



PLASMA RO-FR

31 August - 1 September 2023

INFLPR, Magurele, Romania

1st Romanian-French Workshop on Non-Thermal Plasma

BOOK OF ABSTRACTS PROGRAM





GENERAL INFORMATION / INFORMATIONS GÉNÉRALES

As a continuation of the long-lasting Romanian-French collaboration, the National Institute for Laser, Plasma and Radiation Physics (INFLPR) is organizing a Romanian-French Workshop with the support of the French Embassy in Romania and l'Agence Universitaire de la Francophonie Europe Centrale et Orientale on the topic of non-thermal plasma, covering both fundamental aspects of plasma and applications in various fields, such as nanotechnology, environment, life sciences. The aim is to discuss the latest scientific developments in these areas, to actively exchange new ideas and to globally strengthen the scientific cooperation between France and Romania.

En continuité avec la collaboration roumano-française de longue date, l'Institut National de Physique des Lasers, des Plasmas et des Rayonnement (INFLPR) organise un atelier roumano-français avec le soutien de l'Ambassade de France en Roumanie et de l'Agence Universitaire de la Francophonie Europe Centrale et Orientale sur le thème des plasmas non thermiques, couvrant à la fois les aspects fondamentaux des plasmas et les applications dans divers domaines, tels que les nanotechnologies, l'environnement, les sciences de la vie. L'objectif est de discuter des derniers développements scientifiques dans ces domaines, d'échanger activement de nouvelles idées et de renforcer la coopération scientifique entre la France et la Roumanie.

WORKSHOP TOPICS / THÉMATIQUES DE L'ATELIER

Diagnostics and simulations / Diagnostiques et simulations

Nanotechnology / Nanotechnologie

Environmental applications / Applications environnementales

Applications in life sciences / Applications dans les sciences de la vie

VENUE / LIEU

INFLPR, 409 Atomistilor Street, Magurele, Ilfov/

FOTOPLASMAT - C400 Seminar room / Salle de séminaire FOTOPLASMAT - C400





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Thursday, 31 August / Jeudi 31 Août 2023			
9:00	9:30	Registration / Accueil des participants	
9:30	10:00	Welcome/ Mot d'accueil	
Morning session / Séance du matin 1 - Chair / Présidence: Pascal BRAULT			
10:00	10:30	IL-1	Corina BRADU - Procédés de traitement avancé des eaux usées
10:30	11:00	IL-2	Dunpin HONG - Non-thermal plasma to degrade amoxicillin and sulfamethoxazole antibiotics in water alone or in mixture
11:00	11:15	O-1	Florin BILEA - Insight into the degradation products of an organic pollutant during plasma treatment
11:15	11:45	Coffee break / Pause-café	
Morning session / Séance du matin 2 - Chair / Présidence: Bogdana MITU			
11:45	12:15	IL-3	Thierry BELMONTE - Synthesis, growth mechanism and photocatalytic properties of Bi ₂ O ₂ CO ₃ nanosheets elaborated by discharges in liquids
12:15	12:45	IL-4	Rodica VLADOIU - Advanced materials magnesium-based obtained by implementation of a novel concept of laser-plasma technology
12:45	13:00	O-2	Tomy ACSENTE - A short review on synthesis of W nanoparticles by magnetron sputtering combined with gas aggregation
13:00	13:15	O-3	Valentina MARASCU - Influence of cold plasma on bulk and dust Tungsten materials for hydrogen, deuterium, and tritium gas exposures
13:15	14:30	Lunch / Déjeuner	
Afternoon session / Séance de l'après-midi 3 - Chair / Présidence: Magdalena NISTOR			
14:30	15:00	IL-5	Catherine BATIOT-DUPEYRAT - Plasma-catalysis for syngas production
15:00	15:15	O-4	Zeina AL-ZAYED - Shaped materials of controlled porosity for the direct synthesis of methanol from CH ₄ by plasma-catalysis coupling
15:15	15:30	O-5	Flaviu BAIASU - Influence of the positive pulse on the deuterium retention in Al and Be deposited by BP-HiPIMS
15:30	15:45	O-6	Ovidiu STOICAN - A dc electrical supply unit for cold plasma sources
15:45	16:00	Coffee break / Pause-café	
16:00	17:30	Visit in the Labs / Visite des laboratoires	
19:00	22:00	Workshop Dinner / Diner de l'atelier	



Friday, 1 September/ Vendredi, 1 Septembre 2023

Morning session / Séance du matin 4 – Chair / Présidence: Dunpin HONG

9:00	9:30	IL-6	Philippe GUILLOT - Caractérisations de plasmas à pression atmosphérique et décontamination biologique
9:30	10:00	IL-7	Ionut TOPALA - Cold atmospheric pressure air plasma exposure of cell culture media
10:00	10:15	0-7	Cristina MUJA - Renforcer la sécurité alimentaire des graines germées grâce au plasma froid
10:15	10:30	0-8	Ana-Maria UDREA - Innovative Repurposing Repositioning of Chlorpromazine via Laser Irradiation: A Promising Strategy for Breast Cancer Treatment
10:30	11:00	Coffee break / Pause-café	

Morning session / Séance du matin 5 – Chair / Présidence: Gheorghe DINESCU

11:00	11:30	IL-8	Pascal BRAULT - Molecular dynamics simulations: A powerful virtual microscope for plasma processing
11:30	12:00	IL-9	Catalin VITELARU - Process control in reactive magnetron sputtering: application for the deposition of oxides, nitrides and oxy-nitrides
12:00	12:15	0-9	Stefan IRIMICIUC - Langmuir probe measurements in laser produced plasmas: Implementation, limitations, and perspectives
12:15	13:15	Round-table / Table-ronde	
13:15	14:30	Lunch / Déjeuner	

Procédés de traitement avancé des eaux usées – vers une pollution zéro

Corina Bradu¹, Florin Bîlea², Grégorio Crini³, Nadia Morin-Crini³, Dunpin Hong⁴, Pascal Brault⁴,
Elena-Alina Olaru¹, Sorin-Marius Avramescu¹

1. PROTMED Research Centre, Department of Systems Ecology and Sustainability, University of Bucharest, Spl. Independentei 91-95, 050095 Bucharest, Romania; corina.bradu@g.unibuc.ro
2. Department of Plasma Physics and Nuclear Fusion, National Institute for Lasers, Plasma and Radiation Physics, Atomistilor Street 409, 077125 Magurele, Romania
3. Laboratoire Chrono-Environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, 16 Route de Gray, 25000 Besançon, France
4. GREMI, CNRS - Université d'Orléans, 14 rue d'Issoudun, Orléans, 45067, France

Les activités humaines exercent des pressions multiples sur les systèmes aquatiques affectant leur capacité à fournir des services écosystémiques. Un impact significatif est généré par l'utilisation généralisée de substances chimiques dangereuses qui se retrouvent dans les systèmes aquatiques en raison d'un traitement insuffisant des eaux usées. De ce point de vue, le besoin d'innovation pour développer des méthodes efficaces de traitement de l'eau, capables d'éliminer ces polluants récalcitrants aux méthodes conventionnelles, est devenue une priorité.

