

SURFACES, INTERFACES AND COATINGS TECHNOLOGIES



PLASMA PROCESSING AND TECHNOLOGY



# Book of Abstracts

7 - 9 April, 2021

Paris, France

(Virtual joint Conference)

Organizer



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Conferences & Exhibitions

**SICT / Plasma Tech 2021 Joint Conferences Program**

07 - 09 April 2021 | Paris, France

<b>07 April, 2021</b>		
<b>SICT Session I</b> <b>Surfaces and Coatings processing / Properties</b>		
<b>Session's Chairs:</b> <b>Prof. Alessandro Lavacchi, ICCOM, CNR - Firenze, Italy</b> <b>Prof. Ludmila B. Boinovich, The Russian Academy of Sciences, Russia</b> <b>Prof. Herman Terryn, Vrije Universiteit Brussel, Belgium</b>		
<b>09:00 - 09:30</b>	Tribology of Polymer Composite Coatings for Bearings and Other Applications <b>K. Friedrich</b>	<b>Prof. Klaus Friedrich</b> , Technical University of Kaiserslautern, <b>Germany</b>
<b>09:30 - 10:00</b>	Moving titania nanotube to 3D embedded macrostructure <b>A. Lavacchi</b>	<b>Prof. Alessandro Lavacchi</b> , ICCOM, CNR- Firenze, <b>Italy</b>
<b>10:00 - 10:30</b>	Nano-clustering structures creating a robust superlubricity state under high contact pressure in amorphous carbon films <b>X. Chen</b>	<b>Dr. Xinchun Chen</b> , Tsinghua University, <b>China</b>
<b>10:30 - 11:00</b> Break		
<b>Plasma Tech Session I</b> <b>Plasma fundamentals / Atomic and Molecular Processes</b>		
<b>Session's Chairs :</b> <b>Prof. Tiberiu Minea, Paris-Sud University, France</b> <b>Prof. Gérard Henrion, CNRS University Lorraine, France</b> <b>Dr. Johannes Grünwald, Gruenwald Laboratories, Austria</b>		
<b>11:00 - 10:30</b>	Corona discharges: Physics and Applications <b>O. Eichwald</b> , O. Ducasse, N. Merbahi, J.P. Sarrette and M. Youfifi	<b>Prof. Olivier Eichwald</b> , Paul Sabatier Univ. Toulouse, <b>France</b>
<b>11:30 - 12:00</b>	The strange world of cathodic arc spots: Is plasma formation fractal or periodic or bimodal? <b>A. Anders</b> , K. Oh, M. Golizadeh and R. Franz	<b>Prof. André Anders</b> , Leibniz Institute of Surface Engineering (IOM), <b>Germany</b>
<b>12:00 - 12:30</b>	Non-equilibrium Characteristics of Laser-Induced Plasmas <b>A. Bultel</b> , V. Morel and A. Favre	<b>Prof. Arnaud Bultel</b> , University of Rouen, <b>France</b>
<b>12:30 - 13:00</b>	The role of excited states in the time evolution of gas discharges <b>G. Colonna</b>	<b>Dr. Gianpiero Colonna</b> , CNR-ISTP-Bari, <b>Italy</b>
<b>13:00 - 14:00</b> Break		
<b>SICT / Plasma Tech Joint Session I</b> <b>Surfaces and Coatings processing / Characterization / Properties</b>		
<b>Session's Chairs:</b> <b>Prof. Klaus Friedrich, Technical University of Kaiserslautern, Germany</b> <b>Dr. Monica Bollani, Photonic and Nanotechnology Institute, Italy</b> <b>Prof. Alessandro Lavacchi, ICCOM, CNR- Firenze, Italy</b>		
<b>14:00 - 14:30</b>	Hybrid ALD/CVD towards nanoengineered functional CNT coatings <b>N. Bahlawane</b>	<b>Dr. Naoufal Bahlawane</b> , Luxembourg Inst of Science and Tech., <b>Luxembourg</b>
<b>14:30 - 15:00</b>	Functional polymers and micro/nanoengineering towards advanced manufacturing and sustainability <b>B. Zhao</b>	<b>Prof. Boxin Zhao</b> , University of Waterloo, <b>Canada</b>
<b>15:00 - 15:15</b>	Development of innovative duplex coatings combining cold-spray and plasma electrolytic oxidation processes <b>J. Martin</b> , K. Akoda, G. Ezo'o, G. Marcos, T. Czerwiec and G. Henrion	<b>Mr. Julien Martin</b> , University of Lorraine, <b>France</b>
<b>15:15 - 15:30</b>	Spatio-temporal study of poly (maleic anhydride) plasma deposition using a macroscopic description <b>S. Jebali</b> , A. Airoudj, I. Ferreira, D. Hegemann, V. Roucoules and F. Bally-Le Gall	<b>Ms. Syrine Jebali</b> , Haute-Alsace University, <b>France</b>

15:30 - 15:45	Different plasma nitride layer designs of an AISI D2 tool steel with a new Cr-Al-Ti-B-N PVD hard coating for optimized duplex layer systems <b>T. Weinhold</b> , A. Dalke, C. Wüstefeld, U. Ratayski, D. Rafaja and H. Biermann	<b>Mr. Tom Weinhold</b> , TU Bergakademie Freiberg, <b>Germany</b>
15:45 - 16:00	Plasma nitriding respond of thermal laser or electron beam treated surfaces of austenitic stainless steel <b>A. Dalke</b> and H. Biermann	<b>Dr. Anke Dalke</b> , TU Bergakademie Freiberg, <b>Germany</b>
16:00 - 16:30	<b>Break</b>	
<b>Session's Chairs:</b> <b>Dr. Naoufal Bahlawane, Luxembourg Inst of Science and Tech., Luxembourg,</b> <b>Prof. Boxin Zhao, University of Waterloo, Canada</b> <b>Dr. Zaoli Zhang, Erich Schmid institute, Austria</b>		
16:30 - 16:45	Low-temperature synthesis of gradient composite nanocoating on TiNi substrate <b>K. Dubovikov</b> , G. Baigonakova and E. Marchenko	<b>Mr. Kirill Dubovikov</b> , Tomsk State University, <b>Russia</b>
16:45 - 17:00	Elaboration and characterization of TixHf1-xN thin films <b>G. Desbordes</b> , C. Jaoul, C. Dublanche-Tixier, F. Husson and P. Tristant	<b>Mr. Guillaume Desbordes</b> , Limoges University, <b>France</b>
17:00 - 17:15	Fabrication of Tungsten high aspect ratio micro-tools by electro-chemical etching, by controlling the immersed length and the etching charge. <b>A. Taфраouti</b> , P. Kleimann and Y. Layouni	<b>Ms. Asmae Taфраouti</b> , Nanotechnologies Institute Lyon, <b>France</b>
17:15 - 17:30	Elaboration of high-entropy alloy coating by cold spray with following laser remelting: feasibility study <b>A. Sova</b> , M. Doubenskaia, E. Trofimov, M. Samodurova and V. Ulianitsky	<b>Dr. Alexey Sova</b> , National Engineering School of Saint-Etienne (ENISE), <b>France</b>
17:30 - 17:45	Deposition of Aluminum Nanostructured Films by DC Magnetron Sputtering for Hydrogen Production <b>S. Ibrahim</b> , P. Brault, A. Caillard, T. Sauvage, C. Chauveau, F. Halter and A-L. Thomann	<b>Dr. Sara Ibrahim</b> , University of Orléans, <b>France</b>
17:45 - 18:00	Adjustment of the micromorphology of component surfaces via cold spraying with fine particles <b>M. Bozoglu</b> , P. Breuninger and S. Antonyuk	<b>Mr. Mustafa Bozoglu</b> , TU Kaiserslautern, <b>Germany</b>
18:00 - 18:15	Combined GD-OES and HAXPES for quantified depth profiling through coatings B. F. Spencer, <b>M. Bouttemy</b> , Pia Dally, S. Béchu, P. Chapon and A. Etcheberry	<b>Dr. Muriel Bouttemy</b> , Versailles Saint-Quentin-en-Yvelines University, <b>France</b>
18:15 - 18:30	Multifunctional anti-fouling coatings for building materials: studying the combination of active nano-biocides with passive strategies via hydrophobicity and induced super hydrophilicity. <b>J.J. Cervera</b> , R. Zarzuela, M.L.A. Gil, I. Moreno-Garrido, Giada M.C. Gemelli, M. Luna and M.J. Mosquera	<b>Mr. Jaime Cervera</b> , University of Cadiz, <b>Spain</b>
18:30 - 18:45	Bio-carbon anti-UV properties for wooden façade coatings <b>L. Marrot</b> and D. B. DeVallance	<b>Dr. Laetitia Marrot</b> , InnoRenew Center of Excellence, <b>Slovenia</b>
18:45 - 19:00	Sculptured thin film based all-silica mirrors for high power lasers <b>L. Ramalis</b> , R. Buzelis, L. Grinevičiūtė and T. Tolenis	<b>Mr. Lukas Ramalis</b> , Center for Physical Sciences and Technology, <b>Lithuania</b>
19:00 - 19:15	Impact of Humidity and Deposition Errors on Spectral Parameters of Broadband Chirped Mirror with Sculptured Top Layer <b>S. Melnikas</b> , L. Ramalis, S. Kičas and T. Tolenis	<b>Mr. Simas Melnikas</b> , Center for Physical Sciences and Technology, <b>Lithuania</b>
19:15 - 19:30	Optical properties of highly porous thin films: an overview of optical simulation methods <b>J. Müller</b> , P. Moskovkin and S. Lucas	<b>Dr. Jerome Muller</b> , University of Namur, <b>Belgium</b>

<b>08 April, 2021</b>		
<b>SICT Session II</b> <b>Interface and Interaction Science, Adhesion and Adhesives</b>		
<b>Session's Chairs:</b> <b>Prof. Fabienne Poncin-Epaillard, French National Research institute, France</b> <b>Prof. Auezhan Amanov, Sun Moon University, Rep. of Korea</b> <b>Prof. Ludmila B. Boinovich, The Russian Academy of Sciences, Russia</b>		
<b>09:00 - 09:30</b>	Improvement in Tribological Properties and Interface Adhesion of Thermal Spray Coatings by Surface Severe Plastic Deformation (S2PD) Technique <b>A. Amanov</b>	<b>Prof. Auezhan Amanov, Sun Moon University, Rep. of Korea</b>
<b>09:30 - 10:00</b>	How to study interfacial reactions at the buried interface between organic coatings and metals <b>H. Terryn, S. Pletincx, K. Marcoen, F. Cavezza, L. Fockaert, N. Madelat, J.M.C. Mol and T. Hauffman</b>	<b>Prof. Herman Terryn, Vrije Universiteit Brussel, Belgium</b>
<b>10:00 - 10:30</b>	A study on the quality of adhesively bonded composite aircraft structures based on crack growth monitoring and Acoustic Emission <b>S. Teixeira de Freitas, D. Zarouchas and H. Poulis</b>	<b>Dr. Hans Poulis, TU Delft, The Netherlands</b>
<b>10:30 - 11:00 Break</b>		
<b>Session's Chairs:</b> <b>Dr. Hans Poulis, TU Delft, Netherlands</b> <b>Prof. Herman Terryn, Vrije Universiteit Brussel, Belgium</b> <b>Prof. Auezhan Amanov, Sun Moon University, Rep. of Korea</b>		
<b>11:00 - 11:30</b>	Plasma technologies for enhancing the metallic adhesion or the vulcanization-bonding <b>F. Poncin-Epaillard, M. Ji, L. Benyahia and JF. Coulon</b>	<b>Prof. Fabienne Poncin-Epaillard, French National Research institute, France</b>
<b>11:30 - 12:00</b>	In pursuit of toughness and damage tolerance by controlling material architecture <b>M. Alfano</b>	<b>Prof. Marco Alfano, University of Waterloo, Canada</b>
<b>12:00 - 12:15</b>	Studying the impacts of bonding agents in epoxy adhesives using self-assembled monolayers (SAMs) <b>L. Tomasovic, F. Gilbert, D. Jacquet, F. Bally-Le Gall and A. Ponche</b>	<b>Mr. Lucas David Tomasovic, Institut de Science des Matériaux de Mulhouse, UMR-CNRS/UHA, France</b>
<b>12:15 - 12:30</b>	Polymer thin films nano-engineered by means of femtosecond laser on single spot and scanning. <b>O. Shavdina, H. Rabat, F. Mahut, M. Vayer, C. Sinturel and N. Semmar</b>	<b>Ms. Olga Shavdina, University of Orléans, France</b>
<b>12:30 - 12:45</b>	Laser-based processing of polymeric tribological coatings for engine pistons <b>M. Dahmen, C. Vedder, H. Sändker and J. Stollenwerk</b>	<b>Mr. Marius Dahmen, Fraunhofer Institute for Laser Technology (ILT), Germany</b>
<b>12:45 - 13:00</b>	Hydrophobic Coatings with Low Ice Adhesion as a Passive Anti-icing System <b>J. Marczak, M. Piłkowski and G. Morgiante</b>	<b>Dr. Jacek Marczak, PORT Polish Center for Technology Development, Poland</b>
<b>13:00 - 14:00 Break</b>		
<b>Plasma Tech Session II</b> <b>Plasma-surface interactions / Plasma diagnostics / Modelling and numerical simulations</b>		
<b>Session's Chairs:</b> <b>Prof. Olivier Eichwald, Paul Sabatier Univ. Toulouse, France</b> <b>Prof. André Anders, Leibniz Institute of Surface Engineering, Germany</b>		
<b>14:00 - 14:30</b>	Diagnosing the plasma electrolytic oxidation process: an exciting but complex challenge <b>G. Henrion, J. Martin, C. Tusch, V. Ntomprougkidis, A. Nominé and T. Belmonte</b>	<b>Prof. Gérard Henrion, Institut Jean Lamour- CNRS University Lorraine, France</b>
<b>14:30 - 15:00</b>	Pulsed NS Discharge Development in a Strong Magnetic Field and its Application for MHD Energy Generation <b>A. Yu Starikovskiy, N L Aleksandrov and M N Shneider</b>	<b>Dr. Andrey Starikovskiy, Princeton University, USA</b>

15:00 - 15:30	Theory and Applications of inverted Fireballs <b>J. Gruenwald</b> and G. Eichenhofer	<b>Dr. Johannes Grünwald</b> , Gruenwald Laboratories, <b>Austria</b>
15:30 - 15:45	Ion-induced secondary electron emission coefficient of metal surfaces analysed in an ion beam experiment <b>R. Buschhaus</b> and A. von Keudell	<b>Mrs. Rahel Buschhaus</b> , Ruhr-University Bochum, <b>Germany</b>
15:45 - 16:00	Characterization and analysis of atmospheric pressure air plasma treatment of hard mineral materials <b>V. Grigaitienė</b> , R. Kėželis, R. Uscila, M. Aikas and V. Valinčius	<b>Dr. Viktorija Grigaitiene</b> , Lithuanian Energy Institute, Kaunas, <b>Lithuania</b>
16:00 - 16:30	<b>Break</b>	
<b>Session's Chairs:</b> <b>Dr. Gianpiero Colonna, CNR-ISTP-Bari, Italy</b> <b>Dr Andrey Starikovskiy, Princeton University, USA</b>		
16:30 - 16:45	Plasma nitrocarburizing with an active carbon screen made of CFC: Influence of the active screen power on the reactive gas composition and its effects on surface layer properties of stainless steel AISI 316L <b>J. Böcker</b> , A. Puth, A. Dalke, J. Röpcke, J.-P. H. van Helden and H. Biermann	<b>Mr. Jan Böcker</b> , Technische Universität Bergakademie Freiberg, <b>Germany</b>
16:45 - 17:00	Multiscale simulation of TiAlN film growth in an industrial magnetron-based reactor <b>S. Lucas</b> , P. Moskovkin, J. Müller, A. Haye, P. Zikán and A. Obrusník	<b>Mr. Stephane Lucas</b> , University of Namur, <b>Belgium</b>
17:00 - 17:15	Collisional electronic excitations in the interaction of slow ions with surfaces <b>P. Riccardi</b>	<b>Dr. Pierfrancesco Riccardi</b> , University of Calabria, <b>Italy</b>
17:15 - 17:30	Influence of the transition probabilities and the Hönl-London factors on radiative spectra simulation A. M. Kassir, <b>A. Hleli</b> , Y. Cressault, M. Masquère and P. Teulet	<b>Dr. Ali Hleli</b> , LAPLACE-Toulouse University, <b>France</b>
17:30 - 17:45	Type-I ELM mitigation through lithium pellet injection in EAST with tungsten divertor <b>W. Xu</b> , J.S. Hu, R. Maingi, Z. Sun, Y.Z. Qian, D.K. Mansfield, G.Z. Zuo, X.C. Meng, C.L. Li, M. Huang, Z.L. Tang, J.S. Yuan and D.H. Zhang	<b>Dr. Wei Xu</b> , Hefei Comprehensive National Science Center, <b>China</b>
17:45 - 18:00	Unravelling the limitations of ammonia synthesis by non-thermal plasmas <b>P. Navascués</b> , J.M. Obrero-Pérez, J. Cotrino, A.R. González-Elipé and A. Gómez-Ramírez	<b>Ms. Paula de Navascués Garvín</b> , CSIC-US-Seville, <b>Spain</b>
18:00 - 18:15	Modeling an Atmospheric Pressure Plasma Jet Impinging on a Silver Nitrate Solution for Nanoparticle Synthesis <b>A. L. Raisanen</b> , S. Exarhos, S. Kerketta, P.J. Bruggeman and M. J. Kushner	<b>Dr. Astrid Raisanen</b> , University of Michigan, <b>USA</b>
18:15 - 18:30	Kinetic investigation of electron energization in magnetron discharges: RFMS, DCMS, and HiPIMS B. Zheng, Y. Fu, K. Wang, T. Schuelke and Q. Hua Fan	<b>Dr. Bocong Zheng</b> , Fraunhofer USA Center Midwest, Michigan State University, <b>USA</b>
18:30 - 18:45	Formation of Turing patterns in strongly magnetized plasmas <b>M. Menati</b> , U. Konopka and E. Thomas	<b>Dr. Mohamad Menati</b> , Auburn University, <b>USA</b>

<b>09 April, 2021</b>		
<b>SCIT Session III</b> <b>Coatings for Energy and Environmental Applications</b>		
<b>Session's Chairs:</b> <b>Prof. Alessandro Lavacchi, ICCOM, CNR- Firenze, Italy</b> <b>Dr. Monica Bollani, Photonic and Nanotechnology Institute, Italy</b>		
<b>09:00 - 09:30</b>	The Mechanisms of Corrosion Protection of Metals in Corrosive Medium by Superhydrophobic Coatings <b>L.B. Boinovich</b>	<b>Prof. Ludmila B. Boinovich</b> , The Russian Academy of Sciences, <b>Russia</b>
<b>09:30 - 10:00</b>	Study and optimization of the natural instability in Si-based thin solid films for sensing and photonic applications <b>M.Bollani</b> , M.Abbarchi, C.Barri, I.Berberzier, F.Biccari, M.Bouabdellaoui, P.de Anna, L.Fagiani, L. Favrè, A.Federov, D.Grosso, N.Granchi, F.Intonti, E.Mafakheri, G.Nicotra, M.Salvalaglio, G.Sfuncia, S.Sanguinetti and A.Voigt	<b>Dr. Monica Bollani</b> , Photonic and Nanotechnology Institute, <b>Italy</b>
<b>10:00 - 10:15</b>	PECVD passivation of GaN for transistor threshold voltage control <b>O. Richard</b> , A. Gupta, V. Aimez and A. Jaouad	<b>Mr. Olivier Richard</b> , Sherbrooke University, <b>Canada</b>
<b>10:15 - 10:30</b>	Optimized stoichiometry for CuCrO2 thin films as Sustainable and semi-transparent Hole Transparent Layer in performant and recyclable organic solar cells <b>L. Bottiglieri</b> , A. Nourdine, J. Resende, C. Jimenez and J.L. Deschanvres	<b>Mr. Lorenzo Bottiglieri</b> , LMGP, Univ. Grenoble Alpes/CNRS, <b>France</b>
<b>10:30 - 11:00 Break</b>		
<b>Plasma Tech Session III</b> <b>Plasma diagnostics / Modelling and numerical simulations of plasmas and surfaces</b>		
<b>Session's Chairs:</b> <b>Prof. Achim von Keudell, Ruhr-University Bochum, Germany</b> <b>Prof. André Anders, Leibniz Institute of Surface Engineering (IOM), Germany</b> <b>Dr. Gianpiero Colonna, CNR-ISTP-Bari, Italy</b>		
<b>11:00 - 11:30</b>	On the relation between deposition rate and ionized flux fraction in high power impulse magnetron sputtering <b>J.T. Gudmundsson</b> , H. Hajihoseini, M. Rudolph, T.M. Minea, M.A. Raadu, N. Brenning and D. Lundin	<b>Prof. Jon Tomas Gudmundsson</b> , University of Iceland, <b>Iceland</b>
<b>11:30 - 12:00</b>	Hyper Power Impulse Magnetron glow discharge <b>T. Minea</b> , E. Morel and Y. Rozier	<b>Prof. Tiberiu Minea</b> , Paris-Sud University, <b>France</b>
<b>12:00 - 12:30</b>	On the energy balance of an atmospheric pressure surface barrier discharge <b>H. Kersten</b> , L. Hansen, L. Rosenfeldt and K. Reck	<b>Prof. Holger Kersten</b> , University Kiel, <b>Germany</b>
<b>12:30 - 13:00</b>	Electrical diagnostics for Dielectric Barrier Discharges: from integrated measurements to spatially resolved measurements. Benefits for plasma processes at atmospheric pressure? C.Tyl, A. Belinger, S. Dap and <b>N. Naudé</b>	<b>Dr. Nicolas Naudé</b> , Paul Sabatier University, <b>France</b>
<b>13:00 - 14:00 Break</b>		
<b>Session's Chairs:</b> <b>Dr. Nicolas Naudé, Paul Sabatier University, France</b> <b>Dr Andrey Starikovskiy, Princeton University, USA</b>		
<b>14:00 - 14:30</b>	Controlling atmospheric pressure non equilibrium plasmas for species conversion <b>A. von Keudell</b> , K. Grosse, M. Falke, C. Stewig, T. Urbanietz, P. Preissing, S. Dzikowski, J. Golda, M. Böke and V. Schulz-von der Gathen	<b>Prof. Achim von Keudell</b> , Ruhr-University Bochum, <b>Germany</b>
<b>14:30 - 14:45</b>	TD-LIF measurements and PIC modelling of Titanium sputtered atoms velocity distribution functions in Argon DC magnetron plasma <b>A. El Farsy</b> , A Revel, L. de Poucques, J.Robert, J. Bougdira and T. Minea	<b>Dr. Abderzak El Farsy</b> , Paris-Saclay University, <b>France</b>

<b>14:45 - 15:00</b>	Calculation of thermophysical properties and computational modeling for higher temperature and pressure air plasma <b>M. Alija</b> , Y. Cressault, P. Teulet and M. Kurrat	<b>Mr. Muhamet Alija</b> , Technische Universität Braunschweig, <b>Germany</b>
<b>15:00 - 15:15</b>	Investigation of multi-periodic self-pulsed plasma in a AC Helium Atmospheric Pressure Plasma Jet <b>H. Yang</b> and A. Rousseau	<b>Mr. Hang Yang</b> , Polytechnic Institute-CNRS / Sorbonne University, <b>France</b>
<b>15:15 - 15:30</b>	Optical emission spectroscopy as a diagnostic tool for electron temperature and density measurements in atmospheric pressure liquid plasma reactor <b>N. Milaniak</b> , L. Samard, J-F. Sauvageau and M-A. Fortin	<b>Dr. Natalia Milaniak</b> , Laval University, <b>Canada</b>
<b>15:30 - 15:45</b>	Optical emission spectroscopy and actinometry in SF6/Ar RF discharges for PCE <b>A.A. Osipov</b> , V.I. Berezenko, A.A. Osipov, A.B. Speshilova, A.E. Gagaeva, E.V. Endiarova and S.E. Alexandrov	<b>Dr. Artem Osipov</b> , Peter the Great St.Petersburg Polytechnic University, <b>Russia</b>
<b>15:45 - 16:15</b>	<b>Break</b>	
<b>Plasma Tech Session IV</b> <b>Plasma application for biology, medicine and agriculture</b>		
<b>Session's Chairs:</b> <b>Prof. Achim von Keudell, Ruhr-University Bochum, Germany</b> <b>Prof. Boxin Zhao, University of Waterloo, Canada</b>		
<b>16:15 - 16:45</b>	Cold atmospheric pressure plasma for wound healing: state-of-the-art and perspectives <b>T. von Woedtke</b>	<b>Prof. Thomas von Woedtke</b> , Leibniz Institute for Plasma Science and Technology, <b>Germany</b>
<b>16:45 - 17:15</b>	Plasma in cancer therapy <b>M. Keidar</b>	<b>Prof. Michael Keidar</b> The George Washington Uni., <b>USA</b>
<b>17:15 - 17:30</b>	Effectiveness of plasma activated water on the inactivation of Listeria monocytogenes biofilms <b>P. Fernández-Gómez</b> , A. Alvarez-Ordóñez, M. González-Raurich, M. López, M. Prieto, J. L. Walsh, M. Sivertsvik and E. Noriega Fernández	<b>Ms. Paula Fernández Gómez</b> , University of León, <b>Spain</b>
<b>17:30 - 17:45</b>	Study of antimicrobial and antiviral properties of silver-doped hydro-genated amorphous carbon coatings produced by hybrid PVD/PECVD process <b>V. Job</b> , M. Cardinal, D. Coupeau, B. Muiykens, V. Maloteau, J. Laloy, J-M. Dogné and S. Lucas	<b>Mr. Valentin Job</b> , University of Namur, <b>Belgium</b>
<b>17:45 - 18:00</b>	Low temperature air plasma effects on germination of two Brassica-ceae seeds, Arabidopsis thaliana and Camelina sativa <b>M. Bafoil</b> , M. Yousfi, C. Dunand and N. Merbahi	<b>Dr. Maxime Bafoil</b> , Paul Sabatier University, <b>France</b>
<b>18:00 - 18:15</b>	Application of Dielectric Barrier Discharge (DBD) atmospheric pres-sure plasma for pretreatment of medical textiles <b>I. Pinheiro</b> , J. Padrão, C. Silva, A. Ribeiro, V. Bouça, L. Coelho, A. Carvalho, B. Moura, A. I. Ribeiro, H. Felgueiras, A. P. Souto and A. Zille	<b>Ms. Inês Pinheiro</b> , Centre of Nanotechnology and Smart Materials (CeNTI), <b>Portugal</b>

## Posters Virtual Session

Posters are being displayed through the Virtual event solution (Whova).  
Discussions are to be done through the system chat features available to the attendees.

N.	Poster Title	Author, Affiliation, Country
1.	Hydrogenated amorphous carbon (a-C:H) thin films deposited by low-pressure <b>plasma</b> : linking mechanical and fracture behavior to deposition conditions <b>A. Bagherpour</b> , M-S. Collab, P. Baralb, M. Coulombierb, T. Pardoeb and S. Lucasa	<b>Mr. Alireza Bagherpour</b> , University of Namur, <b>Belgium</b>
2.	Discussion on Dimond-like coatings by HIPIMS W. Gajewski, <b>A.W. Oniszcuk</b> , M. Puźniak, R. Mroczyński and P. Domanowski	<b>Dr. Anna Wiktoria Oniszcuk</b> , TRUMPF Huettinger Sp. z o.o, <b>Poland</b>
3.	Structuration of titanium surfaces using He ions. <b>F. Sanchez</b> , L. Marot, R. Antunes, R. Steiner, M. Kisiel, E. Meyer, M. Astasov-Frauehoffer, I. Hauser-Gerspach, S. Kühn, J. Köser, R. Wagner, J. Hofstetter and K. Mukaddam	<b>Mr Fabien Sanchez</b> , University of Basel, <b>Switzerland</b>
4.	Anodizing of AlSi alloys in sulfuric medium <b>A.Ben Romdhane</b> , D.Veys-Renaux, E. Rocca and K. Elleuch	<b>Mr. Anas Ben Romdhane</b> , University of Lorraine, <b>France/ ENIS, Tunisia</b>
5.	Control of Spokes in Magnetron Discharges. <b>M. George</b> , W. Breilmann <sup>1</sup> , J. Held and A. von Keudell	<b>Mr. Mathews George</b> , Ruhr-University Bochum, <b>Germany</b>
6.	Model Predictive Control and Parameter Identification Analysis of Cascaded H-bridge Multilevel EAST Fast Control Power Supply Based on CPS-PWM Modulation Strategy H. Haihong and <b>Y. Bichen</b>	<b>Mr. Bichen Yan</b> , Hefei University of Technology, <b>China</b>
7.	Single-Shot Spatially Resolved Optical Emission Spectroscopy of Plasma Species within the Spoke <b>M. Šlapanská</b> , M. Kroker, J. Hnilica, P. Klein and P. Vašina	<b>Ms Marta Šlapanská</b> , Masaryk University, <b>Czech Republic</b>
8.	Optical emission spectroscopy mapping for plasma diagnostics during plasma-enhanced chemical vapor deposition <b>R.R. Ismagilov</b> , S.A. Malykhin, A.B. Loginov, V.I. Kleshch and A.N. Obraztsov	<b>Dr. Rinat Ismagilov</b> , Lomonosov Moscow State University, <b>Russia</b>
9.	In Situ Electroanalytical Modelling of the Influence of Bath Hydrodynamics on Nucleation Kinetics for Electrodeposition of Nickel-Cobalt alloy system <b>I. Khazi</b> , U. Mescheder and J. Wilde	<b>Mr. Isman Khazi</b> , Hochschule Furtwangen University, <b>Germany</b>
10.	Influence of chain length of organic modifiers in hydrophobization process on epoxy resin properties <b>G. Morgiante</b> , M. Piłkowski and J. Marczak	<b>Dr. Gianluca Morgiante</b> , PORT Polish Center for Technology Development, <b>Poland</b>
11.	Bulk-modified epoxy resins as a coatings with low ice adhesion <b>M. Piłkowski</b> , G. Morgiante and J. Marczak	<b>Mr. Michał Piłkowski</b> , PORT Polish Center for Technology Development, Wrocław, <b>Poland</b>
12.	Plasma enhanced chemical vapour deposition of ZrO <sub>2</sub> based layers <b>P. A. Maaß</b> , V. Bedarev, S. M. J. Beer, M. Prenzel, M. Böke, A. Devi and A. von Keudell	<b>Mr. Philipp Maaß</b> , Ruhr-University Bochum, <b>Germany</b>
13.	Influence of plasma torch power on the properties of alumina coatings <b>A. Šuopys</b> , V. Grigaitienė, L. Marcinauskas, R. Kėželis, R. Uscila and M. Aikas	<b>Mr. Airingas Šuopys</b> , Lithuanian Energy Institute, <b>Lithuania</b>
14.	Durability Study of the Anti-biofilm Capacity of Plasma-Polymerized Coatings on Stainless Steel for Food Contact Applications R. Múgica-Vidal, P. Fernández-Gómez, I. Muro-Fraguas, A. Sainz-García, M. González-Raurich, A. Álvarez-Ordóñez, M. Prieto, M. López, P. Toledano, M. López, Y. Sáenz, A. González-Marcos, <b>F. Alba-Elías</b> and E. Sainz-García	<b>Dr Fernando Alba-Elías</b> , University of La Rioja, <b>Spain</b>
15.	Methodology for designing the parameters of technological nitriding regime with respect to the relative wear resistance of tool steels for hot working N. Tontchev, <b>E. Yankov</b> and A. Zumbilev	<b>Dr. Emil Yankov</b> , University of Ruse, <b>Bulgaria</b>
16.	The application of organofunctional silanes to protect the wood surface <b>K. Szubert</b> , D. Łoś and H. Maciejewski	<b>Dr. Karol Szubert</b> , Adam Mickiewicz University Poznan, <b>Poland</b>

17.	Development of superhydrophobic CoAl-LDH conversion coating as a novel photocatalytic protective film on AA6082 <b>M. Ahsan Iqbal</b> , H. Asghar and M. Fedel	<b>Mr. Muhammad Ahsan Iqbal</b> , University of Trento, <b>Italy</b>
18.	Enhanced Performance of Solution Processed 2D-MoS <sub>2</sub> Photodetectors upon Ultraviolet-Ozone Treatment. <b>H. Badahdah</b> , R. Altuwirqi and H. Al-Jawhari	<b>Mrs. Hend Badahdah</b> , King Abdulaziz University, <b>Saudi Arabia</b>
19.	Polypropylene vs. Polyester Plasma Ion-Exchange Activated Needle-Punched Non-Woven Geotextiles <b>D. Gospodinova</b> , M. Neznakomova and P. Dineff	<b>Dr Dilyana Nikolova</b> , Technical University Sofia, <b>Bulgaria</b>
20.	Significantly reduced secondary electron yield of electrodeposited silver coatings for multipactor applications <b>J. Belfio</b> , F. Lazar, O. Jbara and M. Belhaj	<b>Mrs. Julie Belfio</b> , Reims Champagne-Ardennes University/ Toulouse University, <b>France</b>
21.	Simulation of multi-layer TiN/TiAlN thin film growth and calculation of its thermal conductivity <b>P. Moskovkin</b> , J. Müller and S. Lucas	<b>Dr. Pavel Moskovkin</b> , University of Namur, <b>Belgium</b>
22.	Mean Absorption Coefficients of air-copper thermal plasmas <b>E. Raveloharinjaka</b> , Y. Cressault, M. Rakotomalala and H.Z. Randrianandraina	<b>Mr. Elisé M. Raveloharinjaka</b> , University of Paul Sabatier Toulouse, <b>France</b>
23.	Catalytic performances of Ce <sub>0.01</sub> Mn in Post-Plasma Catalysis for dilute Trichloroethylene abatement <b>G. Abdallah</b> , J.-M. Giraudon, N. De Geyter, R. Morent and J.-F. Lamonier	<b>Ms. Grèce Abdallah</b> , University of Lille, <b>France</b> / University of Ghent, <b>Belgium</b>
24.	Sequential adsorption followed by plasma assisted catalytic conversion of toluene on Hopcalite in air stream <b>S. Sonar</b> , J.-M. Giraudon, S.K.P. Veerapandian, J.-F. Lamonier, R. Morent, N. De Geyter and A. Löfberg	<b>Ms. Shilpa Sonar</b> , University of Lille, <b>France</b> / University of Ghent, <b>Belgium</b>
25.	Oxygen Plasma Treatment on Silicone Catheter Surface for Enhancement of Antifouling Properties <b>P. Dave</b> , A. Kumar, M. Abdulkhalik, C. Balasubramanian, S. Hans and S. K. Nema	<b>Dr. Purvi Dave</b> , Institute for Plasma Research-Gandhinagar, <b>India</b>
26.	Use of a microwave plasma process at atmospheric pressure for bacterial disinfection <b>L. Renoux</b> , C. Dublanche-Tixier, C. Chazelas, P. Tristant, C. Maftah, P. Leprat, L. Sandoval and N. Picard	<b>Mrs. Laura Renoux</b> , Limoges University, <b>France</b>
27.	Laser-induced breakdown spectroscopy interface tracking (LIBS-IT): application to a W-PVD thin layer on a CuCrZr substrate A. Favre, V. Morel, <b>A. Bultel</b> , G. Godard, S. Idlahcen, B. M. Diez, C. Grisolia and F. Perry	<b>Prof. Arnaud Bultel</b> , University of Rouen, <b>France</b>
28.	Structure and microstructure of high entropy alloy thin films from the AlCrFeMnMo family deposited by magnetron sputtering <b>M. Aly Sow</b> , F. Beclin, C. Cordier, M. Touzin, Laurent Boilet, J.-F. Treclat, A. Tromont and C. Nouvellon	<b>Mr. Mourtada Sow</b> , University of Lille, <b>France</b>

**SICT Session I**  
**Surfaces and Coatings processing /**  
**Properties**

# Tribology of Polymer Composite Coatings for Bearings and Other Applications

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## Abstract

In numerous friction and wear applications, the use of polymers and polymer composites has become state of the art. In many cases the materials are applied as coatings for Bearings and other applications. This presentation describes how to design these polymeric coatings in order to operate under low friction and low wear against various counterparts. Particular emphasis is focused on special fillers (including spherical nanoparticles), often in combination with classical tribo-fillers (such as carbon fibers, graphite flakes, polytetrafluoroethylene (PTFE) microparticles). Finally, a set of practical examples particularly demonstrates how these different fillers act in concert. The industrial applications include polymer - metal hybrid bushings for Diesel fuel injection pumps of the automotive industry, filament wound composite bearings with a thin sliding layer inside and surrounded by a stiffer backing for the use in harsh environments, and high temperature resistant PAI and PBI coatings for automotive engine pistons, bushings, and anti-sticking molds in plastic processing industries.

