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Scientific Report
Of project implementation 269 / 5.10.2011, CNCSIS PN-II-ID-PCE-2011-3-0650, from January to December 2012

Title: The study of polymer-laser radiation interactions in controlled atmosphere. Laser ablation nanostructured thin films layers. Applications

At this stage the proposed objectives were met in the project and directed both to fundamental research, understanding of physical phenomena, but also to find an answer as fully as issues in the taking of physical properties of new chemical materials with high technological impact by using laser pulses action in various experimental conditions. In this research were developed techniques, methods of characterization and preparation of materials of technological interest, and the results were published in international journals and journal indexed BDI national and international conferences as oral papers, poster or invited , as follows:

ISI Papers

1. C. Focsa, S. Gurlui, S. Pellerin, N. Pellerin, D. Pagnon, M. Dudeck, L. Balika, Laser-induced breakdown spectroscopy in a running Hall effect thruster for space propulsion, Spectrochimica Acta - Part B Atomic Spectroscopy, 74-75 pp. 184 - 189, (2012).
2. P. Nica, M. Agop, S. Gurlui, C. Bejinariu, C. Focsa, Characterization of Aluminum Laser Produced Plasma by Target Current Measurements, Jpn. J. Appl. Phys. 51, 106102 (2012).
3. M. Agop, P. Nica, O. Niculescu, D. G. Dimitriu – Experimental and theoretical investigations of the negative differential resistance in a discharge plasma, J. Phys. Soc. Japan 81, 064502 (2012).
4. S. Gurlui, G. O. Pompilian, P. Nemec; V. Nazabal, M. Ziskind, C. Focsa, Plasma Diagnostics in Pulsed Laser Deposition of GaLaS Chalcogenides, Appl. Surf. Science, (accepted for publication 11.10.2012, Ref no: APSUSC-D-12-02356R1).
5. G. Dascalu, G. Pompilian, B. Chazallon, O. Florin Caltun, S. Gurlui, C. Focsa, Cobalt ferrite thin films deposited by femtosecond pulsed laser deposition, submitted to Appl. Surf. Science, 2012.
6. S. Gurlui, D. G. Dimitriu, N. Cimpoesu, E. Buruiana and M. Strat, Photo-(physical and chemical) properties of polyurethane coumarin in polar solvents and thin films state, submitted to European Polymer Journal, 2012.
7. D. G. Dimitriu, M. Aflori, L. M. Ivan, V. Radu, E. Poll, M. Agop – Experimental and theoretical investigations of plasma multiple double layers and their evolution to chaos, submitted to Plasma Sources Science and Technology.

Papers accepted for publication (journal indexed in BDI, etc)

1. D. G. Dimitriu, M. Aflori, L. M. Ivan, E. Poll, M. Agop – Transition to chaos through sub-harmonic bifurcations in plasma. I. Experiment, *Bulletin of the Polytechnic Institute of Iasi, section Mathematics. Theoretical Mechanics. Physics*, accepted.
2. M. Agop, E. Poll, D. G. Dimitriu, M. Aflori, L. M. Ivan - Transition to chaos through sub-harmonic bifurcations in plasma. II. Fractal hydrodynamics, *Bulletin of the Polytechnic Institute of Iasi, section Mathematics. Theoretical Mechanics. Physics*, accepted.
3. E. Poll, M. Agop, D. G. Dimitriu, M. Aflori, L. M. Ivan - Transition to chaos through sub-harmonic bifurcations in plasma. III. Theoretical modeling, *Bulletin of the Polytechnic Institute of Iasi, section Mathematics. Theoretical Mechanics. Physics*, accepted.

Invited papers

1. Silviu Gurlui and Cristian Focsa, Development of Laser-Produced Plasma Technology. Fundamentals and Applications, 8th BPU, the 8th General Conference of **Balkan Physical Union**, 5-7 July 2012, Constanta, Romania.
2. O.G. Pompilian, G. Dascalu, S. Gurlui, C. Focsa, Processing and characterization of advanced materials by laser ablation techniques, 9th **International Conference on Physics of Advanced Materials**, 20 - 23 September 2012, Iasi, Romania;
3. O.G. Pompilian, G. Dascalu, S. Gurlui, C. Focsa, Laser-induced plasma: fundamentals and applications, **Physics Conference TIM-12**, 27-30 November 2012, Timisoara, Romania.