Le développement des procédés d'oxydation avancée (POA) tels quels, ou couplés à des procédés adsorbatives pour l'élimination des polluants prioritaires ou émergents des eaux est un des axes de recherche majeurs de notre groupe. Deux directions principales ont été visées pour les POA : (i) l'oxydation catalytique par l'ozone ou par le peroxyde d'hydrogène et (ii) le traitement par plasma non-thermique (décharges à barrière diélectrique et corona). Ces méthodes ont été testées pour la dégradation de molécules cibles appartenant à différentes classes de polluants, tels que les produits pharmaceutiques (ex. Diclofenac), les pesticides (ex. Acide 2,4-dichlorophenoxyacetic) et les colorants (ex. Reactive Black 5).

Les études ont été portées sur la synthèse de catalyseurs à base de métaux de transition (Cu, Ni, Co, Pd etc.), actifs dans l'oxydation des polluants organiques persistants et sur l'optimisation des paramètres de la décharge électrique.

Pour mieux comprendre le processus de dégradation des polluants cibles par les POA, en élucidant les aspects sur le mécanisme et la cinétique, ont été pris en compte: (i) l'identification et la quantification des espèces oxygénées actives dans le milieu aqueux; (ii) l'identification et la quantification des sous-produits d'oxydation; (iii) l'évaluation du degré de minéralisation des polluants. En outre, la toxicité de l'eau traitée et sa réutilisation potentielle ont été évaluées, ainsi que la stabilité et de la réutilisation des catalyseurs.

Afin de résoudre les problèmes réels générés par les eaux usées industrielles (ex. de l'industrie de la finition de surface métallique) avec une contamination organique-inorganique complexe des POA ont été couplés à des procédés d'adsorption en utilisant bio-polymères à base de cyclodextrines. Le couplage de ces deux procédés de décontamination peut conduire à un abaissement important de polluants organiques auprès des métaux lourds, tendant vers une pollution zéro.

Remerciement - Ce travail a été soutenu par des subventions de l'Autorité Nationale Roumaine pour la Recherche scientifique, CNCS—UEFISCDI : projets BM-PHC 18/2019 et PCE143/2021 ; et du Ministère de la Recherche, de l'Innovation et de la Numérisation : projet PNRR-I5 760010/2022.

Non-thermal plasma to degrade amoxicillin and sulfamethoxazole antibiotics in water alone or in mixture

D. Hong¹, F. Bilea^{2,3}, T. Tian¹, H. Rabat¹, M.-A. Antoissi¹, O. Aubry¹ and C. Bradu⁴

¹GREMI, CNRS Université d'Orléans, 14 rue d'Issoudun, 45067 Orléans, France

²Department for Plasma Physics and Nuclear Fusion, National Institute for Lasers, Plasma and Radiation Physics, Atomistilor Street 409, Magurele, Ilfov 077125, Romania

³Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, Sos. Panduri 90, Bucharest 050663, Romania

⁴PROTMED, Faculty of Biology, University of Bucharest, Splaiul Independenței Str. 91–95, 050095 Bucharest, Romania

e-mail address of the corresponding author: dunpin.hong@univ-orleans.fr

To avoid aggravating the pollution of our precious water resources, wastewater must be treated more effectively with new innovative methods, non-thermal plasma being a viable candidate. Indeed, plasma is able to produce many reactive species and UV radiation to degrade water contaminants, including antibiotics [1]. In this context, a joint study was conducted as part of a Brancusi-PHC collaboration to degrade the mixture of two antibiotics, namely amoxicillin and sulfamethoxazole, in water and compare the result with the removal of each molecule alone.

The reactor consisted of a dielectric barrier discharge with falling water film and was operated at atmospheric pressure with air or oxygen. The discharge was supplied with square waveform high voltage of 11–15 kV in amplitude and 300–1500 Hz in frequency. During plasma treatment, the antibiotic concentrations decreased exponentially and have similar half-life time, in the range 4–9 min, depending on discharge power. Although faster removal of the contaminants was obtained by increasing the power (9.1–20.2 W), the energy efficiency remained almost the same, 3–4 g/kWh at 50% removal. Oxygen considerably reduced the time needed for removal and improved the energy yield by a factor of two as compared with air, due to more effective formation of reactive oxygen species. It was found that the degradation of antibiotics in mixture essentially depends on the overall initial concentration, this behavior being attributed to the similar reactivity of the two investigated compounds.

KEYWORDS: non-thermal plasma, dielectric barrier discharge, water treatment, antibiotics, sulfamethoxazole, amoxicillin

Acknowledgment: The authors thank Dr. Monica Magureanu for her involvement in the Brancusi-PHC joint project.

[1] M. Magureanu, F. Bilea, C. Bradu, D. Hong, A review on non-thermal plasma treatment of water contaminated with antibiotics, *J. Hazard. Mater.* 417 (2021) 125481, <https://doi.org/10.1016/j.jhazmat.2021.125481>

Synthesis, growth mechanism and photocatalytic properties of $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheets elaborated by discharges in liquids

A. V. Nominé¹, V. Milichko^{1,2}, A. Nominé¹, C. Noël¹, Th. Gries¹, T. Belmonte^{1,3}

¹ University of Lorraine, CNRS, IJL, F-54000 Nancy, France

² Department of Nanophotonics and Metamaterials, ITMO University, St. Petersburg, 197101, Russia

³ thierry.belmonte@univ-lorraine.fr

The growth of $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheets through nanosecond-pulsed discharges in liquid environments has been achieved by applying voltages slightly above the breakdown voltage between two bismuth electrodes immersed in liquid nitrogen or water. This growth process involves surface modification of the cathode electrode following an etching pretreatment with Nital.

Remarkably, water and liquid nitrogen as liquid media for discharges do not modify significantly the interaction between the electrodes and the metallic discharge that forms by electrode erosion.

The anisotropic growth of thin nanosheets made of a few monolayers is attributed to ion-assisted deposition via the ledge mechanism, supplemented by the presence of surface defects. Chemical etching is not mandatory but it increases the probability of nanosheet formation from almost zero to nearly one hundred percent. This step eliminates native oxide layers and exposes surface defects. Parallel planes forming combs within polishing scratches are holding flowers of $\text{Bi}_2\text{O}_2\text{CO}_3$ which are assembly of nanosheet (Fig. 1).

