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PLASMA THIN FILM INTERNATIONAL UNION MEETING

Abstract book

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PLATHINIUM

PLASMA THIN FILM INTERNATIONAL UNION MEETING

ORAL PRESENTATIONS

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PLASMAS FOR ULTRAWIDE BANDGAP MATERIALS

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Ultrawide bandgap materials such as diamond and hexagonal boron nitride (hBN) are a class of semiconductors with bandgaps in excess of ~5 eV that are desired for high-power, extreme environment, and ultraviolet applications. While these materials have been been studied for many decades now, new properties continue to be unearthed because of synthetic challenges and advances in measurement tools.

In this talk, I will present two efforts, one related to diamond and the other related to hBN. First, we have recently discovered intervalence band plasmons in boron-doped diamond, defined as collective electronic excitations between the valence subbands.[1] To probe these low-energy (<0.5 eV) transitions, we applied several relatively advanced techniques, including scanning transmission electron microscopy-valence electron energy loss spectroscopy (STEM-VEELS) and scanning near-field optical microscopy (SNOM), and carried out first-principle calculations. While plasmonic behavior in doped semiconductors is well-documented, it has typically been attributed to Drude excitation of free charge carriers (e.g., holes). Our study shows the possibility of other mechanisms for the measured plasmonic response. Second, we have developed an understanding of infrared spectroscopic characterization of hBN which can be applied directly on copper or other metallic substrates that are common growth substrates, unlike Raman spectroscopy.[2] Insight can be obtained into the growth process by analyzing different peaks without the need to transfer, accelerating optimization. Finally, we demonstrate that the addition of a plasma can lower the growth temperature and allow direct growth of hBN on alternative substrates such as silicon and stainless steel.

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PLATH00077

MINIMIZING THE IMPACT OF NEGATIVE OXYGEN IONS ON ALUMINIUM-DOPED ZINC OXIDE THIN FILMS DEPOSITED BY ROTATABLE RF MAGNETRON SPUTTERING

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Thin films attract much attention to the Internet of Things sensors and applications, from smart windows to flexible displays. These devices require low-cost materials, with controlled resistivity and transparency. To reduce the cost of thin film-based devices, controlling the film's properties over large areas is crucial. Aluminum-doped zinc oxide (AZO) can be used to replace more expensive transparent conductive oxides. However, it was proven that during the deposition of AZO, preferential zinc sputtering by energetic negative oxygen ions induces a significant increase in resistivity at locations correlated with the erosion trace.[1] The use of a tuning electrode placed between the substrate and the cathode can mitigate the detrimental influence of the negative oxygen ions. It reduces the DC self-bias of the plasma responsible for the ions energy and offers better control of the AZO properties.[2] So far, this approach has not been tested for rotatable magnetron sputtering targets used for large-area depositions.
This work shows the correlation between the shape of the rotatable magnetron sputtering target and the spatial optoelectronic properties of AZO thin films deposited on 300 cm2 glass substrates. The self-bias responsible for the energy of the negative oxygen ions was lowered by 15V by using the tuning electrode. We found that the minimum self-bias was for pressures around 3.5 mTorr, iindependently from the RF power. Using different pressures and deposition powers, without additional substrate heating, we show improved uniformity when we use the tuning electrode, specifically in the area facing the erosion trace (figure 1). For depositions at equal power, with the tuning electrode, the resistivity is below 5x10-3 ohms cm on 90% of the surface, against only 43% without the tuning electrode. Using optimised parameters, we obtain homogeneous properties on the entire 300 cm2 substrate, as confirmed by XRD and XPS.

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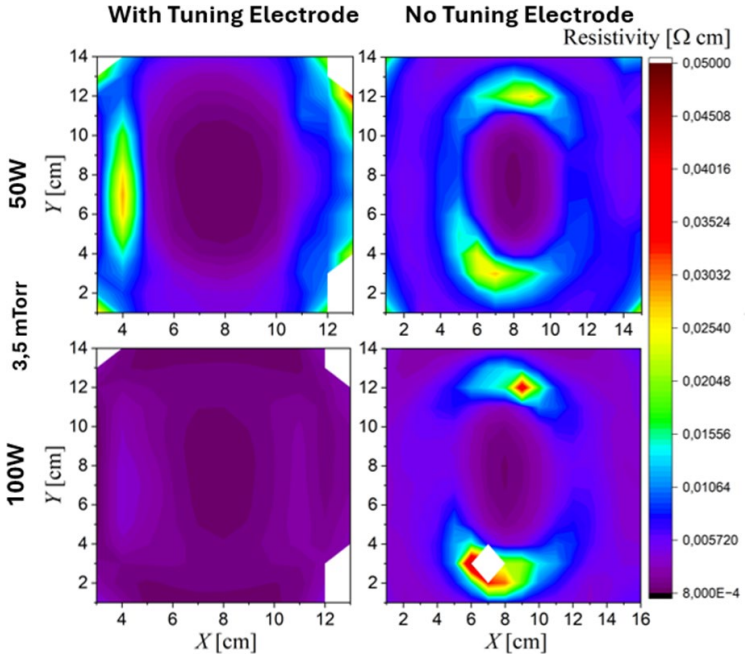

Resistivity mapping of AZO

PLATH00031

CONTROLLING THE STOICHIOMETRY OF COPPER OXIDES DEPENDING ON OPERATING PARAMETERS

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Metal oxide semiconductors, due to their low cost and facile preparation, are key in solar water splitting via photocatalytic and photoelectrochemical (PEC) approaches. Cu_2O is particularly promising for PEC water splitting but faces efficiency limitations due to insufficient electrical properties and defects in electrochemically deposited films[1,2]. To overcome this, RF magnetron sputtering technique is used to create high-quality Cu_2O photocathodes with appreciable electrical properties and diminished defects. By carefully controlling sputtering parameters (e.g., O_2 concentration, pressure, temperature, power, and time), optimal condition were obtained to deposit pure Cu_2O, Cu_4O_3 and CuO films. The films were characterized using X-ray diffraction, Raman spectroscopy, UV-vis absorption, and SEM. The Cu_2O photocathodes showed light response in PEC hydrogen production, and the impact of copper oxide stoichiometry on hydrogen production was examined. To prevent photocorrosion, heterojunctions with materials like WO_3 or TiO_2 were studied for protection, with an emphasis on using earth-abundant materials to avoid noble metals.

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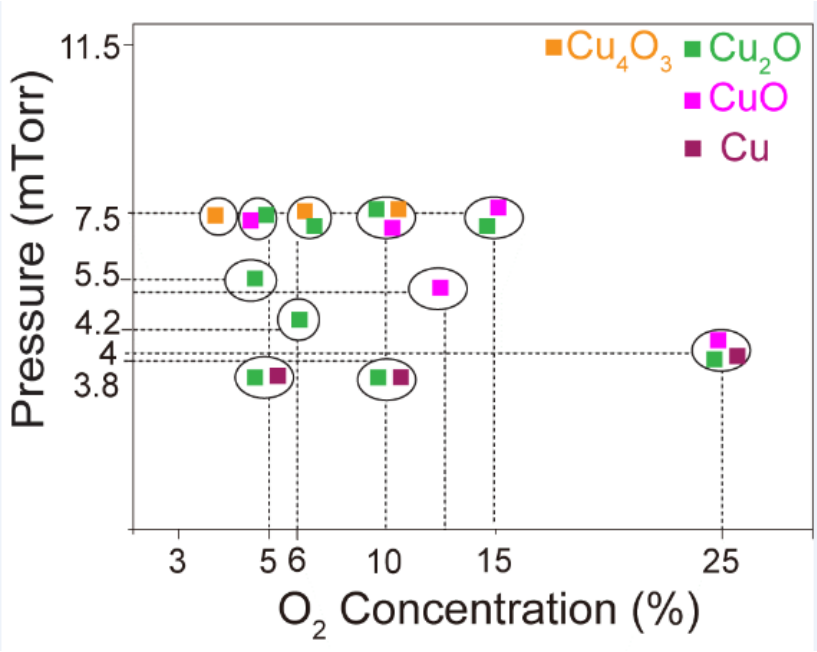

