In our opinion, these phenomena are more important when the substrate is closer to the target surface. Our research was also focused on the study of materials with various atomic masses (aluminum, manganese, copper, tungsten, nickel, tellurium etc.) using femtosecond laser.

A summary of the preliminary results were presented at various conferences (see list above) and also form the basis for a paper submitted for publication in ISI indexed journals.

Project director,
Assoc. Prof. Dr Silviu GURLUI

13 October 2014