**Key Words:** Friction, Wear, Polymers, Composites, Nanoparticles, Applications

# Nano-clustering structures creating a robust superlubricity state under high contact pressure in amorphous carbon films

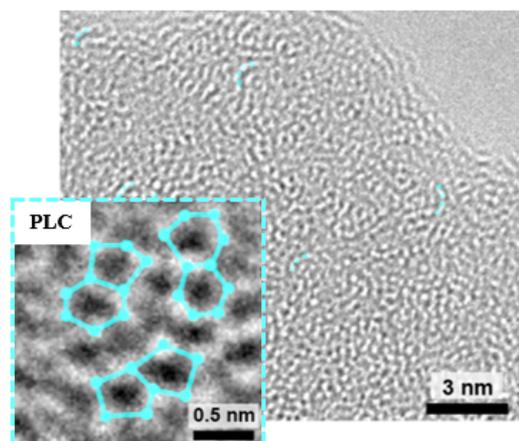
Xinchun Chen\*

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## Abstract:

Recently, anti-friction lubricants such as diamond-like hydrogenated amorphous carbon films have drawn increasing interests in academic and industrial communities. The establishment of the near-zero friction and wear state relies on the intrinsic structure and molecular characteristics of the surface and interface in carbon films. In other words, the state of superlow friction (superlubricity) of carbon films is generally dependent on the tribo-induced interfacial nanostructures, namely tribolayer or transfer film. The growth dynamics and stability of the as-formed tribolayer are not clear yet, mainly due to the fact that most interfacial activities occur in a very thin contact area. The formation of transfer film or nano-ordered shear band is determined by the correlation between the  $sp^2$ -phases and hydrogen atoms in the carbon matrix. This study highlights the critical role of ion energy in growing hydrogenated carbon films, revealing the specific growth mechanism with regarding to the polymer-like structure in the range of low ion energy. The results indicate that a large number of nano-clustered and aromatic  $sp^2$ -structures are sustained in the carbon films when the aromatic hydrocarbon gaseous sources are used as the processed source precursors at specific ion energy during deposition. Meanwhile, a relatively high content of hydrogen is also contained in the film. These findings are totally different from the widely-reported agreement that the structure of superlubric carbon films is dominated by a hydrogen-rich  $sp^3$ -(C-H) architecture. The as-discovered new structure is beneficial for the achievement of superlow friction state. Based on this, a systematic study on the superlubricity mechanisms affected by harsh conditions are conducted.

**Keywords:** diamond-like carbon films, superlubricity, nanostructures, ion energy, nano-clusters, aromatic structures, tribochemistry, robustness, harsh working conditions.



**Figure 1:** HRTEM image illustrating the local nanoclustering structures in carbon matrix from the aromatic hydrocarbon gaseous precursors, which forms some aromatic nano-rings and creating a new bonding structure for achieving superlubricity in a high contact pressure.

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**PlasmaTech Session I**  
**Plasma fundamentals / Atomic and  
Molecular Processes**

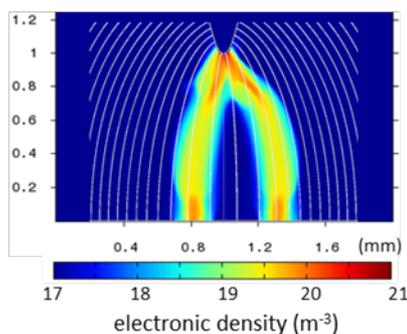
# Corona discharges : Physics and Applications

O. Eichwald<sup>1</sup>, O. Ducasse<sup>1</sup>, N. Merbahi<sup>1</sup>, J.P. Sarrette<sup>1</sup> and M. Yousfi<sup>1</sup>  
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## Abstract:

At atmospheric pressure, corona discharges occur between electrodes when at least one of them show a small curvature radius. Depending on the power supply conditions, several regimes of corona discharges can be generated: glow or breakdown streamer. The latter regime is characterised by the formation of filamentary discharges (having or not a tree structure) and the propagation of primary streamers followed by secondary streamers. The breakdown streamer regime allows the formation of energetic electrons that seed the gas with reactive species at ambient temperature. Nevertheless, the non-thermal plasma discharge thus generated can induce the formation of thermal shocks and redistribution of the initial gas flow. The regimes of corona discharges under positive voltage will be described and analysed using electrical and optical measurements coupled with 2D and 3D simulations in a point-to-plane configuration. The effects of primary and secondary streamers on the formation of chemical reactive species will be clearly identified and will allow a better understanding of the results obtained in corona gas treatment. The hydrodynamic effects of the discharges on the evolution of the gas flow will also be discussed, as well as the challenge of reducing the chemical kinetics needed to choose an optimized set of species and reactions. Several examples of applications will be also described in relation to environmental and biomedical applications.

**Keywords:** Non-thermal plasma physics, Corona discharge, Streamers, Environnemental and biomedical applications, Chemical reduction.



**Figure 1:** (Top) Multi-points corona discharge reactor. (Bottom) 3D simulation of the development of a breakdown corona discharge in a point to plane configuration.

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# The strange world of cathodic arc spots: Is plasma formation fractal or periodic or bimodal?

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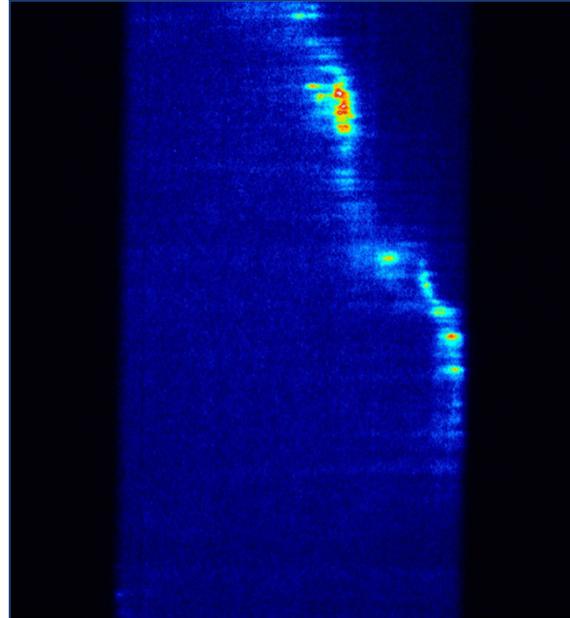
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## Abstract:

High current discharges with generally cold cathodes are characterized by a concentration of power in cathode spots, which are nonstationary and prolific generators of plasma of the cathode material. On the one hand, this plasma system is interesting for some applications since fully ionized plasmas with often multiply charged ions can be obtained at low cost. On the other hand, though, the plasma also contains microscopic droplets or “macroparticles” as the molten material of the cathode is displaced by the high plasma pressure. Cathode spot operation can be described as a sequence of microexplosions [1]. The likelihood to form a cathode spot at a certain location is generally governed by the local electric field strength, which in turn is greatly affected by the chemistry and microscopic geometric features of the cathode location. Using a combination of fast imaging, high frequency analysis of electromagnetic signals, and post-discharge cathode crater analysis on multilayer cathodes [2] we explore whether the statistical nature of cathode spots is fractal or periodic or bimodal. The data indicates fractal behavior for vacuum arcs and arcs in noble gases while bimodal when the gaseous environment contains reactive gases such as oxygen or nitrogen.

**Keywords:** cathodic arcs, vacuum arcs, cathode spots, plasma diagnostics, fractals.



**Figure 1:** Example of a streak camera image of cathode spots for a magnetically steered arc in vacuum ( $6 \times 10^{-5}$  Pa): horizontal is the spatial coordinate, vertical is time (total sweep time 10  $\mu$ s); one sees the average apparent motion to the right while the spot “life time” appears to be of the order 10 ns.

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# Non-equilibrium Characteristics of Laser-Induced Plasmas

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## Abstract:

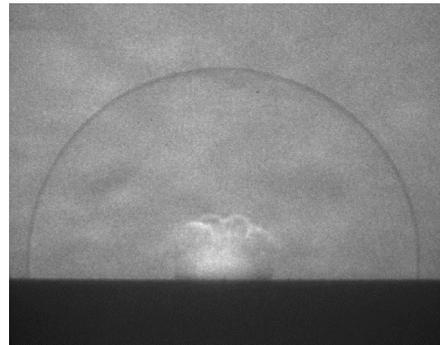
Laser-induced plasmas have been first observed at the beginning of the 60's when the first laser sources have been elaborated. Due to the high irradiance they can reach, above threshold phenomena such as ablation of a solid or liquid surface, or discharge directly in gaseous phase can be put in evidence. They are mainly produced by nonlinear absorption elementary processes. Indeed, inverse Bremsstrahlung (IB) and multiphoton ionization (MPI) play a key role.

Except some specific situations, the laser-induced plasma is mostly produced in a background gas. This gas can be air or rare gas. The related pressure is often atmospheric and at room temperature. The laser source providing the pulse is characterized by irradiance lower than  $\sim 10^{12} \text{ W m}^{-2}$ , therefore under the threshold. The latter is reached by focusing the provided light using a lens. In the vicinity of the focus point, the irradiance is then sufficiently high to produce the first free electrons by MPI if the irradiated medium is dielectric. Then, the laser light is absorbed by IB. If free electrons already exist in the irradiated medium, the MPI processes do not participate so much to the ionization of the plasma. Laser photons are absorbed by IB. In the two cases, the electron temperature  $T_e$  increases, which leads to the increase in the electron density  $n_e$  resulting from the enhancement of the collisional ionization under electron impact. The bonds between particles are broken in the case of the irradiation of a condensed phase, the pressure reaches  $\sim 10^9 \text{ Pa}$ , the temperature  $\sim 50,000 \text{ K}$  and the matter is strongly ejected from the focus point region according to a hypersonic expansion regime. This produces a shockwave expanding at a slightly higher speed than the plasma expansion. Between the plasma core and the shockwave, a shock layer is produced whose thickness increases. During its expansion, the plasma cools down and its pressure decreases. Once the plasma core pressure corresponds to the one of the shocklayer, the shockwave detaches from the plasma core and expands freely in the background gas. The plasma lifetime is of  $\sim 10 \mu\text{s}$ . Finally, we can consider the laser-induced plasma as formed by two regions in mutual interaction (the plasma core and the shocklayer) separated by a fictitious surface called the contact

surface. The background gas is partially dissociated (if molecular) and ionized when crossed by the shockwave. The shocklayer is therefore also a plasma. Two plasmas are consequently produced: the core and the shocklayer (fig.1).

During the expansion of the whole, the collision frequency collapses, which leads to a lack of coupling. In addition to the radiation of the two plasmas, this collapse induces non-equilibrium effects in terms of ionization and electronic excitation. These characteristics yields the study of laser-induced plasmas relatively tricky. This requires not only space and time-resolved measurements [1], but also the development of dedicated models based on state-to-state approaches [2]. Main aspects of the underlying physics will be described during the conference, either from the experimental or modelling point of view.

**Keywords:** Laser, non-equilibrium, shockwave.



**Figure 1:** Strioscopic image illustrating the hemispherical shockwave and the laser-induced plasma produced on a solid sample. The contact surface presents a complex structure far from being hemispherical.

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# The role of excited states in the time evolution of gas discharges

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## Abstract:

The importance of excited states in gas discharges is well known in the plasma community, not only for diagnostic purposes, but also for affecting plasma reactivity. However, solving the Boltzmann equation to calculate the electron energy distribution function (EEDF) and to determine rate coefficients and swarm parameters, excited levels are included in the model only as the final state of electron induced transitions in species in their ground configuration. This approach is known as *Local Field approximation* (LFA) [1,2]. In the last years, models including transitions induced by electron collisions with excited species has been investigated by using complete sets of electron impact cross sections. The Boltzmann solver, considering both inelastic and superelastic processes from excited species, has been self-consistently coupled [3-6] with the gas composition and with the electric field, the latter determined from the power density or circuit equation. This approach will be applied to argon [4], nitrogen [5] and hydrogen discharges [6] sustained by time dependent electric field. The results show that superelastic collisions modify the plasma properties already during the discharge, when the population of excited states grows and starts to affect the evolution of the plasma, till its complete depletion. There are also important effects on the calculation of the electric field due to the dependence of swarm parameters on excited state population. As an example let us discuss the case of argon discharge. The electric field  $E$  is calculated from the power density

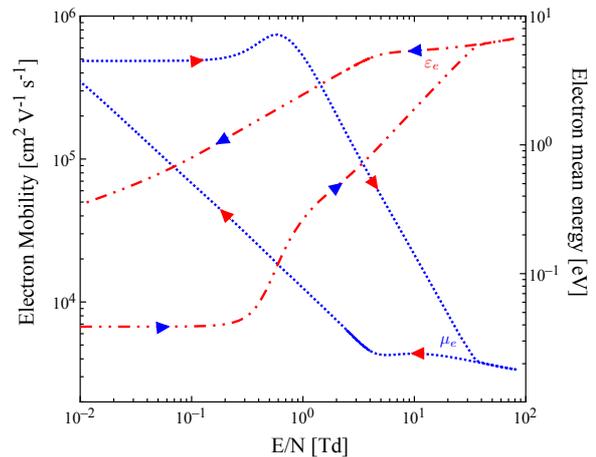
$$w = w_0 x^2 e^{-x}$$

by the equation

$$w = N_e \mu_e E^2$$

where  $w_0 = 10 \text{ W/cm}^3$ ,  $x = t/10^{-3}$ ,  $N_e$  is the electron density and  $\mu_e$  the electron mobility. In figure 1, the electron mobility and the electron mean energy has been reported as a function of the electric field showing an hysteresis profile, and therefore contradicting the LEA assumption, which assumes that the swarm parameters depends only on the electric field. Let us discuss the mean energy.

**Keywords:** Plasma modeling, Boltzmann equation, superelastic collisions, self-consistent kinetics, excited state kinetics.



**Figure 1:** Electron mobility ( $\mu_e$ ) and electron mean energy ( $\epsilon_e$ ) as a function of the reduced electric field. The arrows indicate the direction of time.

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**SICT / Plasma Tech Joint Session I**  
**Surfaces and Coatings processing /**  
**Characterization / Properties**

# Hybrid ALD/CVD towards nanoengineered functional CNT coatings

Naoufal Bahlawane, Vasu P. Prasadam, Hameeda J. Basheer, Kamal Baba, Ali Margot Huerta Flores

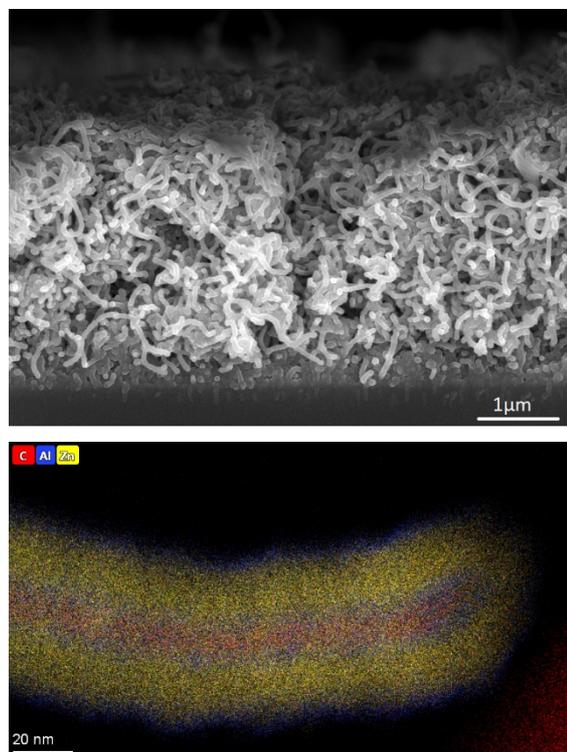
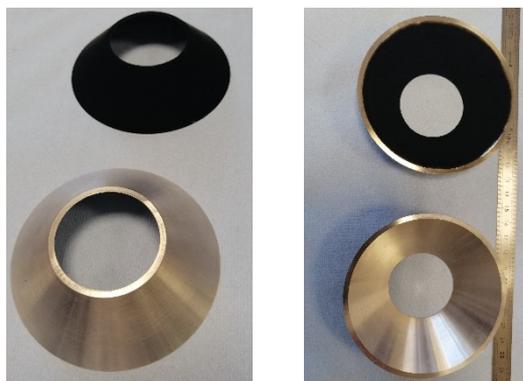
Materials Research and Technology (MRT) Department, Luxembourg Institute of Science and Technology (LIST), Luxembourg

## Abstract:

Owing to their high specific surface area, light absorption, electrical and thermal conductivity, carbon nanotubes are versatile building blocks for the engineering of nanocomposite coatings for various applications including optics, catalysis, sensing and electrochemical energy storage. Nevertheless, involving CNT is always associated with integration challenges, which motivates a continuous development of innovative approaches and chemistries for their synthesis. Here, we report a single-step CVD process implementing a catalyst-promoter approach for the growth of CNT coatings. This purely thermal process allows a sustainable growth of CNTs starting from ethanol vapor at a temperature that is compatible with the implementation of substrates such as aluminium foil.

Promoting the mechanical properties of CNT coatings and tailoring their surface chemistry will be highlighted via the implementation of Atomic Layer Deposition as a second step in the CVD reactor. The one-pot process yields films of randomly oriented CNT/metal oxide core/shell structures with tuneable optical properties, and withstanding aging tests relevant for the space qualification. Associating the electrically conducting CNT core with functional metal oxide is shown as an appealing nanoengineering approach for Photoelectrochemical water splitting and electrochemical energy storage.

**Keywords:** CVD, ALD, CNT deposition, Surface nanoengineering, multifunctional composite coating.



**Figure 1:** Illustrative Photos of coated metallic parts with modified CNT layer, cross-section SEM inspection of the CNT/Al-doped ZnO coating on Si, and STEM-HAADF/EDX mapping of the coated CNTs with a triple shell layer:  $\text{Al}_2\text{O}_3/\text{Al-ZnO}/\text{AlSiO}_x$ .

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# Functional polymers and micro/nanoengineering towards advanced manufacturing and sustainability

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## Abstract:

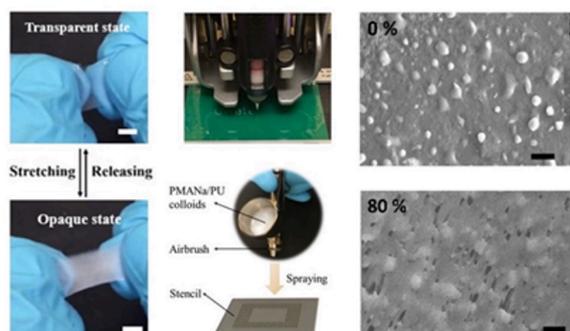
Functional polymers and finely-tuned surface and interfacial properties are essential to the development of advanced materials and manufacturing technologies towards sustainable economy and human well-being. In recent decades, material engineering at the micro and nanoscales have been an innovative and productive approach to design and develop smart materials and engineer material interface to enable desired properties such as super wettability, switchable adhesion, tunable conductivity, switchable optical properties. In this talk, I will present an overview of our research activities on surface science and bionanomaterials and the development of self-cleaning coatings, bio-inspired adhesives, and electrically conductive nanocomposites towards advanced sustainable manufacturing. In particular, I will discuss our latest exploration of water-based polyurethane colloid systems, which have the advantages of sustainability (e.g. low VOCs) and processability (e.g. 3D printing, inkjet printing, spray coating). Our research results show that water-based PU can be incorporated with functional micro/nanoparticles or polyelectrolytes to form colloidal composites that can be printed or coated into functional materials for different applications including stretchable conductive textiles, smart windows (Figure 1), and self-healing electronics.

**Keywords:** functional polymers, smart materials, micro/nano engineering, advanced manufacturing, sustainability

phase separation micro-structure under 0% and 80% strains. [1,2]

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**Figure 1:** Illustration of mechanoresponsive water-based PU/Polymethacrylic acid sodium salt composite smart window, its printability, and

# Development of innovative duplex coatings combining cold-spray and plasma electrolytic oxidation processes

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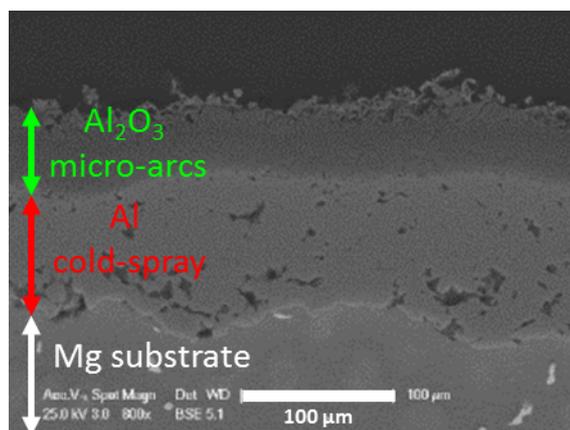
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## Abstract:

Plasma electrolytic oxidation (PEO) is widely used to improve the corrosion and wear resistance of lightweight metals such as aluminium alloys by the formation of a ceramic oxide coating. However, the PEO process remains ineffective for ferrous metals and, when applied to magnesium alloys, oxide coatings are usually thin and porous. To overcome these limitations, the feasibility of applying a duplex treatment combining cold-spray deposition (CS) and PEO is investigated<sup>1</sup>. Aluminium cold-sprayed coatings (Al1050) were pre-deposited on magnesium (EV31) and steel (S235) substrates prior to PEO. Results evidence the efficiency of such a two-steps process to form thick, dense and crystalline alumina coatings on both magnesium and steel substrates. The growth kinetic of the duplex CS-PEO oxide layer is enhanced by a factor of 3 compared to single-step PEO processing of bulk aluminium substrates. Results are discussed by considering the effect of the porosity through the cold-sprayed aluminium coating on the mechanism of oxidation during the subsequent PEO treatment. While porosities in the cold-sprayed coatings are generally undesired, they seem here to have a very positive effect on the PEO growth kinetics. Finally, such a duplex treatment offers new opportunities to protect surface of magnesium alloys and ferrous metals for which direct PEO process remains tricky and even not possible.

**Keywords:** Duplex treatment, cold-spray, plasma electrolytic oxidation, PEO, aluminium, magnesium, Steel.



**Figure 1:** Cross-section SEM micrograph showing the development of a duplex composite coating (Al<sub>2</sub>O<sub>3</sub>/Al) on a magnesium substrate by combining cold-spray and plasma electrolytic oxidation processes.

## References:

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# Spatio-temporal study of poly(maleic anhydride) plasma deposition using a macroscopic description

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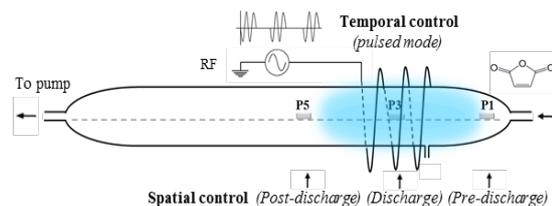
## Abstract:

Plasma polymerization is a vapor-based surface functionalization process consisting of the synthesis and deposition of functional polymer coatings. A macroscopic approach can be chosen to describe plasma polymerization and to control film growth, which relies on the concept of chemical quasi-equilibrium. In fact, for radical-dominated plasma polymerization, the film deposition rate solely depends on the energy provided per particle of the gas mixture flowing through the plasma phase. Taking into account geometrical parameters of the reactor, this macroscopic approach enables the correlation of the polymer thin film deposition rate with an apparent activation energy associated to a specific state of the precursor.<sup>[1]</sup>

Our group works on the engineering of functional polymer films by plasma polymerization which includes investigations on plasma deposition kinetics and mechanisms in order to achieve better control of surface properties.<sup>[2]</sup> The temporal control of plasma species generated during plasma polymerization of maleic anhydride has already been investigated by tuning operating parameters such as the on and off times used for pulsed plasma polymerization.<sup>[3]</sup> In this study, we propose to investigate the possibility to combine a spatial with a temporal control of plasma polymerization by performing pulsed plasma polymerization in an original home-built low-pressure plasma reactor, being 1m long and enabling the deposition of polymer within or outside the glow discharge (figure 1). Hence the evaluation of the poly(maleic anhydride) deposition rate was performed in three different regions of the plasma reactor: pre-discharge, discharge and post-discharge zones for various operating parameters (power, duty cycle in pulsed mode). The plasma discharge has been particularly characterized using the optical emission spectroscopy (OES) while the resulting plasma polymer films have been analyzed by several chemical surface characterization techniques such as infrared and X-ray photoelectron spectroscopies. This fundamental study has enabled the identification of

different growth regimes during the deposition of the plasma polymer as well as a complex growth mechanism including a competition between polymer film deposition and polymer nanoparticles formation. The calculation of the apparent activation energies has also been investigated which can provide interesting results to get more insights into the polymerization mechanisms. This spatio-temporal study of poly(maleic anhydride) plasma deposition thus allowed us to control more precisely plasma polymerization mechanism of this precursor in order to get functional polymer coatings with more diverse surface properties.

**Keywords:** Activation energy, Macroscopic approach, Maleic Anhydride, OES, PECVD.



**Figure 1:** Figure illustrating the spatio-temporal control of maleic anhydride low-pressure pulsed plasma polymerization.

## References:

1. Hegemann, D., Hossain, M. M., Körner, E., Balazs, D.J. (2007), *Plasma Process. Polym.*, 4, 3.
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# Different plasma nitride layer designs of an AISI D2 tool steel with a new Cr-Al-Ti-B-N PVD hard coating for optimized duplex layer systems

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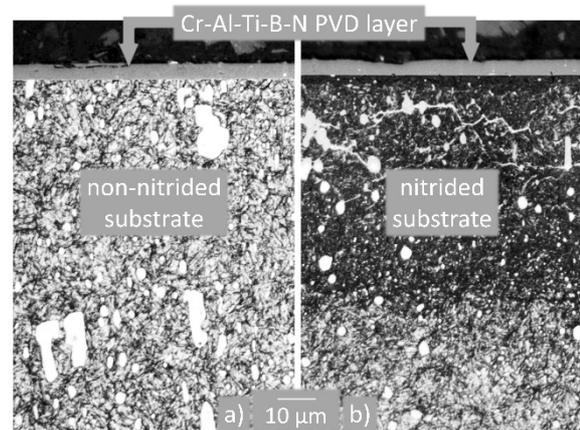
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## Abstract:

Tool steels, especially the widely used AISI D2, are the preferred choice for applications with demanding mechanical and tribological working conditions, such as die casting, stamping and forging. In order to prevent the limited tool lifetime, a common practice is to apply thermochemical treatments to the surface of these steels. Typical surface treatment procedures are plasma nitriding and physical vapour deposition (PVD) hard coating, which both have their process limitations and drawbacks. The duplex surface treatments applied here involve both of these techniques with combined and improved properties that cannot be achieved by the respective single processes. Also a new PVD coating of the type Cr-Al-Ti-B-N was deposited at different coating temperatures, whereby the boron doping can further improve the coating properties by the formation of nanocomposites and enhance the hardness<sup>1</sup>. Another factor worth investigating is the existence of a compound layer, as a part of the nitride layer, which can transform into a "black layer" consisting of soft  $\alpha$ -iron due to the subsequent deposition process of the hard coating. The "black layer" is acting as a kind of interlayer between the nitrogen diffusion zone and the PVD layer<sup>2</sup>. In addition to the surface roughness prior to coating deposition, the general nitride layer design was investigated with respect to the mechanical and structural performance of the resulting duplex system. Therefore, we performed adhesion testing methods such as scratch tests, as well as tribological and structural investigations, including X-ray diffraction analyses and scanning electron microscopy. The results of these investigations represent a new perspective to the duplex coating design and its production, combined with the successful testing of a new PVD coating type.

**Keywords:** tool steel, plasma nitriding, PVD coating, duplex coating, interlayers, adhesion characteristics, mechanical and tribological properties



**Figure 1:** Cross-sections of a) a non-nitrided and subsequently PVD coated AISI D2 steel substrate and b) a plasma nitrided and subsequently PVD coated AISI D2 steel substrate.

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# Plasma nitriding respond of thermal laser or electron beam treated surfaces of austenitic stainless steel

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## Abstract:

Modern methods of material production, such as additive manufacturing, as well as material surface modification by means of high-energy thermal radiation, such as surface texturing or structuring, are excellently suited to meet the requirements of innovative material design, lightweight construction and surface functionalization. The applicability of surface hardening processes, such as thermochemical heat treatment to further improve surface properties in terms of hardness and wear behavior, is still largely unknown for the aforementioned new materials and surface conditions.

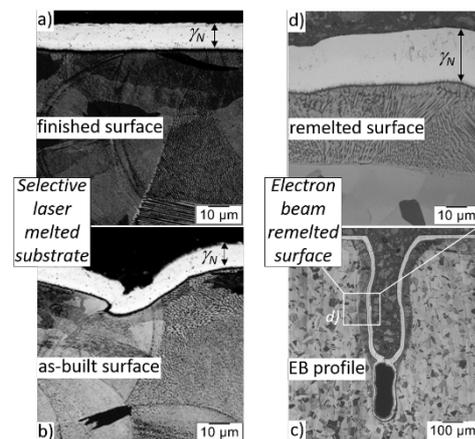
A recently developed technology of active screen plasma nitriding using an active screen made of carbon<sup>1</sup> shows, especially for stainless steels, a more efficient nitrogen/carbon uptake as well as geometry-independent and contour-true treatment results<sup>2</sup>. Therefore, this process is suitable for the application of complex shaped components or profiled surfaces. During the thermochemical heat treatment of austenitic steels, so-called expanded austenite is formed as a result of the diffusion of nitrogen and/or carbon into the surface, which leads to a significant increase in hardness and the formation of a wear-resistant surface layer.

The presented study shows on the example of selected austenitic stainless steels the potentials and the variety in the application of an active screen plasma nitriding/nitrocarburizing process (i) on substrates produced by selective laser beam melting and (ii) on electron beam modified surfaces. In both cases, the interaction of the substrate with thermal radiation to affect the substrate microstructure occurs prior to thermochemical surface treatment.

Using the example of cube geometries produced by selective laser beam melting, it is shown that the surfaces can be homogeneously nitrided both in the finished state and in the as-built state. In addition, thicker layers of expanded austenite are produced compared to conventional plasma nitriding. For the interaction with the electron beam, on the one hand the example of a uniformly remelted surface area and on the other hand the example of a profiling with a high aspect

ratio are used to demonstrate the process engineering possibilities offered by the application of the active screen plasma nitriding in order to vary the nitrogen/carbon element depth profiles and corresponding properties. Material specific investigations are performed including X-ray diffraction analyses, electron probe microanalysis, scanning electron microscopy and complementary hardness measurements.

**Keywords:** austenitic stainless steel, plasma nitriding, active screen technology, expanded austenite, laser beam, electron beam, selective laser melting, surface structuring



**Figure 1:** Cross-sections of different active screen plasma nitrided AISI 316L states: SLM substrate in a) finished and b) as-built condition, and b) electron beam profile with remelted surface d); expanded austenite layer indicated as  $\gamma_N$ .

## References:

1. A. Dalke, I. Burlacov, S. Hamann, A. Puth, J. Böcker, H.-J. Spies, J. Röpcke, H. Biermann, "Solid carbon active screen plasma nitrocarburizing of AISI 316L stainless steel: Influence of  $N_2$ - $H_2$  gas composition on structure and properties of expanded austenite," *Surface & Coatings Technology* 2019, vol. 357, pp. 1060-1068.
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# Low-temperature synthesis of gradient composite nanocoating on TiNi substrate

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Tomsk State University, Tomsk, Russia

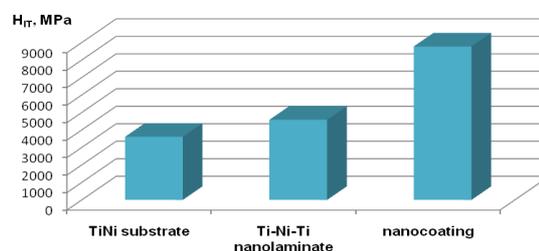
## Abstract:

TiNi alloys are widely and effectively used in medical materials science due to their high corrosion resistance, mechanical properties and biocompatibility [1]. Long-term functioning in a biological environment and under alternating deformations require biomechanical and biochemical solutions to avoid a number of problems: the release of Ni ions at prolonged implantation, poor contact between the implant and the bone tissue due to the incompatibility of their mechanical properties, functional degradation of the material. Biological characteristics of TiNi alloys directly depend on the surface properties, which can be modified by various coating methods. A gradient composite nanocoating was synthesized from a three-layer Ti-Ni-Ti nanolaminate deposited on a TiNi substrate by magnetron sputtering. This study is part of research aimed mainly at producing a dense thin intermetallic biofunctional coating firmly bound to the substrate. Prior to synthesis, the three-layer amorphous nanolaminate deposited by magnetron sputtering is a combination of Ti, Ni, and Ti layers with a thickness of 100 and 50 nm each. Reaction synthesis in argon at 500 °C did not significantly change the coating microstructure and did not affect the overall coating weight. Synthesis resulted in formation of the TiO+TiO<sub>2</sub> oxide layers, a Ni layer and a diffusion zone that mainly consists of the TiNi<sub>3</sub> intermetallic compound. The coating is uniform but not sufficiently dense to identify the shape of the TiO+TiO<sub>2</sub> and Ni crystals. The X-ray spectrum revealed diffraction reflections of two phases of the diffusion zone: bcc-TiNi and fcc-TiNi<sub>3</sub> and diffraction reflections of the coating phases: titanium oxides bcc-TiO, TiO<sub>2</sub>-rutile and fcc-Ni. Synthesis at 500 °C is insufficient for interdiffusion between the deposited layers and their mixing, but it allowed O to diffuse into the Ti layers and form titanium oxides, since Ti is chemically active and easily forms compounds with residual gases. The oxygen concentration in the outer and inner Ti oxide layers is similar, while O diffusion slows down at the interface with the diffusion zone. No signs of diffusion Ni into other layers and substrate elements into the surface layer could be detected.

The hardness of the composite nanocoating after low-temperature synthesis increased two-fold to HIT 8778 MPa at a maximum applied load of 1 mN in comparison with that of the Ti-Ni-Ti nanolaminate and TiNi substrate (Fig. 1). It should be noted that low-temperature synthesis at 500 °C is insufficient to initiate phase transformations (liquid-phase reactions) between the deposited layers in order to obtain the expected intermetallic TiNi-based structure. The temperature of 500 °C was not sufficient for the formation of the expected intermetallic biofunctional coating based on titanium nickelide oxycarbonitride which was obtained at 900 °C [2]. However, an isotropic diffusion zone was formed to ensure a strong coating-substrate bond.

This research was supported by Russian Science Foundation (grant #19-72-10105)

**Keywords:** nanolaminate, coating, Ti-Ni-Ti, magnetron sputtering, reaction synthesis



**Figure 1:** Values of nanoindentation hardness of the TiNi substrate and synthesized coating.

## References:

1. Jani, J., Leary, M., Subic, A., Gibson, M. (2014) A review of shape memory alloy research, applications and opportunities. *Material*. 56. 1078–1113.
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# Elaboration and characterization of $Ti_xHf_{1-x}N$ thin films

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## Abstract:

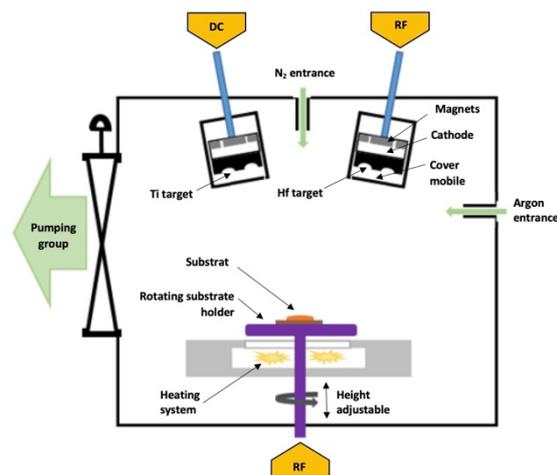
Friction and wear are recurrent problems in many industrial environments where increasing the life of assemblies is a major technological concern. In order to increase the durability of surfaces, it is essential to use thin coatings with a low coefficient of friction and high wear resistance. For mechanical systems operating at a temperature higher than 500°C few tribological solutions are able to protect superalloy based substrates.