The schematic deposition diagram

PLATH00023

EXPLORING ENERGY TRANSFER IN SPUTTER DEPOSITED TUNGSTEN FILMS: EFFECTS OF MAGNETIC FIELD STRENGTH AND PRESSURE-DISTANCE ON PHASE COMPOSITION

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This study investigates the phase composition of magnetron sputter deposited tungsten (W) thin films, with a focus on the impact of energy transfer during film growth. Reflected neutrals play a key role in delivering energy to the growing film, a particularly significant factor for heavy metals like W [1]. The influence of energetic reflected neutrals on the phase composition of 200 nm W films has been studied in some detail under varying deposition conditions [2]. Expanding on this, we explore how variations in magnetic field strength influence energy transfer mechanisms that drive phase stabilization. Additionally, the pressure and target-substrate distance (p·d) affects gas-phase scattering, which in turn controls the energy of particles reaching the substrate [3].

Using X-ray diffraction (XRD) analysis, two distinct phases in W films were observed: the thermodynamically stable α-W phase, and the metastable β-W phase. To study the influence of magnetic field strength on the phase composition, we deposited 200 nm W films with varying target thicknesses (1-5 mm) on Si (100) substrates in a high-vacuum magnetron sputtering system (base pressure: 3×10^{-5} Pa). Also, films were grown under different p·d conditions (3–7 Pa·cm) by varying the Ar pressure (0.3–0.7 Pa) and distance (6–14 cm) at a constant discharge power (180 W) and a target thickness (3 mm).

Our results reveal that increasing the target thickness from 1 to 3 mm raises the discharge voltage, which in turn promotes the formation of the α-W phase (Fig.1a). However, beyond a target thickness of 3 mm, the α fraction begins to decrease, indicating that excessive energy transfer does not necessarily lead to further α-phase stabilization. When the energy input exceeds an optimal threshold, it can lead to increased formation of defects [3]. Additionally, increasing the p·d further reduces the energy of arriving species due to more frequent gas-phase collisions, leading to increased scattering, which can further promote β-W phase formation (Fig.1b).

To quantify these effects, we employ SDTrimSP and SIMTRA simulations, providing deeper insights into the relationship between energy transfer mechanisms and phase evolution in W thin films.

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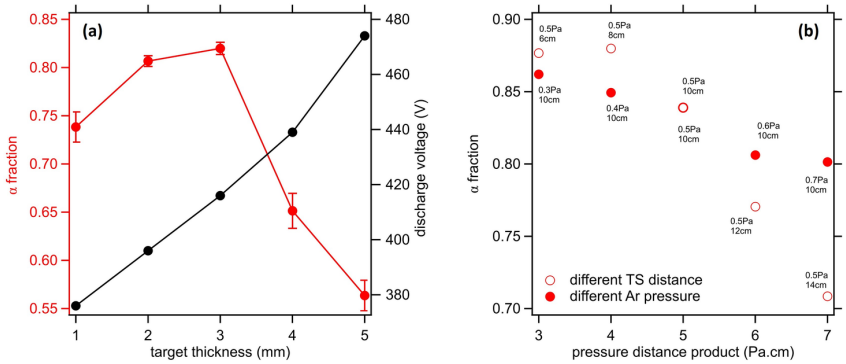

α fraction vs.(a) target thickness, (b)p.d product

PLATH00123

FROM TEMPERATURE-INDEPENDENT TO TUNABLE RESISTIVITY OF HIGH-ENTROPY ALLOYS THIN FILMS

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High-entropy alloys (HEAs) have garnered significant attention across various research and industrial fields owing to their exceptional properties, which originate from their complex structural order and chemical disorder. HEAs represent a promising frontier for next-generation electronic materials and sensing technologies, yet their electrical properties remain largely unexplored. In this work, we demonstrate unprecedented control of electrical characteristics in CrMnFeCoNi thin films through systematic incorporation of elements with distinct metallic radii (Cu, Al, Ag, and Zr). These characteristics suggested potential for systematic control over electrical properties through lattice distortion while maintaining good conductivity, with minimal chemical interaction.

This study unravels the distinct stories of how copper, silver, aluminum, and zirconium additions transform the structure and properties of CrMnFeCoNi Cantor alloy thin films, revealing behaviors that challenge our initial expectations. Using DC magnetron co-sputtering, we systematically investigated these transformations through comprehensive characterization including X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and electrical resistivity measurements.

Our comprehensive structural analysis reveals composition-dependent microstructural evolution: Cu maintains the face-centered cubic (fcc) structure while reducing nanotwin density, Al induces a progressive fcc-to-bcc transition, Zr drives amorphization, and Ag forms distinctive nanoprecipitates through spinodal decomposition. These structural modifications correlate directly with dramatic changes in electrical behavior. Most notably, we achieve a near-zero temperature coefficient of resistance (TCR) of -2.86 ppm/K in CrMnFeCoNiCu37, while CrMnFeCoNiAl25 exhibits enhanced resistivity of 324 μΩ·cm, surpassing conventional alloys like Constantan and Manganin. This approach enables remarkable TCR tunability from +355 to -480 ppm/K across the 80-350K temperature range. The mechanisms underlying these properties involve a complex interplay between lattice distortion, phase transitions, electron scattering at defect sites, and electronic structure modifications. Our findings establish HEAs as superior candidates for precision resistive components, temperature sensors, and thermoelectric applications, offering enhanced performance and stability compared to traditional materials.

PLATH00035

REVERSIBLE FUNCTIONALIZATION OF CITRONELLAL PLASMA POLYMERS - TOWARDS PH RESPONSIVE THIN FILMS

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The deposition of polymer thin films through plasma polymerization offers the possibility of coating a surface with a polymeric material in a solventless way, which is in accordance with the growing demand for environmentally friendly processes. According to the precursor selected, the deposited polymer thin films can either be unreactive or functional. In the case of the latter, the possibility of post-functionalization opens up to a varied range of chemistries and applications that can be targeted [1]. For instance, the selection of a precursor containing an aldehyde functional group, such as citronellal, allows the post-functionalization of the derived plasma polymer through common reactions of aldehydes. Among the aldehyde reactions, imine dynamic covalent chemistry stands as an interest strategy, as a pH-dependent reaction. In this work, the deposition rate and the chemistry of citronellal plasma polymers were evaluated at different input powers, duty cycles and spatial distributions in the reactor. After the determination of the conditions on which aldehyde functional groups were preserved in the thin films, a reversible post-functionalization of that functional group with an amine was evaluated. The proposed strategy allowed to identify the spatio-temporal dependence of the chemistry of citronellal plasma polymers to the deposition conditions. Furthermore, the pH reversible grafting of a model molecule was also observed.