National and international conferences.

1. L. Balika, C. Focsa, S. Gurlui, S. Pellerin, N. Pellerin, D. Pagnon and M. Dudeck, Laser Ablation in a Hall Effect Thruster for Space Propulsion, E-MRS Spring 2012 - Symposium V, Strasbourg, France, 2012.
2. G. Dascalu, G. Pompilian, B. Chazallon, V. Nica, O. F. Caltun, S. Gurlui, C. Focsa, Rare earth doped cobalt ferrite thin films deposited by PLD, E-MRS Spring 2012 - Symposium V, Strasbourg, France, 2012.
3. S. Gurlui, G. O. Pompilian, P. Nemec, V. Nazabal, M. Ziskind, C. Focsa, Plasma Diagnostics in Pulsed Laser Deposition of GaLaS Chalcogenides, E-MRS Spring 2012 - Symposium V, Strasbourg, France, 2012.
4. Ramona Cimpoesu, Silviu Gurlui, Oana Pompilian, Monica Lohan, Nicanor Cimpoesu, Cristian Focsa, Thermo-elastic solicitation of a shape memory alloy enhanced with thin polymer films through pulsed laser deposition technique, 8th BPU, The 8th General Conference of Balkan Physical Union, 5-7 July 2012, Constanta, Romania.
5. Silviu Gurlui, Dan Dimitriu and Mitachi Strat, Optical and Spectral Properties of Polyurethane Coumarine. Self-organization phenomena induces nanoagregate formations, 8th BPU, The 8th General Conference of Balkan Physical Union, 5-7 July 2012, Constanta, Romania.
6. Silviu Gurlui, Nicanor Cimpoesu and Mitachi Strat, Selforganization phenomena in polyurethane coumarine film. The study of formation of nanoagregates by means of AFM and SEM methods, 8th BPU, The 8th General Conference of Balkan Physical Union, 5-7 July 2012, Constanta, Romania.
7. Maricel Agop, Dan G. Dimitriu, Silviu Gurlui, Negative Differential Resistance of the Discharge Plasma through Fractal Space-Time Theory, 5th Chaotic Modeling and Simulation International Conference, 12 – 15 June 2012, Athens, Greece.

8. Maricel Agop, Dan G. Dimitriu, Silviu Gurlui, Modeling of a Scenario of Transition to Chaos in Plasma through Sub-harmonic Bifurcations, 5th Chaotic Modeling and Simulation International Conference, 12 – 15 June 2012, Athens, Greece.

The main research activities were oriented to electrical characterization methods, methods of optical emission spectroscopy spatially and temporally resolved, ultrafast imaging, laser ablation plume both of thin films and special made by PLD technique (Polyurethane coumarin, ferites from cobalt and chalcogenides). Measurements of importance not only in terms of basic research but an application have considered finding various experimental conditions to identify critical values (user mode laser, fluence, working gas pressure, and target polarization PLD thin films substrate, substrate temperature, system geometry, etc.) to ensure obtaining competitive results. Approach and achieve impact on developing nanotechnologies leading applications aimed at obtaining nanocomponents and nanosensors involves the study of new materials governed by quantum effects and physical properties that differ fundamentally from those of the structures of origin (solid material). Thus, in order to understand the effect of the irradiation on particular materials have been devised original experiments (figures 1 and 2), as follows.

1. Were obtained thin layers and stoichiometric cobalt ferrite doped with rare earth elements group (PR) by laser ablation using different values of different the experimental parameters. The analysis of structural properties observed that if doped cobalt ferrite layer is required a higher temperature of the substrate to obtain spinel structure. After analyzing the results of Raman spectroscopy was observed presence of mechanical stress compression webs, with the use of higher temperatures during deposition. PR in the presence of cobalt ferrite thin layers did not cause the formation of residual phase ortoferită PR as if heavy materials. Moreover, structural and magnetic test results confirmed the substitution of Fe spinel structure PR ion. It was noted that the use of higher substrate temperatures resulted in improved magnetic response. To avoid micrometer-sized particle deposition on the substrate, but not significantly diminish the deposition rate for material removal using laser radiation from a fs. Ti-Sapphire laser. The results of structural analysis performed showed the formation of a spinel crystal structure with preferential crystallographic growth direction. Due to much lower fluency and repetition rate laser pulses greater were obtained webs with high uniformity in a much shorter time. Estimated deposition rate was higher by about one order of magnitude than that observed for Nd-YAG laser deposition. In the case of these layers have been detected internal mechanical stresses but expansion.