At the moment, existing tribological solutions whose maximum temperatures of use are the followings (given in brackets): DLC (300°C - 350°C),  $CaF_2$ - $BaF_2$  (250°C to 1000°C),  $WS_2$  (450°C) and  $MoS_2$  (350°C). But, in situations where high contact pressures must be withstood, these coatings do not have sufficient mechanical characteristics (especially hardness). So, it is necessary to choose a coating with initial high hardness and good adhesion. Therefore, a nitride was chosen as a base layer. In many cases, the surface of original nitride coating oxidizes at elevated temperatures and the oxides formed may have a low coefficient of friction. These oxides can reduce the friction and thus the coatings are able to retain lubricating properties during the rise in temperature in a dry environment [1].

This work is dedicated to the synthesis and the characterization of a mixed titanium and hafnium nitrides. Coatings are deposited by simultaneous reactive magnetron sputtering of a titanium target and a hafnium target (**Figure 1**). A wide range of composition  $Ti_xHf_{1-x}N$  has been obtained:  $0,01 < x < 0,70$ . The properties studied are hardness but also thermal stability and resistance to oxidation in air. The Ti-Hf-N coatings have shown general improvement of hardness associated with an improved temperature stability (30 GPa after annealing at 800°C under argon atmosphere).

This study made it possible to identify a composition of interest which was the subject of a transfer to an industrial reactor in order to synthesize thicker layers. A future study will concern the addition of carbon in the coatings in order to decrease the coefficient of friction.

**Keywords:** Reactive magnetron sputtering, Thin films, Mixed titanium and hafnium nitrides, Hardness, Tribology.



**Figure 1:** IRCER laboratory PVD reactor

## References:

1. R. Franz, C. Mitterer, *Surface & Coating Technology* 228 (2013) 1-13

# Fabrication of Tungsten high aspect ratio micro-tools by electrochemical etching, by controlling the immersed length and the etching charge.

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## Abstract:

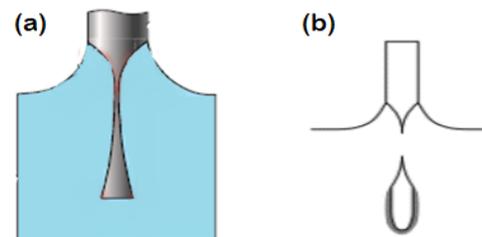
Tungsten wire machining is widely used to fabricate tips for AFM and STM microscopy [1], or for micro-Electrical Discharge Machining ( $\mu$ EDM) of hard materials such as steel [2]. For the later case, it is necessary to form cylindrical micro-tools with small diameters and high aspect ratio [3]. Among the techniques used to fabricate these micro-tools, electrochemical etching is often used thanks to its simplicity, its low cost, and the possibility to obtain diameters lower than 20  $\mu\text{m}$  when the etching parameters are optimized. These small diameters can not be achieved by the mechanical machining techniques.

However, electrochemical etching naturally leads to non-homogeneous profile. Especially, the air/water/electrolyte interface, where a meniscus is formed (Figs. 1 and 2), and could lead to the loss of the micro-tool.

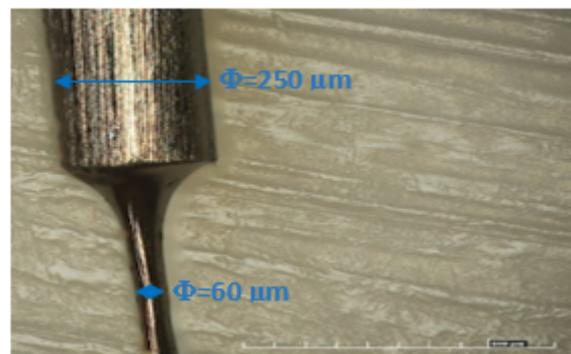
In this work, we were interested in a method consisting in a sequence of etching steps ; varying the etched length and controlling the etching charge, in order to limit the inhomogeneity of etching. This approach has led to the fabrication of cylindrical micro-tools: (i) with a diameter of 30  $\mu\text{m}$ , over a length of 2.5mm with an aspect ratio of 90 in the case of Tungsten wire with initial diameter of 125 $\mu\text{m}$  and also (ii) with a diameter of 90  $\mu\text{m}$ , over a length of 3.5mm with an aspect ratio of 40 for a wire with an initial diameter of 250  $\mu\text{m}$ .

Our perspective is to fabricate, automatically, cylindrical micro-tools with a diameter of 10  $\mu\text{m}$  throughout a length of 1mm. For that, in addition to the control of the etching charge, we propose to use in situ measurement of the diameter by using a high resolution camera. This method may help us to know the amount of etched material in real time in order to readjust the etching charge for the next etching step.

**Keywords:** Tungsten electrochemical etching, High aspect ratio micro-tools, inhomogeneous etching, meniscus effect.



**Figure 1:** physical phenomena influencing the micro-tool etching. (a): a meniscus effect, (b): loss of the micro-tool because of the etching inhomogeneity.



**Figure 2:** Micro-tool profile after etching, at the meniscus level, for Tungsten wire with initial diameter of 250  $\mu\text{m}$ .

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# Elaboration of high-entropy alloy coating by cold spray with following laser remelting: feasibility study

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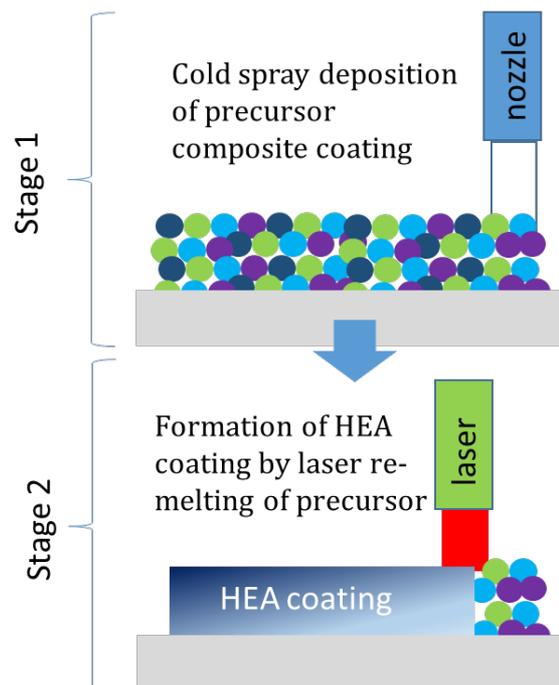
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## Abstract:

High-entropy alloys (HEA) are considered as promising advanced materials with significant application potential in different domains of industry [1]. Recent study demonstrated unique mechanical and tribology properties of HEA coatings deposited on metal substrates [1,2]. Nowadays, the HEA coatings are elaborated by laser cladding, thermal spray or cold spray techniques using pre-alloyed HEA powders. The main drawback of these approaches is the low commercial availability of HEA powders due to significant production complexity. In this study the two-stage approach of HEA coating was proposed. At the first stage, the precursor composite coatings containing the mixture of several low-entropy powders were elaborated by cold spray. At the second stage, the formation of HEA phases in the coating is promoted by laser re-melting.

In current work the feasibility study of elaboration of NiFeMoCrCuAl and NiFeMoCrTiAl high-entropy alloy coatings by two-stage process was performed. In the first stage the precursor composite coatings were deposited on aluminum substrates by cold spray using mechanical mixture of commercial powders of 316L, Triballoy 700, aluminum, copper and titanium. The main challenge in this task was the difference between the coating composition and the initial mixture composition due to different deposition efficiency of the powders. However, proper optimization of cold spray process allowed to obtain the coatings with targeted composition. At the second stage the laser re-melting of the composite coating was successfully carried-out. The microstructure analysis revealed the formation of HEA phases in the coating. However, the coating composition is not uniform due to insufficient element diffusion. The uniformity of the composition could be improved through optimization of laser processing parameters.

**Keywords:** high-entropy alloy, coatings, composite, cold spray, laser melting



**Figure 1:** Figure illustrating the two-stage approach of elaboration of HEA coating consisting of cold spray deposition of precursor composite coating (i) and laser re-melting of precursor coating (ii)

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# Deposition of Aluminum Nanostructured Films by DC Magnetron Sputtering for Hydrogen Production

S. Ibrahim<sup>1</sup>, P. Brault<sup>1</sup>, A. Caillard<sup>1</sup>, T. Sauvage<sup>2</sup>, C. Chauveau<sup>3</sup>, F. Halter<sup>3</sup>, A-L. Thomann<sup>1,\*</sup>

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## Abstract:

Dihydrogen is a clean fuel which has attracted significant attention in different domains, including electricity generation via its conversion in fuel cells. The hydrothermal route to produce hydrogen from aluminium nanopowder was studied few years ago. It was proved that Al nanoparticles exhibit high reactivity [1]. Yet, the manipulation of nanoparticles possesses potential harmful effects on human health and environment. Therefore, in this work, nanoporous Al films with thickness in the range of 1-3  $\mu\text{m}$  were successfully deposited by direct current magnetron sputtering in He/Ar mixed atmosphere. Sputtering using He gas has been little investigated. However, previous researches have reported the formation of porous metallic coatings using pure He plasma [2,3]. Our results reveal that the variation of He to Ar flow rate ratio influences remarkably the film morphology. SEM images demonstrate that films deposited with low He percentage show the typical columnar structure. After that, the grain size decreases as the helium concentration increases until completely nanoporous films are obtained with the 100% He plasma. The amounts of Al and He into the films are determined by Rutherford Backscattering Spectroscopy (RBS) and Proton Elastic Backscattering Spectroscopy (PEBS), respectively. Moreover, Slow Positron Beam analysis (SPB) is performed to investigate the possible formation of vacancy-type defects since the porosity induced by He in metals is often associated with the formation of vacancies and bubbles [4]. The XRD patterns of Al films show that they are crystalline. Peak broadening is observed as the percentage of helium increases, which could be related to metal lattice distortion induced by helium insertion. In addition, the formation of small helium bubbles is investigated by TEM analysis and molecular dynamics simulations of Al film growth in helium atmosphere. These results predict the trapping of He atoms and the formation of a

porous structure. The reactivity of the most porous Al films will be tested for the production of hydrogen.

**Keywords:** Aluminum nanostructured films, DC magnetron sputtering, helium bubbles, molecular dynamics simulation, hydrogen production.

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# Adjustment of the micromorphology of component surfaces via cold spraying with fine particles

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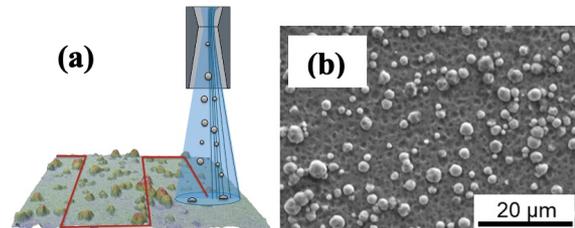
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Kaiserslautern, Germany

## Abstract:

The change of the surface morphology of components is an interesting way for the manufacturing of surfaces with desired properties in special technical applications. A suitable method for the change of the surface properties is cold spraying [1]. In general this particle deposition technique is used for creating a dense coating. In this process particles are accelerated to velocities up to 1000 m/s and impact on a substrate. The high kinetic energy leads to plastic deformation and mechanical interlocking during impact [2]. As a result a strong bond at the interface between the particle and the solid substrate is formed. To obtain high particle velocities a pressurized gas is preheated and then expanded through a Laval nozzle (Figure 1 (a)). The use of inert process gases and the low process temperatures makes the cold spray technique suitable for a big variety of powder feedstock materials.

In this study we use a self-constructed cold spray setup for the generation of microstructured surfaces on different solid components (e.g. titanium, stainless steel and PTFE) by using fine particles in the range of 1-20  $\mu\text{m}$  (Figure 1 (b)). The use of different characterization techniques for the investigation of the manufactured samples permit us to understand the relationships between the process parameters and the produced morphology of the component surface. In addition, we report the improved friction and wetting behavior of the surfaces. The focus of this work is to gain an understanding for the controlled manufacturing of microstructured components with versatile surface properties and their use in technical applications in the area of process and mechanical engineering.

**Keywords:** cold spray, material characterization, morphology



**Figure 1:** Microstructuring of a component surface with fine particles (a) and SEM of a microstructured surface (b).

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# Combined GD-OES and HAXPES for quantified depth profiling through coatings

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## Abstract:

GD-OES enables depth profiling through coatings and interfaces over many microns, however the quantification from photodiode voltage to atomic concentration is not arbitrary when a material system involves many elements and requires a calibration step. The profiling rapidity of this technique offers interesting perspectives for the analysis of coated structures or stacks, enabling to easily reach buried interfaces and specific areas of interest. The GD-OES crater dimension of 2-8 mm diameter is compatible with many chemical, optical or electronic probes that can be directly implemented inside the crater. An important point concerns the reliability of the information inside this crater. Indeed, we have evidenced the systematic presence of an overlayer, damaged by the plasma and resulting from the shutdown procedure, whose physicochemical properties differ from the one of the original layer [1]. The determination of the nature of this layer and its thickness is essential for the development of adjusted procedures to remove it. In a previous paper, we have evaluated the chemical and optical perturbations in the case of InP (100) semiconductor [2]. Combining XPS, EBSD and ellipsometry, we have demonstrated that the morphology and the atomic network are modified over approximately 50 nm (partial loss of crystallinity, superficial In enrichment, optical indexes modifications) but the exact impacted depth has still to be determined. Post-mortem analysis of a GD-OES crater with HAXPES, using a higher energy X-ray source than XPS, will be used to increase the sampling depth from 10 nm up to 30-50 nm for bulk-sensitive measurements, and detect the elemental concentration and chemical state within the whole damaged layer and probably below. Especially, additional core levels become accessible with HAXPES, and thus an extended escape depth range. The In/P ratio can be determined using different photoelectron peak combination, the conventional In 3d/P 2p (as a comparative point with XPS measurements), but also the In 2p/P 1s ratio. For this study, a GD-OES (Profiler 2, Horiba) and an XPS (Nexsa,

Thermo Scientific) are combined with a novel laboratory-based HAXPES spectrometer using a Ga Ka (9.25 keV) X-ray source (Scienta Omicron GmbH) [3] which has recently been calibrated and elemental sensitivity factors calculated to enable quantification [4].

**Keywords:** GD-OES, XPS, HAXPES, depth profiling, crater chemistry, plasma induced perturbation, InP, metrology, quantitative analyses.

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# Multifunctional anti-fouling coatings for building materials: studying the combination of active nano-biocides with passive strategies via hydrophobicity and induced super hydrophilicity.

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## Abstract:

Microbial-induced decay of building elements is an issue that causes numerous economic costs in maintenance and repair interventions and can be associated to multiple health issues (e.g. mold-related diseases, spread of bacterial infections) or occupational hazards. Due to the cumbersome nature of proper disinfection programs, there is a growing demand of surface treatments able to delay or prevent microbial growth, most of them based on limiting water availability (hydrophobic or waterproofing) or leachable biocide components.

The following piece of work consists in an evaluation of different superficial treatments for building materials, specifically concrete and mortars, that combine superhydrophobic and biocidal properties. Additionally, some of these products undergo the so called photoinduced hydrophilia, in other words they change their superhydrophobic surface to hydrophilic when they are exposed to enough light, while the bulk retains its hydrophobic properties. The study of the possible effect this change may have on the biocidal capacity of the treatment is also one of the purposes of the experiment. The products consist in a hydrophobic organically modified silica matrix, synthesized via sol-gel, containing nano-biocides (CuO or Ag) and photo-active TiO<sub>2</sub> nanoparticles to modify surface roughness and wetting properties.

The coatings are being tested against three different types of epilithic photoautotrophic microorganisms (1 alga and 2 cyanobacteria) in an accelerated exposure experiments using transparent methacrylate tanks equipped with a sprinkler system to homogeneously inoculate the surfaces with the algal culture at regular intervals. Algal growth on the surface is mapped by direct measurement of the fluorescence on the surface with a micro-plate reader, and compared with colorimetric analysis, both of them non-destructive analysis techniques.

This experiment is carried out twice, first when the treatments aren't exposed to sunlight (superhydrophobic surface) and second once after preconditioning the surface with UV-Vis lighting so the photoinduced hydrophilia manifests. With this setup, the competing effects of the wetting properties and surface roughness on cell attachment and contact of the biocide with the organisms can be discriminated from each other.

**Keywords:** Superhydrophobicity; Superhydrophilicity; Biocide; Anti-fouling; Coatings; Building materials; Organically modified silica.

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# Bio-carbon anti-UV properties for wooden façade coatings

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## Abstract:

Façades play crucial roles in the building safety, comfort, and aesthetics. As an envelope for buildings, they are in constant interaction with outside environment. Ultraviolet (UV) solar radiation absorbed by lignin – constituting up to 40% of wood – initiates the weathering of wood. The weathering process induces colour changes (Fig. 1), surface fibres to loosen and erode, allowing humidity to penetrate in depth in wood, and causing checks and a raised grain<sup>1</sup>. It is therefore crucial to limit the weathering effects that can then lead to deterioration of wood by using coatings to protect its surface.

UV absorbers enhance the durability of wood outdoors by absorbing incident radiation and by converting it into heat, which is then dissipated. Carbon-based materials are potential UV stabilizers thanks to combined effects of physical screen, UV absorbance, and radical trap<sup>2</sup>. Bio-carbon is a carbon-based product obtained from thermal decomposition of organic materials at elevated temperatures. Organic materials can be wastes from the agricultural or forest industries, with currently little or no economic value. Bio-carbon presents a wide range of properties that can be tailored by the manufacturing process<sup>3</sup>.

In this study, hemp stems underwent thermal treatment in a tube furnace. Several process parameters were studied (pyrolysis rate, final pyrolysis temperature and duration). The composition, particle size distribution, porosity, structure and UV protection potential of the bio-carbon particles were analysed. The effect of biomass carbonization processes on the structure and properties of bio-carbon were investigated and the critical properties needed for UV protection were identified. The most suitable particles for UV-protection were introduced in a drying oil and dispersed on beech wood to form a coating. The wooden surface underwent an artificial weathering in a QUV machine. Thickness, colour, gloss, surface morphology, hydrophilic behaviour, antibacterial effect, UV-resistance, and tensile properties have been investigated for the un-weathered (controls) and weathered coating materials in order to assess the efficiency of the coating.

**Keywords:** bio-carbon, biochar, sustainable coating, carbonization, pyrolysis, hemp, UV protection, anti-UV, UV absorber, wood, wooden façades, weathering.



**Figure 1:** Figure illustrating the undesired uneven discoloration of wooden façade exposed to an outside environment: an adequate protective anti-UV coating limits the weathering effects that can then lead to deterioration of wood.

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# Sculptured thin film based all-silica mirrors for high power lasers

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## Abstract

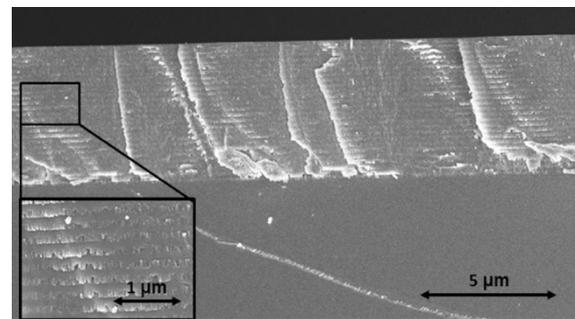
Optical coatings resistance to laser radiation plays an important role in photonics topic. In order to increase the resistance, optical elements are modified in different ways, including material engineering or electric field distribution optimization in formation of multilayers structure. At high energy nanosecond laser pulses materials tend to gain stress after laser exposure due to thermal expansion. Thus, porous nanostructured singlelayers, which are characterized by low inner stress, need to be investigated. Moreover, the main resistance to laser radiation is limited by material itself. Therefore, material which excels low absorption and high band-gap, such as silica, should be investigated in detail for promising applications. Porous all-silica anti-reflection coatings are already demonstrated as a viable commercial elements [1]. By applying an innovative materials engineering technique in formation process – GLancing Angle Deposition (GLAD), the porosity modulation is achieved in this work and laser-induced damage threshold (LIDT) is measured for different materials produced layers. Moreover, it is shown, that using GLAD technique high reflection and more resistant mirrors may be formed using only silica material.

Singlelayers of several different materials such as aluminium, hafnium oxides are investigated to achieve LIDT dependance on structure porosity. Afterwards, Bragg mirror is formed using GLAD, where multilayer structure of porous silica (as low refractive index layer) and dense silica (as high refractive index layer) are combined (Figure 1.).

Such optical element exhibits high reflectance (>99%) at 355 nm wavelength and has superior resistance to nanosecond laser radiation (>60 J/cm<sup>2</sup>) [2]. Unfortunately, such coatings tend to absorb water and other harmful particles from the environment, thus insulation of the element must be implemented. Several storage conditions such as glass desiccator with oxygen gas and nitrogen gas environments of sample are investigated to avoid porous structure LIDT degradation.

GLAD coatings exhibit superior resistancy compared with standart Bragg mirrors.

Singlelayers of several materials including silica were investigated as well as all-silica coating of Bragg mirror. Different environments were tested in order to achieve the most stable optical resistivity and spectra properties. Structural and optical characterization is demonstrated and compared with conventional deposition methods. GLAD technology provided a new concept of increasing the optical resistivity of optical coatings.



**Figure 1:** Electron microscopy image of cross section structure of all silica mirror [2].

**Keywords:** Glancing angle deposition, laser-induced damage threshold, sculptured thin films, porosity, high reflection mirrors.

## References:

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# Impact of Humidity and Deposition Errors on Spectral Parameters of Broadband Chirped Mirror with Sculptured Top Layer

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## Abstract:

Chirped mirrors (CMs) are optical interference coatings designed for manipulation of phase properties of ultrashort optical pulses. Multilayer structure of CMs allows to customize the CM design to necessary spectral bandwidth thus ensuring a wide field of applications for ultrashort laser devices. However, several limitations restrict parameters of CMs. Main of them is optical impedance mismatch between chirped mirror and ambient medium (i.e. air) which causes oscillations of CM main spectral parameter — group delay dispersion (GDD). Such oscillations may inflict an increase in pulse duration or even additional satellite pulses in chirped pulse compression optical lines.

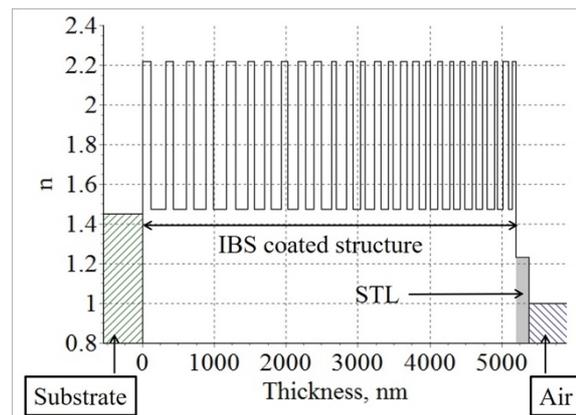
In order to decrease or avoid such issues, various CM types were introduced: double CMs, complementary CM pairs, and other. The most recent type is a CM with sculptured top layer (STL). Refractive index of STL may be lower than refractive index of dense material layer and therefore better impedance matching may be achieved. However, such mirrors are extremely sensitive to deposition errors and STL is formed less accurately than dense material layers. Furthermore, a water content in air may be adsorbed within the STL because of its porous structure and may change the spectral parameters of the mirror.

In this work, we investigated the dependence of spectral parameters of CM with STL to deposition errors and change in relative humidity (RH). For this reason, a 52-layer CM with STL (Figure 1) was deposited for 400 nm spectral bandwidth ( $\lambda=600-1000$  nm). Dense layers of the structure ( $\text{Nb}_2\text{O}_5$  and  $\text{SiO}_2$  materials) were deposited by ion beam sputtering (IBS) technology and sculptured layer ( $\text{SiO}_2$  material) was deposited by glancing angle deposition method within the electron beam evaporation coating plant. After deposition spectral parameters of the mirrors were measured at different RH conditions as well as reverse engineering procedure was carried out to determine the errors of deposited layers.

Amplitude of measured GDD oscillations was at least two times smaller than it would be expected for a single CM without STL. Deposition error analysis indicated that the amplitude of GDD oscillations might have been reduced at least by half if IBS

deposition errors had been avoided. Furthermore, low impact of RH change to final CM parameters was observed.

**Keywords:** optical interference coatings, chirped mirrors, femtosecond pulse compression, sculptured films



**Figure 1:** Structure of deposited CM with STL: different refractive index values indicate separate layers of CM.

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# Optical properties of highly porous thin films: an overview of optical simulation methods

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## Abstract:

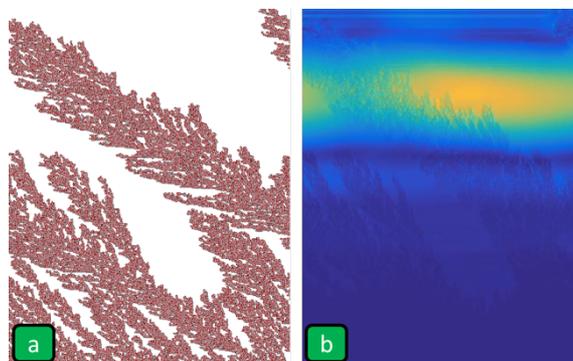
Thin film technology presents a large range of applications in various fields like anti-scratching coatings, optoelectronic devices, optical coatings... However, physical behavior of thin films highly depends on intrinsic properties, especially the film structuration or porosity and it is mandatory to develop efficient analytical or numerical methods to predict such properties, especially in optics.

In the case of optical coatings, it is generally admitted that if one knows the refractive index, and films thicknesses, one can compute the optical properties easily by using for example transfer-matrix analytical method.

Such method has very strong limitation when the coating is porous. The purpose of this work is to evaluate the validity of various optical models applied to porous coatings. To do so, we will first deposit in-silico a 3D TiO<sub>2</sub> porous coating by using NASCAM k-MC modeling taking place in GLAD mode [1,2]. 3D coating optical properties are then computed by using conventional effective medium theory based on Maxwell-Garnett and/or Bruggeman models [3], and are benchmarked against more adequate simulations performed by Rigorous Coupled Wave Approximation (RCWA [4]) or Finite Difference Time Domain (FDTD [5]). The last two models solve directly the Maxwell equations and then act as benchmark because they are de facto more suitable to take into account nanometric and micrometric size features like occluded pores or open pores (filled or unfilled) as observed in films deposited by GLAD. Figure 1 shows the modeling of a TiO<sub>2</sub> porous coating and its optical characterization by FDTD.

Special care will be put on determining the optical model strengths and limitations, required inputs and generated outputs, and defining their range of validity.

**Keywords:** thin film, PVD, GLAD, high porosity, transfer-matrix, effective medium theory, FDTD, RCWA.



**Figure 1:** Modelling and characterization of TiO<sub>2</sub> thin film deposition in GLAD (vertical cross-section). a - film growth modeling by kinetic Monte-Carlo. b - FDTD simulation: representation of the electric field modulus when illuminating the film with a plane wave.

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## **SICT Session II**

### **Interface and Interaction Science, Adhesion and Adhesives**

# Improvement in Tribological Properties and Interface Adhesion of Thermal Spray Coatings by Surface Severe Plastic Deformation (S2PD)

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## **Abstract:**

Although the application of surface severe plastic deformation (S2PD) methods such as surface mechanical attrition treatment (SMAT), shot peening (SP), laser shock peening (LSP) to metallic materials has attracted considerable attention, but there have been a lack of attempts to make use of these technologies for thermal spray coatings due to the several reasons. For example, S2PD methods may produce metallic materials having simultaneous high strength and high ductility, which cannot be applicable for thermal spray coatings. Also, the hardening mechanisms of thermal spray coatings by S2PD methods are not understood and recent experiments showed remarkable dissimilarities to hardening mechanisms of metallic materials. In this study, the advantage will be taken to provide an understanding of the hardening mechanisms and the microstructural evolution occurring in thermal spray coatings by ultrasonic nanocrystal surface modification (UNSM) technology, which is one of the S2PD methods. In the UNSM process, not only the static load, but also the dynamic load are exerted. The UNSM processing is conducted striking a work-piece surface up to 20K or more times per second with shots of an attached ball/tip to the horn in the range of 1K-100K per square millimeter. Moreover, a post-deposition development of procedures for the successful utilization of UNSM technology in manufacturing will be discussed.

Finally, the effects of UNSM technology on tribological properties and interface adhesion of thermal spray coatings are investigated and the related mechanisms are comprehensively discussed. It is certain that the results of this study help improve the performance of thermal spray coatings for many applications such as nuclear, aerospace, automotive, etc.

# How to study interfacial reactions at the buried interface between organic coatings and metals

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<sup>2</sup> Delft University of Technology, Department of Materials Science and Engineering, Corrosion Technology and Electrochemistry, Delft, The Netherlands

## Abstract:

Interfacial interactions between metals and an organic coating are mainly determining the durability of the entire organic/inorganic hybrid system. However, analyzing this solid/solid interface is challenging. Since this region is covered by a  $\mu\text{m}$ -thick polymer layer on one side and a metal oxide matrix on the other, the use of conventional surface analysis techniques to probe this region is hindered and this region is therefore often referred to as the buried interface. To understand this region, there has been a tendency to model the organic over layer by organic molecules with the functional groups of interest. Another accessing approach focuses mechanical removal of the coating by a destructive technique. (1) However, none of these approaches resemble the true buried interface or allow in situ investigations. Here, we characterize interfacial interactions of several polymeric films with metal oxide by utilizing novel methodologies. This approach leads to the in situ characterization of a more realistic model interface and this even when the systems are exposed to relevant environmental conditions such as water ingress, etc. The use of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is employed to describe the behavior of interfacial interactions in the presence of water vapor. (2,3) Furthermore, combined ATR-FTIR Kretschmann (2,3,4) with ORP- EIS (5) is utilized to obtain a near-interface infrared spectrum while simultaneously, the influence of an above-the-polymer electrolyte (such as water) on the interface is characterized. The local deposition of organic molecules we try to probe by Nano IR or TOF-SIMS/AFM approaches. This work shows that by using ultrathin films and a set of recently developed techniques, it is possible to non-destructively and in situ probe interfacial changes in hybrid systems. We believe that this approach can contribute in understanding the contribution of the molecular interfaces in adhesion and delamination processes of organic coatings on metals and their oxides. In this contribution we will

elaborate on the simultaneous ORP-EIS and in situ IR measurements to prove that this approach allows to study the formation and destruction of the interfacial bonds between polymers and aluminium oxides in real time.

Within the lecture we will emphasize the approach and end up with a link to more industrial type of coating applications on Al and galvanized steel surfaces.

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# A study on the quality of adhesively bonded composite aircraft structures based on crack growth monitoring and Acoustic Emission

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## **Abstract:**

In the aerospace industry adhesive bonding is one of the most promising technologies for joining parts because of its benefits in weight and performance. Its application is already implemented in secondary structures which failures should not be detrimental for aircraft safety. However, for primary aerospace structures adhesive bonding technology is still not accepted as the only joining method. In this case, the use of mechanical fasteners (the so called chicken rivets) are always implemented as a safety measure in case the adhesive bond fails. This procedure is clearly limiting the benefits of the application of composite bonded joints. The lack of acceptance can mainly be justified by the inability to guarantee the adhesion quality of adhesive bonding.

The prediction of flaws such as interfacial- or adhesive failures have been researched by linking non-destructive to destructive test results. Thus, two studies were performed: (1) Composite Bell Peel Test correlated with Hyper-Spectral Imaging and (2) Acoustic emission analysis during DCB Tests.

The first study compares the adhesive strength in non-contaminated and contaminated areas in combination with hyper-spectral imaging analysis. This allows for the determination and quantification of the amount of contamination during manufacturing process which influences the adhesive strength and the failure types at the surface. With a consistent spectral signature of the contaminants, it would be possible to identify contamination before bonding; reducing the chances of a weak (or often called “kissing”) bond.

The second study was performed to identify the different failure types during the in-service. The acoustic emission method was used during DCB Testing to map the acoustic pattern of the different failure types, allowing for a future development of an in-flight monitoring system of the condition of the aircraft.

Both studies are complementary; as the first one focuses on the manufacturing process and the second one on the in-service of the adhesive bond.

**Keywords:** Peel, acoustic emission, kissing bonds, adhesive bond strength, surface treatment, composites, aerospace

# Plasma technologies for enhancing the metallic adhesion or the vulcanization-bonding

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## Abstract:

Current environmental recommendations lead to the development of eco-friendlier surface coatings, particularly in the preparation of metals / polymers (or elastomers) assemblies widely used in the automotive and aerospace industry. Plasma technologies either applied as surface functionalization, texturing or deposition could substitute these processes.

Poly-ether-ether-ketone (PEEK), a thermoplastic requires a surface modification because of its low surface energy. Low pressure plasma allows both chemical functionalization and texturing of surfaces. The effect of the surface morphology, generally defined as the surface roughness, on the adhesion during the plasma treatment of certain polymers was already studied<sup>1,2</sup>. Our recent study shows that the chemical functionalization by ECR plasma<sup>3</sup> induces an ionic texturing effect produced by a polarization of the substrate useful for further increase the Al adhesion. Plasmas of argon, dioxygen and dinitrogen and their mixtures were explored with different treatment parameters. The different results issued from AFM, XPS and FTIR allow us to bring out models that could explain the mechanisms leading to these surface modifications. Then, PVD coatings of aluminum layers made it possible to test the assembly on these adhering surfaces using the pull-of test. The results showed the correlations between the morphology of the surface and the adhesion of the assembly. These topographies allow the adhesion performance of a functionalized polymer surface to be increased by the same plasma process.

Rubber material is particularly suitable for various applications<sup>4</sup>. However, the adhesive bonding between substrate and rubber is currently prepared by one or more adhesive layers often run by repetitive manual coatings<sup>5</sup>. In addition, these adhesive layers are liquid and highly toxic products and solvents. We propose a new approach to reach a unique bonding and homogeneous layer by plasma enhanced chemical vapor deposition

(PECVD) method using the technique of pulsed RF plasma polymer deposition which is eco-friendly and without solvent. We studied the deposit of different organic precursors (acetylene, acrylic acid, maleic anhydride) in order to preserve the chemical function of the different precursors. All treated surfaces and obtained interfaces are characterized by XPS, FTIR, AFM and wettability. Then, the vulcanization of different elastomers was followed by rheological measurements. Finally, the adhesion strength was measured directly after the vulcanization by tensile testing.

**Keywords:** plasma, functionalization texturing, deposit, adhesion, metallization, vulcanization.

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# In pursuit of toughness and damage tolerance by controlling material architecture

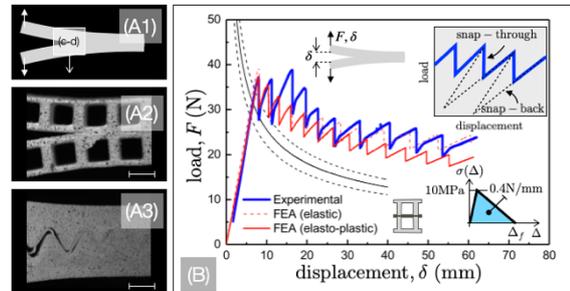
Marco Alfano

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## Abstract:

Current aerospace, automotive, and shipbuilding are pursuing the fabrication of strong and damage-tolerant components using advanced joining techniques. In that respect, adhesive bonding plays a crucial role because it eases the assembly process and provides increased design flexibility. Adhesive properties and morphology/topography of mating surfaces control the mechanical performances of the joints. Recent work has shown that substrate architecture represents a new scale for the joint design and allows us to tune deformation and fracture mechanisms, crafting layered structures with enhanced strength and toughness. Unprecedented developments in additive manufacturing are hastening this approach. This talk will support this point of view and leverage the results of the most recent research work on the analysis of deformation and fracture of layered materials. I will initially showcase the results of ongoing collaborative efforts that focus on tailoring bondline and interfacial architectures to achieve enhanced mechanical behavior [1-4]. After that, I will dive into current research to unravel the existing interplay between the architecture of adjoined layers and the resistance to interfacial separation [4]. In particular, the discussion will be mainly framed into the latest experimental results that include 3D printing, fracture testing, high-resolution in-situ imaging of the fracture process [5]. I will highlight that material architecture promotes a snap-through cracking process represented by a sequence of non-equilibrium transitions accompanied by sudden load drops and a local release of strain energy. Using design exploration and computational fracture mechanics, I will speculate on the tantalizing opportunity of tuning energy dissipation by tailoring material architecture [6].