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PLATH00038

ON THE OCCURRENCE OF INTERNAL PARTIAL DISCHARGES INSIDE ALUMINIUM MATRIX COMPOSITE LAYERS DURING PLASMA ELECTROLYTIC OXIDATION PROCESS

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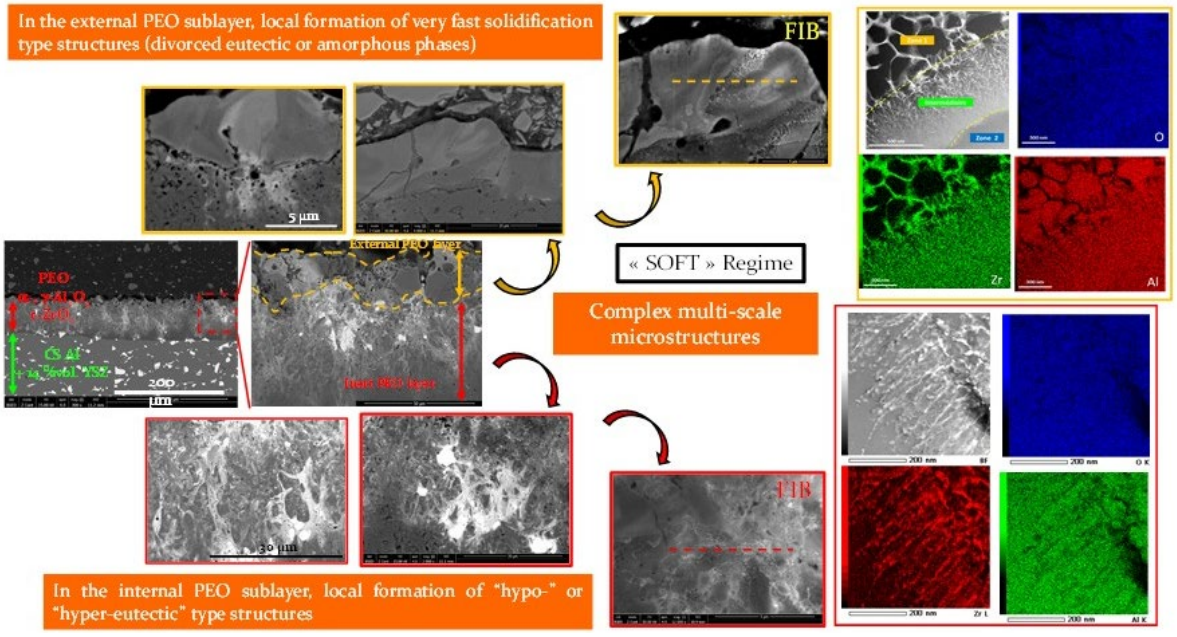
Plasma electrolytic oxidation (PEO) is a plasma-assisted electrochemical conversion technique used to grow a protective oxide layer on light metals such as aluminum. This process is a credible industrial alternative to anodizing in terms of the environment. One of the obstacles to the development of the PEO process is the lack of knowledge of the physical phenomena involved. A very promising innovation consists in manufacturing layers containing aluminum and particles by cold spraying (Cold Spray CS) and performing PEO treatments on these layers. In this communication, we will show that the presence of particles in the aluminum layer deposited by CS constitutes an opportunity to understand the physics of PEO. The application of bipolar currents makes it possible to obtain a particular PEO regime called "soft" regime, characterized by a very strong reduction in surface discharges compared to treatments performed in the conventional regime with "arc". Scanning and transmission electron microscopy observations of CS layers containing particles and treated with PEO in the arc and soft regimes have revealed for the first time traces of partial discharges inside the PEO layers. We will discuss the mechanisms to explain the existence of internal partial discharges during the PEO process.



Traces of internal partial discharges

PLATH00016

INVESTIGATION OF THE CHEMICAL BEHAVIOUR OF AN ELECTROLYTIC DISCHARGE USED TO SYNTHESIZE LOW-DENSITY MESOPOROUS METALS

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As part of laser matter interactions experiments carried out, at the Laser Mégajoule (LMJ) facility, CEA needs to synthesize low-density materials with specific characteristics. In this context, cutting-edge materials in the form of low-density metallic foams are employed, with a specific focus on those produced through the technique of plasma electrolysis deposition.
This synthesis method, patented by the CEA [1], differs from commercial and industrial synthesis techniques for metallic foams and aerogels due to the specific properties it provides. These materials have an apparent density equivalent to approximately 1% of the bulk metal, pore sizes of about a micrometre, and a purity higher than 95%.
Because the synthesis processes for these innovative materials are complex and the underlying mechanisms have not been fully elucidated yet, studies have been undertaken to improve the understanding of the phenomena occurring during synthesis. Specifically, the different species present in solution and their influence on the reaction leading to the formation of metal foams have been examined. Additionally, the functional heterogeneity of similar solutions and cathodic and anodic processes in an aqueous medium have been the subject of specific studies. The objective of these investigations is to improve control of the structural organization and characteristics of the material, with the aim of optimizing the synthesis process and obtaining a final material that meets the required criteria.

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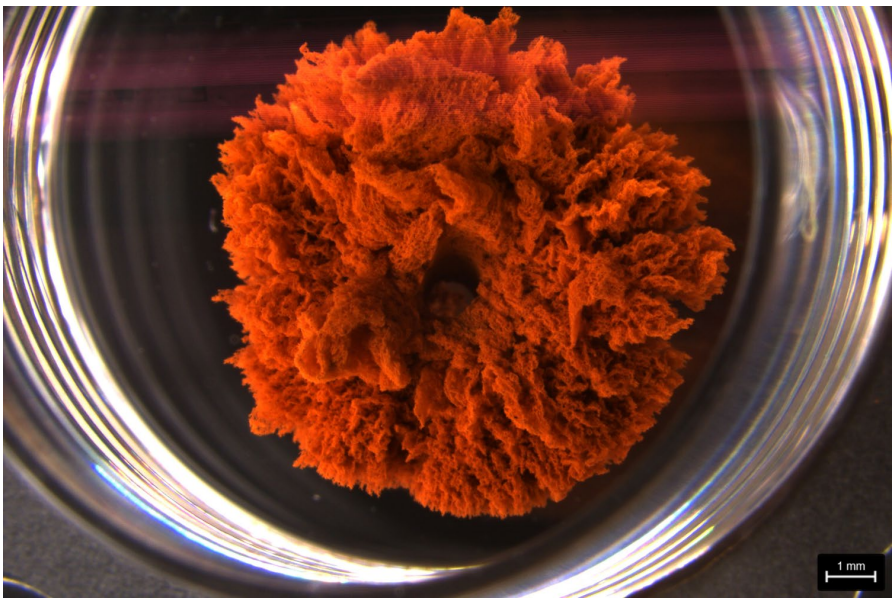

Gold foam synthetized by plasma electrolysis

PLATH00103

DEGRADATION OF METHYLENE ORANGE IN AQUEOUS SOLUTION USING NON-THERMAL PLASMA

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Water pollution caused by organic dyes from industrial wastewater poses significant environmental challenges. Among various treatment methods, non-thermal plasma (NTP) has emerged as a promising advanced oxidation process due to its ability to generate reactive species capable of degrading organic contaminants efficiently. In this study, we investigate the degradation of Methylene Orange (MO), a model organic dye, in an aqueous solution using a pulsed DC plasma system. The primary objective is to understand the degradation mechanisms and assess the efficiency of this plasma-based treatment.