The removal of nanosheets from the cathode and their release into the liquid is ensured by the mechanical movement of the liquid-bubble interface along the electrode, which breaks the nanosheets away from their substrate.

The photocatalytic activity of nanosheets was evaluated by following the decomposition of different dyes. It turns out that it is much higher than Bi_2O_3 nanoparticles.

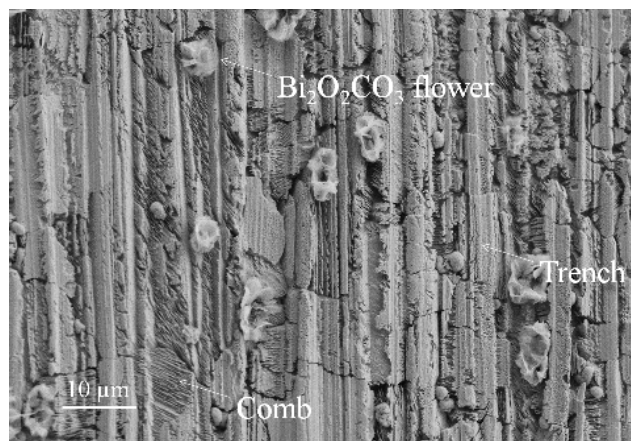


Fig. 1: Surface of the bismuth cathode after synthesis.

Advanced materials magnesium-based obtained by implementation of a novel concept of laser-plasma technology

R. Vladoiu^{1,2}, A. Mandes¹, V. Dinca¹, S. Polosan^{2,3}

¹*Ovidius University of Constanta, Faculty of Applied Sciences and Engineering, Dept of Physics, Mamaia Av. No 124, Constanta, 900527, Romania*

²*Academy of Romanian Scientists, Splaiul Independentei No. 54, Bucharest 050094, Romania*

³*National Institute of Materials Physics, P.O. Box MG-7, Bucharest-Magurele 077125*

²*e-mail: rvladoiu@univ-ovidius.ro*

1. Introduction and experimental methods

The aim of this paper is to investigate the growth and structure properties of Mg-based composites thin films deposited by Thermionic Vacuum Arc (TVA) technology in one electron gun configuration. TVA method offers convincing advantages for multi-component depositions, such as high rate of deposition, low thermal energy transfer, very stable discharge conditions, no cathode' impurities, and very good adherence. [1]

In order to come closer to applications and technological control, a great interest has been paid to develop a combination technique to deposit thin films by using laser-induced high current arc which has the advantages of high ion energy and high-density. This work offers insight into the influence of the deposition parameters on morphology and properties in the TVA plasma induced by an adjustable power laser beam (Laser-induced Thermionic Vacuum Arc - LTVA). In the LTVA configuration the laser beam is provided by a QUANTEL Q-Smart 850 Nd:YAG compact Q-switched laser with second harmonic module.

2. Results and discussions

The plasma/surface interactions combined with photonic processes and growth mechanisms are relevant for finding the best combination of the magnesium based complex nanocomposites with tailored properties. [2] We analyzed the Mg:X (X=Zn, Ag, Si, Zr) thin films and find the deposition parameters, which include the intensity of the heated current by electron gun, the fluence of the laser beam, film thickness, and choice of the substrate have a huge impact on the nanocrystallinity and morphology

The properties of the deposited Mg-based composites were investigated in terms of wettability, morphology, and tribology. The surface free energy was determined by means of Surface Energy Evaluation System and the morphology were determined from BF-TEM image performed by Philips CM 120 ST TEM system. Compositional and topographical analyses were also undertaken by using Scanning Electron Microscopy with Energy-Dispersive X-ray detection (SEM/EDX).

[1] R. Vladoiu, M. Tichy, A. Mandes, V. Dinca, P. Kudrna, **COATINGS**, Vol: 10 Issue: 3, Article Number: 211, 2020

[2] R. Vladoiu, A. Mandes, A. V. Dinca, P. Kudrna, M. Tichy, S. Polosan., **J. Alloys Comp.**, 869 (2021) 159364.

Caractérisations de plasmas à pression atmosphérique et décontamination biologique

Ph. Guillot

*Laboratoire Diagnostics des Plasmas Hors Equilibre (DPHE), Université de Toulouse, INU
Champollion, Albi, France
philippe.guillot@univ-jfc.fr*

De nos jours, au niveau international, de nombreux laboratoires effectuent des recherches dans le domaine des plasmas appliqués à la biologie, notamment pour décontaminer des surfaces et traiter des liquides. De nouvelles sources plasma et de nombreuses applications ne cessent d'apparaître montrant ainsi un fort intérêt scientifique et un grand potentiel socio-économique. Le laboratoire DPHE s'inscrit modestement dans ce travail collectif et dans cette trajectoire. L'objectif de cette présentation sera double : 1) présenter des sources plasma et les résultats expérimentaux correspondants 2) identifier des voies de collaboration potentielles.

En introduction, le laboratoire DPHE sera rapidement présenté ainsi que ces deux grandes thématiques de recherche : plasma et chimie analytique, plasma et biologie. Ensuite, dans le cadre de la présentation, un focus sera fait sur les plasmas à pression atmosphérique appliqués à la décontamination, en se concentrant sur les jets de plasma. Dans un premier temps, les sources plasma et leurs fonctionnements seront décrits. Ensuite des résultats de caractérisations expérimentales de jets de plasma seront présentés. Pour les émissions du plasma, les caractérisations optiques sont réalisées pour la spectrométrie à partir d'un spectromètre Princeton SpectraPro HRS-750 et pour les variations spatio-temporelles à partir d'une caméra Princeton Instruments PI-MAX3:1024i. Pour l'ionisation, les spectres de masse sont obtenus à partir d'un spectromètre de masse à temps de vol TOF-MS TOFWERK. Cet appareil est équipé d'une interface à pression atmosphérique permettant un couplage simple entre le jet de plasma et l'entrée du spectromètre de masse. Par la suite en qui concerne la décontamination par plasma, la partie du laboratoire dédiée à la microbiologie et la méthodologie employée pour notamment évaluer l'efficacité des traitements pas plasma seront décrites. Des exemples de décontamination de surface et de liquides seront alors présentés. Enfin la conclusion sera centrée sur les aspects collaboratifs principalement autour de la spectrométrie de masse et du potentiel de la partie microbiologie du laboratoire.