**Keywords:** adhesive bonding, composite materials, additive manufacturing, fracture toughness, architected materials.



**Figure 1:** (A) Double cantilever beam adhesive joints featuring bio-inspired architected substrates obtained using 3D printing (A2: subsurface channels; A3: sinusoidal patterned interface). (B) Typical load-displacement response obtained in repeated tests (and Finite Element counterpart) highlighting the snap-through cracking process (i.e., sequence of non-equilibrium transitions) what is accompanied by sudden load drops and a local release of strain energy.

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# STUDYING THE IMPACTS OF BONDING AGENTS IN EPOXY ADHESIVES USING SELF-ASSEMBLED MONOLAYERS (SAMs)

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## Abstract:

New materials and coatings have been introduced in car manufactures to reduce vehicle weight and reach the European legislation of CO<sub>2</sub> emission. This mix of materials is joined using mainly structural adhesives. Moreover, adhesive bonding is extensively used in automotive industry as joining technique to ensure features as crash resistance, stiffness, fatigue resistance and the assembly of different materials types and thickness. An adhesion issue has been observed on new surfaces using the old generation of crash adhesives where the failure pattern was adhesive. This adhesive failure is not accepted by carmakers. To overcome this issue, the adhesive suppliers have developed new generation of epoxy adhesives which gave fully cohesive failure on new surfaces.

ArcelorMittal as steel manufacturer developed new coatings such as Zagnelis® which must be compatible with the new generation of adhesives. First screening using single lap shear tests confirmed good adhesion. According to adhesive suppliers, it might be related to the addition of bonding agent (organosilanes) in new formulations.

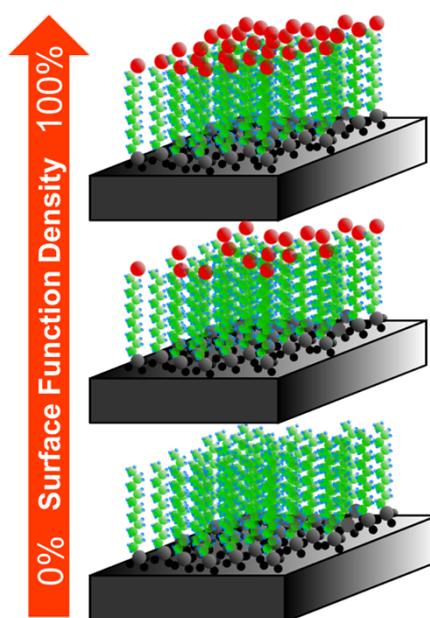
It is known that the silanes react strongly with hydroxyl groups of metallic surfaces. Therefore, it seems interesting to study the reactivity of the silanes with the hydroxides of the steel surface. First step is to manufacture controlled hydroxyl density surface. IS2M lab had developed silanization methodologies enable to control the density of grafted functional groups on wafer surfaces. The methodology is a multi-step procedure to get well-organized functional Self-Assembled Monolayers (SAMs) (Figure 1a) by depositing simultaneously the organofunctional silane with an aliphatic silane.

The objective aims to use these model surfaces to investigate the reaction mechanism with industrial epoxy- and amino-functionalized silanes. Different analytical techniques are used: ellip

sometry to control layer thickness; contact angle measurements and High-Resolution X-Ray Photoelectron Spectroscopy (HR-XPS) to study

surface chemistry (function density). Finally, the chemical reactivity will be correlated to adhesion tests.

**Keywords:** Structural adhesives, epoxy/epoxides, surface modification, interface, coupling agents, adhesion by chemical bonding,



**Figure 1** Silanized silicon wafer with a controlled surface density of functional groups (red dots).

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# Polymer thin films nano-engineered by means of femtosecond laser on single spot and scanning.

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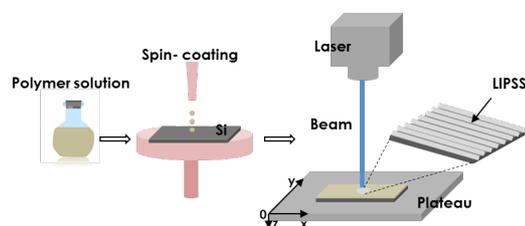
\*Corresponding authors: olga.shavdina@univ-orleans.fr

## Abstract:

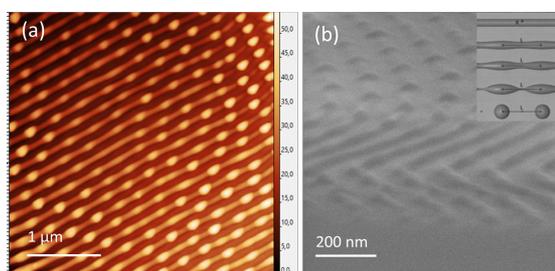
Laser patterning of a wide range of materials is increasingly a powerful technique for high resolution surface nanoengineering[1]. It is a non-contact maskless and flexible method with direct generation of nano and micro structures so-called laser-induced periodic surface structures (LIPSS) [2]. Several studies on LIPSS generation in Polymer films were conducted using nanosecond laser sources from the fundamental wavelength, typically 1032 nm with Nd:YAG sources down to the fourth state at 266 nm[3] and in some works with excimer sources [4]. Femtosecond laser-polymer interaction less investigated with UV beam is considered in our present work. It seems interesting to study the effect of the nonlinear optical phenomena with multiples photochemical reactions. The period of LIPSS can be modified by varying several process parameters as the laser beam wavelength, the angle of incidence and/or the beam polarization. For example, by increasing the angle of incidence it is possible to increase the period between the induced structures. Linear polarization makes it possible to form parallel structures called regular ripples parallel to the polarization vector[3]. In this work (see the schematic in **Fig.1**) we performed the study of femtosecond laser treatment by multipulse irradiation on polystyrene (PS) spin-coated thin film. More specifically, we studied the influence of laser frequency and number of laser pulses on the surface morphology and the LIPSS main features (period, amplitude, bifurcation). We also optimized the process parameters to create the ripples within a single spot and after on several processed lines with the control of the size and morphology of the periodic structures. Our experimental results illustrate several morphological features of surface nanostructures characterized for example by the bending and bifurcation of ripples as illustrated on **Fig.2**.

Correlation to pulse energy, focalization length as well as accumulation effect will be considered in the discussion part of the present work.

**Keywords:** femtosecond laser; nanoengineering; polymer films, multi-pulse irradiation.



**Figure 1:** Schematics of main steps Laser-polymer films nano-engineering.



**Figure 2:** PS irradiated at 266nm and 50 Hz by fs laser : (a) AFM image; (b) SEM image.

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# Laser-based processing of polymeric tribological coatings for engine pistons

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## Abstract:

Automotive engineering is characterized by an ever-increasing reduction in energy consumption, especially due to restrictions imposed by government regulations. This leads to new innovations for reducing friction and wear inside the engine. Especially engine pistons are in permanent friction contact with the cylinders and show high potential for further improvement on tribological properties. High-performance polymers like polyether ether ketone (PEEK) are potential candidates to substitute state of the art bonded coatings due to their excellent properties in terms of temperature resistance, friction reduction as well as corrosion and wear protection.

Conventionally, PEEK is applied to the component in a microparticulate dispersion. It is then melted in an oven-based process, whereby the entire component is heated above the melting temperature of PEEK ( $T_M = 340\text{ °C}$ ) for minutes up to hours [1]. Due to the high thermal load on the component, temperature-sensitive materials cannot be processed without a significant reduction in the hardness of the component. Engine pistons are usually made of an aluminum alloy, which is why it is not possible to apply these coatings using conventional methods.

An innovative approach to overcome this deficit is to form a dense and adhesive protection layer by melting the microparticulate PEEK layer using laser radiation. Due to the rapid heating and cooling rates, laser radiation offers the possibility to achieve the necessary melting temperature within the coating while reducing the thermal load on the substrate material. This leads to new challenges in obtaining sufficient adhesion between coating and substrate due to the comparably low substrate surface temperature during the process [2,3].

The current investigation deals with different approaches for the laser-based processing of tribological coatings made of PEEK, examining the entire process chain. This includes, first of all, a laser-based surface pretreatment of the substrate to improve adhesion between coating and substrate. Apart from adapting the substrate's surface roughness, a modification of the surface's optical properties is made to achieve higher

absorbance and, thus, improve the substrate surface temperature during the following laser melting process. Second, the deposition of the microparticulate PEEK to the component is investigated. Different approaches are suitable for this purpose depending on the required selectivity/layout, inline capability and process speed. Third, the laser-based melting of the particulate PEEK layer is investigated. Different approaches are characterized with respect to their advantages for different production scenarios.

**Keywords:** Laser-based processing, Laser melting, High-performance polymers, Polyether ether ketone, PEEK, Tribological coatings, Surface treatments, Coating application, Temperature sensitive materials



**Figure 1:** Figure illustrating a polymeric tribological coating on an engine piston produced in a laser-based process. The PEEK-based coating can significantly reduce the friction between pistons and cylinders compared to state of the art bonded coatings.

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# Hydrophobic Coatings with Low Ice Adhesion as a Passive Anti-icing System

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## Abstract:

Ice adhesion to the surface – one of the main problems in the aeronautics, needs to be solved. Anti-icing systems, prevent to form the icing of the protected surface. Many systems are used and they are quite popular in general aviation aircraft. The most common include: heating the surfaces, or spraying on them anti-freeze liquid (e.g. propylene glycol or ethylene glycol).

Passive anti-icing system preparation is crucial for many industry and life aspects. Mentioned solution does not need electrical energy to work. Reduction of ice adhesion to the substrate and thereby ice formation prevention is a serious issue, which has not been sufficiently addressed. Conventional anti-icing systems require electrical energy to work or special chemical treatment every time before the use.

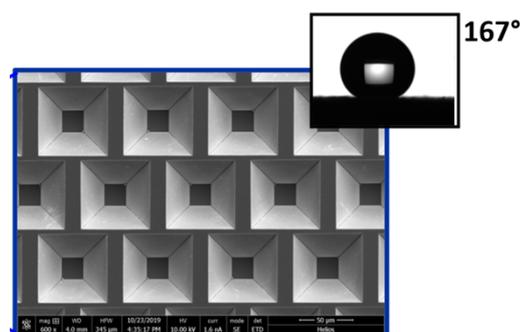
For this reason in this work hydrophobic (modified epoxy resin coatings) and superhydrophobic (surfaces with regular geometry structures based on epoxy nanocomposites) materials have been presented. Different epoxy resins have been used for hydrophobic coatings preparation. Moreover chemical structure of epoxy resins (volume modification of the materials) has been modified using different kind of fluorinated compounds. It has been shown that the obtained superhydrophobic coatings delayed the ice formation on their surfaces. Hydrophobic and superhydrophobic coatings showed low ice adhesion. Moreover prepared coatings properties were stable in temperature ranging from -25 °C to 30 °C and 98% humidity. Additionally their efficiency did not change upon exposure to UV radiation. The resistance of obtained coatings to atmospheric conditions is important factor. These tests were performed in aging chambers. Opposite to traditional anti-icing approaches, the proposed passive system and prepared surfaces did not need electrical energy to work efficiently. The research results may have strong application potential for defined recipients of the developed technology, such as aerospace and wind energy industry. We report the influence of different parameters (hydrophobicity, surface free energy,

surface topography, chemical modification of obtained materials) on the ice adhesion for prepared coatings.

This work was supported by the National Centre for Research and Development under the LIDER programme through the project contract No. LIDER/47/0194/L-9/17/NCBR/2018.

## Keywords:

hydrophobicity, hydrophobic coatings, epoxy resin, composite, anti-icing coatings, superhydrophobic coatings.



**Figure 1:** SEM image of superhydrophobic nanocomposite coating topography with water contact angle value (167°).

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## **PlasmaTech Session II**

**Plasma-surface interactions / Plasma  
diagnostics / Modelling and numerical  
simulations**

# Diagnosing the plasma electrolytic oxidation process: an exciting but complex challenge

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## Abstract:

Plasma Electrolytic Oxidation (PEO) also known as Micro-Arc Oxidation (MAO) is a powerful process to grow protective oxide coatings on light metallic alloys (e.g. Al, Mg, Ti...). However, PEO is a quite complex process involving chemistry, electrochemistry, plasma physics, material science & engineering. Complexity of the process is emphasized because of the multiple interfaces it has to face with, ceramic/metal, liquid/gas, liquid/solid, gas/solid, while considering the plasma surface interaction as well.

Over the last 30 years, there has been an abundant scientific literature dedicated to PEO. However, since there is a huge industrial demand, the published works mostly deal with the performances and properties of the processed materials, and only few of them rely to the process and the mechanisms underlying the material conversion. One way to progress in the understanding of underpinning mechanisms of PEO consists in deeply investigating the discharges that result from the dielectric breakdown under the applied voltage or current. Plasma diagnostics can indeed provide essential parameters that can bring useful information in the description of the growth mechanisms, or in the coating structure properties. As examples, plasma diagnostics can access the gas temperature that can be related to the material phase transformation; micro-discharge behavior can be correlated with the coating thickness and evenness.

The PEO process will be presented first with a focus on the so-called soft regime. The complexity of the process will be pointed out. The presentation will then review plasma diagnostics studies that have been carried out to get new insights into the PEO process. A particular attention will be paid to optical emission spectroscopy and to fast video imaging. From the plasma characterization, growth mechanisms will be inferred. In view of the presented results, related energetic issues will be discussed as well.

**Keywords:** Plasma electrolytic oxidation, plasma diagnostics, optical emission spectroscopy, fast video imaging, alumina.

# Pulsed NS Discharge Development in a Strong Magnetic Field and its Application for MHD Energy Generation

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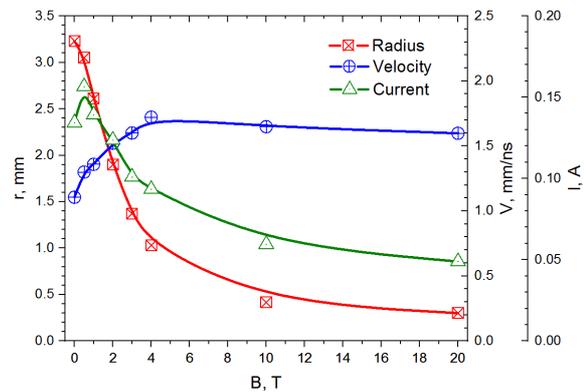
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## Abstract:

The numerical simulation of the development of a streamer discharge in a gap with an external longitudinal magnetic field was used to demonstrate the self-focusing of such discharges. Self-focusing is caused by a sharp slowdown in the speed of the radial ionization wave due to a change in the EEDF, a decrease in the average electron energy, electron mobility, and the rate of electron impact ionization in the crossed electric and magnetic fields as compared with the case of the discharge development without magnetic field. Simultaneously with the deceleration of the radial ionization wave, the ionization wave accelerates along the axis of the discharge gap due to a decrease in the radius of the streamer head and an increase in the electric field on it. Since the electric and magnetic fields are parallel to each other on the axis of symmetry, for the longitudinal wave there is no decrease in the average electron energy and ionization rate with an increase in the magnetic field value. In a weakly ionized plasma, a transverse magnetic field slows down the heating of electrons in an external electric field. The effect of magnetic field on the electron properties is determined by the Hall parameter and turns out to be different for electrons belonging to different parts of their energy distribution function. In particular, in weakly ionized CO<sub>2</sub> plasma, the effect of magnetic field is most profound for electrons with energies in the 0.1–4 eV range and is less important for electrons with higher energies. The self-focusing effect of a streamer discharge in an external longitudinal magnetic field is observed for both polarities of the discharge. At the same time, the self-focusing of the positive streamer is limited by a decrease in the photoionization efficiency as the streamer radius decreases to values less than the propagation distance of ionizing radiation in the gas. This limitation is absent for the negative streamer. The estimates of the critical magnetic field obtained in this work lead to the conclusion that the effective interaction of the external magnetic field with the ionization wave occurs when the Hall parameter exceeds unity. For a qualitative

assessment of this effect, it is proposed to consider the critical value of the reduced electron gyrofrequency  $\omega_e/n \sim 10^{-13} \text{ rad}\times\text{m}^3/\text{s}$  (in CO<sub>2</sub>), which may be somewhat different for other gases.

**Keywords:** nanosecond discharge, streamer, magnetic field, electric field, electron energy distribution function, electron mobility, ionization coefficient, nonequilibrium plasma, Hall parameter, reduced gyrofrequency



**Figure 1:** Streamer velocity, discharge current and channel radius versus magnetic field. Positive polarity,  $t = 7.0 \text{ ns}$ .  $P = 50 \text{ Torr}$ , CO<sub>2</sub>,  $U = 20 \text{ kV}$ .

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# Theory and Applications of inverted Fireballs

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## Abstract:

Inverted Fireballs have been proven to be a viable tool for large area surface modifications [1,2] and for a direct conversion from a dc input signal to a rf output signal [3]. This technology enables energy efficient deposition for various fields of applications. Its suitability for surface modifications in general and for deposition technologies in particular is owed to their very homogeneous plasma potential and their high charge densities. It has been shown that a substantial increase in ionisation in the deposition plasma is feasible. This work will outline theoretical investigations into inverted fireballs, such as analytical models and particle-in-cell simulations [4-6] and the application of these findings to technologically relevant topics. Details of how these plasma phenomena can be utilised in possible areas of surface technology, will be shown. Furthermore, it will be demonstrated that inverted FBs exhibit a number of plasma instabilities. However, they can be stabilised over a long period of time, which is necessary for industrial applications. It will also be outlined in this talk where the limitations of fireball research are at the moment and what needs to be done in order to gain a deeper scientific understanding in the future and establish commercial utilisation.

**Keywords:** Inverted Fireballs, Plasma Diagnostics, Instabilities, PECVD, Surface Modification



**Figure 1:** Illustration of an inverted fireball (IFB) setup in a low pressure PECVD chamber with a DC argon plasma.

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# Ion-induced secondary electron emission coefficient of metal surfaces analysed in an ion beam experiment

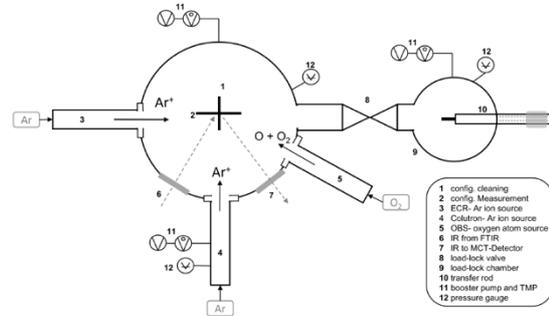
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## Abstract:

In glow discharges the generation of secondary electrons at surfaces plays an important role for ignition and maintenance of a plasma. The ion-induced secondary electron emission coefficient (iSEEC)  $\gamma$  depends on the chemical state of the surfaces and is defined as number of released electrons per incident ion. The iSEEC varies depending whether metal surfaces are clean or oxidized [1]. In magnetron sputtering discharges e.g. knowledge about the interaction of plasma and metal ions with the metal target, described by  $\gamma$ , is important for the occurrence of different discharges regimes [2]. Moreover,  $\gamma$  is an important input parameter for many plasma simulations. The coefficients of some metals are already published in literature and measured by different techniques [3]. As the applied techniques measure often directly in the plasma, the determination of the iSEECs remains rather indirect though. Moreover, any energy dependence is mostly missing. The unique feature of the here presented experiment is the possibility of analysis of surface processes induced by single and multiple ionized argon ions impinging on metals or their oxides within a broad energy and mass range. The elementary plasma processes on surfaces are mimicked by sending quantified beams of ions to metal foils in an ultra-high vacuum reactor. Different thin metal foils are exposed to a beam of argon ions, which are extracted from an inductively coupled plasma. This ion beam is mass and energy selected before reaching the metal foil. The iSEEC is measured by comparing target currents with currents on a biased collector surrounding this target [4]. We will present  $\gamma$  of different clean and oxidized metal surfaces in a broad energy range and compare them with calculations.

**Keywords:** ion beam experiment, ion-induced secondary electron emission, oxidized metal surfaces



**Figure 1:** Schematic top view of the ion beam reactor.

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# Characterization and analysis of atmospheric pressure air plasma treatment of hard mineral materials

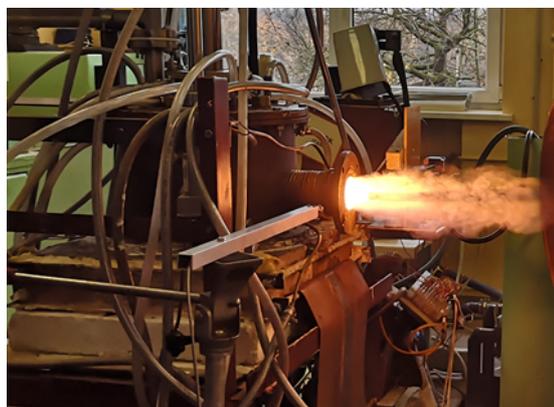
V. Grigaitienė, R. Kėželis, R. Uscila, M. Aikas, V. Valinčius

Plasma Processing Laboratory, Lithuanian Energy Institute, Kaunas, Lithuania

## Abstract:

The applications of atmospheric pressure thermal plasma technology are constantly expanding as it is a novel technique for the manufacture of novel and better materials, modification of surfaces, hazardous waste treatment, and etc. Plasma reactor provides high-power density, high temperature and velocity gas flow and plasma treatment, unlike other thermal methods, does not involve dangerous elements and compounds, does not change the basic properties of the treated material [1]. Plasma technology with a prototype volumetric plasma reactor [2] for destruction of different materials and waste decomposition has been realized at Lithuanian Energy Institute, Plasma Processing Laboratory. The main operating parameters of the plasma torch were established at power of plasma source of 35–55 kW, arc current – 150–160 A, arc voltage – 215–350 V. By using a specially designed plasmachemical reactor, connected directly to the plasma torch, the flow was heated up to 1800–2500 K of temperature, the gasification/decomposition process of selected mineral waste materials was realized (clay and phosphogypsum, hydroquinone mixtures, corundum). Contact and non-contact methods for plasma flow diagnostics have been applied in this research. One of them is an optical spectroscopy method with analytical system for rapid measurements and investigation of gas and treated materials emission spectra peaks in a wavelength range of 250–800 nm. The examination of plasma element optical emission spectra was performed and it revealed presence of emission lines for N, O, Si, Al, C, Ca, Fe, etc. with varying intensities. The summarized results of experimental research can help to develop systems for hazardous waste treatment, to establish optimal parameters for stable operation of plasma reactor and regulate the parameters of the process.

**Keywords:** air plasma, plasma torch, plasma treatment, optical emission spectroscopy, waste decomposition.



**Figure 1:** Plasmachemical reactor in operating regime.

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## Acknowledgement

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# Plasma nitrocarburizing with an active carbon screen made of CFC: Influence of the active screen power on the reactive gas composition and its effects on surface layer properties of stainless steel AISI 316L

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## Abstract:

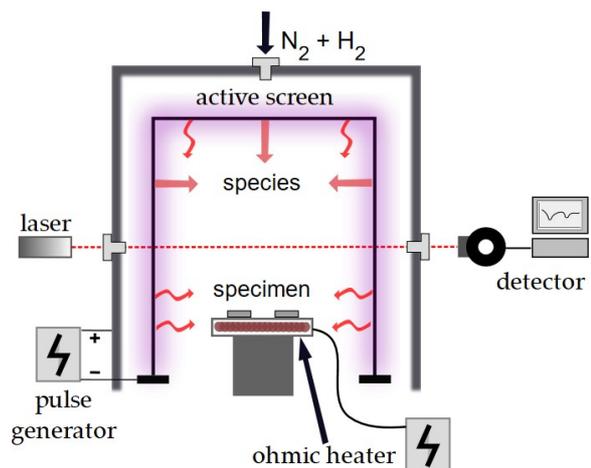
Austenitic stainless steels are widely used in automotive, offshore, chemical, and medical industries due to their excellent corrosion behavior. However, low hardness and poor wear resistance limit their applications. To improve the surface properties, plasma-assisted thermochemical heat treatment technologies, such as active screen plasma nitriding/nitrocarburizing (ASPN/ASPNC), are favorable. During the plasma-enhanced diffusion processes, the steel surface is enriched with nitrogen and carbon atoms resulting in a supersaturated solid solution, the “expanded austenite”. The incorporated elements cause strong lattice distortions and increase the lattice parameters, resulting in high compressive residual stresses.

Recently, a new ASPNC technology was suggested operating with an active screen made of carbon fiber-reinforced carbon (CFC). The active screen serves for heating the components to process temperature and generating highly reactive gas species, such as unsaturated hydrocarbons and CN-radicals by chemical sputtering. Since the active screen technology is implemented in cold wall reactors, the production rate of reactive gas species is connected to the process temperature. At high treatment temperatures, a high erosion rate of the CFC screen leads to unwanted material effects and a reduced service time of the screen.

In the present study, an additional heat source installed at the workload in the reactor decouples the heating from the production of reactive species. Thus, the temperature can be set independently from the active screen power. Laser-based absorption spectroscopy is used to monitor the absolute concentrations of reactive species in dependence of the power applied to the CFC screen, and for various ratios of the N<sub>2</sub>-H<sub>2</sub> feed gas composition (Fig. 1). The variation of the plasma parameters allows the modification of the expanded austenite in a broad range. For selected process conditions, the obtained correlation between the resulting process gas composition

determined by absorption spectroscopy and the nitrogen and carbon distribution within the expanded austenite surface layer is presented. On the basis of the specimens’ properties, the optimal concentrations of reactive species is assigned in order to use the AS carbon as efficiently as possible.

**Keywords:** active screen plasma nitrocarburizing, infrared laser absorption spectroscopy, afterglow nitrocarburizing, austenitic stainless steel, solid carbon source, surface engineering, expanded austenite.



**Figure 1:** Schematic illustrating of the ASPNC process and measurement of the process gas atmosphere by laser absorption spectroscopy.

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# Multiscale simulation of TiAlN film growth in an industrial magnetron based reactor

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<sup>1</sup>Laboratoire d'Analyse par Réactions Nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, Namur, Belgium

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## Abstract:

TiAlN coatings have very interesting properties that make them suitable for applications requiring heat, corrosion or wear resistance. Their find numerous applications like in the cutting tools coating market for example. When deposited in a large scale machine it is always a challenge to predict and tune their characteristics versus the deposition conditions.

In this work, we propose a multiscale simulation approach to predict the morphology and chemical composition of such coatings deposited in an industrial dual magnetron system like the one depicted in the next figure. Gas phase simulation was performed using DSMC method that solves the propagation of metal vapours from the targets toward the substrates together with the collisions with the neutral argon and nitrogen gas. That was completed with a 0D (global) model with detailed plasma kinetics has been used for the computation of the poisoning of the targets.

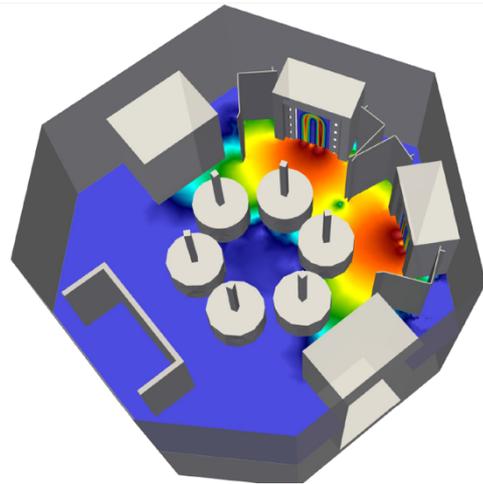
The presented model enables a prediction of reactive gas distribution, reactive gas depletion, and target poisoning for each cathode separately. It overcomes the “multiscale” nature of reactive magnetron sputtering, which poses a problem for efficient simulation of this process for a 3D fully loaded industrial chamber like the one considered here.

From those gas phase simulation, the condensing species were determined as well as their fluxes, energy and angular distribution at “sensors” placed at different locations in the chamber, on the sample holder. That serves as input for film growth simulations as performed by NASCAM [1]. NASCAM is 3D inetic Monte-Carlo based code for the simulation of deposition, surface diffusion, nucleation, film growth, and evolution of surface structures. It allows the simulation of metallic and reactive deposition, and each flux of condensing species is characterized by its own energy and angular distribution of particles.

After checking if the prediction of the pressure and hysteresis behaviour evolves similarly to the experimental one, several simulations were performed in various deposition conditions for

samples placed at different locations in the chamber. Film thickness, composition, porosity, morphology and roughness were then assessed and these simulation results were benchmarked with experimental ones like relative thickness or deposition rate (profilometry), chemical composition (XPS), surface and cross section morphology (SEM) and porosity (SEM). A general good agreement is found.

**Keywords:** thin film, monte-carlo simulations, film growth, NASCAM,



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# Collisional electronic excitations in the interaction of slow ions with surfaces

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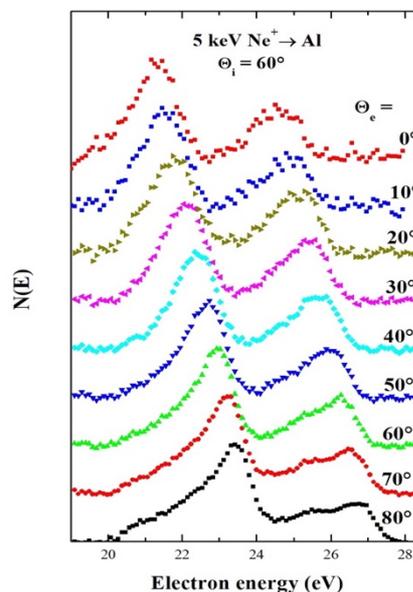
## Abstract:

The energy lost by atomic particles moving through solid materials governs important effects, such as scattering, sputtering, electron emission, and damage, that are of importance in many areas of research and technology, including astrophysics, plasma physics, materials science, and biomedical research. Energy losses involve both nuclear and electronic stopping, meaning that the projectile kinetic energy is transferred to both the electronic subsystem of the solid, producing excitation and ionization [kinetic electron excitation (KEE)], and the nuclei, via the elastic scattering of the projectiles with target atoms. At low projectile velocity, both the nuclear and the electronic processes are sizeable. The basic known mechanisms of KEE, in the interaction of slow ions with metal targets, are excitation of valence electrons (mostly treated as an idealized Fermi gas) in binary projectile-electron collisions and electron promotion in close atomic collisions. Electron promotion occurs when atomic collisions transiently create quasimolecular systems in which some electronic levels are promoted to higher orbital energies. These processes are characterized by well-defined energy thresholds, which depend on the particular combination of collision partners and which can be experimentally determined and theoretically estimated from molecular-orbital (MO) correlation diagrams.

For atomic collisions in a solid environment, it is commonly accepted that excitation results from promotion of one electron into the continuum of conduction band states [1,2]. For the most investigated He and Ne projectiles, this process entails an inelastic loss of about 20 eV, due to the promotion of the projectiles' 1s and 2p levels, respectively. Here, we show that such a commonly accepted view of electron promotion in atomic collisions in solids is quite far from reality. We demonstrate that the electrons promoted in collisions of slow sodium projectiles with Al target atoms are located into atomic outer shells, rather than being transferred into the empty conduction states of the metal surface. We study Autoionization electron emission from decay of 2p

excited Ne and Na projectiles scattered from Al surfaces (figure 1). We discuss experimental evidence demonstrating that the excitation of two 2p electron in neon and sodium occur simultaneously, in a single scattering event and not in two consecutive collisions, as expected in the one-electron excitation model.

**Keywords:** Plasma Surface Interactions, Secondary Electron Emissions, Auger Electron Emissions, Ion Scattering, Noble Gases, Aluminum



**Figure 1:** Detection-angle-resolved Ne autoionization spectra for a primary energy of  $E_i = 5$  keV for an incidence angle of  $Q_i = 60^\circ$  relative to the surface normal. The spectra have been background subtracted, normalized to the same height, and arbitrarily shifted on the vertical scale. The shift and the broadening of the autoionization lines due to the motion of the emitting atoms in vacuum show that the double 2p excitation in Neon projectiles occurs simultaneously in a single scattering event and not in two consecutive collisions, as commonly assumed.

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# Influence of the transition probabilities and the Hönl-London factors on radiative spectra simulation

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## Abstract:

Numerical simulation of radiative spectra serves as an efficient diagnostic tool to study plasmas. For instance, emission spectra contain a wealth of information on the radiative mechanisms occurring in the plasma and the species involved in those mechanisms, e.g., atomic lines, molecular bands, and atomic and molecular continua [1]. The description of these phenomena via the numerical simulation of synthetic spectra proves to be a useful method in the experimental characterization of laboratory-generated plasmas. By comparing simulated and experimental spectra, one can calculate several characteristic parameters of the medium, such as the temperatures associated with the various energy modes (vibration, rotation, excitation, electron, etc.) and the electron number density.

In order to study and characterize plasmas used for nanostructures growth (Ar-N<sub>2</sub>-He-C), syngas production (CO-H<sub>2</sub>) [2], and surface treatment (Ar-N<sub>2</sub>) [3], a spectra simulation code under thermal and non-thermal equilibrium conditions was developed, taking into account the radiative contributions of the most prominent molecules encountered in these mixtures, including C<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, and CN. From a theoretical point of view, radiative spectra modeling requires several assumptions (the molecular potential energy function, Hund's coupling case, the importance of hyperfine structure, etc.) and necessitates knowledge on fundamental spectroscopic data, such as the transition probabilities and the Hönl-London (HL) factors. Regarding C<sub>2</sub>, CN, N<sub>2</sub>, and N<sub>2</sub><sup>+</sup> molecules, numerous bibliographic sources are available in the literature [4,5]. Unfortunately, the use of these sources in our simulation code led to notable discrepancies when comparing our calculated spectra with that of well-known software (e.g., Specair, Lifbase, and Spartan) and measured spectra.

This work illustrates the impact of the transition probabilities and the HL factors on the emission spectra of the C<sub>2</sub> (Swan system) and N<sub>2</sub>(second positive) molecules. This study also highlights the influence of the bibliographic sources related to these two physical quantities on the simulated

spectra, as well as those quantities' role in understanding the differences observed with software or experimental spectra. The results suggest that the choice of transition probabilities have a noteworthy effect on the rovibrational lines' intensities, while the HL factors affect the rotational structure of the spectrum and, to a lesser degree, the lines' intensities.

**Keywords:** plasmas, radiative spectra, thermal and non-thermal equilibrium, transition probabilities, Hönl-London factors.

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# Type-I ELM mitigation through lithium pellet injection in EAST with tungsten divertor

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X.C.Meng<sup>1,2</sup>, C.L. Li<sup>2</sup>, M. Huang<sup>2</sup>, Z.L. Tang<sup>2</sup>, J.S. Yuan<sup>2</sup>, D.H. Zhang<sup>2</sup>

<sup>1</sup>Institute of Energy, Hefei Comprehensive National Science Center, Anhui, Hefei, 230031, China

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<sup>4</sup>Princeton University Plasma Physics Laboratory Princeton, NJ 08543, USA

## Abstract

High confinement mode with periodic type-I edge localized modes (ELMs) plasma operation has been determined as basic operational scenario in ITER with tungsten divertor. But the periodic ELMs will create huge transit heat and particles flux on the plasma facing components, which cause serious damage and sputter great impurities into main plasmas [1].

The results of lithium pellet injection in EAST show that the type-I ELMs were successfully mitigated with higher frequency and lower amplitude ELMs. This result extends the lithium triggered ELMs operational range, which the previous experiments mostly focus on the type-II or type-III ELMs phase [2]. The ELMs frequency was increased to almost 150 Hz from the 30 Hz. And the ELMs amplitude was reduced by almost half. The results of Langmuir probe on the tungsten divertor shows that the peak heat flux reduced sharply with the ELMs stimulated by lithium pellets. And the result of EUV impurity diagnostic shows that the high-Z metal impurities obviously reduced in the plasma core during the type-I ELMs mitigation phase, especially the tungsten impurity. Further, the high-speed camera diagnostic successfully captured the lithium pellets ablation process in the plasma edge, lasting almost 1.56 msec. And this ablation process was exactly corresponding with the normal color camera monitor, which shows a clear green light emission located at the pellets ablation position.