A pulsed DC plasma reactor was employed to generate reactive species, including hydroxyl radicals (•OH), and hydrogen peroxide (H_2O_2), which play a crucial role in the oxidation and breakdown of MO molecules [1,2]. The degradation process was analyzed by monitoring the absorbance spectra of MO at different treatment times using UV-Vis spectrophotometry. The effects of key operational parameters, including applied voltage, treatment duration, and initial dye concentration, were systematically studied to determine their influence on the degradation rate.

Our results indicate that the MO concentration decreases 100% within 5 minutes of plasma treatment time. Kinetic analysis suggests that the degradation follows a pseudo-first-order reaction model, with the rate constant dependent on the applied voltage and the presence of reactive species. Additionally, the effects of solution pH and conductivity on the degradation efficiency were examined. The results show that an acidic environment enhances the degradation process, likely due to increased formation of hydroxyl radicals. The presence of electrolytes in the solution influences plasma-liquid interactions, affecting the production and diffusion of reactive species.

These findings demonstrate the potential of pulsed DC plasma as an effective method for degrading organic dyes in wastewater treatment applications. The ability of plasma to generate highly reactive species without the need for additional chemical reagents makes it an environmentally friendly alternative. Future work will focus on optimizing the process parameters, scaling up the plasma system, and exploring its application for real industrial wastewater containing a mixture of organic contaminants.

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PLATH00102

PLASMA TECHNOLOGY FOR TETRODOTOXIN INACTIVATION IN *LAGOCEPHALUS SCELERATUS* FISHMEAL

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In recent years, the Mediterranean has seen a massive influx of non-native and invasive marine species. A clear example is the pufferfish "*Lagocephalus sceleratus*", which is not a target species for inshore fisheries due to its toxicity and consequent trade ban for human consumption. The toxicity is due to the presence of tetrodotoxin (TTX) in the tissues of the species, consumption of which can cause respiratory disorders, circulatory failure, muscle paralysis, and even death. The rapid growth of the pufferfish population has a major impact on the fishing industry, through gear wear and bycatch, but also on tourism and local economies, particularly in the southern Mediterranean. A solution for the utilization of *L. sceleratus*, which combines environmental and socio-economic benefits, is the production of fishmeal, after TTX inactivation.

The aim of this study is to investigate the effectiveness of plasma technology in inactivating TTX in *L. sceleratus* fishmeal. There is only one relevant study [1] on plasma treatment of liquid solutions of chemically produced TTX. Four plasma reactors are being developed to fulfil this purpose. The first is a plasma jet reactor, with He as the feed gas, and is used to process liquid samples, i.e., the *L. sceleratus* stickwater. The second and third reactors, where the plasma is generated by a dielectric barrier surface discharge with air as the feed gas, are used for the direct processing of fishmeal. The sample is stagnant in the second reactor and stirred in the third. The fourth is a multiphase dielectric barrier discharge jet reactor with air as the feed gas. It is used to treat fishmeal samples indirectly by producing plasma "activated" water, i.e., water enriched in reactive oxygen and nitrogen species (RONS), in which the samples are then immersed.

TTX inactivation is assessed by measuring the TTX concentration using high performance liquid chromatography-tandem mass spectrometry (LC-MS/MS). The reduction in TTX concentration of the fishmeal was ~2-fold in the direct and ~7-fold in the indirect treatment. The results of the study show that plasma technology can support the innovative idea of exploiting pufferfish to produce fishmeal, turning a challenge for the aquaculture sector into an economic opportunity.

Thanks/Acknowledgement
The work was supported by the project "LagoMeal" (Operational Programme for Fisheries and Sea, MIS 5067491)

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PLATH00112

AEROSOL-ASSISTED ATMOSPHERIC PRESSURE PLASMA DEPOSITION OF ACTIVE COATINGS BASED ON NATURAL ANTIOXIDANT COMPOUNDS

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Food packaging ensures safety and quality by shielding food from external factors. The rising demand for healthier, longer-lasting food products has has led to significant advancements in packaging technologies, particularly in the development of active packaging (AP). AP integrates various components, such as antioxidants, antimicrobial agents, and scavengers, to improve food freshness, safety, and shelf life by either releasing beneficial substances or absorbing unwanted compounds from the internal or external environment of the package. [1] Among the various strategies explored, the incorporation of natural antioxidant compounds, such as polyphenols, has shown great potential in improving packaging functionality and extending the shelf life of perishable foods. Polyphenols, including flavonoids like quercetin, possess strong antioxidant and antimicrobial properties, making them ideal candidates for AP applications.[2]
Cold plasma surface modification, especially thin film deposition, is an effective strategy to obtain AP. Conducted at room temperature, it allows treatment of thermolabile materials like natural and synthetic polymers or deposition of biomolecules and microorganisms. These traits make the process eco-friendly and highly appealing to industries.[3]
Here we report a study on plasma deposition of active films based on polyphenols, like quercetin. Films were deposited using aerosol-assisted atmospheric pressure plasma. This technique allows for a high deposition rate and a reduction in process costs due to the limited need for pumping systems and time. Water or a solution of antioxidants were employed to feed plasma discharge jointly to helium as a gas and ethylene as monomer. To better understand the nature of the deposited films, they were characterised using FTIR, SEM, UV-vis, thickness and contact angle measurements. The antioxidant properties of the films were assed through DPPH assay.

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ON NOVEL MERITS OF (PLASMA-ASSISTED) ATOMIC LAYER DEPOSITION FOR NEXT-GENERATION ENERGY APPLICATIONS

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NiO and Co_3O_4 find major application in energy conversion and storage devices, such as photovoltaics, batteries and electrocatalysis. We have recently shown that combining these chemistries is beneficial for selected applications. We synthesize these layers by atomic layer deposition, which enables accurate control over film conformality, uniformity and stoichiometry, opto-electrical properties, crystal orientation and texture.
In this contribution, we will review selected merits of ALD when combined with plasma processing by presenting case studies where the above mentioned chemistries are investigated for the preparation of NiO hole transport layers for metal halide perovskite devices and of NiO and $NiCoO_x$ electrocatalysts for H_2O splitting.
Specifically, plasma-assisted ALD NiO is found to outperform the thermal ALD counterpart in terms of current density during the oxygen evolution reaction [1], because the plasma-ALD NiO layer is efficiently converted to the β-NiOOH phase. At the same time, plasma-assisted ALD NiO films are characterized by a Ni-to-O ratio of 0.82 ± 0.04, lower than the thermal ALD counterpart (0.94 ± 0.04). This comparison indicates that the plasma-assisted NiO films rich in Ni^{3+} acceptor states: while inducing an improvement in film conductivity, these are also responsible for redox reactions with the metal perovskite absorbed in photovoltaic devices, thereby negatively affecting the device performance.
The plasma-assisted ALD approach for the synthesis of $NiCoO_x$ with tunable chemical composition and crystallographic structure between rock-salt and spinel, enables to unravel the dual electrochemical behavior of these films [2]. In detail, Co-rich spinel type films display an electrochemical behavior which is confined at their surface, whereas Ni-rich rock-salt films exhibit a dynamic bulk-activation. Moreover, the plasma-ALD approach leads to film texture control, when NiO and Co_3O_4 are combined in heterostructures: Co_3O_4 adapts its growth direction to align with the <100> texture of NiO, while NiO similarly mimics the <111> textured Co_3O_4 [3].