Cold atmospheric pressure air plasma exposure of cell culture media

A.B. Stache^{1,2}, C.T. Mihai³, I.C. Gerber⁴, I. Mihaila⁴, V. Pohoata⁵, L. Gorgan¹, I. Topala⁵

¹Faculty of Biology, Alexandru Ioan Cuza University of Iasi, 700505 Iasi, Romania

²Center of Fundamental Research and Experimental Development in Translational Medicine—TRANSCEND, Regional Institute of Oncology, 700483 Iasi, Romania

³Praxis Medical Investigations, 700376 Iasi, Romania

⁴Integrated Center of Environmental Science Studies in the North-Eastern Development Region (CERNESIM), Alexandru Ioan Cuza University of Iasi, 700506 Iasi, Romania

⁵Faculty of Physics, Alexandru Ioan Cuza University of Iasi, 700506 Iasi

Correspondence: ionut.topala@uaic.ro

Atmospheric pressure plasma sources are optimum technological solutions to be used for water and biological environments activation (e.g., culture media, phosphate-buffered saline (PBS), acidified buffers) [1]. A new approach in the field of plasma medicine was the use of plasma-activated medium (PAM), an alternative to directly delivering cold atmospheric plasma to cancer cells *in vitro* or *in vivo*. Plasma generation directly into cell culture plates was selected in our studies (Figure 1). The effects of PAM are attributed to persistent reactive molecular and ionic chemical species, like H_2O_2 , NO_2^- and NO_3^- , present in the solution following CAP treatment. The stability of various reactive oxygen and nitrogen species and their interactions with biomolecules, which result in oxidized products, are influenced by the composition of the cell culture medium. The critical nutrient deposits are reduced, which ultimately results in cytotoxicity [2,3].

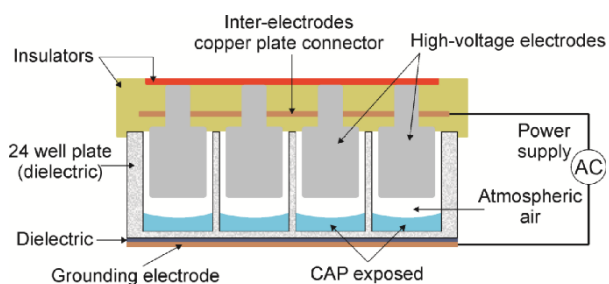


Figure 1. Sketch of the experimental set-up for air DBD plasma experimental exposure system for cell culture medium activation [2,3].

Our results proved the synergy of PAM use (DMEM) in addition with Paclitaxel to improve the *in vitro* antitumoral effect, as well the effect of PAM alone against breast cancer cells (MCF-7 and MDA-MB-231). In the case of human osteosarcoma cells (HOS cell line) and human osteoblasts (HOB cell line), exposing RPMI 1640 medium to our custom-built cold atmospheric pressure air plasma source was found to present selective dose-dependent cytotoxic effects on HOS cells.

- [1] I.C. Gerber, I. Mihaila, V. Pohoata, I. Topala, Evolution of Electrical and Optical Parameters of a Helium Plasma Jet in Interaction With Liquids, *IEEE Trans Plasma Sci*, **49(2)** (2021) 557-562
- [2] C.T. Mihai, I. Mihaila, M.A. Pasare, R.M. Pintilie, M. Ciorpac, I. Topala, Cold Atmospheric Plasma-Activated Media Improve Paclitaxel Efficacy on Breast Cancer Cells in a Combined Treatment Model, *Curr. Issues Mol. Biol.* **44** (2022), 1995–2014
- [3] A.B. Stache, I. Mihaila, I.C. Gerber, L.M. Dragos, C.T. Mihai, I.C. Ivanov, I. Topala, D.L. Gorgan, Optimization of Indirect CAP Exposure as an Effective Osteosarcoma Cells Treatment with Cytotoxic Effects, *Appl. Sci.* **13** (2023), 7803

Molecular dynamics simulations: A powerful virtual microscope for plasma processing

P. Brault¹

¹*GREMI, CNRS - Université d'Orléans, 14 rue d'Issoudun, 45067 Orléans Cedex 2, France*
pascal.brault@univ-orleans.fr

1. Principles

As plasma processes are atomic and molecular by nature, simulations at the molecular level will be relevant for providing us with insights into core and interface plasma chemistry basic phenomena. Moreover, statistical averaging allows to provide/predict macroscopic data as reaction rates, diffusion coefficients, etc., directly comparable with experiment outputs. Recent developments relevant for plasma processing and applications to plasma assisted sputtering deposition, nanoparticle growth and reactivity on plasma produced reactive oxygen species on pollutant molecules in water are reviewed.

Among all the available molecular simulation tools, reactive and ab-initio molecular dynamics (MD) simulation techniques are a good compromise between quantum mechanical and kinetic Monte-Carlo methods, especially due to the availability of robust and accurate reactive force fields and fast quantum chemistry methods. MD simulations calculate the trajectories of a set of particles, by solving the appropriate set of Newton equations of motion leading to the ability of these simulations to address reactivity of relatively large molecular systems (up to 109 atoms). It is now possible to directly include the electrons, but it is limited to some specific situations as plasma breakdown. Nevertheless, MD simulations can be carried out with initial conditions including expected plasma composition (ions, neutrals) from experimental measurement, such as mass spectrometry or fluid models. Addressing reactive plasma processes, thus, remains a quite challenging and useful task.

2. Applications

Three examples nicely illustrate the interest of carrying out molecular dynamics simulations:

1) Plasma sputtering deposition

Selection of initial velocity conditions can be done from either experimental data (energy resolved mass spectrometry) or SRIM simulations of sputtered atom energy distribution (EDF) for thermal evaporation, dc magnetron, HiPIMS and bipolar HiPIMS.. Moreover, it is possible to describe, in a single MD simulation, sputtering, transport and deposition using scaling arguments.

2) Nanoparticle growth and hydrocarbon plasma chemistry

The simulation box is composed of the plasma forming gas (Argon here), a metal vapor originated from a sputtered target and, if relevant, a reactive gas. As nanoparticles are also of concern in hydrocarbon plasma chemistries: volume and at surfaces for polymer film growth will be addressed.

3) Insight into plasma-liquid interactions

MD simulations are particularly relevant for addressing effects of ROS on pollutant molecules in water.