These results are encouraging as a possible technology for mitigating type-I ELM in future long pulse and high power injection plasma discharges operation in EAST.

**Keywords:** ELM control, Lithium pellet, Plasma, EAST

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# Unravelling the limitations of ammonia synthesis by non-thermal plasmas

P. Navascués<sup>1\*</sup>, J.M. Obrero-Pérez<sup>1</sup>, J. Cotrino<sup>1,2</sup>, A.R. González-Elipe<sup>1</sup> and A. Gómez-Ramírez<sup>1,2</sup>

<sup>1</sup>Laboratory of Nanotechnology on Surfaces and Plasma. Instituto de Ciencia de Materiales de Sevilla (CSIC-US). Seville, Spain

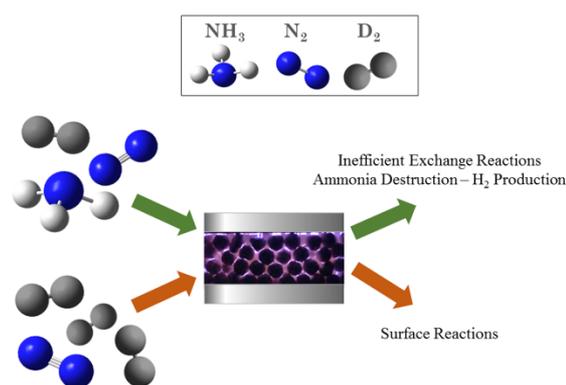
<sup>2</sup>Departamento de Física Atómica, Molecular y Nuclear. Universidad de Sevilla. Seville, Spain

## Abstract:

Ammonia synthesis by means of atmospheric pressure non-thermal plasmas is thought to be a feasible alternative to the Haber-Bosch process. Nevertheless, and although many plasma devoted research groups are now working on this topic,<sup>1-3</sup> energy efficiencies and chemical yields are still under those provided by the classical method.

In this work we analyse the ammonia synthesis process in a ferroelectric packed-bed reactor, paying special attention to the factors that hinder higher nitrogen conversions and better energy performances.<sup>4</sup> Between them, the occurrence of the reverse reaction (it is, destruction of ammonia by the plasma after being formed) and inefficient exchange reactions (ammonia can exchange H atoms with H<sub>2</sub> molecules in the plasma bulk or –OH groups at the surfaces) could play an important role. With the aim of quantifying the occurrence of those energy wasting processes, we apply an isotope labelled technique. By using different reactive gases (composed by NH<sub>3</sub>, H<sub>2</sub>, N<sub>2</sub>, D<sub>2</sub> or their mixtures) and varying their residence time in the plasma reactor, we have obtained valuable information about reaction mechanisms. Our results point to an important proportion of decomposed ammonia, that alternatively can be seen as a hydrogen production process, and a high number of H↔H inefficient exchanges. Furthermore, this methodology allows us to quantify, for the first time up to our knowledge, the relative amount of processes taking place in the plasma bulk or at the ferroelectric surface.

**Keywords:** atmospheric pressure plasmas, ammonia synthesis, packed-bed plasma reactors, hydrogen production, ferroelectric materials.



**Figure 1:** Sketch of the analyzed processes

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# Modeling an Atmospheric Pressure Plasma Jet Impinging on a Silver Nitrate Solution For Nanoparticle Synthesis

Astrid L. Raisanen<sup>1</sup>, Stephen Exarhos<sup>2</sup>, Sanjana Kerketta<sup>1</sup>, Peter J. Bruggeman<sup>2</sup> and Mark J. Kushner<sup>1</sup>

<sup>1</sup>Electrical Engr & Computer Sci. Dept., University of Michigan, Ann Arbor, MI 48109-2122, USA

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## Abstract:

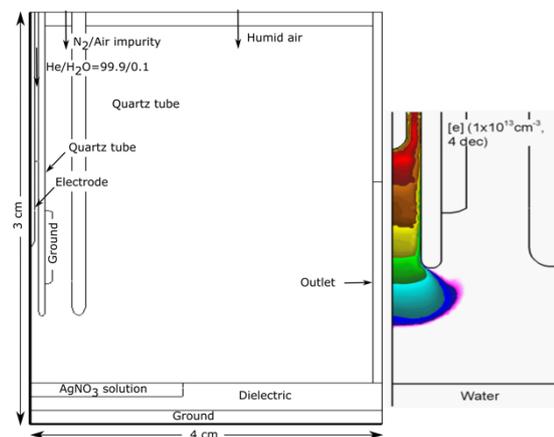
Atmospheric pressure plasmas impinging upon liquids are now being investigated for materials synthesis. In plasma-driven solution electrochemistry (PDSE), electrons, radicals and ions are produced in a gas phase plasma and solvate into an interfacing liquid solution. These species then act as initiators and sustainers of material synthesizing processes, such as nanoparticle production. To achieve selective and controllable chemical synthesis, an improved understanding of the underlying fundamental plasma processes is necessary.[1] To that end, in this work we discuss results from a computational investigation of the reduction of silver ions in a silver-nitrate solution treated by an atmospheric pressure plasma jet. These results are compared to experimental measurements.

The two-dimensional computational platform *nonPDPSIM* is used to model the plasma processes that occur when an atmospheric pressure plasma jet impinges on an aqueous solution containing silver nitrate. *nonPDPSIM* is a multi-fluid plasma hydrodynamics model that utilizes time-slicing algorithms to address disparate time scales for the transport of various species. [2] The model accounts for transport and chemical reactions of both charged and neutral species and is capable of addressing plasma activation of liquids.

The model conditions are a radio-frequency (RF) or pulsed direct current (DC) driven atmospheric pressure plasma jet sustained in helium with molecular additives flowing into humid air incident on an aqueous solution containing silver nitrate. This setup results in the reduction of silver ions, forming nanoparticles. The plasma jet is shown schematically in Fig. 1. The electron density during RF excitation in a non-plasma touching configuration is also shown. The reaction mechanism for plasma activated  $\text{Ag}^+$  reduction has significant uncertainties. To quantify those sensitivities, a parametric study was performed to quantify the relative importance of plasma parameters to achieve silver reduction. For example, what are the consequences of the incident electron and

ion fluxes on  $\text{Ag}^+$  reduction for a given molarity of the silver nitrate solution? Plasmas parameters to be discussed include RF power, DC pulsed voltage amplitude or power, gas flow rate and molecular additives to the helium jet (e.g.,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ).

**Keywords:** atmospheric pressure plasma, plasma jet, modeling, plasma-liquid interaction, electrochemistry



**Figure 1:** (Left) the computational domain for an atmospheric pressure plasma jet incident on a solution containing silver nitrate. (Right) electron density during RF excitation.

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# Kinetic investigation of electron energization in magnetron discharges: RFMS, DCMS, and HiPIMS

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## Abstract:

We demonstrate a self-consistent and complete description of electron dynamics in magnetron sputtering discharges. The electron energization in radio frequency magnetron sputtering (RFMS), direct current magnetron sputtering (DCMS), and high power impulse magnetron sputtering (HiPIMS) discharges is studied via fully kinetic 1d3v/2d3v particle-in-cell/Monte Carlo collision (PIC/MCC) simulations. The interplay between the fundamental plasma parameters is analyzed through their spatiotemporal dynamics. In RFMS discharges, the electron power absorption can be primarily decoupled into the positive Ohmic power absorption in the bulk plasma region and the negative pressure-induced power absorption near the target surface. Ohmic power absorption is the dominant electron power absorption mechanism, mostly contributed by the azimuthal electron current. The contribution of secondary electrons is negligible under typical RFMS discharge conditions. In DCMS discharges, however, secondary electrons are necessary to maintain the discharge. Scale-invariant breathing oscillations are observed in similar DC magnetron discharges and microdischarges. Breathing oscillations are suppressed at higher pressures  $p$  and enhanced at stronger magnetic fields  $B$ . As the similarity invariant  $B/p$  increases, the electron mobility approaches the ion mobility, inducing plasma instability as well as an appreciable time-averaged potential drop outside the sheath. With the onset and development of breathing oscillations, the electron energization mechanism shifts from sheath energization to Ohmic heating in the ionization region. The characteristics of breathing oscillations and the transition of electron energization mechanism are scale-invariant under similar discharge conditions due to the electron kinetic invariance. Lastly, for the simulation of HiPIMS discharges some additional physical processes need to be

considered, such as Coulomb collisions between charged species, sputtering winds, i.e. gas rarefaction due to momentum exchange between the sputtered species and the background gas, and metal ions ionized from the sputtered species, as well as secondary electron emission induced by these multiply charged metal ions. During the discharge runaway, i.e., the transition from the low-current DCMS regime to the high-current HiPIMS regime, metal ions gradually replace gas ions as the dominant, the sheath width decreases drastically with the increase in plasma density, and the electron energization transforms from sheath energization to Ohmic heating. These results are beneficial for the design, optimization, and scaling of magnetron sputtering discharges under various power sources in practical applications.

**Keywords:** magnetron sputtering, electron energization, electron heating, plasma simulation, particle-in-cell, plasma instability, similarity law, RFMS, DCMS, HiPIMS.

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# Formation of Turing patterns in strongly magnetized plasmas

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## **Abstract:**

Emergence of self-organized patterns in a variety of biological and non-biological systems can be explained through activator-inhibitor model. Here, we will show how the presence of strong magnetic field in a low-pressure electric discharge results in the formation of Turing patterns. Theoretical investigations revealed that the fluid equations for a magnetized plasma can be rearranged to take the mathematical form of an activator-inhibitor system. In this model, electrons can be considered as the activator and the ions as the inhibitor. The effect of strong magnetic field on the mobility of electrons/ions enables the ions to diffuse much faster than the electrons perpendicular to the magnetic field which initiates self-regulation in the magnetized plasma. Numerical simulations using these fluid equations were able to reproduce the various patterns observed in the experiments. Also, it will be shown that unlike an unmagnetized plasma, a non-zero transverse electric field exist in the bulk of the strongly magnetized plasma that maintains the filamentary patterns over time scales much longer than the characteristic time scales of the plasma.

**Keywords:** Magnetized Plasmas, Turing Patterns, Filamentation, Pattern Formation, Fluid Simulation of Plasma

## **SCIT Session III**

# **Coatings for Energy and Environmental Applications**

# The Mechanisms of Corrosion Protection of Metals in Corrosive Medium by Superhydrophobic Coatings

Ludmila B. Boinovich

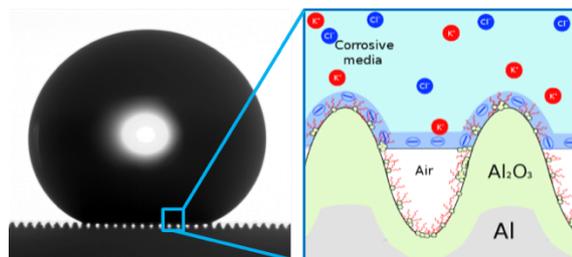
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## Abstract:

Over the last 10 years, many field and laboratory investigations conducted on the corrosion of metals protected by superhydrophobic coatings (SHCs) show the very high efficiency of protective properties of the SHCs [1,2], which are considered as very prospective materials for the automotive industry, shipbuilding, aviation, construction, and medicine. The overwhelming majority of these studies mainly relate the improved corrosion resistance of the SHCs to their water repellency. Such interpretation of the nature of the SHCs protective effect does not explain the diversity of the behavior and the stability of superhydrophobic coatings on metal substrates in corrosive liquids having different compositions, pH, temperature, etc. It is a well-known fact that in some cases the superhydrophobic coatings give excellent anti-corrosion results, while in other cases they fail to sustain the corrosion attack. However, the most recent publications revealed a more complex nature of the physico-chemical phenomena determining the protective properties of SHCs [3].

In this lecture, we will review the recent studies on corrosion protection potential of superhydrophobic coatings on the surface of various metals and alloys, with the emphasis on the methods of SHCs fabrication and conditions of functioning. Basing on the combined analysis of different types of experiments, including EIS and surface polarization, FE SEM, EDX and XRD, analysis of wetting and capillary electrokinetics, we will discuss in detail the physical insight and various aspects of complex corrosion protection mechanisms provided by SHCs. Using the numerous experimental data for different metallic systems with deposited superhydrophobic coatings we will demonstrate the contribution of the discussed corrosion protection mechanisms and highlight the areas of reliable application of such coatings for prolonged protection against corrosion.

**Keywords:** superhydrophobic surface, corrosion resistance, corrosion mechanism, laser processing, durability



**Figure 1:** Schematic illustration of main mechanisms, defining the improved corrosion resistance of metals with SHC.

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# Study and optimization of the natural instability in Si-based thin solid films for sensing and photonic applications

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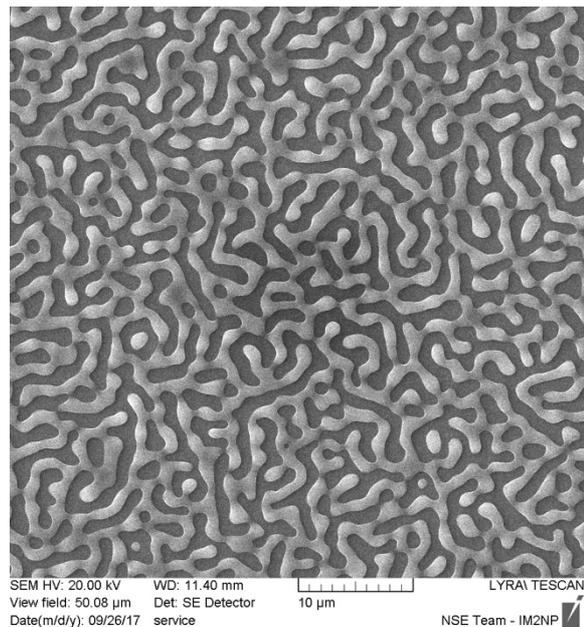
## Abstract:

The Horizon 2020 program represents a paradigm shift with respect to the past introducing a strong focus on innovation. In fact, two of the three pillars of the European program and numerous instruments are aimed to promote and develop innovation processes. Despite the resources committed by the H2020 program and various national and regional programs, the effects on society and the productive system are in many cases below expectations. An emblematic case is that of nanotechnologies, which have the potential to strongly affect vital fields such as healthcare, energy, environment and manufacturing. To unlock potential benefits at the most, it is necessary to reduce the ‘valley of death’ and enhance the track record in transforming breakthroughs into commercially valuable innovations.

Meeting these challenges involves understanding the internal (to the innovation process) and external (related to the surrounding environment) bottlenecks of the innovation cycle. In this context we will present the case of “NARCISO” FET-OPEN project. Manufacturing at the nano and micrometer scale provides access to distinct physical and chemical properties as compared with bulk counterparts. Nanometric monocrystalline islands and micrometric stable monocrystalline structure can be formed by exploiting the instability of ultra-thin solid semiconductor films when annealed at high temperature. This instability, in analogy with a liquid film beading up over time, is known as solid-state dewetting where the shape instability is driven by surface tension and mass transport. Upon heating, indeed, atoms diffuse away from the film edges to reduce the total surface energy [1, 2]. By squeezing the natural instability of the solid system down to the nanoscale, the dewetted semiconductor material

can challenge existing technological limits and help to devise Si based photonic and devices for colloids filtration with enhanced performances [3].

**Keywords:** solid state dewetting, SiGe instability, hyperuniform systems.



**Figure 1:** SEM image of SiGe solid state dewetting on SiO<sub>2</sub> substrate.

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# PECVD passivation of GaN for transistor threshold voltage control

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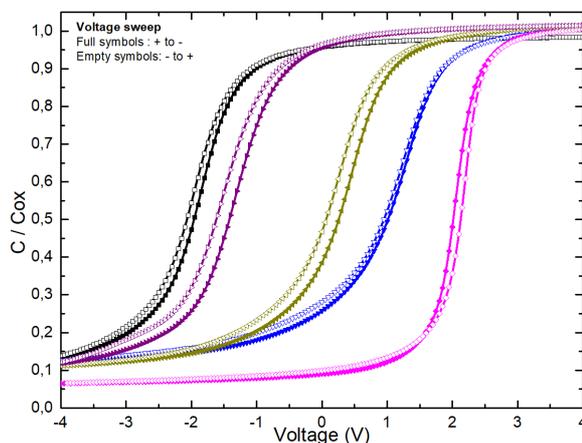
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## Abstract:

GaN and other III-N compound semiconductors are increasingly used for high-power/high-frequency electronic devices such as heterostructure field effect transistors (HFET). This is due in particular to their high electron mobility and breakdown electric field. However, current commercial technologies are only available as normally-on devices, which means the transistor gate must be polarized by an external circuit to be turned off. Several gate designs have been studied in the past in order to produce a normally-off HFET, such as fluor implantation or gate recess, but they tend to degrade performances, increase instabilities in device characteristics and complicate the fabrication process. Metal-insulator-semiconductor (MIS) gates are frequently used in these devices, in particular to reduce gate leakage. The chemical pretreatment and process conditions for the formation of the insulator layer are also of great importance to minimize defects at the interface with III-N semiconductors, which are responsible for threshold voltage instabilities and drain current collapse. We report state-of-the-art plasma-enhanced chemical vapor deposition (PECVD) of SiO<sub>x</sub> for surface passivation of unintentionally doped n-GaN, but also show the potential to control the threshold voltage of HFET devices. Several MIS capacitors were fabricated in a systematic study of the following PECVD parameters: SiH<sub>4</sub>/N<sub>2</sub>O ratio, RF power, pressure and temperature. With C-V measurements (fig. 1), we demonstrate that these parameters can be optimized in order to shift the flatband voltage of MIS capacitors towards positive values, while maintaining a high-quality interface. This voltage shift is caused by insulator charges and current work is ongoing to identify their chemical origin and location (bulk or interface). If successful, this approach could lead to a cost-effective solution for normally-off III-N HFET technologies.

**Keywords:** GaN, PECVD, passivation, MIS gate, normally-off, HFET



**Figure 1:** Example of 1MHz C-V measurements of Al/SiO<sub>x</sub>/GaN MIS capacitors with 20-30 nm SiO<sub>x</sub>. The same chemical pretreatment was used for all devices and only the parameters of PECVD vary. Note the wide flatband voltage variations for the different samples, low hysteresis and good surface potential modulation in all cases.

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# Optimized stoichiometry for CuCrO<sub>2</sub> thin films as Sustainable and semi-transparent Hole Transparent Layer in performant and recyclable organic solar cells

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## Abstract:

A promising approach to improve the performances and photochemical stability of Organic Solar Cells (OSC) in atmospheric conditions, is the replacement of chemical unstable and hygroscopic PEDOT:PSS<sup>1</sup> used as Hole Transport Layer (HTL) with p-type Transparent Conductive Oxides (TCOs'). In this work, CuCrO<sub>2</sub> thin films with various Cu/(Cu+Cr) cationic contents, synthesized by Aerosol Assisted Chemical Vapour Deposition, were optimized to find a good compromise between transparency, conductivity, band alignment, and devices performance. The resistivity, the transparency, and the energy gap are reduced increasing Cu/(Cu+Cr) ratio in the film.

The composition of the CuCrO<sub>2</sub> film used as HTL was correlated to the performances of the solar cells. The strong chemical stability and mechanical resistance of the CuCrO<sub>2</sub> HTL allowed, through a simple chemical method, the recycling of the functionalized substrate composed of glass/ITO/CuCrO<sub>2</sub>. This peculiar feature permitted the assembly of new solar cells over the same functionalized substrates, allowing the optimization of the Active Layer (AL). The greatest Power Conversion Efficiency (PCE) was achieved for Cu/(Cu+Cr) of 77% as the best trade-off between HTL's resistivity, energy gap, and morphology, resulting in a PCE of 3.75% and a Fill Factor of 32% after the AL optimization. As highlighted results, we successfully substitute unstable PEDOT:PSS, traditionally used as HTL in organic solar cells, with CuCrO<sub>2</sub> out of stoichiometry able to enhance the performances and the stability of the devices. Moreover, we report the recyclability of the functionalized substrate which could open many promising routes in microelectronic and prototyping, reducing the required materials and processes i.e. the manufacturing costs and time. This will favor and fasten the development of performant and sustainable organic photovoltaic devices.

**Keywords:** Transparent conductive oxides, oxides based HTL, organic solar cells, sustainable photovoltaic, solar cells recycling.



**Figure 1:** Figure illustrating the successful replacement of unstable PEDOT:PSS with CuCrO<sub>2</sub> thin films out of stoichiometry. The assembled cells are electrically characterized. Then, a simple chemical approach is used to recycle the substrate/electrode/HTL structure, allowing the test of different Active Layers and the conception of new cells, finally, enhancing the performances.

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## **Plasma Tech Session III**

**Plasma diagnostics / Modelling and  
numerical simulations of plasmas and  
surfaces**

# On the relation between deposition rate and ionized flux fraction in high power impulse magnetron sputtering

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## Abstract:

The deposition rate in high power impulse magnetron sputtering (HiPIMS) is always somewhat lower than that obtained with dc magnetron sputtering (dcMS) when operating at the same average power [1], typically in the range of 30-85 % of the dcMS rates, depending on target material [2]. Back-attraction of ions of the sputtered species to the cathode target is believed to be the main reason for this, while some other mechanisms have also been suggested as well. This includes the nonlinear sputter yield effect, guiding effect of the magnetic field, the increased density of the deposited film, the effect of different ion species on the sputter yield and that the sputtered material are being transported radially outward in the vicinity of the cathode. Some approaches to increase the deposition rate are discussed. We discuss how the magnetic field strength  $|\mathbf{B}|$  and geometry (degree of balancing) influences the deposition rate and ionized flux fraction  $F_{\text{flux}}$  in dcMS and HiPIMS operation both axially [3] and radially [4]. We then relate the deposition rate and the ionized flux fraction to the internal parameters that describe ionization probability  $\alpha_i$  and the back attraction probability of the sputtered species  $\beta_i$ . A significant transport of the film forming material is found to travel radially or parallel to the target surface for both dcMS and HiPIMS operation. This radial deposition decreases with increasing axial distance from the target surface and it is always higher in dcMS than HiPIMS. There are significantly higher number of ions traveling radially in the HiPIMS discharge. We find that the relative radial flux of the film forming material is greater in dcMS compared to HiPIMS for almost all cases investigated. It is therefore concluded that the commonly reported reduction of the (axial) deposition rate in HiPIMS compared to dcMS does not seem to be linked with an increase in sideways material transport in HiPIMS. We discuss the

tradeoff between a high ionized flux fraction of the sputtered species and a high deposition rate referred to as the HiPIMS compromise [5], and other approaches to optimize the sputter process such as shortening the pulse length [6].

**Keywords:** magnetron sputtering discharge, high power impulse magnetron sputtering discharge, ionized physical vapor deposition, deposition rate, ionized flux fraction.

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# Hyper Power Impulse Magnetron glow discharge

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## Abstract:

High Power Impulse Magnetron Sputtering (HiPIMS) becomes nowadays a very versatile way to tailor the film properties and better control the growth of the thin films. However, looking back to the initial idea, HiPIMS has been proposed by the end of the last century to overcome the arc transition, but allowing the glow operation of the discharge beyond the regular abnormal regime, *i.e.*, achieving high currents with high operating voltages. The transition to arc is, in this case, simply avoided by the pulse duration control, typically 100  $\mu$ s. The average power is comparable with the direct current (dc) operation, choosing the duty cycle in the same ratio as the current density ratio in HiPIMS over dc mode, namely within a factor of 100 to 1000, leading to average peak current densities up to 10 A/cm<sup>2</sup> in respect to the target surface

In this communication, we report a new glow discharge mode obtained with a regular magnetron cathode, in pulsed mode, but with current density much higher than the upper HiPIMS limit. Moreover, the pulse duration is very long ( $\sim$ 1 ms) corresponding to a quasi-steady state. It is clearly different from both, HiPIMS and arc discharge, since the operation voltage stays well between the two typical ranges, which are beyond 500 V for HiPIMS and below 100 V for arcs. The power density approaches 0.5 MW per pulse for a 2 inch target, so we call it Hyper Power Impulse Magnetron (HyPIM) glow discharge.

The first diagnostics of HyPIM mode are presented and discussed, as well as the behaviour of the discharge in HiPIMS and the phenomena leading to arc transition. A typical image of the glow discharge in HyPIM regime is depicted in Fig. 1, taken with a high speed camera.

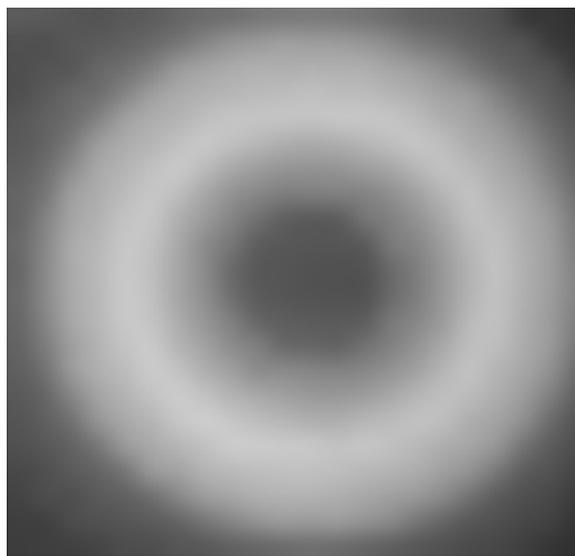
Three target materials have been successfully tested: carbon (C), molybdenum (Mo) and tungsten (W) in helium atmosphere 10-30 Pa. Two key parameters have been identified as necessary to be fulfilled for reaching HyPIM mode:

(i) the operation voltage must be externally limited and

(ii) the pre-ionization of the gas is mandatory before the pulse application.

In addition, we will introduce this glow regime on the well-known current-voltage characteristic of the discharges and will discuss on optimal (E x B) design compared with other high current configurations. We will also emphasize some possible applications of this novel discharge mode.

**Keywords:** HyPIM, ExB, glow discharge, HiPIMS, glow to arc transition



**Figure 1:** Typical HyPIM glow discharge.

# On the energy balance of an atmospheric pressure surface barrier discharge

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## Abstract:

Energy flux measurements by a passive thermal probe (PTP) were performed for a (diffuse) coplanar surface barrier discharge (DCSBD) [1] to determine the transferred energy from plasma to substrate in dependence on the distance to the electrode and the working gas (air, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>) of the discharge (Figure 1).

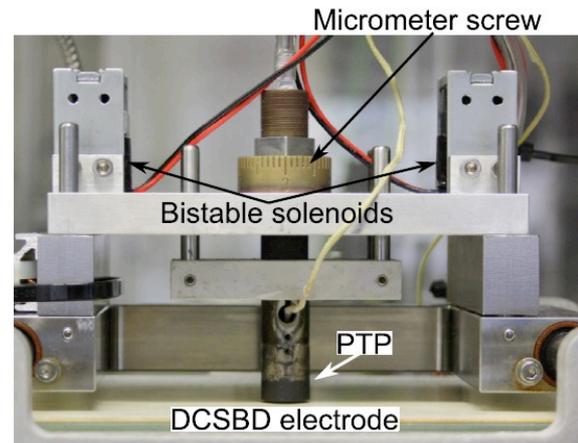
The PTP is based on the determination of the temporal change of surface temperature of the probe during a heating phase with plasma operation and a cooling phase with plasma off [2]. By knowing the heat capacity of the sensor, the difference of the time derivatives yields the deposited power to the surface. It should be noted that the PTP measures time and energy integrated values.

Overall input power and applied electrical power were measured to obtain information on the energy conversion for the plasma processes. The highest energy flux was found at ~300–400 μm above the electrode surface to be about 500 mW/cm<sup>2</sup> using air. Conversion efficiencies of the available electrical power via discharge to the power used for substrate treatment of 35–50% depending on the working gas (highest for air, lowest for CO<sub>2</sub>) were determined. Investigation on the spatial expansion of the surface discharge showed a pronounced dependence of the energy flux from the distance above the electrode. The energy flux maximum shifts to larger distances if no oxygen is present in the working gas [3,4].

In addition, measurements of the temperature gradient for the electrode oil cooling were performed to identify the power loss due to cooling. With about 50% of the applied electrical power, it turned out to be the largest loss term.

An active substrate cooling mechanism could be identified within the plasma caused by convective flows for very small distances between electrode and substrate. Variation of the working gas (argon, molecular gas) indicates also the importance of the gas and surface reactivity for the transferred energy from plasma to substrate. Molecular gases result in a remarkably higher energy flux compared to rare gas due to molecule association and chemical surface reactions.

**Keywords:** surface barrier discharge (DCSBD), energy flux measurements, passive thermal probe (PTP).



**Figure 1:** Experimental setup for the energy flux measurements. The PTP is mounted above the electrode [3]. A micrometer screw and two bistable linear solenoids are used to place the PTP in the plasma.

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# Electrical diagnostics for Dielectric Barrier Discharges: from integrated measurements to spatially resolved measurements. Benefits for plasma processes at atmospheric pressure?

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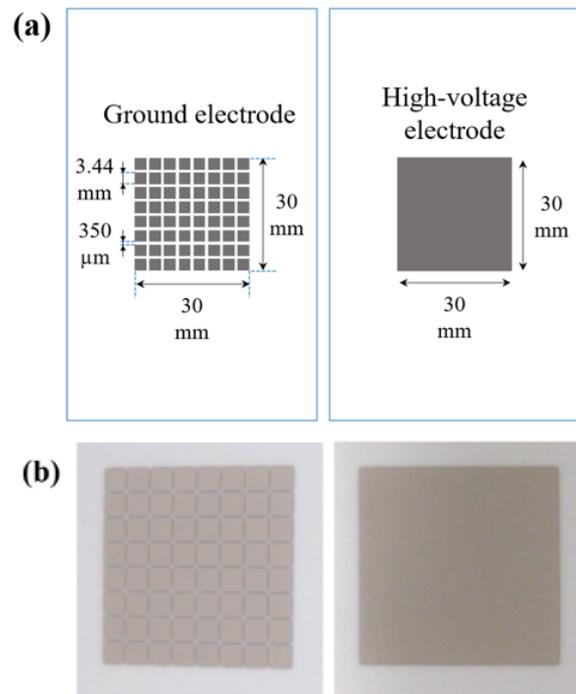
## Abstract:

Dielectric Barrier Discharges (DBDs) can be used in many processes as thin-film coating, sterilization, treatment of gases, aerodynamic flow control, and lighting devices [1]. Depending on the gas, electrical operation parameters and discharge geometry, the plasma operates in the classical filamentary mode or in a homogeneous regime [2]. Homogeneous regimes are interesting for surface modification applications as it allows to uniformly transfer the energy to the surface. Consequently, it is easier to get homogeneous and dense layer deposition with a homogeneous discharge than with a filamentary plasma [3].

Electrical measurements are a more convenient than optical measurements to characterize the discharge regime and to study the discharge behavior. However, and because of the dielectric presence, it is not possible to directly measure the electrical parameters of the discharge. Usually, the electrical parameters (gas voltage, discharge current, charge transferred within the discharge, discharge power, ...) are calculated from the measured quantities (*e.g.* total current or charge) under usage of an electrical equivalent circuit [4-5]. Among other parameters, the electrical equivalent circuit depends on the DBD geometry. The key parameter for this approach is the determination of the discharge area, which is usually considered to be equal to the electrode surface as long as the discharge is homogeneous. However, even if the plasma seems to cover the electrodes uniformly, its electrical properties (current density, breakdown voltage, duration of discharge, ...) are not exactly the same at any time and at any point of the surface. The spatial variation can be due to the gas flow circulation as observed in a homogeneous discharge ignited by Townsend breakdown in nitrogen [6].

For example, in surface treatments applications, a gas flow is usually injected from one side of the planar DBD arrangement. The residence time of the gas increases as a function of the position from the gas inlet to the gas outlet. Thus, the species densities are not the same along the gas flow because of the kinetic processes and chemical reactions in the discharge [6]. The discharge

current and the gas voltage are not uniform along the spatial DBD dimensions. Therefore, determination of discharge current and gas voltage from macroscopic parameters of the DBD is often inaccurate. In the best case, the calculated values are spatially averaged but do not allow the interpretation of localized plasma treatment.

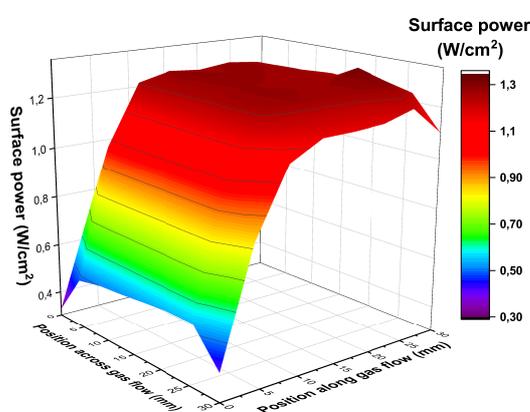


**Figure 1:** Diagram (a) and photograph (b) of the segmented electrode and the high-voltage electrode.

The spatial inhomogeneity of a diffuse DBD in nitrogen is particularly highlighted with the addition of oxidizing gases or precursors [6]. For example, in the case of a Townsend discharge in  $N_2$  with 30 ppm of NO the discharge is visually different from the gas inlet to the gas outlet; the color changes from violet to green along the gas flow [6]. Even if the discharge is a diffuse one (*i.e.* without filaments appearing on the electrical and optical measurements), its behavior changes along the gas flow direction and, therefore, the electrical characteristics are also varying in the same way.

In order to have a more accurate characterization of the discharge behavior, a measurement of the

local current density is required. To get a 2D mapping of the discharge electrical parameters, the ground electrode is prepared as a segmented electrode with 64 equally spaced square segments. The high voltage electrode still remained full. This electrode is a  $3 \times 3 \text{ cm}^2$  square, while each square of the segmented electrode has a 3.44 mm side length, a distance of  $350 \text{ }\mu\text{m}$  spaced each segments (Figure 1). A prototype, using a ground electrode divided into 64 identical squares and a data acquisition system is developed. This system can be used to study the spatial electrical behavior of a DBD (Figure 1). This set-up allows to correlate the discharge current and light emissions from different species in time and space.



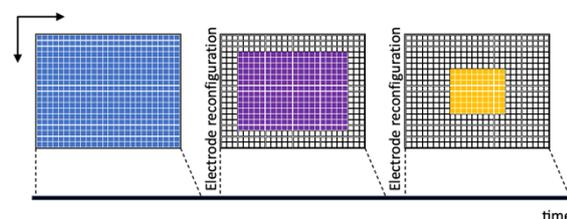
**Figure 2:** 3D mapping of surface power density from measurements with the segmented electrode in  $\text{N}_2 + 30 \text{ ppm NO}$  (gap=2 mm, 2 kHz, 17.12 kVpp, 4 sLm).

It has been successfully validated on planar DBD by the comparison with short exposure time photos taken by a camera from above the discharge cell. It has been used to study the diffuse discharge (APTD) and shows the effect of a gas flow on the local electrical behavior of the discharge. In the case of diffuse DBDs with sinusoidal voltages at frequencies from 1 to 20 kHz, the temporal and spatial resolutions are high enough to characterize the behavior of the discharge with sufficient spatial information.

This electrode arrangement and measuring systems allows a 2D mapping of the discharge electrical parameters (discharge current, power dissipated, gas voltage, etc.) of Townsend but also for Glow discharges, hybrid or patterned regimes. Concerning the plasma processes for surface coatings, this system can be used to monitor the evolution of the local discharge power which defines the local deposition rate. If we use this segmented electrode as the high voltage electrode

with adequate high-voltage switches and power supply, we could reconfigure the electrode (Figure 3) and the power transfer to the discharge. Then this system could be used to realized patterns (Figure 4).

All of this opens up new directions which will be discussed during the presentation.



**Figure 3:** Illustration of the reconfigurable electrode concept.



**Figure 4:** Illustration of a pattern coating which could be achieved using the configuration of the Figure 3.

**Keywords:** DBD, APTD, Townsend discharge, electrical measurement, local current, spatially resolved, segmented electrode.