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PLATH00022

THE ROLE OF NITROGEN ADDITIVE ON THE GROWTH OF ULTRATHIN SILVER FILMS: IN SITU AND REAL-TIME STUDIES DURING MAGNETRON SPUTTERING DEPOSITION

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Ultrathin silver films with thickness below a few nanometers are interesting candidates for use in various applications (e.g., flexible electronics and low-emissivity glazing). However, early growth stages of Ag films deposited on weakly interacting substrates are dominated by a natural tendency to form disconnected 3D islands, which manifests itself in high electrical resistivities and broad absorption bands in the visible range. Growth strategies to produce continuous and ultrathin Ag films without compromising their electrical conductivity and optical transparency have lately been deployed. Among them, the use of gaseous additives appears to be an effective means of promoting wetting of Ag on the substrate surface [1-3].
Overall, there is a need for a thorough understanding of the nanoscale mechanisms of thin film formation, which requires implementation of real-time techniques during growth. In particular, the widely used ex situ diagnostics can provide misleading information, as the films evolve even under high vacuum conditions. In the present work, we study nitrogen-mediated growth of Ag on SiO_x and SiN_x surfaces. We employ a simultaneous combination of real-time techniques during Ag deposition by magnetron sputtering, including grazing incidence small-angle x-ray scattering (GISAXS), grazing incidence diffraction (GID), substrate curvature measurements (fig. 1), and surface differential reflectance spectroscopy (SDRS). In particular, GISAXS reveals changes in nanoscale morphology, GID gives insight into the crystallinity of thin films, while substrate curvature measurements and SDRS provide information about the average intrinsic stress and optical properties, respectively. Using the information from all four techniques, we will discuss the impact of nitrogen additive from the very first stages of growth (island nucleation, growth, and coalescence) up to formation of percolated and continuous films, including the evolution of the film after growth interruptions.

Thanks/Acknowledgement
This work is part of the IRMA project funded by the ANR and DFG (reference ANR-21-CE09-0041-01). It also pertains to the French Government programs “Invertissements d’Avenir” (EUR INTREE, reference ANR-18-EURE-0010) and LABEX INTERACTIFS (reference ANR-11-LABX-0017-01).

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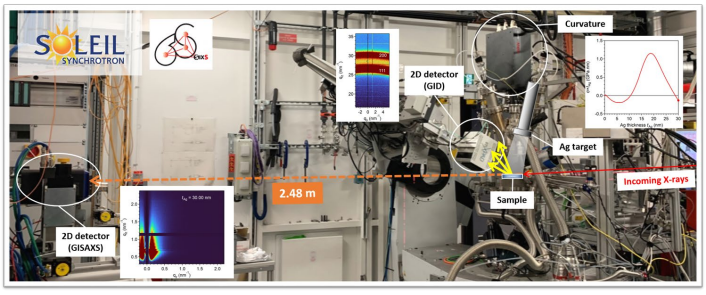

Photograph of the experimental setup.

PLATH00117

IMPROVING TiO_2 ANATASE CRYSTALLIZATION USING A LOW POWER DIELECTRIC BARRIER DISCHARGE AT ATMOSPHERIC PRESSURE IN A SINGLE STEP PROCESS: A PRECURSOR AND PARAMETRIC STUDY

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Titanium dioxide (TiO2) coatings are widely investigated for their whole set of properties including biocompatibility, corrosion resistance or even photoactivity. The latter one is the focus of the present work. It is well known that photoactivity depends on crystal size and on the crystal structure of the materials [1]. Many researchers investigated the deposition of TiO2 using low pressure plasma enhanced chemical vapor deposition (PECVD) demonstrating different important results such as lowering the substrate temperature from 400 °C to 250°C and a tunability of the crystal size and structure [2]. These low-pressure processes are mature and well-developed techniques which enable good control of the different deposition and growth modes. However, around 90% of the electrical consumption of a typical process is used for pumping and maintaining vacuum of the different equipment [3]. Nowadays, a growing number of researchers, for sustainability reasons, work with atmospheric pressure PECVD that comes with new challenges. This requires a new approach to recreate the previously obtained results with low pressure PECVD. In the specific case of TiO2, we have already evidenced [4] the major effect of deposition parameters on the crystalline behavior of TiO2 anatase films, exhibiting a maximum crystal size of 20 nm and a crystalline TiO2 layer could be deposited at low temperature (250°C). In the present work titanium tetraisopropoxide (TTIP) used as precursor, combined with low substrate temperatures and nitrogen as plasma gas, lead to different crystal sizes ranging from 20 to 55 nm. By combining a higher bubbler temperature (80°C) with a pulse voltage signal and using nitrogen as plasma gas, an average crystal size of 40 nm could also be obtained for various samples. A less common precursor for anatase crystallization is also used in this study, titanium ethoxide (TEOT) which is more water resistant than TTIP. Depending on the TEOT mass flow, crystal size ranging from 10 to 40 nm were obtained. These results demonstrate the potential of crystallizing TiO2 anatase films using atmospheric plasma deposition.

Thanks/Acknowledgement
This project is funded by the F.R.S. - FNRS under the CrystallizaTiO2(N) project (Fosseur Nicolas PhD FRIA grant).

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PLATH00130

EXPERIMENTAL AND THEORETICAL STUDY OF PLASMA POLYMERIZATION INTO 3D STRUCTURES

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Understanding the role of substrate geometry is crucial for optimizing deposition on non-planar substrates. Our study was motivated by special substrate materials requested for tissue engineering, such as porous ceramics [1] or polymer nanofibrous mats [2,3]. We studied the penetration depth of the plasma enhanced chemical vapor deposition of organic films with amino, anhydride, or carboxyl groups into these microporous materials [4,5]. Besides, we developed a theoretical, analytical description of the deposition into nanofibrous material, the usefulness of which was proved by comparing it with a Monte Carlo simulation [6]. The experimental and theoretical study was extended by investigating the altered transport of film-forming species into different well-defined 3D geometries, such as microtrenches [5], cavities with a slit opening and a cavity with an undercut [7]. The deposition thickness profile in CO2/C2H4/Ar low-pressure capacitively coupled plasma with CO2:C2H4 ratio of 2:1 and 6:1 is demonstrated in Fig. 1 for cavities with three different slit widths.

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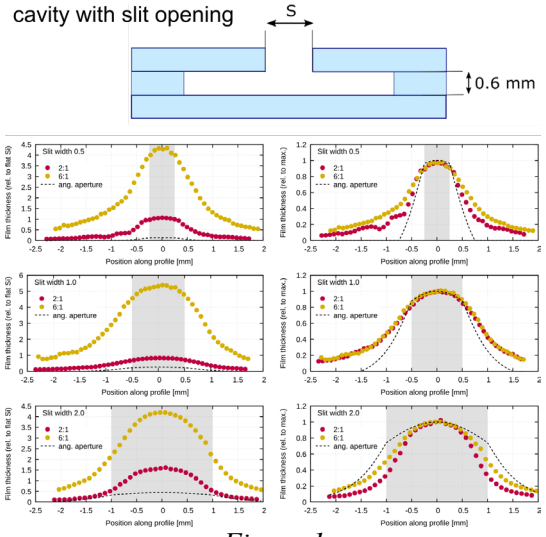