Acknowledgments: I wish to warmly thanks all collaborators who contribute to these works. Among them: A.-L. Thomann, A. Caillard, G.O. Otakandza-Kandjani, S. Fazeli, M. Mikikikian, A. Michau, K. Hassouni, M. Mgreanu, C. Bradu, F. Bilea

Process control in reactive magnetron sputtering: application for the deposition of oxides, nitrides and oxy-nitrides

Catalin Vitelaru^{*}, I.Pana, A.C. Parau, M.Dinu, L.R. Constantin, A.E Kiss, C.N Zoita, M.Braic

¹National Institute for Optoelectronics, 409 Atomistilor St., Magurele-Bucharest, P.O.Box MG 05, Romania

catalin.vitelaru@inoe.ro

Reactive sputtering is a widely known technique, implemented both in research laboratories and industrial setups. It allows to obtain a wide range of compound materials, such as oxides, nitrides, oxy-nitrides, carbides etc, with properties that are highly dependent on the reactive gas element. It is therefore crucial to be able to control the process in such a way that the composition of the thin film is tunable and reproducible over long durations of deposition process. In this contribution we propose a systematic approach of the reactive process, with the purpose of controlling the process and tuning the properties of the thin films.

The process tunability was achieved by using optical emission spectroscopy as a tool to monitor and control the gas composition in the process chamber. Active control loops using PID controllers are implemented by using the ratio of selected emission lines intensities. The magnetron plasma emission is used as the main source of radiation, having the emission lines of metal atoms and the reactive gas as parameters to monitor and control the reactive process. In addition, a modified version of the control loop is proposed, using the emission lines specific for the Penning pressure gauge. In this case the emission lines of argon and the reactive gases are used to monitor and control the reactive process. This version has the advantage of being independent on the sputtering source, being able to monitor the gas composition changes in the chamber.

The performance of control loops is assessed both for processes with one reactive gas, either oxygen or nitrogen, as well as for the processes where two reactive gases are used simultaneously. The stability of the process is proven for a series of perturbations and the ability to stabilize the process inside the hysteresis loop is also demonstrated. The tunability of material properties is exemplified both for oxides (CuO_x) and oxy-nitrides (TiO_xN_y , TaO_xN_y).

Keywords: reactive sputtering, magnetron, optical emission spectroscopy, oxides, oxy-nitrides

Acknowledgment: This research was funded by the Romanian Ministry of Research, Innovation and Digitalization, through Program 1- Development of the national research-development system, Subprogram 1.2 - Institutional performance - Projects to finance the excellent RDI, Contract no. 18PFE/30.12.2021 and Romanian National Core Program no. PN 16.40.01.01/02 and PN11N-03-01-2023.

Insight into the degradation products of an organic pollutant during plasma treatment

F. Bilea¹, C. Bradu², M. Magureanu¹

¹National Institute for Lasers, Plasma and Radiation Physics, Magurele, Romania

²Faculty Of Biology, University of Bucharest, Bucharest, Romania
florin.bilea@inflpr.ro

The main side effect of intense antibiotics use around the globe is the dissemination of bacteria resistant to commonly prescribed antimicrobials. Thus, in the past decade, less known antibiotics have seen a rise in popularity [1]. One such antibiotic is sulfamethoxazole [2], which persists following conventional water treatment methods and can pose an environmental risk by stimulating antimicrobial resistance [3,4].

Sulfamethoxazole degradation was investigated using a pulsed corona discharge coupled with ozonation [5]. The plasma was generated in oxygen, above the pollutant solution using a multi-wire to plate reactor geometry. This configuration allows the formation of excess ozone, which is bubbled through the liquid in a second vessel. The sulfamethoxazole solution (330 mL) was circulated between the plasma and ozonation reactors. The plasma was generated using 100 ns (FWHM – full width at half maximum) high voltage pulses with an amplitude of 18 kV, at a frequency of 25 Hz, resulting in an average dissipated power of 5.5 W. The pollutant concentration was varied in the range 0.1-0.5 mM and the solution was prepared with tap water or distilled water (+ NaHCO₃), of 300 µS/cm conductivity. The pollutant removal was assessed using high performance liquid chromatography, while the degradation products were analyzed by liquid chromatography coupled with mass spectrometry.

In the time frame of the experiments (maximum 60 minutes treatment time) complete pollutant removal was achieved for all tested concentrations. The degradation of sulfamethoxazole was characterized by apparent reaction rate constants in the range of 0.21 – 0.49 min⁻¹, depending on the initial concentration. The experimental setup has also proven cost effective, with the highest recorded energy yield of 64.5 g/kWh at 50% pollutant removal. During treatment, 38 degradation intermediates were detected and identified based on the mass spectra recorded in both positive and negative ionization modes using an electrospray ionization source. Of these intermediates, only 9 were still present after 60 minutes of treatment. Based on the identified compounds, hydroxyl radicals and ozone were confirmed as the main contributors to the degradation of sulfamethoxazole and its intermediates, leading to the formation of hydroxylated compounds, ring opening and fragmentation.

Acknowledgment: This work was supported by UEFISCDI, Grant no. PCE 143/2021.

Keywords: non-thermal plasma, water treatment, pulsed corona discharge, sulfamethoxazole

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A short review on synthesis of W nanoparticles by magnetron sputtering combined with gas aggregation

T. Acsente¹, G. Dinescu¹

¹INFLPR, Atomistilor 409 str., Ro 077125, Magurele, Romania

²tomy@infim.ro

Magnetron sputtering combined with gas aggregation (MSGGA) becomes in the last decades a traditional technique for synthesis of nanoparticles from diverse materials at a moderate synthesis rate, pointing to diverse specific applications in nanotechnology [1]. This method is based on the condensation in an inert gas flow of the supersaturated metallic vapors obtained from a magnetron discharge.

In this work we will present a review of our results on synthesis of tungsten nanoparticles (W NPs) using MSGGA and some of their application. We will point out on the possibility of controlling the morphology and dimension of the W NPs by proper tuning of the process parameters [2, 3]. Supplementary we will shortly present the possibility of obtaining core shell nanoparticles (W core and W compound in shell) using the MSGGA cluster source operated in plasma jet mode (MSGGA-JET); in this mode a plasma jet expanding from the exit aperture of the cluster source [4].

Supplementary, the use of W NPs as laboratory model for dust generated in fusion reactors will be presented. We will point out on the evaluation of tritium retention in W dust obtained by MSGGA when compared to bulk W [5] and on the cytotoxic effect of the W NPs on human dermal fibroblasts [6].

Acknowledgments. This research was supported by the Romanian Ministry of Research, Innovation and Digitization under Romanian National Core Program LAPLAS VII-contract no. 30N/2023 of National Institute for Lasers, Plasma and Radiation Physics.