2. To understand the dynamics of laser plasma ablation of the various stages of evolution of plasma formations have been proposed structured self-study methods characteristic of specific transient plasmas. For simplicity aluminium targets and cylindrical probe were chosen to investigate the plasma plume behaviour in conditions of pressure and various target potential. It turned out the importance of target polarization upon the laser ablation plasma evolution, the transient characteristics dynamics (oscillatory regime, self- structuring plasma, etc). Preliminary results indicate a possible structure type plasma double layer (DL) in certain experimental conditions.

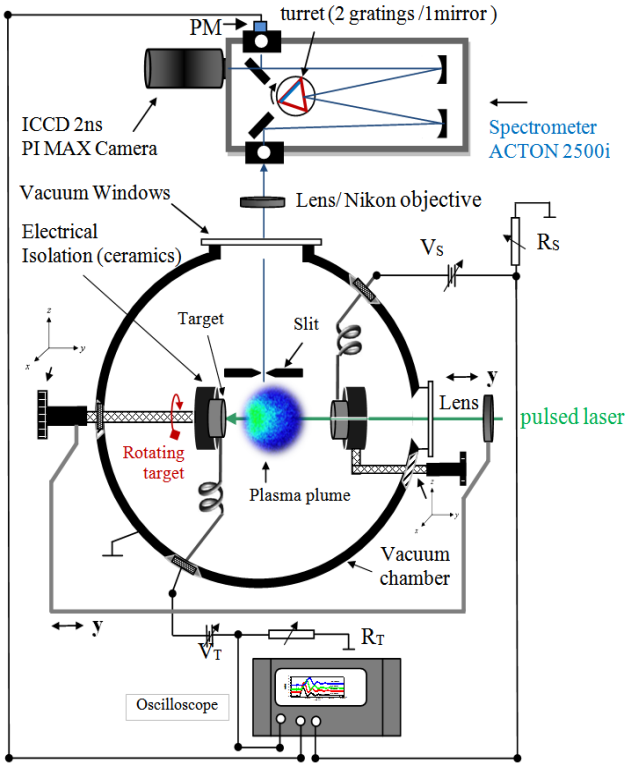


Figure 1. Experimental device used to study both the bihaviour of the plasma plume (fast optical emission spectroscopy and electrical diagnosis) and to obtaining PLD thin layer

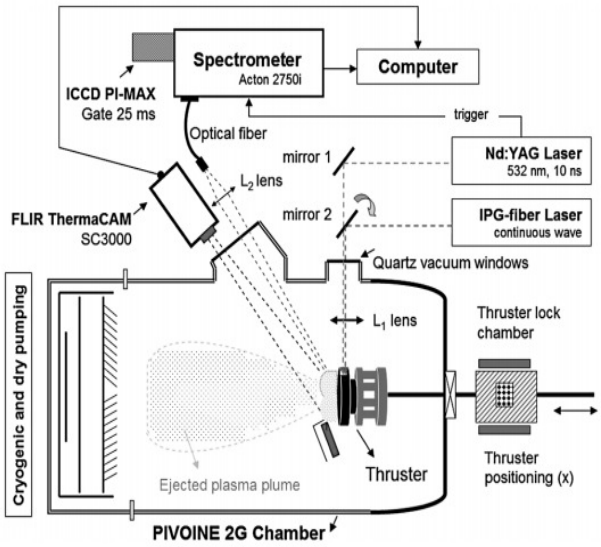
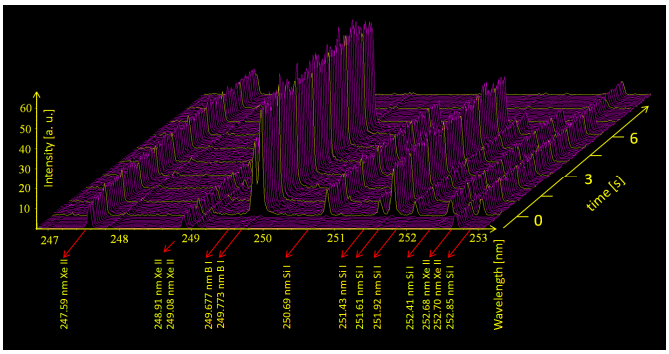