Figure 1

PLATH00045

METAL THIN FILMS GROWTH BY MAGNETRON SPUTTER DEPOSITION IN He: NUMERICAL AND EXPERIMENTAL APPROACH

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The design of porous and nanostructured materials has been of great interest to the materials science community in recent decades, as nanostructures modify the material properties and increase the specific surface area. Nanostructured thin films have improved the performance of many technological devices used in energy generation and storage, optics, catalysis etc. Magnetron sputter deposition is a versatile technique that can produce films of a large range of elements and compounds. Widely used in industry, this technique has the advantage of controlling the film microstructure and porosity by playing with different parameters (pressure, reactor geometry, power supply etc.). More recently authors have investigated the effect of the sputtering gas nature on the film characteristics. They have shown that, when He gas is used, highly porous nanofiber films or He-gas/solid composites can be elaborated [1]. Even if several studies have tried to evidence how the growth mode is affected when Ar is replaced by He, the mechanisms leading to one or the other type of films are not clearly understood [1]. The role of fast neutrals (backscattered gas ions neutralized at the target and directed towards the substrate) is suspected to be significant [2].
In this contribution we investigated the deposition of metal elements (Al, Cu, Ti) and of some of their alloys in Ar and He. Deposition was carried out by DC magnetron sputtering of pure targets in 1 Pa of Ar or He gas. SEM (scanning electron microscopy) and EDS (energy dispersion spectroscopy) were used to determine the microstructure, surface morphology and composition of the films. RBS (Rutherford backscattering spectroscopy) and EPBS (Elastic proton backscattering spectroscopy) gave the number of deposited metal atoms and the amount of He inserted in the film. The crystalline properties were analyzed by Xray diffraction.
Numerical study of the growth was conducted by molecular dynamics. SRIM simulation of the sputtering process was carried out coupled with a model to describe the transport of the emitted particles from the target to the substrate [3]. Using the calculated kinetic energies as inputs in simulations, the growth process was simulated. The main features (film morphology and porosity, He content and organization, x-ray patterns, atomic stress) of the numeric films were compared to the experiment.

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PLATH00005

INFLUENCE OF THE NATURE OF THE TRANSITION METAL IN OBLIQUE ANGLE DEPOSITION

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GLancing Angle Deposition (GLAD), also known as Oblique Angle Deposition (OAD), is a powerful technique for controlling the microstructure of thin films and, consequently, their properties [1]. This process relies on the orientation of the substrate relative to the vapor source and the resulting shadowing effect that occurs during growth. This configuration produces films with inclined columns and increased porosity.
The Tait's rule and the tangent rule are the two models commonly used to correlate the column tilt angle with the incidence angle. While the column tilt angle is typically obtained through SEM cross-sectional observations, the incidence angle can be easily calculated using numerical simulations, such as SIMTRA [2]. However, these models do not account for the chemical nature of the deposited material, including atomic mass and crystalline structure.
In this study, we investigate the deposition of nine transition metals from three different groups: Ti, Zr, and Hf (hcp structure), Cr, Mo, and W (bcc structure), and Cu, Ag, and Au (fcc structure). The surface morphologies and columnar microstructures are analyzed and discussed. An emphasis is put on the prediction of column tilt angle related to the deposition angle facing simulated and experimental architectures. A classification of these sputter-deposited metals is even suggested as function of their crystalline structure, and atomic number in periods and groups.

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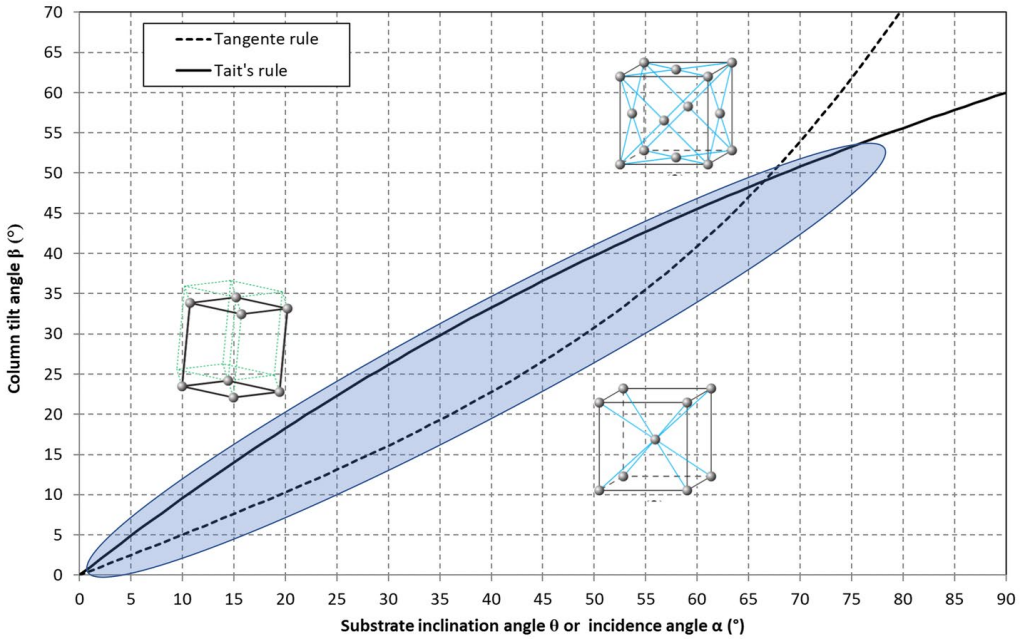

Colum tilt angle vs. incidence angle

PLATH00108

KINETIC MONTE CARLO SIMULATION OF HETERO-EPITAXIAL DEPOSITION OF METAL ONTO SILICON SUBSTRATE; INFLUENCE OF MULTISTEP DEPOSITION PROCESS

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Over the years, numerous studies have demonstrated a complex dependence of the thin film microstructure and the resulting properties on the deposition conditions and the characteristics of the deposited species. In this respect, prior work using real-time growth monitoring of polycrystalline Cu films on SiO_2 substrate has revealed that the thickness at which the film becomes continuous is affected by multistep deposition process, but in opposite way depending on whether the interruption of the deposition process occurs before or after the percolation threshold. In the framework of the INTEGRAL project, a dedicated Kinetic Monte Carlo (KMC) model based on 3D rigid lattice has been developed to study the sputter deposition of Cu thin films. To better understand these experimental findings, we have performed simulations of deposition of copper on both Cu (100) and Si(100) substrate. Beside deposition and diffusion events, atomistic mechanisms relevant to growth under energetic deposition conditions, such as re-sputtering, bulk defect creation, have been explicitly considered.
The present contribution is focused on simulation results on reentrant smooth growth and on the effect of multistep deposition process for homoepitaxial (Cu on Cu(001)) and heteroepitaxial (Cu on Si(001)) systems. So specific diffusion mechanisms of Cu on Si(001) and their energetic quantities, have been calculated and are taken into account as well as the anisotropy of Cu surface diffusion. To study the reentrant smooth growth, simulations have been done at temperatures varying between 150K and 450K and deposition rates from 0.1ML/s to 100ML/s. Considering the funneling mechanism and Ehrlich-Schwoebel barrier, the simulation results agree with the experimental and simulation ones. Concerning the effect of multistep deposition process, the temperature was fixed at 350K and the initial deposition time was chosen in such a way that the relaxation period starts before and after the 2D percolation of the deposited film. Different deposition rates and relaxation times were considered. The results show that the variation of the continuity thickness, depending on when the interruption of the deposition process is done, is in a good qualitative agreement with the experimental results mentioned before.