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Influence of cold plasma on bulk and dust Tungsten materials for hydrogen, deuterium, and tritium gas exposures

V. Marascu^{1,*}, C. Stancu¹, M. Payet², A. Bonciu³, A. Bercea⁴, S.D. Stoica¹, C. Constantin^{1,5}, V. Mertens⁶, F. Miserque⁷, G. Pieters⁸, E. Bernard², C. Grisolia²

¹Low Temperature Plasma Department, INFLPR, RO-077125, Magurele, Romania

²CEA, IRFM, F-13108, St Paul Lez Durance, France

³Fotoplasmal Department, INFLPR, RO-077125, Magurele, Romania

⁴Laser Department, INFLPR, RO-077125 Magurele, Romania

⁵Faculty of Physics, University of Bucharest, RO-077125 Magurele, Romania

⁶CEA Saclay, DRF, IRAMIS, NIMBE, LEDNA, F-91191, Gif-sur-Yvette, France

⁷CEA Saclay, DES, ISAS, DPC, SCCME, LECA, F-91191, Gif-sur-Yvette, France

⁸Universite Paris-Saclay, CEA, INRAE, DMTS, SCBM, F-91191, Gif-sur-Yvette, France

*Corresponding author: valentina.marascu@gmail.com

1. General

Due to the development of future fusion facilities like ITER, SPARC, DEMO, etc., the fusion research sector offers alternative views on the production of clean energy. Thus, due to security issues, complementary experiments are in demand, in order to avoid scenarios that could affect the environments, during their operations. Herein, in the current paper, we present an approach for obtaining fusion-relevant materials, by using cold plasmas. In addition, tungsten bulk and dust were exposed to cold plasmas, in RF (13.56 MHz) [1, 2], and in microwaves (2.45 GHz) [3], in order to analyze the impact of hydrogen, deuterium, and tritium gases. Exposing tungsten to hydrogen plasma leads to nanostructure formation on top materials (Fig.1). In the case of deuterium plasma, blisters occur (Fig.2). Also, tritium retention was studied on submicronic tungsten dust, pre-treated in a hydrogen plasma discharge. These lab-scale experiments can be comparable with tungsten material phenomena behavior, during ITER operation.

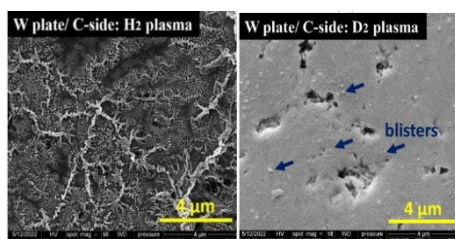


Fig.1: SEM image of the W surface plate, exposed to hydrogen plasma. [2]

Fig.2: SEM image of the W surface plate, exposed to deuterium plasma. [2]

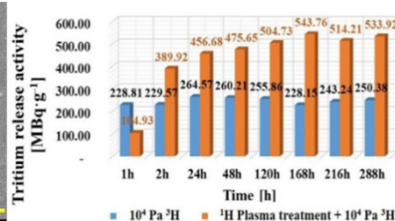


Fig.3: Tritium release activity:-Room temperature desorption results of W dust shows the comparison between the tritium release activity of dust pre-treated in pure hydrogen gas vs dust pre-treated in hydrogen plasma. [3]

Keywords: cold plasmas; tungsten surfaces and dust; hydrogen, deuterium, tritium gas exposure; fusion-relevant materials.

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Shaped materials of controlled porosity for the direct synthesis of methanol from CH₄ by plasma-catalysis coupling

Al Zayed Zeina¹, Fourré Elodie¹, Rossignol Sylvie², and Batiot-Dupeyrat Catherine^{1,3}

¹ENSIP, University of Poitiers, 86000, Poitiers, France

²IRCER, University of Limoges, Limoges, France

³catherine.batiot.dupeyrat@univ-poitiers.fr

Methanol is a key building block in the synthesis of chemicals. It can be used as fuel and fuel additive in combustion-based vehicles, and also a promising energy carrier in fuel cells. Methanol can be synthesized from several feedstock, including natural gas, coal, oven gas, biomass, and CO₂. Direct methanol synthesis through catalytic reactions has limitations due to the high thermal energy required to selectively activate C-H bonds leading to unwanted methane oxidation into CO or CO₂. [1] Plasma has been proposed as an alternative method to overcome these limitations, as it can activate methane at low temperature. [2] Combining a heterogeneous catalyst to plasma was proposed to increase the selectivity in the desired product. [3] Gas-solid interactions significantly influence the control of reaction interfaces. However, using catalysts in powdered form, as often seen in academic papers, might not be the most suitable choice due to limited gas-phase volume for plasma reactions. In this study, we adopted a novel approach by depositing the catalyst support on the inner electrode. Geopolymers were chosen for their proven ability to adhere well to stainless steel surfaces, as previously demonstrated in IRCER [4]. Geopolymers result from the activation of an aluminosilicate source by an alkaline silicate solution. And so, the use of geopolymers as catalyst supports showcases their potential for sustainable and eco-friendly applications in catalysis due to their low-temperature synthesis.

The plasma tests were conducted at atmospheric pressure and a temperature of 100°C within a quartz reactor featuring a wire-cylinder configuration with an internal gap of 0.2cm and a 6.2 cm³ volume of plasma. A controlled gas flow, consisting of a methane and oxygen mixture, was introduced into the reactor diluent. The resulting gas effluent was carefully examined using micro-gas chromatography to accurately determine the conversion of methane and oxygen, as well as the selectivity towards methanol and other products.

A parametric study was conducted on the reactor to optimize the conditions for achieving the highest methanol yield. This study involved manipulating key parameters, namely residence time (5.27, 6.15, 7.37 and 9.22 s), deposited power was fixed at ≈5.5W, and the CH₄/O₂ ratio (0.04, 0.1, 0.3, and 0.5). The best yield in methanol 1.8% was achieved when the reactor operated at a CH₄/O₂ ratio of 0.5 and a residence time of 9.22 seconds resulting in a conversion of 14% for CH₄ and a selectivity of 12.6% in methanol. Under these optimal conditions the selectivity in CO was of 66% and so a yield of 9.5%.

After establishing the optimal conditions, a series of tests were performed using geopolymer alone and geopolymer incorporating copper oxide to examine their respective effects. The results obtained from these tests will be presented and discussed to demonstrate the outcomes of the study.

Keywords: Plasma, geopolymers, methanol, biofuel.

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Influence of the positive pulse on the deuterium retention in Al and Be deposited by BP-HiPIMS

F. Baiasu^{1,2}, P. Dinca^{1*}, B. Butoi¹, C. Staicu^{1,2}, C. Lungu, C. Porosnicu¹, E. Grigore¹, M. Gherendi¹, M. Mocanu¹, C. Ruset¹

¹National Institute for Laser, Plasma and Radiation Physics, 077125 Magurele, Romania;

²Faculty of Physics, University of Bucharest, 077125 Magurele, Romania;

In nuclear fusion, the bombardment of the plasma facing materials (PFM) with intense particle flows can cause unwanted consequences such as erosion, melting, nuclear fuel retention that affect the reactor lifetime. The purpose of this work is to assess the influence of the positive pulse and the effect of the positive impinging ions on the deuterium retention in the beryllium and aluminum [1-3] coatings deposited under ITER-relevant conditions in terms of ion energy. Also, considering the safety issues in working with Be, the scientific community had to find a surrogate element-Al [1-3] which allow a safe manipulation in laboratory studies to simulate T retention through deuterium (D) retention, which is quite similar.