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# Controlling atmospheric pressure non equilibrium plasmas for species conversion

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## Abstract:

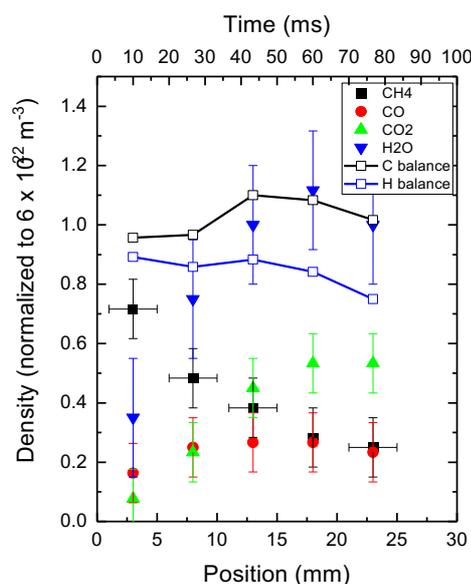
Non equilibrium atmospheric plasmas form the unique basis for a multitude of applications ranging from thin films, surface modification, plasma chemistry to plasma medicine. In all these cases atmospheric pressure plasmas exhibit an intimate coupling to the bounding surfaces that trigger surface and conversion processes. The complexity of these processes makes a detailed understanding very challenging. A prominent example is the plasma catalytic conversion of gases in atmospheric plasmas and the plasma supported electrolysis in nanosecond plasmas in liquids.

The excitation and dissociation of CO<sub>2</sub> or CH<sub>4</sub>/O<sub>2</sub> admixed to argon and helium atmospheric pressure radio frequency plasmas and DBD plasmas is analyzed. The absorbed plasma power is determined by voltage and current probe measurements and the excitation and dissociation of the molecules is analyzed by transmission mode Fourier-transform infrared spectroscopy (FTIR) and emission spectroscopy. It is shown, that the vibrational temperatures of the molecules are significantly higher in an argon compared to a helium plasma. The rotational temperatures remain in both cases close to room temperature. The plasmas allow an efficient conversion of the species, as illustrated by the position dependent data along a plasma stream in Fig. 1 for the oxidation of methane in a methane oxygen RF plasma [1].

As a second example, nanosecond plasmas in liquids are presented that are monitored with respect to the temporal variation of species densities and temperatures. The plasmas are generated by high voltages (HV) between 14 kV and 26 kV and pulse lengths of 10 ns applied to a tungsten tip with 50 μm diameter immersed in water. Ignition of the plasma causes the formation of a cavitation bubble that is monitored by shadowgraphy and compared to cavitation theory. The dissipated energy by the plasma drives the adiabatic expansion of water vapor inside the bubble from its initial super critical state to a low pressure, low temperature state at maximum bubble expansion reaching values of 10<sup>3</sup> Pa and 50 K, respectively. The ignition of those plasmas occurs via field effects at the electrode liquid interface, the plasma propagation via charge multiplication in nanovoids or

in the supercritical fluid. Such plasmas are then used to support and to regenerate the catalytic surfaces of an electrolysis cell.

**Keywords:** Plasma catalysis, plasma supported electrolysis.



**Figure 1:** Conversion of a CH<sub>4</sub>/O<sub>2</sub> mixture along a plasma stream. From [1]

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2. Nanosecond pulsed discharges in distilled water - Part II: Line emission and plasma propagation, A. von Keudell, K. Grosse, V. Schulz-von der Gathen, *Plasma Sources Science and Technology* 29, 085021 (2020)

# TD-LIF measurements and PIC modelling of Titanium sputtered atoms velocity distribution functions in Argon DC magnetron plasma

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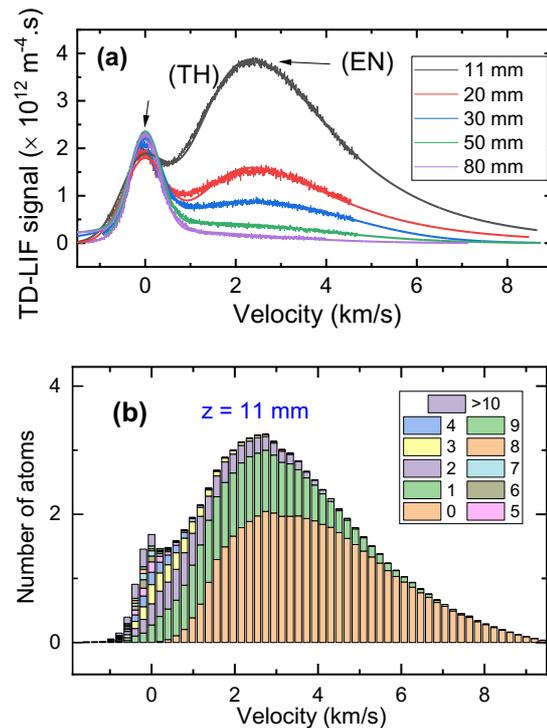
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## Abstract:

Tunable diode laser induced fluorescence (TD-LIF) was optimized to measure accurately Titanium (Ti) sputtered atoms velocity distribution functions (AVDF) in a magnetron discharge operating in direct current mode. The TD-LIF measurements have been carried out with high spatial and spectral resolutions to characterize the transport of titanium atoms. The experimental setup is described in a previous work [1]. Figure 1 (a) shows TD-LIF measurements of the Ti sputtered AVDFs. When the distance from the target increases, fully thermalized atoms (distribution centred at 0 m/s, noted TH) and less energetic atoms (peak at 2500 m/s, noted EN) are measured. The sputtered atoms leave the target following the Stepanova energy distribution (modified Thomson distribution). The fitting of the measurements shows that distribution is easily degraded by collisions with the gas towards a Gaussian function. A deep study of this phenomenon lead to determining the similarity parameter, i.e. pressure  $\times$  distance, for which this transition occurs. Simulated AVDF by particle-in cell Monte Carlo collision (PIC-MCC) model, detailed elsewhere [2], are shown in figure 1 (b). A very good over all agreement is obtained for measured and calculated AVDFs. That leads to an improved cross section for Titanium - Argon momentum transfer, based on the *ab initio* formulae of the interaction potential derived from noble gases interaction. In the presentation, the model results will be used to discuss and explain what we see experimentally: the thermalisation, the vapor cooling, the backscattering and the relaxation of EN atoms from Stepanova distribution to Gaussian one.



**Figure 1:** (a) AVDFs of Ti sputtered atoms measured by TD-LIF technique at  $p = 0.4$  Pa and  $P = 5$  W.cm<sup>-2</sup>. (b) Simulated AVDFs of Ti sputtered atoms by PIC-MCC as function of the number of collision at 0.4 Pa and  $P = 1.5$  W.cm<sup>-2</sup>.

**Keywords:** Transport of sputtered atoms, DC magnetron plasma, TD-LIF, PIC-MCC.

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# Calculation of thermophysical properties and computational modeling for higher temperature and pressure air plasma

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## Abstract:

Computational models as well as sophisticated experiments are needed to understand the complex phenomena in a plasma [1-3]. For the implementation of a computational model, the thermophysical properties of the gassystem need to be calculated for a suitable temperature and pressure range quite accurately [1,3].

In this article the thermophysical properties of the gassystem air are calculated and applied in 2D axisymmetric plasma model. The gassystem is described by its thermophysical properties for a wider temperature and pressure range. Starting with the elementary concepts in statistical thermodynamics the gassystem is in the first step described by the calculation of the plasma composition. For this a gas mixture of real air is considered. This is accompanied by the calculation of the partition functions for all species of the gassystem for the temperature and pressure range. The calculated thermodynamic properties are the mass density, the enthalpy, the internal energy, the specific heat by constant pressure and the velocity of sound.

The transport properties are calculated by solving the integro-differential equation of Boltzmann. Applying the Chapman-Enskog theory [1-2] with a slightly perturbed Maxwell Boltzmann distribution function the relevant collision integrals for the air species are obtained. Together with the number densities of the air gassystem the elementary transport coefficient: the binary diffusion, the viscosity, the thermal conductivity and the electrical conductivity are calculated over the temperature and pressure range.

The fully calculation of the thermophysical properties covers also the radiative properties of the air gassystem. Therefore, the calculation of absorption coefficient and subsequently the net emission coefficient is developed. The results of the calculation over the selected temperature and pressure range are also presented and discussed. In the computational model the plasma is described by the MHD equations as a fluid. The differential equations are derived and the thermophysical properties are applied.

This article is organized as follows. Section I gives brief introduction on the theoretical background and basic methods to calculate the thermophysical properties of a gassystem forming a plasma. Section II starts with the concepts of statistical thermodynamics and gives the basic input data for the calculation, that is the plasma composition with the chemical constituents and the partition functions of the gassystem. In Section III the result of the thermophysical is then presented. In Section IV the elementary equations for the computational model using the thermophysical properties are shown. This article is then concluded with Section V.

**Keywords:** thermophysical properties, air thermal plasma, transport properties, thermodynamic properties, radiative properties, chemical equilibrium, thermal equilibrium, computational plasma model.

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# Investigation of multi-periodic self-pulsed plasma in a AC Helium Atmospheric Pressure Plasma Jet

Hang Yang and Antoine Rousseau

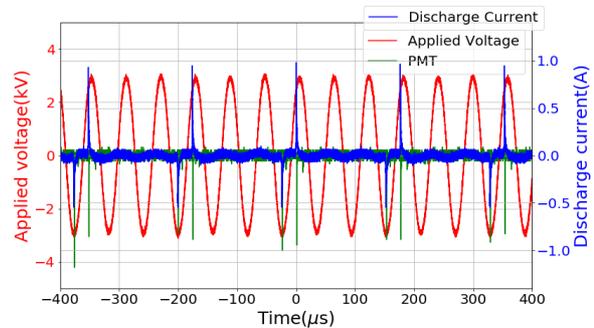
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## Abstract:

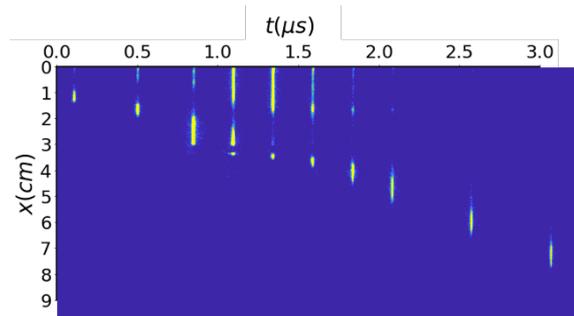
Numerous works have been dedicated to the Helium Atmospheric Pressure Plasma Jet (APPJ) in pulsed mode where an ionization wave, often called plasma bullet, travels over long distances. Contrary to pulsed discharge AC low frequency voltage are known to produce randomly ignited ionization waves<sup>1</sup>; only few works have reported the propagation of bullets showing a periodic or multi-periodic stability<sup>2</sup>. For instance, Ning et al. observed periodic short plasma bullet in a He-APPJ using AC voltage<sup>3</sup>. In this report, multi-periodic plasma bullets are observed with the periodicity of 2 to 3 periods and can propagate over 13cm. Depending upon voltage, gap distance and frequency, some remarkable self-pulsed behavior is observed: bullet ignition is “self-triggered” within a time delay less than 100 ns; The bullets are also very reproducible with the same velocity and distance per shot. The plasma jet is generated by a 15 to 18kHz, 0 to 15kV sinusoidal power supply in a 15cm long glass capillary and the focus is made on the propagation of the ionization front (plasma bullet). A grounded ring electrode, is located on the outer surface of the capillary, at a gap distance of 25 to 40mm downstream the high voltage electrode.

An example of discharge current waveform of this kind of multi-periodic plasma is shown in figure 1. Each 3 cycle, a negative bullet is ignited, followed by a positive bullet, which propagates over 11cm. Figure 2 shows the fast imaging of the positive long bullet, and 1 $\mu$ s in figure 2 corresponds to the positive discharge current in figure 1. The properties of multi-periodic plasma bullets with different period are investigated with different diagnostics, including fast imaging and spectroscopy. Such self-triggered bullets travel at a velocity of 25 km/s.

**Keywords:** plasma bullets, periodic, self-pulsed



**Figure 1:** The discharge current, and light signal measured by photon multiplier tube(PMT) plotted with the applied voltage. The applied voltage amplitude is 3.1kV. The plasma bullet is ignited every 3 AC cycles.



**Figure 2** Fast imaging of the plasma bullet's ignition and early stage of propagation corresponding to *Error! Reference source not found.* The exposure time for each photo is 200ns.

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# Optical emission spectroscopy as a diagnostic tool for electron temperature and density measurements in atmospheric pressure liquid plasma reactor

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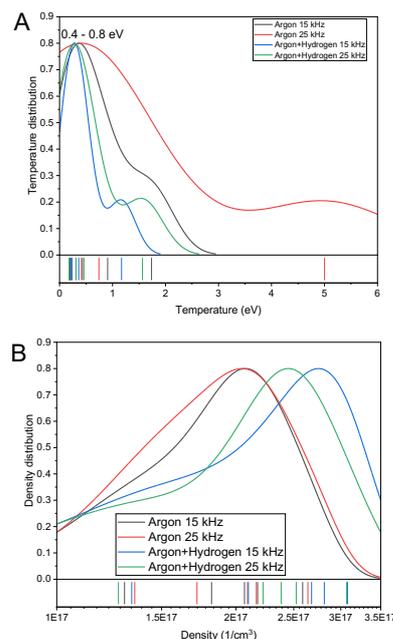
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## Abstract:

Atmospheric pressure plasma technologies can be used to extract metal ions from aqueous effluents. In certain conditions and for a whole range of precursors, such plasma treatment can convert the metal ions into nanoparticles (NPs) that can be later collected by either filtration or centrifugation. Due to their level of purity and absence of surfactants, these particles can be advantageously introduced in catalytic and biomedical applications<sup>1, 2</sup>. Whereas parameters such as precursor concentration, temperature, gas flow and gas chemistries have been thoroughly investigated, the impact of plasma characteristics on the conversion of metal ions into NPs have not been comprehensively elucidated. In this work, a bench-top atmospheric pressure plasma technology (dielectric barrier discharge configuration) was characterised at different conditions (carrier gas, excitation frequency, voltage amplitude, gas flow) with optical emission spectroscopy (OES): argon emission lines, OH radicals and second positive system (SPS) of N<sub>2</sub>. Electron temperature and density were extracted from these measurements, as well as the discharge power was assessed, all performed in conditions allowing an optimal conversion of metal ions and molecules into NPs.

In the presented plasma parameters (15 and 25 kHz frequencies, argon and argon + H<sub>2</sub> as carrier gases), relatively low, but confirmed by literature, electron temperatures (T<sub>e</sub>) were found (0.4-0.8 eV). Upon addition of H<sub>2</sub> to argon, the average T<sub>e</sub> decreased by half; however, much narrower temperature distributions were found, suggesting a more stable discharge mode. Addition of 5% H<sub>2</sub> into argon also shifted the distribution to higher electron densities (D<sub>e</sub>). A complete analysis of the reactive oxygen and nitrogen species was also performed, which confirmed the generation of high concentrations of OH radicals. These results are consistent with the strongest nucleation of metal NPs observed in such conditions, as reactive oxygen species and H<sub>2</sub>O<sub>2</sub> are directly associated with the mechanism of NP nucleation. These studies allowed to identify the optimal frequency for plasma operation guaranteeing the most efficient and rapid nucleation of NPs (25 kHz at 15 kV<sub>p-p</sub> voltage amplitude). Overall, these studies unveiled the impact of plasma on the

optimal conditions of metal NP nucleation in plasma-treated aqueous effluents.



**Figure 1:** OES characterization of argon and argon + 5% hydrogen plasmas at 15 and 25 kHz excitation frequencies: Above: T<sub>e</sub>; Below: D<sub>e</sub>.

**Keywords:** atmospheric pressure plasma, optical emission spectroscopy, electron temperature (T<sub>e</sub>), electron density (D<sub>e</sub>), plasma characterization, dielectric barrier discharge.

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# Optical emission spectroscopy and actinometry in SF<sub>6</sub>/Ar RF discharges for PCE

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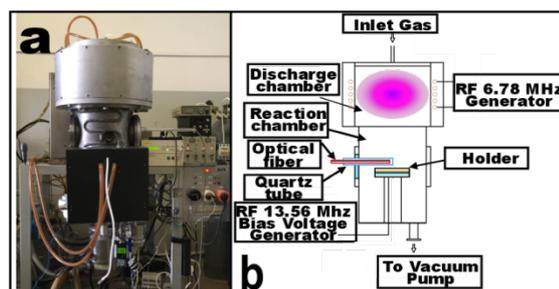
<sup>2</sup> Higher School of Physics and Materials Engineering, Peter the Great St. Petersburg Polytechnic University, Saint Petersburg, Russian Federation

<sup>3</sup> Southern-Urals Federal Research Center of Mineralogy and Geoecology, Institute of Mineralogy, Ural Branch, Russian Academy of Sciences, Miass, Russian Federation

## Abstract:

In this paper, an investigation of the optical-emission spectra (OES) of SF<sub>6</sub>/O<sub>2</sub> inductively-coupled plasma (ICP) is presented. The spectra were obtained using a HR4000 spectrometer by Ocean Insight which provide registration of an optical signal within wavelength range of 200 – 1120 nm with ~0.02 nm resolution. The optical signal from plasma discharge was transmitted to the entrance slit of spectrometer via a fiber optic patch cable (Figure 1). The influence of operational parameters of the plasma chemical etching (PCE) process on fluorine radicals concentration in plasma was studied using optical emission actinometry technique. For instance it has been shown that reducing the pressure during PCE process from 1.65 Pa to 0.65 Pa results in increased (more than 1.5 times) concentration of atomic fluorine, while increase of plasma power from 500 W to 700 W provide only 1.27 times higher concentration of the fluorine atoms. The influence of operational parameters on the optical signal intensity for 6 gas ratios of SF<sub>6</sub>/Ar was also investigated viz. SF<sub>6</sub>(1.5 sccm)/Ar(9.2 sccm), SF<sub>6</sub>(7.8 sccm)/Ar(10.8 sccm), SF<sub>6</sub>(4.7 sccm)/Ar(6.0 sccm), SF<sub>6</sub>(7.0 sccm)/Ar(4.9 sccm), SF<sub>6</sub>(11.7 sccm)/Ar(5.4 sccm), SF<sub>6</sub>(9.4 sccm)/Ar(3.3 sccm).

**Keywords:** plasma etching, ICP, OES, plasma diagnostics, optical emission actinometry.



**Figure 1:** a) general view of the PCE system, b) schematic drawing of the processing and plasma chambers

## Acknowledgments

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## **Plasma Tech Session III**

**Plasma diagnostics / Modelling and  
numerical simulations of plasmas and  
surfaces**

# Cold atmospheric pressure plasma for wound healing: state-of-the-art and perspectives

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## Abstract:

Plasma medicine means the direct application of physical plasma on or in the human body for therapeutic purposes. For a direct application on living tissue, cold atmospheric pressure plasma (CAP) is used, i.e. plasma generated in atmospheric air environment causing temperatures lower than 40°C at the target site. During recent years, mainly two basic concepts of CAP devices were tested and partially applied for medical purposes: dielectric barrier discharges (DBD) and plasma jets [1]. Because CAP is dominated by nitrogen and oxygen gas chemistry, biological plasma effects that are potentially useful for medical applications are mainly based on reactive (redox-active) oxygen and nitrogen species (ROS, RNS) [2]. From the beginning, main focus in plasma medicine is in dermatology and notably wound healing, based on both the very effective inactivation of a broad spectrum of microorganisms by CAP and its ability to stimulate tissue regeneration. A huge number of in vitro studies based on cultivated cells and tissue as well as animal studies could give detailed insight into molecular-biological mechanisms of plasma-based stimulation of tissue regeneration [3,4]. Based on comprehensive physical and biological research as well as advanced technical development, a few CAP sources are CE-certified as medical devices now opening up the possibility of broad clinical use of CAP in wound healing and dermatology [5,6]. In a recent search, 17 clinical trials or case reports could be evaluated related to 7 different CAP devices, 4 of them are approved as medical devices yet. The studies and reports include in total more than 450 patients or volunteers, respectively, with both acute and chronic wounds in experimental as well as clinical settings. Together with a very satisfactory feedback from a growing number of clinical applications, – that is not yet well documented unfortunately, – we can state that CAP is much more than a “physical disinfectant”. Its exclusive and unique feature is to directly stimulate tissue regeneration processes at the cellular level making it a useful tool to supplement clinical therapy. Based on this

knowledge, there is nothing to prevent scientifically founded clinical application of CAP. Currently in Germany a consensus-based clinical guideline on “Rational therapeutic application of cold physical plasma” [7] is in preparation to foster the clinical use of CAP and to allow a regular reimbursement of such therapies by health insurance. In November 2020, the official consensus building commission has already reached the level of unanimity: Cold physical plasma is recommended for the treatment of chronic wounds.

**Keywords:** plasma medicine, cold atmospheric-pressure plasma, medical plasma devices, redox biology, wound healing

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# Plasma in cancer therapy

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## **Abstract:**

The chemical factors such as reactive oxygen and nitrogen species (RONS) generated by cold atmospheric plasma (CAP) have been regarded as the main factors to cause cellular changes and cell death. These factors work mainly through apoptosis pathway during the CAP treatment *in vitro* and *in vivo*. Utilising new treatment approach that eliminate RONS, we observed the strong killing effect on melanoma and glioblastoma cells by the physical mechanisms. Such CAP treatment causes a novel cell death on the cancer cells.

This new model of cell death is characterized by the leaking of bulk water from distinct points on the cellular membrane with the subsequent shrinkage of the cytoplasm. This discovery builds a foundation to use the CAP as an anti-cancer tool independent of the reactive species. Such a new observation may also have wide applications in other branches of medicine.

# Effectiveness of plasma activated water on the inactivation of *Listeria monocytogenes* biofilms

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## Abstract:

The use of water activated by exposure to non-thermal atmospheric-pressure plasma (known as Plasma Activated Water, PAW) in decontamination of food products and food processing environments has gained interest in the last years, due to its advantages such as storage capacity, offsite generation, possibility for self-sanitation and reactivation, and sustainable production (Zhao et al., 2020). Although several studies have demonstrated the efficacy of PAW in the inactivation of microorganisms in planktonic state, there is scarce information on its effectiveness against sessile cells.

The aim of the present study was to evaluate the influence of PAW storage conditions (4 °C / 24 h and -80 °C / 6 months; in order to resemble potential industrial scenarios) on the pH and NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and H<sub>2</sub>O<sub>2</sub>-content, as well as on the inactivation efficacy (logarithmic cycles) of *L. monocytogenes* biofilms on stainless steel and polystyrene surfaces, two relevant food-contact materials in the food industry. Additionally, the antimicrobial efficacy was compared to that obtained with conventional disinfectants (0.5% v/v sodium hypochlorite and peracetic acid).

The antimicrobial effectiveness of PAW stored at 4 °C for 24 h was assessed on biofilms of a cocktail of three *L. monocytogenes* strains (CECT911 and two isolates from a meat processing plant). After a 15 min treatment, a reduction of the recovered CFU/cm<sup>2</sup> of 1.8 and 1.2 logarithmic units was observed on stainless steel and polystyrene, respectively (Table 1). However, an identical treatment with PAW stored at -80 °C for 6 months against biofilms grown on stainless steel resulted in the inactivation of only 0.9 logarithmic units. The loss of antimicrobial effectiveness could be partially related to the observed % reduction in the NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub> levels (Table 2), more pronounced in NO<sub>2</sub><sup>-</sup> (76 %) than in NO<sub>3</sub><sup>-</sup> (14 %). On the other hand, results showed that sessile cells of *L. monocytogenes* grown on stainless steel were more sensitive to both sodium hypochlorite and peracetic acid after a 15 min-

treatment, where reductions of bacterial counts > 4.3 logarithmic cycles were achieved. An increase in PAW exposure time led to higher inactivation efficacy for the pathogenic microorganism on both surface materials. Thus, a 60 min-PAW treatment was able to reduce the bacterial population in > 4.6 and 3.9 logarithmic units on polystyrene and stainless steel, respectively. In conclusion, the potential of PAW as an effective and safer alternative to conventional chemical disinfectants used in the food industry has been demonstrated in the present study.

**Keywords:** Plasma Activated Water (PAW), *Listeria monocytogenes*, biofilm inactivation

**Table 1.** Inactivation (logarithmic cycles) of a cocktail biofilm of *L. monocytogenes*.

Surface		Exposure time (min)		
		15	30	60
Polystyrene	PAW stored at 4 °C (24 h)	1.9±0.1	4.5±0.4	> 4.6
	PAW stored at -80 °C (6 mo)	0.9±0.2	-	-
Stainless steel	PAW stored at 4 °C (24 h)	1.8±0.2	> 3.9	> 3.9
	PAW stored at -80 °C (6 mo)	0.9±0.2	-	-
	Sodium hypochlorite 0.5% v/v	> 4.3	-	-
	Peracetic acid 0.5% v/v	> 4.3	-	-

**Table 2.** PAW composition (mg/L) and pH.

	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>	pH
PAW stored at 4 °C (24 h)	32.4±5.6	462.3±1.2	8.8±0.4	2.3
PAW stored at -80 °C (6 mo)	7.7±0.3	399.6±7.2	3.3±0.7	2.2

## References:

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# Study of antimicrobial and antiviral properties of silver-doped hydrogenated amorphous carbon coatings produced by hybrid PVD/PECVD process

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## Abstract:

The surfaces are transmission vectors of pathogens such as bacteria and viruses. By indirect contact mode between our hands and fomites, these microbes spread in our environment and contaminate us. That is all the more true in the hospitals where the immunosuppressed patients are most likely to contract infections. These latter are responsible for a significant part of morbidity and mortality worldwide, not only but also, a financial burden on our society.

The emergence of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) and the exponential growth of COVID-19 (Coronavirus disease 2019) pandemic have created a global health crisis. SARS-CoV-2 is stressing every country it touches and has the potential to create devastating social, economic and political crises. Thus, every effort made to block viral transmission chains will participate to pandemic mitigation following World Health Organisation's recommendations. In addition to spreads through droplets, it was also demonstrated that most of the touchable surfaces in hospital handling COVID-19 were heavily contaminated [1].

In this work, we evaluate the possibility to produce antimicrobial and antiviral coating to be applied on any surfaces. Amorphous hydrogenated carbon matrix doped with silver (a-C:H:Ag) were produced by a hybrid low pressure PVD/PECVD process and deposited on stainless steel substrates. The colony-forming unit (CFU), live/dead bacterial viability and modified Kirby-Bauer diffusion assays were used to assess the toxicity of this coating against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacteria. The antiviral properties were evaluated by infectivity assays, Tissue Culture Infectious Dose 50% - (TCID<sub>50</sub>) calculated by Reed-Muench Method, and by quantitative reverse transcription PCR, RT-qPCR. We used a

Porcin Respiratory Coronavirus (PRCV), a virus of the *Coronaviridae* family that shares the same common features with SARS-Cov-2.

The antimicrobial and anti-viral properties of the coatings assessed and compared with various level of Ag doping and with Cu or glass surfaces (controls). The coatings main features were characterized by X-Ray Photoelectron Spectrometry (XPS) and Scanning Electron Microscopy (SEM). The results obtained during this work shows very promising antibacterial and antiviral activities.

**Keywords:** antimicrobial coating, antiviral coatings, a-C:H, silver incorporation, *S. aureus*, *E. coli*, virus, COVID-19

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# Low temperature air plasma effects on germination of two Brassicaceae seeds, *Arabidopsis thaliana* and *Camelina sativa*

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## Abstract:

The seeds treatment using low temperature atmospheric pressure plasma is nowadays known as an interesting technology to increase the speed and/or rate of seed germination. The *Arabidopsis thaliana* seeds were previously (ref 1 and 2) investigated to try to better understand the plasma effects since it is a powerful model in plant biology. Nevertheless, due to its small submillimetric size, certain experiments are difficult to be carried out, in particular the direct observation of the change of the seed surface wettability. Indeed, under direct plasma treatment, it is essential to analyse the changes appearing on the surface of the treated seeds, in order to contribute to the understanding of the mechanisms involved in responses to the plasmas.

To do this, seeds of *Camelina sativa* were selected, on the one hand because the two considered seeds are very close phylogenetically since they both belong to Brassicaceae family. On the other hand, the morphology of the seed is very similar with a size four times larger. Finally, *Camelina* is a species of agronomic interest by itself used for its oil. This communication focuses on the effects induced by cold air DBD plasma treatment at atmospheric pressure on germination but also on the changes induced at the surface. Comparisons of the two plasma treated seeds will be shown during the conference more particularly on SEM pictures and membrane test permeability while the wettability test are done only on *Camelina sativa*.

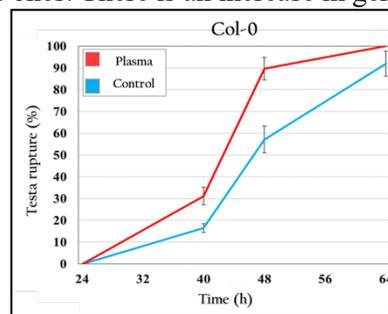
Figure 1 depicts an increase in the seed germination rate of *A. thaliana* after plasma treatment. The plasma treatment having a dose dependent effect, the germination of *Camelina* could also be affected by this treatment.

Figure 2 shows a change in the contact angle between a *Camelina* seed and a drop of water. These results show that the air plasma treatment seems to affect the surface making it as expected more hydrophilic.

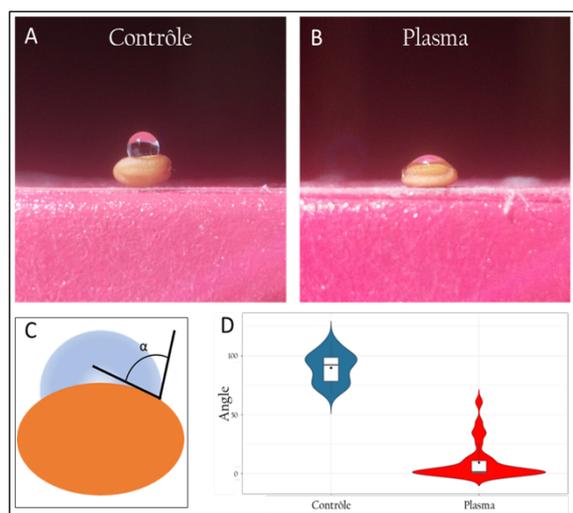
**Keywords:** Cold plasma, Germination, *Arabidopsis thaliana*, *Camelina sativa*, Seeds, Reactive species, Plasma-agriculture

**Figure 1:** Augmentation of the percentage of testa rupture after DBD air plasma treatment of 15 min on *A. thaliana* seeds. The blue curve represents the control seeds and the red, the plasma

treated ones. There is an increase in germination



rate and speed versus time.



**Figure 2:** Reduction of the contact angle after DBD air plasma treatment of *C. sativa* seeds.

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2. Bafoil M., Jemmat A., Martinez Y., Merbahi N., Eichwald O., Dunand C., Yousfi M. (2018) Effects of low temperature plasmas and plasma activated waters on *Arabidopsis thaliana* germination and growth. *PLoS One*.

# Application of Dielectric Barrier Discharge (DBD) atmospheric pressure plasma for pretreatment of medical textiles

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## Abstract:

Conventional pretreatment by wet chemistry and/or low-pressure plasma have several drawbacks [1]. Atmospheric plasma is an alternative and cost-competitive method to low-pressure plasma and wet chemical pretreatments, allowing continuous and uniform processing of fibers, substrates and films surfaces, improving its functionalization performance [2]. This technology has been studied in the field of the R&D project - PLASMAMED. The main objective of this project is to produce a new generation of coatings containing nanoparticles (NPs) and enzybiotics, with controllable antibacterial activity, on medical textiles, with special emphasis in antimicrobial dressing for pressure injury and hernia meshes. To achieve this goal, a dielectric barrier discharge (DBD) atmospheric pressure plasma was used as a pretreatment sustainable alternative.

In this sense, medical-grade 100% polyester (PES) fabrics were pretreated by atmospheric plasma technology, where various processing conditions were tested. Different treatment speeds and discharges powers have been considered, as well as the application of various gases (such as helium, oxygen and nitrogen) and a corona treatment (air), with a carrier gas (argon). The characterization of these pretreated textiles was carried out by contact angle (CA), through the sessile drop technique, with 3  $\mu$ L water droplets on the surface of the textile. In general, contact angles exhibit a significant decrease (between 40° and 60° for all studied gases), when compared with the standard values for substrate without treatment (around 120°). Therefore, plasma pretreatment significantly improved the hydrophilicity of these fabrics (Figure 1), which reveals to be an advantage for the further functionalization steps.

**Keywords:** textile pretreatment, atmospheric plasma, hydrophilicity, nanotechnology, medical textiles.



**Figure 1:** Contact angle results. Effect of plasma pretreatment on the hydrophilicity of medical-grade 100% PES fabric: before (on the left) and after plasma pretreatment with oxygen (on the right).

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# Posters Session

# Hydrogenated amorphous carbon (a-C:H) thin films deposited by low-pressure plasma: linking mechanical and fracture behavior to deposition conditions

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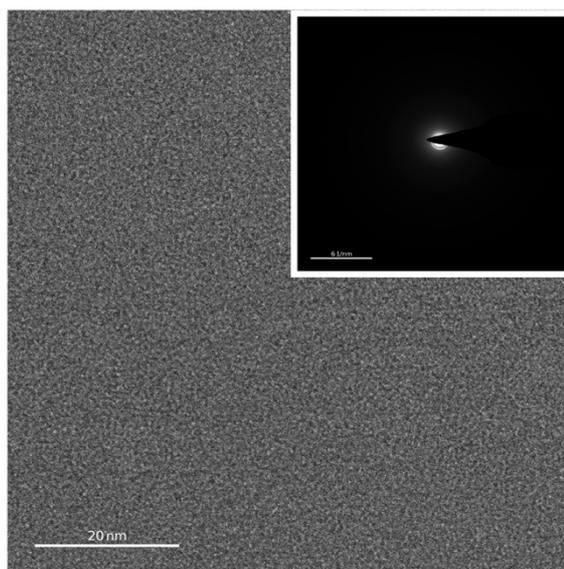
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## Abstract:

Carbon-based coatings have drawn attention in the last decades because of their eye-catching properties. The commercial interest of amorphous carbon coatings is significant, as they are used in a large variety of applications as protective tribological coating, radiation protection, electron field emitters, and biomedicine<sup>1,2</sup>. Hydrogenated amorphous carbon films (a-C:H) belong to the carbon-based material category with different carbon bonding configurations (mainly  $sp^2$  and  $sp^3$ ) and usually containing a hydrogen amount between 20–50%. a-C:H thin films are mostly used as a protective coating against corrosion and abrasion<sup>3,4</sup>. These films can be deposited by magnetron sputtering, and their properties can be adjusted by altering the deposition conditions. For instance, for low negative bias voltage (<40 V) the films are very soft, have a low residual stress, and a high concentration of hydrogen (40–60 at. %) while increasing bias voltage leads to harder films with higher compressive residual stress (1-2 GPa) and lower hydrogen concentration<sup>1,5</sup>. In the present work, the mechanical and fracture behavior of thin amorphous carbon films (Fig. 1) related to deposition conditions were quantitatively characterized by SEM in-situ tensile tests and nanoindentation. The results show that the denser films exhibit a higher fracture toughness and fracture stress and a lower crack density. Overall, better mechanical and morphological properties were observed in high bias and low sputtering pressure.

**Keywords:** hydrogenated amorphous carbon, Magnetron sputtering, Tensile testing, Fracture.



**Figure 1:** TEM image of a-C:H film obtained by plasma-enhanced vapor deposition.

## References:

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# Discussion on Dimond-like coatings by HIPIMS

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## Abstract:

Diamond-like carbon (DLC) coatings are a multifunctional materials which exhibits excellent mechanical, electrical and optical properties making it suitable for wide range applications from tribological, biomedical to optical fields. Because of its wide range of application in various fields, over last two decades, the industry and scientists were focusing on diamond-like carbon (DLC) coating improvements. Recent trials on diamond-like carbon show high demand on high transparency with low friction and wear rate DLC coatings for protection of electrical, optical and decorative components.