Thanks/Acknowledgement
Acknowledgment:this work is supported by the French ANR project “INTErface reactivity, microstructure and stress Evolution during thin film GRowth: multi-scALe modelling and experimental validation (INTEGRAL)” (Reference ANR: # ANR-19-CE08-0024-01)

PLATH00075

DRY ETCH PROCESS DEVELOPMENT OF GAPLESS SILICON NITRIDE MICROLENS ARRAY FOR CMOS IMAGER SENSORS

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CMOS Image Sensors (CIS) are composed of three critical functional layers above CMOS. Photodiodes converts photons into electrical signal. For visible applications, color filter array selects the wavelengths sent to the photodiodes. Finally, microlenses array focuses photons towards the photodiodes through the color filters.
Microlenses are usually made of a cross-linked polymer material. In order to improve the focusing properties of microlenses, the implementation of high refractive index (>1.7) microlenses could be a promising alternative. We propose to investigate the patterning of silicon nitride (SiN) microlenses at small pitch (<1.5µm).
The process flow is as follow. First, photoresist (PR) microlenses are obtained by photolithography followed by thermal reflow. Then, the PR microlenses are transferred into SiN using plasma etching. The etch step is critical because it must close the gap between microlenses to minimize signal loss by non-focalized photons [1]. In addition, the hemispherical shape of microlenses need to be preserved.
The goal of this work is to identify the etch parameters controlling structures morphology and to achieve gapless SiN microlenses with hemispherical shape. Studies are conducted in a 300mm Dual Frequency Capacitively Coupled Plasma etch reactor using SiN and PR blanket wafers, and patterned wafers with PR microlenses on SiN. Etch rate, etch selectivity and microlens morphology are characterized using ellipsometry, SEM and 3D AFM.
As a result, three parameters are identified to reduce the gap between microlenses during transfer: temperature, LF and HF plasma power. Figures 1&2 show SEM pictures of microlenses before and after optimized etch process, demonstrating SiN gapless microlenses and good morphology.

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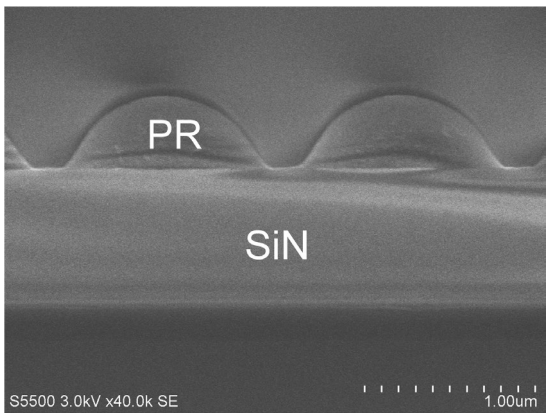
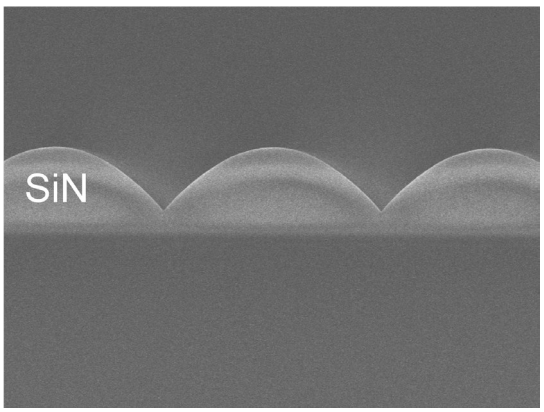


SEM of microlenses after PR thermal reflow



SEM of microlenses after etch transfer

PLATH00104

DEVELOPMENT OF PLASMA ALE FOR B-Ga_2O_3 USING THE GAS MIXTURE SF_6/Ar AND CH_4/H_2

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Atomic Layer Etching (ALE) is a cyclic process aimed at controlling etching at the nanoscale or at the atomic monolayer level. In this process, the etched thickness is controlled by plasma-surface reactions [1]: two half-reactions—modification and activation. Additionally, ALE process can enable surface smoothing and better control of morphological and stoichiometric defect density, potentially leading to improved material performance in advanced fabrication applications. Despite the general advancement of ALE processes, questions remain about the fundamental mechanisms involved in both the modification and activation steps depending of the target material.

This work aims to characterize plasma atomic layer etching processes for β-Ga_2O_3 using the gas mixture SF_6/Ar and CH_4/H_2. The growing interest in this material is due to their promising applications in the fields of power electronics (SBD, Field Effect Transistors (FETs), RF switches) and optoelectronics (UV-VIS optical devices). Indeed, β-Ga_2O_3, a wide bandgap semiconductor, has a low intrinsic carrier density at high temperatures, a high breakdown electric field (8 MV/cm), and a large electron-hole pairing energy. The study aims to investigate the mechanisms involved in the modification and activation steps and examine the impact of process parameters such as plasma species flux, energy, and exposure time on the etching process. Additionally, the evolution of the surface's chemical composition, structure, and morphology after both steps, as well as the etch rate, will be examined. These surface changes after ALE etching will be determined using in situ and ex situ characterization techniques, such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD).

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PLATH00046

PLASMA CRYOGENIC PROCESSES APPLIED TO SiO_2 DEEP ETCHING

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Cryogenic etching was first dedicated to silicon deep etching [1]. The standard process consists in lowering the temperature of the substrate holder down to typically -100°C while running a SF_6/O_2 plasma. At this very low temperature, a SiO_xF_y layer forms on the silicon trench sidewalls. This is the so-called standard cryoetching process. Then, the STiGer process was introduced to enhance the passivation by SiF_4/O_2 plasma [2]. Cryogenic processes were also applied to the structuration of porous low-K material and to atomic layer etching. [3, 4]. More recently, cryoetching has attracted the attention of industrialists for 3D-NAND applications, for which alternatively stacked thin layers of SiO_2 and Si_3N_4 must be deeply etched. Even if fluorocarbon gases have traditionally been employed to etch such dielectrics, it turns out that some limitations are encountered, which could delay the development of such devices. A cryogenic process involving HF and H_2O plasma mixture was proposed in 2023 to form 100 nm diameter holes having a depth as high as 10 µm. [5]
SF_6/H_2 plasma mixture can be used to form HF at the SiO_2 surface cooled down to a low temperature. Such a process has been investigated in an Inductively Coupled Plasma reactor. As shown in figure 1, the etch rate (ER) can be enhanced by a factor of three, reaching a value close to 1 µm.min^{-1} for a H_2 content of 62.5%. The involved mechanism was studied using different diagnostics such as Optical Emission Spectroscopy, in-situ Spectroscopic Ellipsometry and mass spectrometry. The role of the low temperature was investigated and the desorbed species were analyzed during the wafer warming indicating some favored chemical reaction schemes at the surface.