The deposition method, Bipolar-High Power Impulse Magnetron Sputtering (BP-HiPIMS) stood out due to its advantages such as high ionization degree of the plasma species, the ability to control the ion flux and energy during the deposition process. Also, this technique can provide coatings relevant to ITER conditions where the ions energies of the plasma species can vary up to 200 eV.

The present study reports the deuterium retention for samples deposited by BP-HiPIMS, produced in 2 batches one for Al and one for Be. The energy of the impinging ions after the positive pulse was varied in 3 steps: 50 eV, 100 eV, 200 eV. The depositions were carried in a constant mixture of Ar+D gaseous atmosphere, and the D inventory of Al+D/Be+D samples was analyzed in correlation with the kinetic energy of impinging ions after applying the positive pulse. In order to assess the influence of different parameters on the processes of ionization and transport of ions in the plasma, plasma properties, retention and release behavior of D from the deposited samples, plasma-diagnosis was performed. Moreover, in this work we addressed comprehensive evaluation such as: deuterium depth profile measured by GDOES [4], thermal desorption outgassing by TDS, structural and morphological characterization by XRD and SEM.

Keywords: BP-HiPIMS, Deuterium retention, Aluminum, Beryllium.

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A dc electrical supply unit for cold plasma sources

O. S. Stoican

*INFLPR, Atomistilor Street, 409, Magurele, RO-077125, Romania, P. O. Box MG-36
ovidiu.stoican@inflpr.ro*

A standalone unit aimed to supply the plasma generators operating at atmospheric pressure is presented. The unit is a practical implementation of the circuit topology described in [1]. Basically, it consists of a voltage multiplier [2] with five stages serving both to initiate and to maintain a dc electrical discharge. The output voltage varies between about 5.3 kV (open circuit) and a few hundred volts (at 13-23 mA load current), depending on the state of the plasma jet. Due to the specific configuration of the electric circuit, the transition between the different discharge regimes is done "naturally", without to be necessary any additional electronics or user action. This feature allows to apply the plasma jet to a probe for a predefined amount of time and to reignite the electrical discharge in the case of its erratic interruption. In this way the robustness and reliability of the operation for the system comprising the power supply and plasma generator is obtained. The ballast resistor, necessary to achieve the plasma stability [3], can be electronically switched in the range from 10 k Ω to 50 k Ω in steps of 10 k Ω . By varying the ballast resistor, the plasma gas temperature can be changed as a function of the specific purpose, e.g. biological or material processing applications. Additionally, the unit is equipped with a solenoid valve to turn on/off the carrier gas and a Wi-Fi module allowing the remote control of the plasma generator operation. By using a pure dc electrical discharge to generate the plasma jet, the need for RF or microwave power electronic components and matching networks is avoided. Because of lack of matching networks or tuned circuits the unit can drive a wide range of plasma generating devices with different geometries and sizes. The whole design is based, as much as possible, on usual and readily available components, materials and electronic boards.

This work was performed in the frame of PN 23 03 01.

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Keywords: plasma electrical supply; cold plasma sources; dc electrical discharges; voltage multiplier; material processing.

Renforcer la sécurité alimentaire des graines germées grâce au plasma froid

C. Muja^{1*}, Ph. Belenguer², L. Rigodanzo¹, T. Maho¹, Ph. Guillot¹

¹Laboratoire DPHE, INU J.F. Champollion, Université de Toulouse, Albi, 81012, France

²Laboratoire LAPLACE, CNRS, Université de Toulouse, Toulouse, 31000, France

*e-mail cristina.muja@univ-jfc.fr

Ces dernières années, la consommation mondiale de graines germées a fortement augmenté en raison de leur teneur élevée en nutriments tels que les vitamines, les minéraux, les enzymes et les antioxydants. Néanmoins, l'un des risques les plus importants pour la sécurité de ces produits est la contamination par des bactéries potentiellement pathogènes présentes dans les graines. Le développement de ces bactéries est favorisé par les conditions de température et humidité utilisées pour la germination de ces graines. Au cours des vingt dernières années, un nombre important de toxiinfections alimentaires (TIA) associé à la consommation de graines germées a été rapporté. Ces épidémies sont produites principalement par des souches d'*E. coli* pathogènes ou de *Salmonella* spp [1]. Bien que plusieurs techniques de décontamination puissent être utilisées pour réduire la charge bactérienne sur les graines à germer et les graines germées, la plupart d'entre elles ont un impact négatif sur les caractéristiques physiques et chimiques et sur la qualité finale des aliments.

Dans ce travail, nous avons examiné l'utilisation d'une décharge plasma dans l'air à pression atmosphérique comme solution potentielle pour la décontamination des graines à germer. Cette décharge corona a été générée dans un réacteur à l'aide d'une alimentation continue (HEINZINGER PNC30000-20POS). La caractérisation du plasma a été réalisée à l'aide d'un spectromètre optique (SpectraPro HRS-750). De plus, la concentration en ozone à l'intérieur du réacteur a été mesurée à l'aide d'un détecteur d'ozone (106M, 2BTechnologies).

Des graines de luzerne (*Medicago sativa*) et de lentilles (*Lens culinaris*) ont été utilisées comme modèles dans ce travail. L'efficacité biocide du traitement plasma a été évaluée en utilisant la flore mésophile présente dans les échantillons. De plus, des graines à germer inoculées avec *E. coli* (ATCC 700728) ont été utilisées pour évaluer l'effet bactéricide. Enfin, l'effet du traitement plasma sur les caractéristiques physicochimiques (par exemples, la couleur, la teneur en eau ainsi que le potentiel de germination) a été étudié.

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Innovative Repurposing Repositioning of Chlorpromazine via Laser Irradiation: A Promising Strategy for Breast Cancer Treatment

Ana-Maria Udrea¹, Angela Staicu¹, Speranta Avram², Madalina-Andreea Badea², Ionut-Relu Andrei¹, Mihail-Lucian Pascu¹, Patricia Preduna², Mihaela Balas².

¹ INFLPR, 409 Atomistilor Street, Magurele, ana.udrea@inflpr.ro; angela.staicu@inflpr.ro; ionut.andrei@inflpr.ro; mihai.pascu@inflpr.ro; RO-07712.