Figure 2. Experimental device: PPS100-ML, Hall Effect Thruster) used for orbital correction of the geostationary satellite, Pivoine-2G (ICARE laboratory), CNRS Orleans, France. Were analyzed changes induced by plasma ion bombardment effect due to erosion or laser ablation (local and accelerate erosion control operating parameters in situ analysis)

3. Were performed also research on simulating operation of engines Hall effect (PPS100-ML, Hall Effect Thruster) propulsion used at geostationary satellite orbit correction, (**see Pivoine-2G, ICARE laboratory, CNRS Orleans, France**). During engine operation different conditions were induced by irradiation of critical work laser beam pulsed or continuous wave. Were analyzed changes induced by laser ablation plasma, temperature variations, etc. There were induced variations in discharge current, temperature regime, etc. Under the interaction with the pulsed laser beam, significant changes in plasma discharge parameters (Figure 3) and emission spectrum have been evidenced. A notable result obtained here is that the rate of erosion function for calibration using spectral measurements

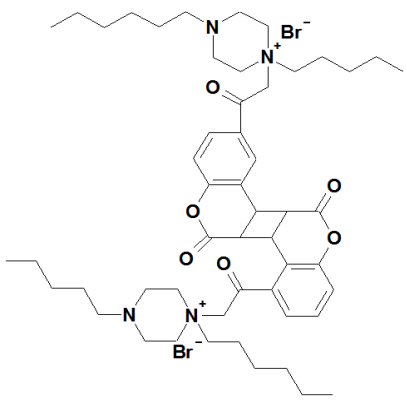


Typical spectrum of $BnSiO_2$ laser ablation over the Xe discharge plasma. Important changes occur with the action of laser pulses.

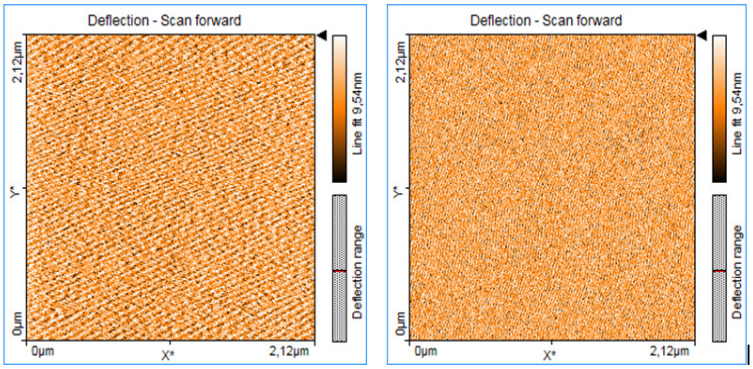
techniques. Were made also simulations of ion engine in critical experimental conditions. Results do were published in ISI journals and conferences in the field.

4. We have analyzed a number of high applicative potential chalcogenides (with important applications in many branches of science: biology, medicine, chemistry, physics, etc.), as noted in particular by low cost and tend super miniaturized: ultra-fast memory, amplifiers and laser sources, optical sensors, etc. Using PLD techniques, chalcogenides single or multilayer amorphous films having special physicochemical properties (mechanical, thermal, optical, homogeneity, etc.) have been studied. Preliminary research has been directed towards the analysis chalcogenides type GST / Galas doped with rare earths. Preliminary results have shown the importance of laser ablation plasma parameters to obtain thin PLD films with superior mechanical and optical characteristics and can be found in the list of publications attached to this report.