Essential properties of DLC thin films are determined by the bonding configuration - sp<sup>3</sup>/sp<sup>2</sup> fraction of its carbon atoms. In order to prepare DLC thin films for desired applications, it is essential to control and estimate the sp<sup>3</sup>/sp<sup>2</sup> fraction precisely. The bonding configuration can be controlled with the ionization energy of the sputtered carbon atoms.

Moreover, other process variables (e.g., bias voltage, etching, current, precursor gas, time, and substrate temperature), also affect the tribological characteristics of DLC coatings as surface roughness, hydrogen incorporation or coating thickness.

In this research utilization of High Power Impulse Magnetron Sputtering (HIPIMS) for control of the DLC thin films parameters is instantiated. First the influence of HIPIMS (peak current, voltage, power, pulse time and frequency) and process (pressure, gas flow) parameters are investigated. Next effect of incorporation of hydro-carbon gas during deposition process is studied.

Following, DLC film properties were investigated with the Raman Spectroscopy. The ID/IG carbon peak ratio is found in the range of

0.2-1.49. However, certain samples don't show characteristic carbon peak in range of 800-2200 cm<sup>-1</sup>. Microscopic analysis reveals that most of coatings has non homogeneous coating distribution along the sample, which was confirmed by the Raman Spectroscopy. Optical parameters changes with an increase of deposition energy. For low ionization (low power or current) samples have low optical transmittivity in the visible spectrum. With increasing ionization the transmittivity increase, however for high ionization it starts to decrease. This behavior is consistent with the sp<sup>3</sup> content depending on energy per C ion of 100 eV.

# Structuration of titanium surfaces using He ions

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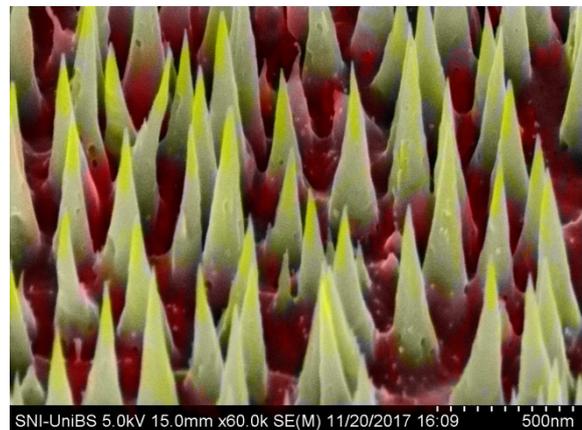
## Abstract:

Firstly discovered on Cicada wings, the surface patterning with spikes shows interesting antibacterial properties. By reproducing a similar structure on titanium, preliminary work has showed the possibility of developing antibacterial properties [1]. Within the Nano-Argovia grant A15.11, we aim at developing dental implants with such antibacterial properties using helium ions to produce spikes on a titanium surface.

In this work, we used a Kaufmann high flux ion gun source (eH1000) and a target electrode with 15 mm disc diameter samples to study the impact of the source parameters (eg., discharge voltage, emission current) on the ion flux and on the mean ion energy. The former was determined by measuring the ion current using home-made Faraday cups, whereas the latter was quantified with a Retarding Field Analyser (Semion single sensor by Impedans). We also studied the effect of the temperature using a thermocouple attached on the electrode's surface. Throughout the experiments, the He ion flux was constant and equal to  $1.03 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}$ , corresponding to a fluence of  $2.04 \times 10^{24} \text{ m}^{-2}$  (time of experiment: 330 min).

We produced samples with different mean ion energies (70 to 130 eV) and temperatures (300 to 380°C) and we characterized them using scanning electron microscopy (SEM). The results evidence the influence of the ion mean energy and the surface temperature on the peak density and its height variability.

**Keywords:** surface structuration, titanium, He ions, high flux ion gun, Faraday cups, Retarding field analyser, ion mean energy, ion flux, Scanning electron microscopy



**Figure 1:** SEM micrograph of titanium surface after exposure to He ions forming spikes of about 600 nm height.

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# Anodizing of AlSi alloys in sulfuric medium

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## Abstract:

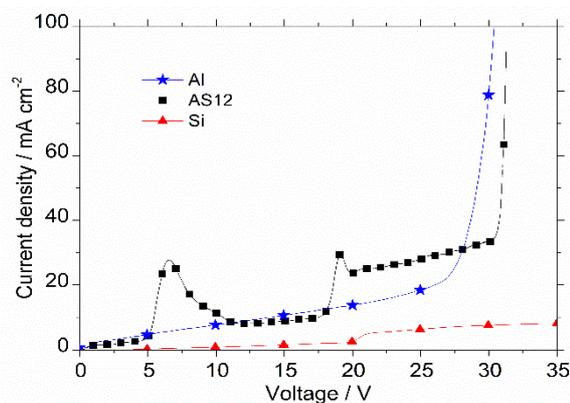
Thanks to very good mechanical strength and excellent coulability, AlSi alloys cover a very wide range of industrial and domestic applications. In order to protect aluminum alloys, surface treatment by anodizing in diluted acidic media is largely used.

The aim of the present work is to investigate the growth mechanisms and the properties of oxide layers formed on AlSi alloys (13% m Si) in sulfuric acid over a wide range of anodic potentials. For this, a fundamental in situ electrochemical study of the anodizing of AlSi alloys was carried out up to 35V in comparison with pure aluminum and pure silicon, in order to get a deep understanding of the different electrochemical processes successively involved in the oxidation. Results show that the passivation range can be divided into two different steps, likely related to two different steps of silicon anodizing. As for pure aluminum and commonly studied alloys, the passivation range is limited by a current wall corresponding to a sudden high conductivity of the interface. This disruption potential decreases with the concentration of the sulfuric acid in the electrolytic solution.

The morphological aspect of the anodized layer was observed by SEM. According to the measured thicknesses, the growth rate of the anodic layer is reduced in presence of silicon and large silicon particles are embedded in the final coating. The internal barrier layer properties were estimated by electrochemical impedance spectroscopy performed ex situ in a non-corrosive K<sub>2</sub>SO<sub>4</sub> medium. They are modified by the incorporation of silicon as well.

From the corrosion point of view, the performances were evaluated by electrochemical impedance spectroscopy in NaCl 0.1M. Only judiciously chosen anodizing parameters induce improvement of the AlSi alloy corrosion behavior, combining high dielectric properties of internal the barrier layer and resistance of the porous surmounting layer..

**Keywords:** sulphuric anodization, AlSi alloy, corrosion, electrochemical study, oxide layer



**Figure 1:** Figure illustrating the fundamental question that we are tempting to solve experimentally: what is the effect of silicon in the electrochemical behavior of AS12 in sulfuric medium

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# Control of Spokes in Magnetron Discharges.

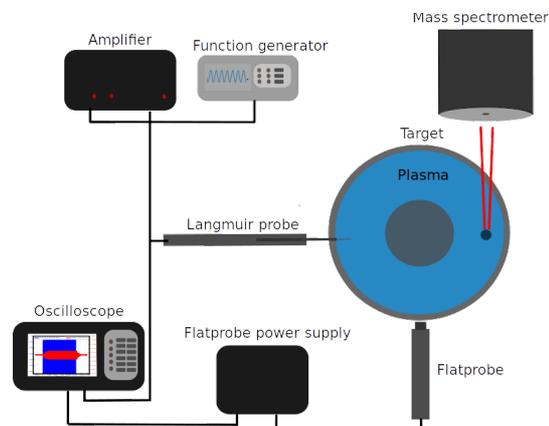
Mathews George<sup>1</sup>, Wolfgang Breilmann<sup>1</sup>, Julian Held<sup>1</sup> and Achim von Keudell<sup>1</sup>

Experimentalphysik II, Ruhr-University Bochum, Germany

## Abstract:

Magnetron Sputtering is a Plasma Vapour Deposition (PVD) process widely used in industry and scientific communities. HiPIMS (High Power Impulse Magnetron Sputtering) produces plasma pulses of very high density of the order of  $10^{19} \text{ m}^{-3}$  without overheating the target. The plasma appears to be homogeneous to the human eye, but shows localised zones of high brightness rotating in the  $E \times B$  direction when observed with an ICCD camera with exposure times below  $1 \mu\text{s}$  [1][3]. These local ionization zones, also called 'spokes' are assumed to play a role in the transport of particles and energy away from the target [2]. This anomalous transport results in an enhanced deposition rate by counteracting the return effect [4]. The primary objective of this project is to control spoke frequency in HiPIMS in order to study its influence on the IEDF and metal ion flux from the target. Controlling metal ion flux from the target would lead to a better deposition rate and quality of the film. DCMS was chosen for the development of spoke control as an initial test object since the spokes in DC regime are more uniform compared to HiPIMS. Amplified rectangular signals are applied to a Langmuir probe to draw electron current from the plasma at the highest gradients in the  $E \times B$  direction. The responses of the spoke frequency and intensity to the applied signal are measured with a flat probe. The metal ion flux from the target surface is measured time and energy resolved with a mass spectrometer. This study is then further extended to HiPIMS spokes by applying signals on multiple probes to achieve an effective control of spokes.

**Keywords:** Anomalous transport, local ionisation zones, overheating, DCMS, HiPIMS, control, spoke frequency, mass spectrometer, Langmuir probe, applied signal, ion flux, deposition rate, magnetron,



**Figure1:** Schematic depiction of the experimental setup.

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# Model Predictive Control and Parameter Identification Analysis of Cascaded H-bridge Multilevel EAST Fast Control Power Supply Based on CPS-PWM Modulation Strategy

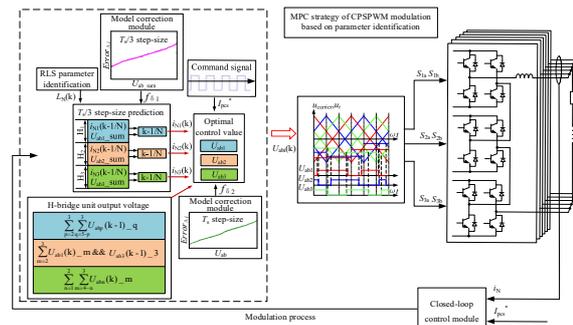
H. Haihong<sup>1\*</sup>, Y. Bichen<sup>1</sup>

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## Abstract:

The EAST(Experimental Advanced Superconducting Tokamak) fast control power supply based on the cascaded H-bridge(CHB) topology is used as the external power supply for the fast control coil.<sup>1</sup> The research is to realize the optimal control of current through the model predictive control(MPC)<sup>2</sup> and carrier phase shift pulse width modulation(CPSPWM)<sup>3</sup>, improve the magnetic confinement ability and dynamic suppression performance. Regarding a single H-bridge unit as an independent power supply, calculate the optimal control value with digital delay at the corresponding sampling time of CPSPWM modulation, and realize balance output power. Aiming at the model error, by offline testing the dynamic unmodeled items and establishing a linear fitting function with the average value of the PWM voltage period, the model was revised to reduce the prediction error. The system parameters are identified by the recursive least square(RLS) algorithm with forgetting factor, and the arithmetic mean is used to approximate the average switching period of the state variable, which overcomes the problem of the degradation of MPC quality when the parameters change. The identification of the injecting step-signal continuous excitation conditions and error accuracy are analyzed. The control strategy is shown in Figure 1. This research proposes a model predictive optimization control for the EAST fast control power supply when the parameters of the coil change, and combines MPC with CPSPWM to obtain an algorithm suitable for any cascaded H-bridge. This method has been used in EAST fast control power supply prototype platform.

**Keywords:** cascaded H-bridge multilevel, EAST fast control power supply, CPSPWM, model predictive control, parameter identification analysis, dynamic unmodeled items.



**Figure 1:** Figure illustrating the question that we are tempting to solve experimentally: Through the combination of CPSPWM modulation and MPC, the optimal control quantity of the fast control power supply of the cascaded H-bridge is obtained to cope with the optimal control of the current when the parameters are changed. It provides solutions and analysis for model deviation and parameter identification.

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3. S. R. Mohapatra and V. Agarwal,(2019), Model Predictive Controller With Reduced Complexity for Grid-Tied Multilevel Inverters, *IEEE Trans. Ind. Electron.*, 66, 11, 8851-8855.

# Single-Shot Spatially Resolved Optical Emission Spectroscopy of Plasma Species within the Spoke

M. Šlapanská\*, M. Kroker, J. Hnilica, P. Klein, P. Vašina

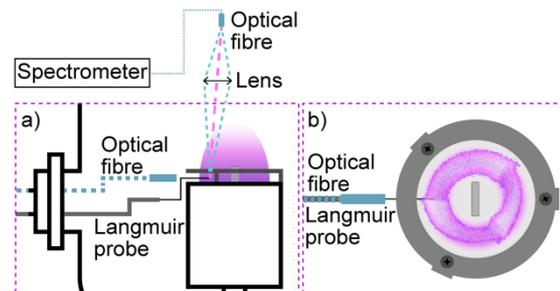
Department of Physical Electronics, Masaryk University, Brno, Czech Republic

## Abstract:

Using the fast cameras it has been revealed, that the plasma above the race track rearranges under certain conditions into localised rotating regions of increased light emission and intense excitation, commonly known as spokes or ionization zones<sup>1,2,3</sup>. Over time, the spokes have been observed in many types of magnetron sputtering discharges, including the reactive processes. The spokes have been studied due to their potential impact on the sputtering process and, consequently, thin film deposition. It has been discovered, that spoke's parameters, such as the mode number, shape and speed of rotation, are dependent on practically all experimental conditions, including the magnetic field and target material in combination with working gas<sup>4</sup>.

This contribution presents the single-shot spatially resolved optical emission spectroscopy (OES) of the titanium and argon species present within the spoke captured by the Langmuir probe and the optical fibre both placed in the deposition chamber in a non-reactive high power impulse magnetron sputtering (HiPIMS) discharge (Figure 1). The argon gas pressure in the range of 0.4 – 1.6 Pa has been set to investigate both triangular (< 0.5 Pa) and round (> 1.0 Pa) spokes<sup>5</sup>. The Langmuir probe recorded the floating potential of the passing spoke in each HiPIMS pulse, therefore the time-resolved measurement could be utilized to spatially resolve the passing spoke. It was always possible to distinguish at least two spokes on the electrical and the optical signals, therefore, determining where one spoke begins and where it ends. By processing those signals, we were able to calculate a spoke length distribution, and consequently, by creating a normalised time scale of each spoke, the unified spoke has been created. To reveal additional spoke's inner parameters the spatially resolved excitation temperature and the ionisation fraction were obtained from the emission signal.

**Keywords:** spoke, ionisation zones, HiPIMS, OES, optical emission spectroscopy, argon, titanium, spoke length distribution, UNI-spoke, excitation temperature, ionisation fraction.



**Figure 1:** Simplified scheme of the a) side and b) top view of the experimental setup for the spatially resolved optical emission spectroscopy of the plasma species present within the spoke.

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# Optical emission spectroscopy mapping for plasma diagnostics during plasma-enhanced chemical vapor deposition

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<sup>2</sup> Department of Physics and Mathematics, University of Eastern Finland, Joensuu, Finland

<sup>3</sup> Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, Russia

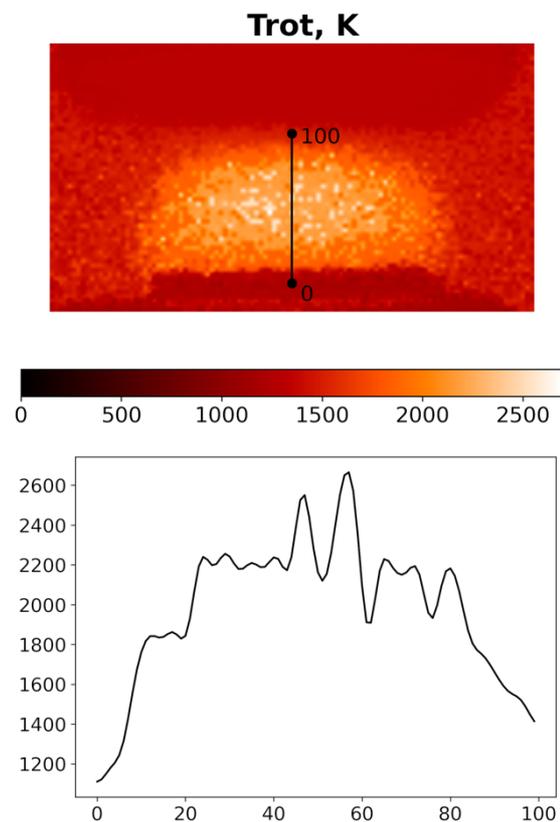
## Abstract:

We present results of optical emission spectroscopy study of a plasma-enhanced chemical vapor deposition of carbon films. The materials produced in this study were the diamond films, containing unique pyramidal diamond crystallites [1], and the films, consisting of vertically oriented carbon nanowalls [2]. These carbon films were deposited from a hydrogen and methane gas mixture activated by a direct current discharge (typical parameters: methane flow rate 10 sccm, hydrogen flow rate 130 sccm, total pressure 10 kPa, voltage 700 V, current 6 A, Si substrate's temperature at anode 950 °C). The optical emission spectra were recorded at different scanning points of the plasma discharge to provide a spatial mapping of the electron and gas temperatures, as well as any emission line from the available spectrometer range.

Slightly resolved ro-vibrational optical emission spectrum of the C<sub>2</sub> Swan band system was used for gas temperature measurements. Gas temperature was estimated by comparison method: the calculated spectrum was compared with the experimental one until the best match. In order to increase comparison procedure speed and to reduce it's subjectivity, comparison work was delegated to the machine learning algorithms. This, in turn, allowed to create temperature distribution maps in a reasonable time [3]. The obtained results might be used for optimization of the deposition process and for revealing new mechanisms explaining formation of the carbon materials with different properties.

The work was supported by RSF #19-79-00203 and by RFBR #18-29-19071 (CVD, Optical parts and Si purchase)

**Keywords:** molecular plasma technology, plasma diagnostics, OES mapping, machine learning, plasma-enhanced CVD, carbon film materials.



**Figure 1:** A typical spatial distribution map of the rotational temperature (top) and its profile along electrodes axis (bottom).

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# In Situ Electroanalytical Modelling of the Influence of Bath Hydrodynamics on Nucleation Kinetics for Electrodeposition of Nickel-Cobalt alloy system

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## Abstract:

The approach of using current transients to model the nucleation rate as reported in the seminal work of Scharifker and Mostany [1] is limited to electrodeposition system without bath hydrodynamics (BHD) [2]. Therefore, in this work in situ electroanalytical approach is proposed to unveil the influence of BHD on the nucleation kinetics of electrochemically deposited Nickel-Cobalt alloy system (eNiCo). Using the Hydrodynamic linear sweep voltammetry (HLSV) technique, the limiting current density as function of BHD is computed, wherein it increased (for eNiCo alloys) from 186 mA/cm<sup>2</sup> to 222.6 mA/cm<sup>2</sup> on increasing BHD from 0 to 42 cm/s, respectively. Consecutively, the diffusion layer thickness is found to decrease from 19 μm to ca. 15.8 μm on increasing BHD from 0 to 42 cm/s, respectively. Additionally, from Nyquist plots (Figure 1) recorded using the Galvanostatic Electrochemical Impedance Spectroscopy (GEIS), the charge transfer coefficient ( $R_{ct}$ ), exchange current density ( $i_0$ ) and double layer capacitance ( $C_{dl}$ ) as a function of BHD is computed. It is found that  $R_{ct}$  decreased and  $i_0$ ,  $C_{dl}$  increased (Figure 2) as function of BHD. Thereby, indicating the enhancement in the charge transfer on the cathode surface and reduction in the thickness of the diffusion layer. Hence, with the use of BHD, it is possible to control the nucleation kinetics, therefore enabling the deposition of tailor-made materials possessing specific required properties.

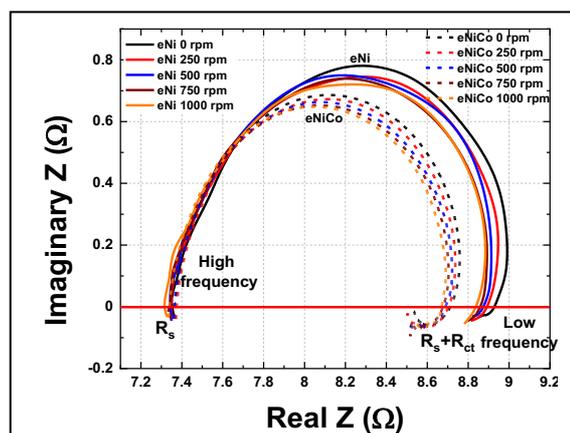
**Keywords:** nanostructured materials, electrodeposited nickel-cobalt alloys, in situ electroanalytical modelling, hydrodynamic linear sweep voltammetry, Galvanostatic electrochemical impedance spectroscopy

## References:

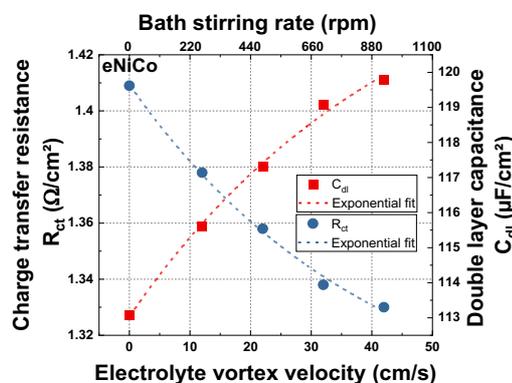
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**Figure 1:** Nyquist plots recorded from the GEIS analysis for nickel and nickel-cobalt alloys as a function of varying BHD conditions.



**Figure 2:** Computed  $R_{ct}$  and  $C_{dl}$  values for eNiCo alloys from the record Nyquist plot as function of varying BHD conditions.

# Influence of chain length of organic modifiers in hydrophobization process on epoxy resin properties

G. Morgiante<sup>1\*</sup>, M. Piłkowski<sup>1</sup>, J. Marczak<sup>1</sup>

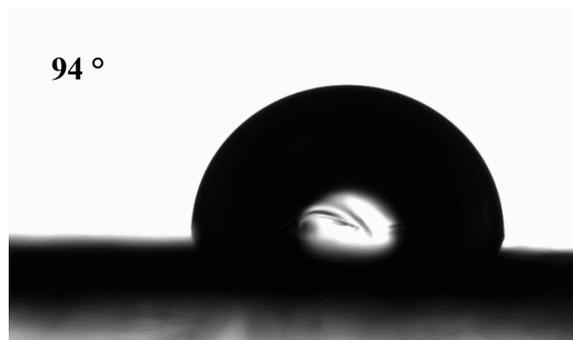
<sup>1</sup>Łukasiewicz Research Network – PORT Polish Center for Technology Development, Wrocław, (Poland)

## Abstract:

Resins have been widely used in a variety of industry fields for more than a century such as coatings, adhesives or automotive. Their low cost and workability are extremely useful in creating more and more advanced materials due to their chemical structure<sup>1</sup>. Common problem today is the wetting tendency of various materials which in the end can result in further damage in the structure because of atmospheric conditions. Nowadays, scientists are trying to find better ways to improve the properties of coatings or composites in cases like hydrophobicity or icephobicity. One of the examples are fluorinated organic compounds with good linking properties to the substrate<sup>2</sup>. Because of that, to improve the properties of a basic epoxy resin, its chain has been modified with hydrophobic compounds with different chain lengths. Influence of modifiers molecule size on hydrophobic and ice adhesion properties of obtained epoxy resins have been tested. Chemical composition of prepared coatings were analysed by FTIR. Moreover their thermal stability was investigated using TG and DSC measurements. Additionally wettability of the samples was analysed with goniometer. Furthermore, their ice adhesion tests were performed on a dedicated apparatus. As a result, presented work provides a critique overview and concept of promising icephobic and hydrophobic coatings in the industry. Moreover, these products have a high chance to be developed further.

This work was supported by the National Centre for Research and Development under the LIDER programme through the project contract No. LIDER/47/0194/L-9/17/NCBR/2018.

**Keywords:** epoxy resin, chemical modification, organic modifiers, coatings, surface wettability, cross-linking, ice adhesion



**Figure 1.** Figure illustrating the hydrophobic property of the surface which was modified with one of the used fluorinated compounds.

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# Bulk-modified epoxy resins as a coatings with low ice adhesion

M. Piłkowski <sup>1\*</sup>, G. Morgiante <sup>1</sup>, J. Marczak <sup>1</sup>

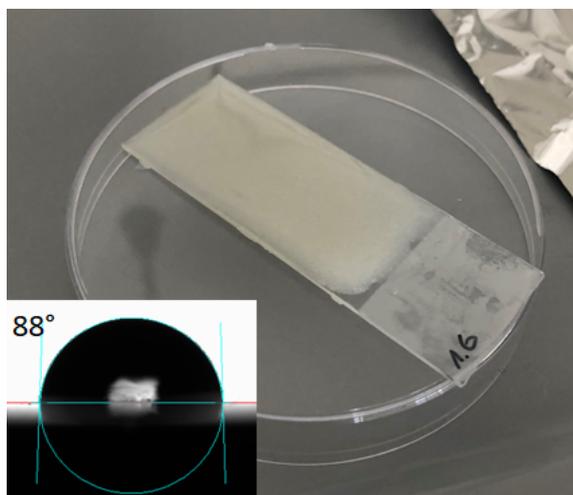
<sup>1</sup>Łukasiewicz Research Network – PORT Polish Center for Technology Development, Wrocław Poland

## Abstract:

Surface icing can cause several problems in aviation, which leads not only to lower safety but also to higher energy input to remove ice from wings. To deal with it, most of planes use active anti-icing systems, those are effective however they have several disadvantages. Recent research in hydrophobic/ icephobic materials lead us to idea of development coatings with low ice adhesion as a passive anti-icing systems [1]. In opposite to active systems, passive ones don't need energy to work, and get rid of toxic glycol based anti-icing liquids.

In order to do that we decided to modify commercially available epoxy resins with chosen fluorinated organic compound [2]. Newly obtained resins were used to prepare coating and were tested. Obtained samples had lower surface free energy than unmodified one, leading to higher hydrophobicity which allows for higher anti-icing properties [2, 3]. Different resins were used to, check modifier impact on prepared materials. Modified resin was first tested using FTIR, TG and DSC techniques – allowing for better understanding of material properties and its chemical composition. Samples wettability was measured with WCA (water contact angle) and SFE (surface free energy by van Oss- Good method) [4]. Anti-icing properties were estimated by ice adhesion measurements. Obtained results suggest that presented materials are suitable for further research and tests cooperation with industry.

**Keywords:** epoxy resin, ice adhesion, fluorinated organic compounds, aircraft, wettability



**Figure 1:** Figure illustrating fluorinated epoxy resin after curing process with water contact angle values.

This work was supported by the National Centre for Research and Development under the LIDER programme through the project contract No. LIDER/47/0194/L-9/17/NCBR/2018.

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# Plasma enhanced chemical vapour deposition of ZrO<sub>2</sub> based layers

P. A. Maaß<sup>1\*</sup>, V. Bedarev<sup>1</sup>, S. M. J. Beer<sup>2</sup>, M. Prenzel<sup>1</sup>, M. Böke<sup>1</sup>, A. Devi<sup>2</sup>, A. von Keudell<sup>1</sup>

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<sup>2</sup>Inorganic Chemistry II, Ruhr-University, Bochum, Germany

## Abstract:

Chemical vapour deposition (CVD) is a widely applied technique used for thin film deposition. The combination with a plasma source (PECVD) enables the fine-tuning of parameters, opening new possibilities for the fabrication of functional coatings. The aim of the current research project is the development of thin thermal barrier coatings using (PE)CVD. The evaporated metalorganic precursor is transported into the reaction chamber by a nitrogen-flow of 25-50 sccm at pressures of about 100 Pa. A ZrO<sub>2</sub> layer is deposited onto a heated substrate in the centre of the chamber. The desired layer growth rate is expected to be > 500 nm/h and the layer thickness < 30 µm.

To influence and improve the reaction chemistry, a microwave plasma source is to be mounted opposite the substrate surface. The discharge is to interact with the incoming precursor molecules, with the aim to reduce the reaction temperature.

During this process, the growth rate and substrate temperature are monitored by in-situ ellipsometry to obtain insights into growth characteristics at different process conditions. The deposited layers are characterised in thickness and stoichiometry, using profilometry and X-ray photoelectron spectroscopy (XPS).

To gain insight into the thermal conductivity of the thin layers, the 3ω method is set up.

Especially the change of the thermal conductivity depending on the morphology of the layer is investigated.

**Keywords:** PECVD, Thermal barrier coatings, ZrO<sub>2</sub>

# Influence of plasma torch power on the properties of alumina coatings

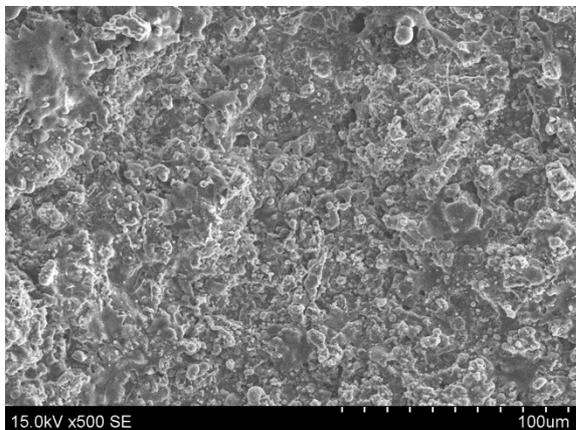
A. Šuopys, V. Grigaitienė, L. Marcinauskas, R. Kėželis, R. Uscila, M. Aikas

Lithuanian Energy Institute, Laboratory of Plasma Processing, Breslaujos str. 3, LT-4440, Kaunas, Lithuania

## Abstract:

Plasma spraying is one of the branches of thermal spraying and is widely used for development of various protective coatings [1]. Coatings deposited by atmospheric plasma spray are being used for many applications that require protecting components against corrosion, high temperatures and wear. Depending on plasma spray parameters properties of formed coatings can be modified. The quality of the coatings depends on the surface roughness, thickness, porosity and hardness [2]. The power of the plasma torch is one of the main control parameters. It directly affects the speed and temperature of the plasma jet, where the feedstock particles are accelerated and melted, or partly melted before they flatten on the substrate and solidify (Fig 1). This can have a major impact on the structure and quality of the coating. Alumina coatings were formed using atmospheric plasma spray, increasing torch power from 25 kW to 42 kW. The properties of coatings were determined using scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and profilometer. The results indicate that increasing the plasma torch power, the amount of  $\gamma$ - $\text{Al}_2\text{O}_3$  phase in the coating also increased and the surface roughness  $R_q$  decreased from 7  $\mu\text{m}$  to 5.5  $\mu\text{m}$ . Elemental composition changes were minimal.

**Keywords:** Plasma spraying, plasma torch,  $\text{Al}_2\text{O}_3$



**Figure 1:** SEM image of  $\text{Al}_2\text{O}_3$  coating

## References:

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2. Sreekumar Rajesh T., Venkata Rao R., (2018) Experimental Investigation and parameter optimization of  $\text{Al}_2\text{O}_3$ -40% $\text{TiO}_2$  atmospheric plasma spray coating on SS316 steel substrate

## Acknowledgement:

This research is funding by the European Regional Development Fund according to the supported activity 'Research Projects Implemented by World-class Researcher Groups' under Measure No. 01.2.2-LMT-K-718.

# Durability Study of the Anti-biofilm Capacity of Plasma-Polymerized Coatings on Stainless Steel for Food Contact Applications

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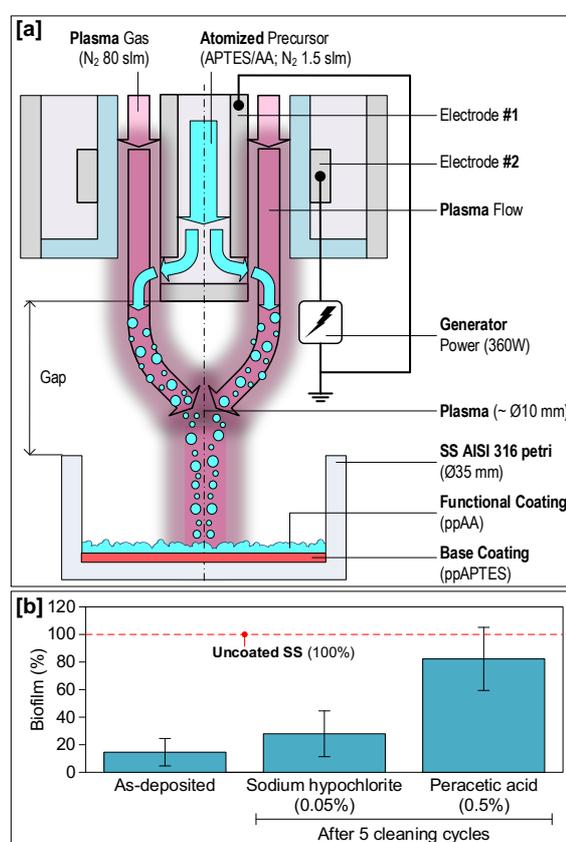
<sup>2</sup> Department of Food Hygiene and Technology and Institute of Food Science and Technology, University of León, León, Spain

<sup>3</sup> Molecular Microbiology Area, Center for Biomedical Research of La Rioja (CIBIR), Logroño, Spain

## Abstract:

Biofilms, which are organized bacterial communities embedded in an extracellular polymeric matrix and attached to a surface, are a major concern in food industries. The formation of these persistent communities on food contact surfaces can cause cross-contamination of the products, posing a threat to the consumer's health. This study is the continuation of our recently published work<sup>[1]</sup> in which anti-biofilm coatings were deposited by an atmospheric-pressure plasma jet system on AISI 316 stainless steel (SS) (Fig. 1(a)). The present study assesses the durability of the anti-biofilm capacity of the most promising coating of our previous work (as-deposited coating AP10 + AA6), which has a base coating of (3-aminopropyl)triethoxysilane (APTES) and a functional coating of acrylic acid (AA). Coated and uncoated (control) SS samples were subjected to 5 cleaning cycles with sodium hypochlorite (0.05%) and peracetic acid (0.5%), which are commonly used disinfectants. Finally, biofilm formation by *Listeria monocytogenes* (cocktail of CECT911 and two strains isolated from food industries) after incubation at 12 °C for 6 days was quantified by crystal violet staining. According to the obtained results (Fig. 1(b)), coating AP10 + AA6 preserved its anti-biofilm capacity (biofilm production <100%) to some extent after 5 cleaning cycles with any of the two disinfectants. More remarkably, after cleaning with sodium hypochlorite (0.05%), the biofilm production on the coating was still substantially lower than on the uncoated SS. These results suggest that coating AP10 + AA6 is compatible with a common disinfectant for the removal of surface contamination while keeping an acceptable degree of anti-biofilm capacity. This is a promising finding for enabling the implementation of the proposed anti-biofilm coating in real industrial environments.

**Keywords:** durability, anti-biofilm, plasma-polymerization, cleaning, disinfectants, food contact.



**Figure 1:** (a) Scheme of the plasma-polymerization process; (b) Biofilm production on coating AP10 + AA6, relative to that on the uncoated SS, after 5 cleaning cycles with two different disinfectants and as-deposited (i.e., without cleaning).

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# Methodology for designing the parameters of technological nitriding regime with respect to the relative wear resistance of tool steels for hot working

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## Abstract:

The present study aims to create a methodology for decision making in the process of designing the regime of the technological process of ion nitriding. The methodology is applied about the relative degree of wear  $K_v$  for grade tool steels for hot working BH10, BH11 and BH21 and thus the stages of its application are demonstrated. Main procedures such as Design of Experiment, single and multi-criteria optimization are used. With the help of the numerical methodology the tendency in the change is determined for establishing technological regimes and modeling properties of wear, which are finally clarified by nitride zone forming the layer. Since similar steels are analyzed in the study, the general treatment regime is established, which leads to the desired relative wear resistance. The result of the study is obtaining accurate values for the relative degree of wear  $K_v$  and their corresponding regimes for the three tested steels. A general range is determined for the whole grade, through the stages of the applied methodology, in which the steels have high wear resistance.

**Keywords:** ion nitriding, plasma nitriding layers, modeling properties of wear, grade tool steels for hot working.

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# The application of organofunctional silanes to protect the wood surface

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## Abstract:

Wood should serve us for many years and enjoy its natural beauty. However, it is constantly exposed to harmful external factors, therefore it should be properly protected against biocorrosion and weather conditions. Appropriate protection of wood leads to its longer life and hence, huge reduction in maintenance costs [1].