² University of Bucharest, Faculty of Biology, Splaiul Independentei speranta.avram@gmail.com; mihaela.balas@bio.unibuc.ro; badea_andreea08@yahoo.com. No 91-95, 050095 Bucharest, Romania;

1. Abstract

Breast cancer stands out as one of the most prevalent cancers, contributing significantly to global mortality rates. Conventional treatment methods encompass chemotherapy, radiotherapy, surgery, or their combinations. Our study introduces an innovative treatment by repurposing a novel technique involving laser irradiation and an antipsychotic drug, chlorpromazine, aimed at refining breast cancer treatment.

Employing a multidisciplinary approach, our investigation merges *in silico* methodologies with laser irradiation and *in vitro* validation, showcasing a pioneering strategy for the repositioning of established pharmaceuticals in the realm of cancer treatment. The irradiation procedure involves a pulsed laser beam operating at a 266 nm wavelength, delivering an average pulse energy of 6.5 mJ with a pulse repetition rate of 10 pps and irradiation durations spanning varied intervals.

Through molecular docking simulations, we predict the biological interactions with key cancer-associated receptors for laser-irradiated chlorpromazine.

To assess the cytotoxic effect on breast cancer cells (MCF-7 cell line), we adopted the MTS assay and live/dead staining methods. Our computational insights reveal that the photoproducts generated via laser irradiation have similar or higher biological functionality to chlorpromazine. Moreover, our *in vitro* investigations show the enhanced cancer-inhibitory activity of irradiated chlorpromazine, surpassing that of the unirradiated. This augmented effect could be attributed to the independent or synergistic actions of the photoproducts.

A comprehensive understanding of the mechanism underlying this synergistic enhancement may represent a novel modality for the repositioning of established pharmaceutical agents for breast cancer treatment. This research may bridge existing gaps in cancer therapeutics and holds promise for advancing oncological therapies.

Keywords: breast cancer, laser irradiation, chlorpromazine, cancer therapeutics, molecular docking.

Acknowledgment: This research was funded by the Ministry of Research, Innovation and Digitization, CCCDI UEFISCDI, within PNCDI III, CNCS-UEFISCDI, project number PN-III-P1-1.1-PD-2021-0225, and Nucleu Program LAPLAS VII - contract no. 30N/2023.

Langmuir probe measurements in laser produced plasmas: Implementation, limitations, and perspectives

Stefan Andrei Irimiciuc^{1,2}, Radu Udrea^{3,4}, Sergii Chertopalov², Michal Novotný², Jan Lancok²,
Valentin Craciun¹

IINFLPR, 409 Atomistilor street, Magurele, RO-077125, ROMANIA

2 Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, Prague, Czech Republic

3Apel Laser, Bucharest, Romania

4 Physics Faculty, University of Bucharest, Bucharest-Magurele, Romania

5Extreme Light Infrastructure for Nuclear Physics, Romania

One of the key research directions within the thin film technology is the controlling and tailoring of the any plasma-based deposition techniques via fundamental development. Controlling and tailoring PLD has been the main developmental pillar in its history with the focus on external factors (laser fluence, gas pressure, target bias, target-substrate distance, etc.). Recent results have showed that the laser produced plasma can be considered active medium in the deposition. Therefore, developing suitable diagnostics systems to understand the plasma kinetics and to control the complex chemistry occurring during the deposition becomes mandatory in order to develop a complete picture of the deposition process.

Aside the obvious applications for deposition monitoring, plasma dynamics is highly relevant for ELI related irradiation regimes. Reports of what was named “peculiar” effects were found for plasma plumes generated by laser ablation on wide range of materials. Theoretical approaches were also proposed based on fractal physics or a collisional model based on the plasma ions frequency and electron-ion collision rate. Recent advancements in charge current temporal traces interpretation combined with time-of-flight mass spectrometry measurements raised concerns on the interpretation of modulated probe current. Understanding the limitation of the probe will help the interpretation of the charge current temporal traces and the effect of charge fluctuation on the calculated plasma parameters. This goal is achieved by implementing a complex analysis of laser produced plasma with Langmuir probe coupled with time-resolved optical emissions spectroscopy. Correlations between the oscillation length, drift velocities and the charge density gradients are used to build a new explanation for oscillations in laser produced plasmas.

Acknowledgement: This work was supported by Romanian Ministry of Education and Research, under Nucleus Project LAPLAS VII – contract no. 30N/2023 and ELI-RO_2020_12.



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CONTACT

Monica Magureanu: monimag@gmail.com; monica.magureanu@inflpr.ro;
Bogdana Mitu: mitu.bogdana@inflpr.ro
Tel: +40766457701



SHORT PROGRAM / PROGRAMME COURT

31 August/ 31 Août 2023		1 September/ 1 Septembre 2023	
9:00 - 9:30	Registration / Accueil des participants	9:00 - 9:30	IL-7 Philippe Guillot
9:30 - 10:00	Welcome/ Mot d'accueil	9:30 - 10:00	IL-8 Ionut Topala
10:00 - 10:30	IL-1 Corina Bradu	10:00 - 10:15	O-7 Cristina Muja
		10:15 - 10:30	O-8 Ana-Maria Udrea
10:30 - 11:00	IL-2 Dunpin Hong	10:30 - 11:00	<i>Coffee break / Pause-café</i>
11:00 - 11:15	O-1 Florin Bilea	11:00 - 11:30	IL-9 Pascal Brault
11:15 - 11:45	<i>Coffee break / Pause-café</i>	11:30 - 12:00	IL-10 Catalin Vitelaru
11:45 - 12:15	IL-3 Thierry Belmonte	12:00 - 12:15	O-9 Stefan Irimiciuc
12:15 - 12:45	IL-4 Rodica Vladoiu	12:15 - 13:15	Round-table / Table-ronde
12:45 - 13:00	O-2 Tomy Acsente		
13:00 - 13:15	O-3 Valentina Marascu		
13:15 - 14:30	<i>Lunch / Déjeuner</i>	13:15 - 14:30	<i>Lunch / Déjeuner</i>
14:30 - 15:00	IL-5 Catherine Batiot-Dupeyrat		
15:00 - 15:15	O-4 Zeina Al-Zayed		
15:15 - 15:30	O-5 Flaviu Baiasu		
15:30 - 15:45	O-6 Ovidiu Stoican		
15:45 - 16:00	<i>Coffee break / Pause-café</i>		
16:00 - 17:30	Visit in the Labs / Visite des laboratoires		
19:00 - 22:00	<i>Conference Dinner / Diner de la conférence</i>		