5. The electronic spectra, absorption and fluorescence of polyurethane coumarin were obtained in various polar solvents and film state. Electronic absorption bands in polar solvents suffer shifts towards higher wavelengths. Electronic absorption spectrum of polyurethane-coumarin has two bands, and they π-π transitions assigned*. Electronic spectra of the fluorescence of polyurethane coumarin were obtained in dimethyl-formamide (DMF), tetrahydrofuran (THF) and in the film state. In order to obtain fluorescence spectra were used the following sources of radiation: 310nm Hg; 365nm Hg; N2 laser radiation (337nm) and Nd-YAG laser radiation (Quantel) 266nm, 532nm respectively. It has been found that shifts of the fluorescence maxima in polar solvents bands are greater than the displacement of the absorption bands peaks in the same solvent. This shows that the electric dipole moment in the excited state (μe) is higher than the ground state dipole moment (μg) (μe> μg). These shifts to higher wavelength peak of electronic bands (Δν = 3000-5000 cm^{-1}) indicated that the state of the film and solutions of DMF and THF are nano-aggregates of the polyurethane-coumarin. To get more information about these nanostructures were studied photo-physical properties and photo-chemical properties of polyurethane-coumarin excitation under the action of molecular systems using λ_{exc} = 266nm respectively λ_{exc} = 532nm. Studies of absorption and fluorescence spectra showed that, under the action of radiation with λ> 310nm, polyurethane- coumarin forming photodimers. By comparing the fluorescence intensity of the bands at 375nm and 375nm in a state film and DMF showed that photodimerization of polyurethane coumarine film state is produced, in particular its surface. To confirm this result we studied the photodimerization of polyurethane coumarin in film state using AFM methods. We studied also the surface of a film obtained by spin-coating in two cases. Surface area non-irradiated and irradiated with the nitrogen laser pulses (λ = 337nm). AFM images produced by the deflection are given in Figure 4.



Formation of photodimers in the polyuretan-cumarine



Figur 4. The images deflection of polyurethane-coumarin film obtained by spin-coating irradiated (left) and irradiated with 337nm laser N2 (right).

Images deflection confirms that nanoagregates formats appear in greater numbers when the film surface is irradiated with nitrogen laser radiation with, λ = 337nm. Main results mentioned above summary is sent for publication in European Polymer Journal.

6. There have been highlighted some preliminary results on action pulsed laser beams (2 picoseconds) on the same polyurethane-coumarin-type polymers. Spectral measurements were performed and ICCD imaging of laser ablation plume and PLD thin layers of different thicknesses. Preliminary results will be correlated and interpreted in accordance with the literature.

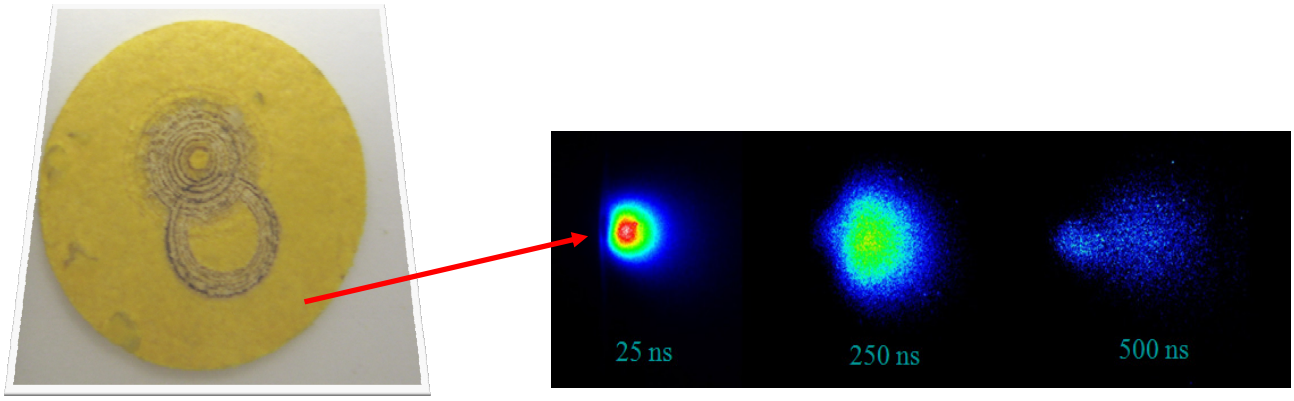


Figure 5. The polymer target under the action of the (2 ps, 100 Hz and energy 1.6 mJ / pulse) laser radiation. Different delay times of the plasma expansion phase were recorded using the ICCD high-speed camera (100 ns gate).

Project manager,
S. Gurlui