Unfortunately, many of the wood preservatives used so far are highly toxic to humans and hence, much attention has been paid to development of nontoxic materials/methods for protecting wood [2]. Recently, several reports have been published on the use of inorganic-organic hybrid coating for protecting wood substrates. The sol-gel process to generate hybrid coatings is versatile and even allows room temperature deposition of hybrid inorganic-organic films on various substrates, including wood [3]. Wood surface modification with multifunctional alkoxysilanes by sol-gel process is one of promising method to improve and provide new properties for wood materials. The advantage of the sol-gel process is that it allows the deposition of thin inorganic-organic layer on various substrates because of controlled hydrolysis and polycondensation of alkoxysilanes [4]. The sol-gel coatings created on the wood surface provide barrier properties, moisture control and repellency properties.

In this communication, we present a new silicon containing fatty acid derivatives and their application to produce hydrophobic coatings on wood surfaces.

**Keywords:** Renewable resources, fatty acids, sol-gel processes, organically modified silanes, wood protection.

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# Development of superhydrophobic CoAl-LDH conversion coating as a novel photocatalytic protective film on AA6082

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## Abstract

We reported the novel photocatalytic protective CoAl-Layered double hydroxides (CoAl-LDH) based uniform, the dense thin film developed directly on the aluminum AA6082 substrate. Further, the low surface energy molecules (1H, 1H, 2H, 2H perfluorododecyl trichlorosilane) were incorporated inside the LDH network through anion exchange mechanism to obtain superhydrophobic CoAl-LDHs surface for enhanced corrosion resistance properties and adding self-cleaning characteristics. The developed films were characterized by Scanning electron microscopy (SEM-EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) while further contact angle measurements were made to evaluate superhydrophobicity against different household items. The static water contact angle (WCA) for the prepared surface was observed to be about 152°. The high charge transfer resistance observed from the results of electrochemical impedance spectroscopy (EIS) tests indicated the significant corrosion resistance properties of the CoAl-LDHs and modified CoAl-LDHs. The research in photocatalytic protective thin films brings insights into the understanding of new aspects of surface protection against contaminations. This will address the possibility of new challenges in many engineering applications. The photocatalytic activity of CoAl-LDHs in the degradation of the model pollutant was investigated under visible light irradiation. It is found that reductive sites of Co(II) of LDHs and the conductive substrate improve the separation of photogenerated charges and prevent the particle aggregation of LDHs and exhibit higher visible light photocatalytic performance.

**Keywords:** CoAl-LDH, Self-cleaning, EIS, photocatalytic.

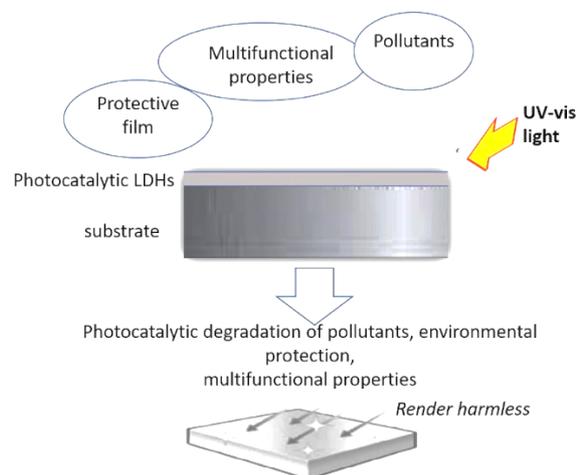


Figure 1. General photocatalytic LDHs concept for protective coatings and pollutants degradation.

# Enhanced Performance of Solution Processed 2D-MoS<sub>2</sub> Photodetectors upon Ultraviolet-Ozone Treatment.

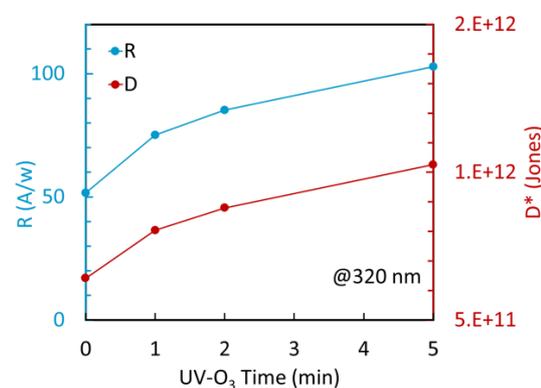
Hend Badahdah <sup>1\*</sup>, Reem Altuwirqi <sup>1</sup> and Hala Al-Jawhari <sup>1</sup>

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## Abstract:

Molybdenum disulfide (MoS<sub>2</sub>) nano-sheets, with their direct bandgap of 1.8 eV, have become excellent candidates for NIR photodetectors. Nonetheless, covering a wide range of wavelengths, from UV to IR, has developed into a requirement for diverse applications. It has been reported that treating MoS<sub>2</sub> nano layers with UV-O<sub>3</sub> will lead to formation of S-O and Mo-O bonding and transfer some of the upper layers to MoO<sub>3</sub> [1-3]. Due to the large band gap (3-3.2 eV) of MoO<sub>3</sub> [4], it is predicted that it will enhance the detection at the UVA range. In this study, we investigate the influence of exposing 2D-MoS<sub>2</sub> layers to UV-O<sub>3</sub> on their photodetecting properties. Our MoS<sub>2</sub> thin film photodetectors were fabricated using facile solution process at low temperature. As UV-O<sub>3</sub> exposure time was increased, significant enhancement of both responsivity and detectivity have been observed for 320 nm irradiation as shown in (Figure 1). An excellent responsivity of 103 A/W along with a high detectivity of  $1.03 \times 10^{12}$  Jones were achieved at 320 nm irradiation under light intensity of  $300 \mu\text{W}\cdot\text{cm}^{-2}$  after 5 minutes exposure to UV-O<sub>3</sub>. On the other hand, for 750 nm irradiation, a reduction of 14% in responsivity and around one order of magnitude in detectivity were noticed after the UV-O<sub>3</sub> treatment. These results are in agreement with the formation of the wide band gap semiconductor MoO<sub>3</sub> as a result of the exposure to UV-O<sub>3</sub>. Such findings provide a new route for modulating the optical properties of MoS<sub>2</sub>-based optoelectronics.

**Keywords:** 2D-MoS<sub>2</sub>, photodetector, solution-processed MoS<sub>2</sub>, Ultraviolet-ozone treatment,



**Figure 1:** Responsivity and detectivity as a function of UV-O<sub>3</sub> exposure time for the wavelength of 320 nm under low illumination of  $300 \mu\text{W}\cdot\text{cm}^{-2}$ .

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# Polypropylene vs. Polyester Plasma Ion-Exchange Activated Needle-Punched Non-Woven Geotextiles

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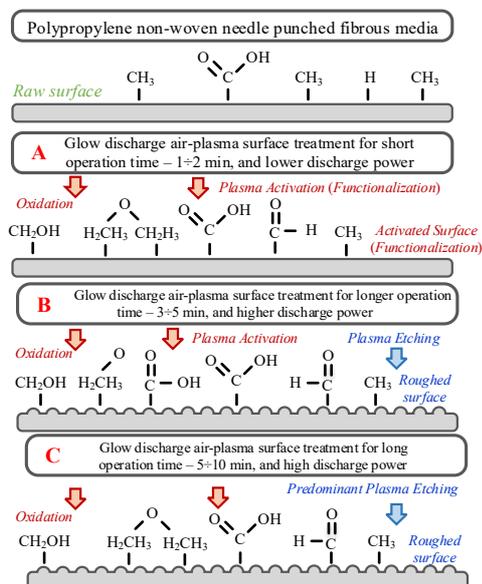
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## Abstract:

Low-pressure plasma processing was considered an attractive alternative to adding new functionalities to geotextiles. Activation processes happen when a nonwoven geotextile surface was treated with a glow discharge air plasma. Glow discharge activation may be related to both productions of nonwoven geotextiles with soil-friendly properties and non-woven ion exchangers for water purification and conditioning applications. It was the end-step for producing ion-exchange activated polyester (PES) and polypropylene (PP) needle-punched nonwoven geotextiles. The appropriate choice of the most effective glow discharge mode – abnormal glow discharge (160÷640 Pa), results in the creation of the necessary amount of functionality suitable for the production of ion-exchanging geotextiles with soil-friendly properties. Cation exchange capacity (CEC) is an important determinant of soil fertility as it measures a soil's ability to hold nutrients and water. Indeed, most of the geotextile functions which are an object in this study were dealing with the interaction between geotextiles and water in the manner of the interaction between soils and water. The maximum of cation-exchange capacity of low-pressure plasma-activated PP and PES needle-punched highly porous geotextiles (500 g/m<sup>2</sup>) was achieved: at 640 Pa for PP – 15.1 mEq/100g vs. 160 Pa for PES – 32.0 mEq/100g. Both the PP and PET cation-exchange activated geotextiles can be categorized on the base of the CEC soil-related data of ESDAC as follows: PP in the soil category with moderate CEC: 10<CEC<20 mEq/100g vs. PES – soil category with high CEC: 20<CEC<40 mEq/100g.

**Keywords:** ion-exchange capacity, geotechnical and geoenvironmental engineering, low-pressure plasma activation, needle-punched non-woven, non-woven geotextile, polyester, polypropylene, soil-friendly property.



**Figure 1:** Three main oxidative effects can be obtained on polymer (including PP and PET) fibrous textile surfaces depending on the plasma treatment conditions - operating time and power: A – cleaning effect and low chemical activation; B – chemical activation (functionalization by scissoring and oxidation) and production of radicals to obtain hydrophilic surfaces, and low etching; C – etching (increasing of microroughness and anti-pilling finishing) and intensive activation. After the stage C, the etching becomes dominant and the surface activation is suppressed very fast.

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# Significantly reduced secondary electron yield of electrodeposited silver coatings for multipactor applications

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## Abstract:

The multipactor effect is an electron avalanche like phenomenon that can occur in microwave components when electrons are accelerated by radio-frequency (RF) fields in their vacuum. This undesirable effect results from the synchronism between the RF-wave and the electron emission phenomenon of microwave-components materials. The new trend in the space telecommunication is to increase the RF power density which leads to an increased multipactor occurrence probability. To circumscribe this risk, an interesting strategy consists to produce surfaces with low Total Electron Emission Yield (TEEY). For this purpose, many technics were used such as laser ablation [1], copper nanowires [2] or micro-structured gold/silver coatings [3].

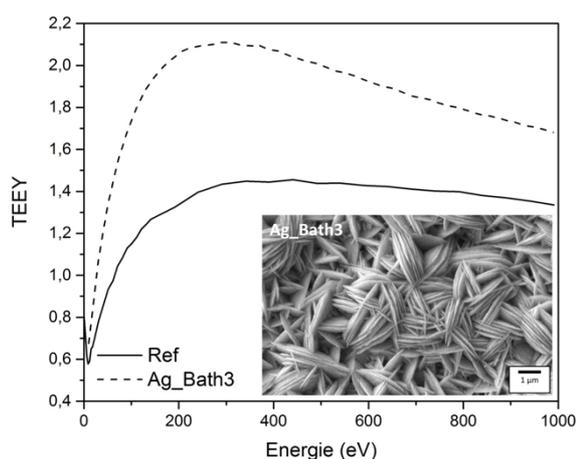
In this work, we explore the capabilities of electrodeposition techniques to produce low TEEY surfaces.

Silver was electrochemically deposited on nickel substrate at ambient temperature. Different bath compositions were used to explore the effect of electrodeposition parameters on the surface morphology and on the TEEY.

We will show that some produced morphologies lead to a substantial overall decrease of the TEEY as shown in Figure 1 where the TEEY of a standard silver reference sample is compared to that of a silver electrodeposit surface. A scanning electron microscopy (SEM) with electron dispersive X-ray analysis were used to link the TEEY to surface morphology and chemical composition.

The consequences of TEEY drop on the multipactor power threshold were analyzed with the help of simulations of multipactor effect in parallel plate wave-guide geometry.

**Keywords:** electrodeposition, silver, coating, total electron emission yield, roughness, particles morphology.



**Figure 1:** The evolution of the TEEY as a function of primary electron energy for a silver reference sample (Ref) and a silver coating obtained in “Bath3” (Ag\_Bath3).

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# Simulation of multi-layer TiN/TiAlN thin film growth and calculation of its thermal conductivity

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## Abstract:

Multi-layer titanium nitride/titanium aluminium nitride film growth was simulated by means of kinetic Monte Carlo code NASCAM [1]. Results of the simulation were compared to experimental data [2]. Film growth was simulated for different number of bi-layers TiN/TiAlN, with the number of bi-layers equals from 5 to 50. The total thickness of the whole stack was the same for all samples. That means that the thickness of bi-layers became smaller with the increase of bi-layer numbers.

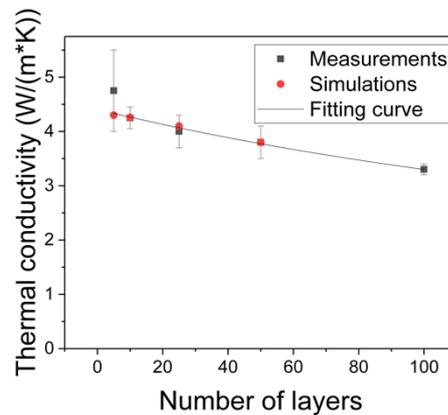
Calculation of the thermal conductivity of simulated multi-layer film was conducted in two steps. Firstly, the thermal conductivity of the single layer was calculated by using Landauer relation based on effective medium theory [3]. Secondly, the thermal conductivity of the whole stack  $k$  was calculated the following equation:

$$\frac{1}{k} = \sum_{i=1}^N \frac{l_i/l}{k_i} + \sum_{j=1}^{N-1} r_j,$$

where  $k_i$  is a thermal conductivity of a sub-layer “ $i$ ”,  $l_i$  is a thickness of the sub-layer “ $i$ ”,  $l$  is the total thickness of the layer, and  $N$  is the number of sub-layers, and  $r_j$  are thermal resistivities of the interfaces between each TiN and TiAlN layers.

Simulation results were compared to the experimental data and to the results of the calculation by means of the equation given above and it was found the perfect agreement between all the data.

**Keywords:** Multi layer thin films, thermal barrier coating, thermal conductivity, film growth simulations.



**Figure 1:** Experimental values of thermal conductivity of TiN/TiAlN multi layer film [2] and values simulated by NASCAM.

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# Mean Absorption Coefficients of air-copper thermal plasmas

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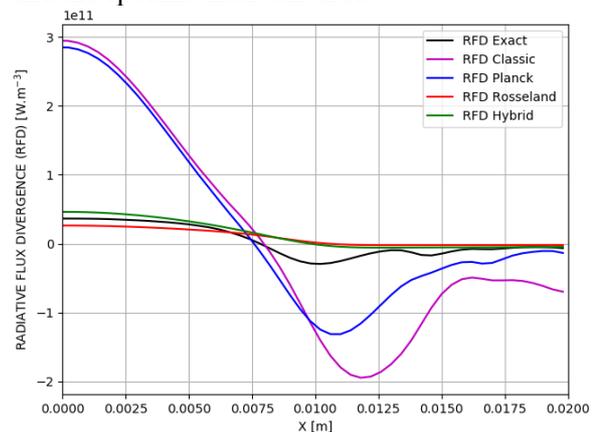
## Abstract:

In Madagascar, the transport of the electrical energy is difficult because of aging electrical installations. One of the main problems is the creation of electric arcs between electrical lines, greatly facilitated by a high moisture content in the country. After the creation of the arc, a plasma of air mixed with copper (vapours resulting from the erosion of the cables) is formed and releases a strong energy by radiation. The study of the radiative losses is essential to protect surrounding materials. Consequently, numerous numerical modelling are developed to better understand the behaviour of the arc, the energy transfers inside the plasma and to external environment. The radiative heat transfer is considered in the energy equation through the Radiative Flux Divergences (RFD). This work proposes a database of the Mean Absorption Coefficients (MACs) used in P-N Models to solve the Radiative heat Transfer Equation (RTE). Compared to other methods [1], it allows to describe not only the emission and absorption in the hot regions but also the absorption in the cold regions of the plasma especially in the tepid regions near its edge. However, this method involves carefully selecting the spectral intervals and the averages to determine the coefficients.

In this work, we have decided to split the total spectral absorption coefficient into eight spectral intervals. We used and compared five averaging methods: the classic, the Planck, the modified Planck, the Rosseland and the hybrid Planck-Rosseland averaging methods [2]. In the literature, it is well-known that Rosseland mean is useful for optically thick plasmas, classic mean for molecular plasma at low temperatures, Planck mean must be modified to consider the self-absorption of the atomic lines [1]. The recent published work on this topic deals with the

**Keywords:** Mean Absorption Coefficients, radiative properties, thermal plasma, metallic vapour, Air, Copper, Radiative Flux Divergence, luminance.

development of a hybrid methods (a mix between the different mean functions) as a solution to well describe the radiative transfer in the plasma through the MACs. For an air-copper plasma, the presence of an important numbers of copper lines with strong emissions and strong absorptions requires precise analysis. As result, we will present a comparison between the exact resolution of the RTE method and the approximate methods using the MAC in order to test the validity of the means and the specific intervals used.



**Figure 1** : RFD of 1D exact resolution and MACs (Classic, Planck, Rosseland and Hybrid means) for pure air thermal plasma and P=1 bar.

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# Catalytic performances of Ce<sub>0.01</sub>Mn in Post-Plasma Catalysis for dilute Trichloroethylene abatement

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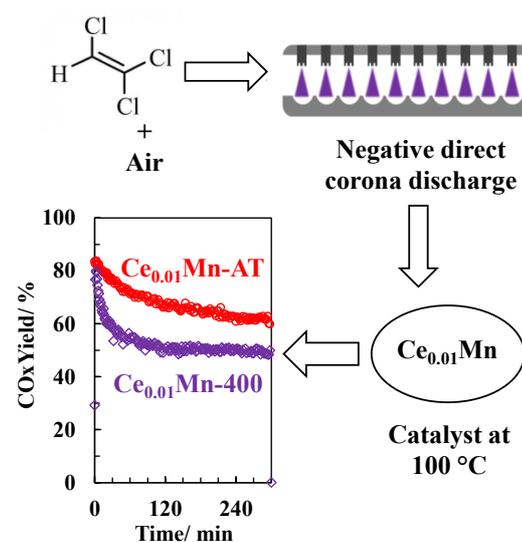
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## Abstract:

Trichloroethylene (TCE) is a chlorinated volatile organic compound commonly used in industry as a solvent and acts as a degreaser. TCE is detected in all media but mostly in air due to its high volatility. It is known to be harmful to human health as well as to the environment [1]. Therefore, an effective method for TCE abatement is required. Over the last two decades Non Thermal Plasma (NTP) technology has partly regained interest through Post-Plasma catalysis (PPC) which results from coupling a NTP reactor with a downstream catalytic reactor. This resulting hybrid technology can outperform NTP and total oxidation catalysis in terms of selectivity, efficiency and energy cost [2]. In PPC configuration catalytic reactions can take advantages of ozone emitted from NTP as a potential source of active oxygen species for further oxidation at very low temperatures of untreated parent VOC and of potential gaseous hazardous by-products from the NTP. One of the key point is to adapt the molar ratio  $[O_3]/[TCE]_0$  to 4 according to the following accepted formal reaction:  $C_2Cl_3H + 4O_3 \rightarrow 2CO_2 + HCl + Cl_2$ . The design of the catalyst has to be performed taking into account some basic requirements such as ozone decomposition ability, oxygen mobility, high CO<sub>2</sub> selectivity coupled with a chlorine and water tolerance. On purpose Ce doped birnessite ( $\delta$ -MnO<sub>2</sub>) are of prime importance due to their remarkable amount of defects, easy cycling of Mn<sup>4+</sup>/Mn<sup>3+</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup> and the high mobility of surface and lattice oxygen. In this paper the TCE abatement is investigated in PPC configuration in dry and moist air (15 %) with NTP using a 10 pin-to plate negative DC corona discharge and with PPC using Ce<sub>0.01</sub>Mn as catalyst calcined at 400 °C or treated with nitric acid (Ce<sub>0.01</sub>Mn-AT). Plasma assisted Ce<sub>0.01</sub>Mn-AT catalyst (100°C) presents the best CO<sub>2</sub> yield in dry air with of minimization of the formation of gaseous chlorinated by-products. This result can be explained by (i) the high specific surface area, (ii) the high mobility of oxygen

at low temperature and the strong surface acidity of Ce<sub>0.01</sub>Mn catalyst treated with nitric acid.

**Keywords:** Post-Plasma catalysis, Ozone, dilute TCE, Ce<sub>0.01</sub>Mn.



**Figure 1:** TCE abatement in PPC configuration using Ce<sub>0.01</sub>Mn calcined at 400°C or treated with nitric acid (ED = 150 J/L, Q = 1L/min, [TCE]<sub>0</sub> = 150 ppmv).

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# Sequential adsorption followed by plasma assisted catalytic conversion of toluene on Hopcalite in air stream

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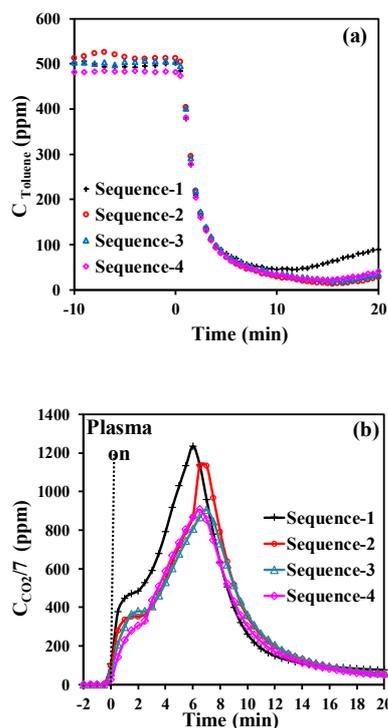
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## Abstract:

Volatile organic compounds (VOCs) such as toluene are emitted primarily from automobiles, industrial activities, waste water and so on [1]. Therefore, pertinent technologies removing toluene before its emission is necessary for environmental protection and for human health concern. Non-thermal plasma (NTP) is a promising technology for the removal of VOCs due to its wide adaptability and fast reaction time under ambient conditions. Nevertheless, plasma alone has some drawbacks including the formation of some unwanted by-products, low selectivity to CO<sub>2</sub> and high energy consumption. The combination of NTP/catalysis helps for the improvement in the CO<sub>2</sub> selectivity and suppress the by-products formation, the energy cost is still inadequate because of the huge amount of energy consumed during continuous discharge. To reduce this energy consumption a sequential adsorption-plasma oxidation system is proposed. First, toluene is adsorbed on the material in the absence of plasma. Subsequently the plasma is ignited in order to perform the catalytic combustion of adsorbed toluene assisted by NTP [2]. In this way, the energy consumption occurs only during the second step. For such process the catalytic materials should have good adsorption capacity and redox properties. We report the influence of different parameters (adsorption time, plasma power) on the reactivity and stability of Hopcalite (Figure 1). These parameters influence the formation of product selectivity and yield by changing the interaction between the catalyst and the plasma species. The optimized experimental conditions leads to good selectivity toward CO<sub>2</sub> selectivity (80-90 %), CO<sub>2</sub> yield (71-79 %) and low energy cost (11.6 kWhm<sup>-3</sup>). Furthermore, the cyclic process has been performed for four times, indicating stability of Hopcalite which was further confirmed by materials characterization (XPS, XRD, and Raman). The results pave the way for the plasma catalytic technique to be used in environmental applications to remove low concentrated pollutants from the air.

**Keywords:** Adsorption, adsorption plasma-catalysis, Hopcalite, non-thermal plasma, Toluene removal.



**Figure 1:** Toluene adsorption (a) and CO<sub>2</sub> evolution during plasma treatment

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# Oxygen Plasma Treatment on Silicone Catheter Surface for Enhancement of Antifouling Properties

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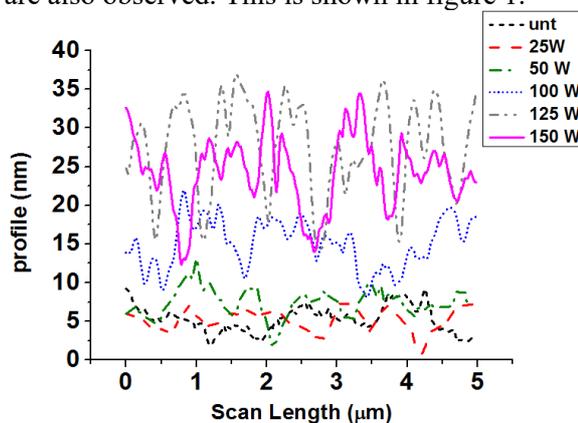
## Abstract:

Indwelling medical devices such as catheters, orthopedic implants, endotracheal tubes, vascular grafts, pacemakers, heart valves, breast implants and many more have become an unavoidable part of modern medical practice [1-3]. Silicone catheters are prone to bacterial adhesion /growth during insertion as well as post insertion. Researchers are continuously exploring the ways to control the bacterial adhesion on catheter surfaces. A lot of work has been reported on plasma surface modification of silicone / PDMS surfaces for various applications such as for improving adhesion between two PDMS surfaces, improving bonding between PDMS and glass surfaces, for better bonding of antibiotic / other bio-molecules to the PDMS surfaces, enhancing wettability for microfluidic devices etc. [4-6]. Only few literature report plasma treatment as the complete solution to treat catheter surfaces. Leila Taheran et.al [7] has reported that biofilm formation on catheter surface can be reduced by DC nitrogen plasma treatment. DC plasma has certain limitations for its usage in treating non-conducting substrates such as i) DC plasma cannot be formed if one of the electrode is entirely covered by non-conducting substrate as it works on the principle of conduction current and ii) substrate surface may experience unwanted damage due to continuous bombardment of charged particles during the process.

In order to overcome these limitations radiofrequency (RF) plasma has been chosen for the present work. A systematic study of evolution of desired surface properties as a function of RF power and its decay as a function of time is reported. Our study reveals that not only the roughness but other morphological parameters such as profile wavelength, peak to valley height, peak density etc. plays an important role in determining bacterial adhesion. Bacterial cells approaching the surface to settle down experience environmental stress due to significant change in these

parameters which ultimately resulted in less bacterial attachment on plasma treated and aged surfaces. This hypothesis was validated by our results.

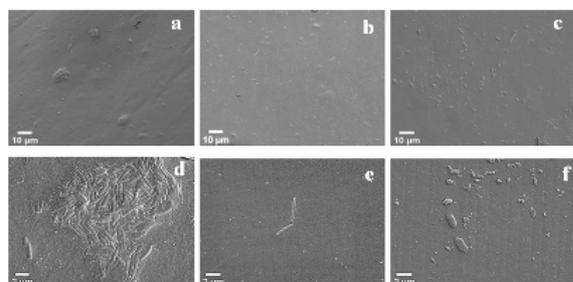
Experiments were carried out using oxygen plasma under capacitively coupled radio frequency (*CCP-RF*) configuration. Properties such as morphology, surface chemistry, surface energy and anti-fouling behaviour of plasma treated catheter surfaces have been studied as a function of RF power in the oxygen plasma. The plasma processed surfaces were characterized by different techniques such as Fourier Transform Infrared Spectroscopy (*FTIR*), Atomic Force Microscopy (*AFM*), and Scanning Electron Microscopy (*SEM*). Wettability of the surface was estimated by contact angle measurements followed by calculation of surface free energy. Plasma induced oxygen containing functional groups and morphological changes resulted in ~ 6 fold increases in total surface energy and ~ 4 fold increases in  $R_a$  value. Substantial changes in other morphological parameters such as average wavelength of the profile ( $L_a$ ) and Peak to Valley distance ( $S_t$ ) are also observed. This is shown in figure 1.



**Figure 1:** 2D line Profiles of bare and plasma treated silicone catheter surfaces

Substantial bacterial growth in the form of clusters / colonies of E-coli bacterial cells is found at random locations on untreated silicone catheter

surface whereas only few numbers of randomly scattered cells are found on plasma treated as well as aged surfaces as shown in figure 2. Reduced growth on aged surfaces reveals that only physical changes on the silicone catheter surface can also result in reduced bacterial growth. Study towards quantification of bacterial adhesion on the silicone catheter surface is underway.



**Figure 2:** SEM images of bacterial adhesion on untreated (a, d), plasma treated surfaces (b, e) and aged surface (c, f)

This study brings out an important process to control the growth/ adhesion of bacterial cells on silicone catheter surface.

**Keywords:** Anti-fouling surface, Silicone catheter, Oxygen Plasma, Surface Energy, AFM, FTIR

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# Use of a microwave plasma process at atmospheric pressure for bacterial disinfection

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## Abstract:

Currently, plasma torches find applications in a wide variety of fields such as production of thin layers, surface cleaning or even sterilization. The use of plasma has a significant advantage from an environmental point of view compared to processes using liquid phases which generate effluents to be reprocessed. The device used for this study is composed of a plasma torch operating at atmospheric pressure called an "Axial Injection Torch" (or TIA for "Torche à Injection Axiale").

At IRCER, the TIA is mainly used for thin layers deposition and surface treatments. In this study, the plasma jet generated by the TIA is characterized by optical emission spectroscopy in order to better understand the role of the plasma active species on the disinfection mechanisms of metallic surfaces contaminated with bacteria. The tests of disinfection were conducted in conditions allowing to maintain the temperature of the surface lower than 45°C in order to avoid the thermal effect of plasma.

The first measurements carried out aimed to determine the influence of the microwave power and the presence of a substrate in the axis of the discharge onto the characteristic temperatures and the species present in the plasma. They were made for an argon plasma gas flowrate of 10 slpm at different microwave powers [200-450 W] and nozzle/substrate distances [10-35 mm]. The results showed that the more the power increases the more the excitation temperature increases. In addition, when a substrate was placed in the axis of the discharge, a confinement was created therefore the excitation temperature increased in the vicinity of the substrate. Excitation temperatures ranging from 7200K to 9800K were obtained, depending on the operating conditions. To complete this study, acquisitions were also performed for argon plasma gas flowrates of 5 and 7 slpm will be made.

To determine the effectiveness of the plasma treatment, a E.Coli bacterial suspension was laid out on a steel substrate. Then, these substrates were exposed to the plasma discharge at different distances and microwave powers, Ar flowrates and exposure times. These first tests made it possible to obtain a reduction in the rate of bacteria. Other tests will have to be done to determine the optimum operating points and the action radius of the plasma.

**Keywords:** plasma torch, surface treatment, disinfection, optical emission spectroscopy

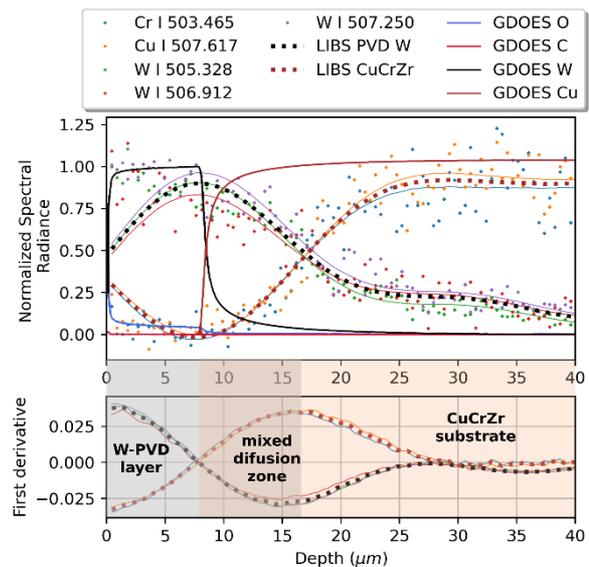
# Laser-induced breakdown spectroscopy interface tracking (LIBS-IT): application to a WPVD thin layer on a CuCrZr substrate

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## Abstract:

Surface characterization is not an easy task. Indeed, different material parameters such as roughness, hardness or even purity can limit the precision in this characterization. Depending on the application, several experimental methods exist<sup>1</sup>. Among them, a laser-based ablation method derived from LIBS (Laser-Induced Breakdown Spectroscopy)<sup>2</sup> can be used. The determination of the multi-elemental composition of solid samples can be derived. The radiative signals spectroscopically monitored are proportional to the target's ablated mass. Consequently, a high-controlled ablation is mandatory to ensure an accurate diagnostic. This method is not fitted to deduce the absolute composition due to significant matrix and screening effects. However, LIBS can be used as an interface tracking (IT) method in the case of a thin layer deposited on a substrate (Fig. 1). This communication aims at discussing the accuracy of the LIBS-IT applied to a W plasma vapor deposited (PVD) thin layer on a massive Cu-Cr-Zr substrate<sup>3</sup>. A detailed quantitative discussion based on a comparison with Glow Discharge Optical Emission Spectroscopy (GDOES) illustrates the potential of such an analytical process.

**Keywords:** LIBS, Laser-Induced Breakdown Spectroscopy, Ablation, Surface, Coating, Interface tracking, PVD, Plasma Vapor Deposition, Tungsten, Copper, Chromium, Zirconium, OM, Optical Microscopy, SEM, Scanning Electron Microscopy.



**Fig. 1:** Normalized LIBS lines cross sections compared to GDOES depth profiles. Three regimes are identified from the good agreement of GDOES and LIBS data: pure coating deposition, mixed diffusion/rough region and substrate region. On this figure, GDOES signals are displayed by solid lines, LIBS signals by points (acquired data), elemental filtered contribution by thin colored solid lines. The dashed lines stand for mean deposition and substrate filtered contributions (respectively in black and brown). The first derivative of normalized spectral radiance is devoted to the analysis clarity.

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# Structure and microstructure of high entropy alloy thin films from the AlCrFeMnMo family deposited by magnetron sputtering

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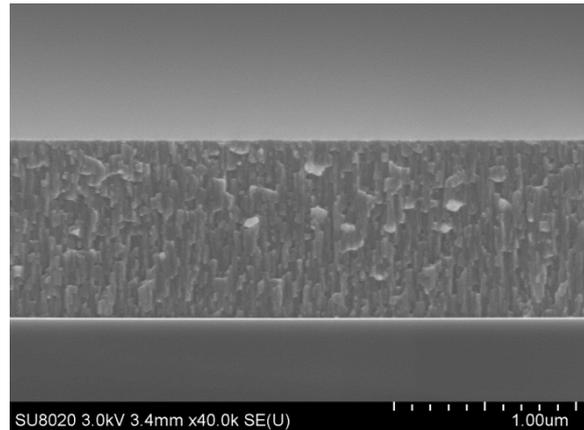
## Abstract:

High Entropy Alloys (HEA), which constitute a new concept of alloys, were described for the first time in 2004 [1]. Consisting of at least 5 elements in equiatomic or quasi-equiatomic composition, these new alloys have remarkable thermomechanical and chemical properties. However, the cost of the raw material and the difficulty to produce bulk HEA by casting lead us to explore new applications such as HEA coatings. In this work, HEA thin films from the new AlCrFeMnMo family were prepared by magnetron sputtering technique on silicon wafer and steel substrates. The coatings were obtained from a  $\text{Al}_{19}\text{Cr}_{22}\text{Fe}_{34}\text{Mn}_{19}\text{Mo}_6$  quinary target obtained by sintering of:

- a powder obtained by mechanical alloying in a planetary ball milling;
- A mixture of the elemental powders.

Thin films with different thicknesses were obtained by controlling the deposition time. Subsequently, the structure and microstructure of the deposits on both substrates are investigated by XRD, SEM, EDS and TEM. Structural analysis by XRD has shown that the films are amorphous. SEM coupled with EDS revealed a columnar cross-sectional microstructure (Figure 1), smooth and dense on the surface. In addition, a chemically homogeneous composition identical to that of powder alloys are obtained. Nanodomains structures are detected in the amorphous thin films of the HEA and have been finely characterized by the HRTEM image.

**Keywords:** high entropy alloy thin films, magnetron sputtering, high entropy alloy, powder metallurgy, microstructure.



**Figure 1:** Cross-section of High entropy alloy thin film obtained by magnetron sputtering from  $\text{Al}_{19}\text{Cr}_{22}\text{Fe}_{34}\text{Mn}_{19}\text{Mo}_6$  quinary target, prepared by sintering a mechanical alloying powder and deposited on Si wafer.

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