Thanks/Acknowledgement
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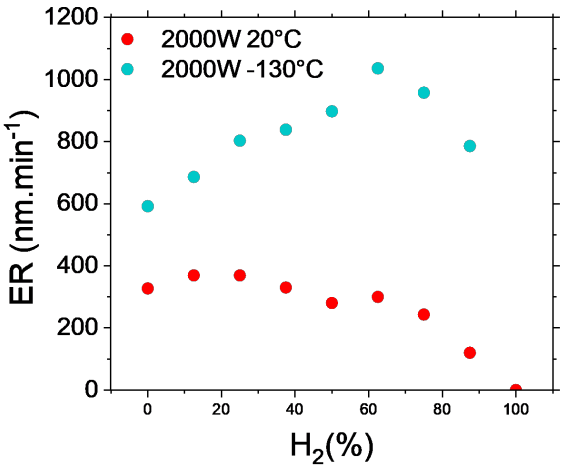

SiO2 ER Vs H2 % in SF6/H2 plasma at 20C and -130C

PLATH00090

NUMERICAL SIMULATIONS AND ION BEAM EXPERIMENTS FOR THE ANALYSES OF SURFACE REACTIONS FOR REACTIVE ION ETCHING

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Molecular-dynamics (MD) simulations of reactive ion etching of Si, SiO2, and SiN with halogen-based ions such as F+, Cl+, Br+, I+, CFx+, NFx+, and SFx+ as well as physical sputtering of those materials by inert-gas ions such as Ne+, Ar+, Kr+, and Xe+, have been performed to predict the etch yields (i.e., sputtering yields) as functions of the ion incident energies and to clarify the associated surface chemical reactions. Mass-selected ion beam experiments with surface chemical analyses have also been used to determine the etch yields and chemical states of the etched surfaces. If both simulation and experimental results are available, they have been compared and used to clarify the etching mechanisms. In this presentation, the author will first review classical schemes to construct the interatomic-force fields and potential functions needed for MD simulations and, then discuss the recent methods to construct them with machine learning techniques and interatomic potential and force data obtained from density-functional-theory (DFT) calculations of small atomic clusters. Using some of the latest examples of MD simulation and ion beam experimental data, the author discusses the difficulties and challenges of MD simulation methods to predict thermally-driven dry chemical etching processes.

PLATH00107

ENHANCING PLASMA ETCHING EFFICIENCY VIA PHYSICS-BASED MODELING, EXPERIMENTAL MEASUREMENTS, MACHINE LEARNING, AND OPTIMIZATION ALGORITHMS

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The optimization of plasma etching processes using multidimensional physics-based models (PBMs) entails a very high computational cost due to the heavy computations required for the solution of the models. In this study, a generic framework for the optimization of the plasma etching process is developed following a holistic approach, which combines multidimensional PBMs, experimental data, machine learning, and optimization algorithms.
The development of the PBM of the framework starts with the compilation of the reaction sets for volumetric and surface reactions followed by the construction of a 2D axisymmetric reactor-scale model, incorporating mass balances for the heavy species and electrons, electron energy balance, momentum conservation equation, gas energy balance, Ampere's law, and Poisson's equation. The PBM is calibrated with apt experimental measurements and then is iteratively run to generate training data for a feedforward neural network model (FNNM). The FNNM predicts the etching rate along the wafer's radial direction based on the reactor operating conditions. In a case study of PMMA etching (blanket samples) by Oxygen plasma in an ICP reactor, the FNNM achieves a maximum deviation of 7.5% from PBM results; in Figure 1, the distribution of the % deviations as well as the etching rate along the wafer's radius for the maximum deviation is demonstrated. Besides and beyond the high accuracy, the computational cost of the FNNM is three orders of magnitude smaller than that of PBM rendering the optimization of the process feasible. An optimization problem is formulated with an objective function that considers the process efficiency (etching rate magnitude and uniformity for the case study), as well as the resources' consumption, energy cost, and environmental footprint. Using successive quadratic programming and the FNMM for search acceleration, an optimal solution is reached.
We envisage that the proposed generic framework will be a universal solution to provide answers to important questions regarding the cost, the uniformity, the process drifts, the environmental footprint, and the design of new plasma etching recipes.

Thanks/Acknowledgement
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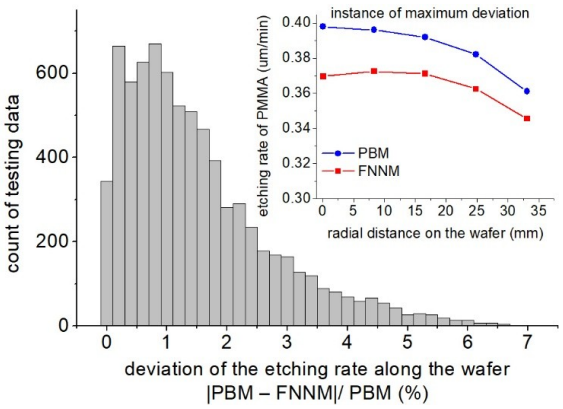

PLATH00049

FORMATION OF BLACK SILICON MICROSTRUCTURES BY THE STIGER ETCHING PROCESS FOR MICROFLUIDIC APPLICATIONS

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Wettability is a key parameter that plays a crucial role in microfluidic devices, especially for geoscience applications. One of the main challenges in these devices is controlling wettability at interfaces and along the inner walls of microfluidic chips. Previous work has demonstrated that chemical surface treatments using atmospheric plasma jets injected directly into the microchannels can control surface wettability. However, this approach is complex, and its effect is short-lived, diminishing after only a few passes of the microfluidic flow [1].
To overcome these limitations, we propose an alternative approach: forming black silicon (BSi) directly on the surfaces and walls of the microchannels by plasma etching. BSi exhibits exceptional intrinsic properties: it can be either hydrophilic or hydrophobic depending on plasma process conditions. Moreover, this method requires no masking step and results in a high surface area, making it a promising candidate for microfluidic applications.
This study focuses on the formation of BSi on all the inner surfaces of microfluidic channels using a cryogenic etching process with an SF_6/O_2 plasma in an over-passivation regime. This method creates very rough surfaces, providing an extended control of flow in microfluidic devices. For this approach to be effective, it is essential that the plasma sheath penetrates the etched cavity, with a good conformity with the sidewalls, as shown in figure 1. Therefore, wettability can be controlled on all the channel surfaces.
The STiGer [2] process was used to form BSi, alternating plasma etching steps (typically using SF_6/O_2) with passivation steps (using SiF_4/O_2 plasma) at cryogenic temperature. Our results show that, in an over-passivation regime, the oxygen fraction in the SiF_4/O_2 plasma and the bias voltage are the most critical factors for controlling the surface morphology and consequently its wettability.

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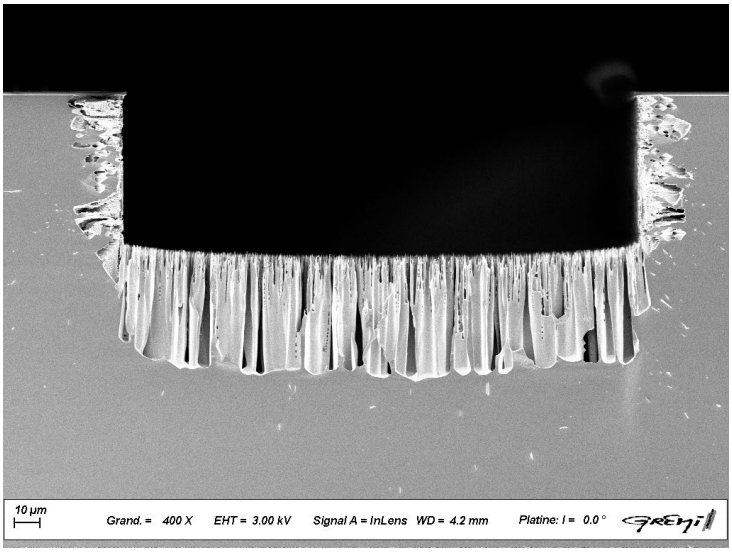

BSi microstructures on microchannel sidewalls

PLASMA RESPONSES TO TAILORED VOLTAGE WAVEFORMS IN CAPACITIVELY COUPLED PLASMAS

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Because of developments in pulsed power supplies, tailored voltage waveforms are becoming available for semiconductor etching tools. This feature was initially proposed to provide nearly monoenergetic ion energy distributions at the wafer surface. However, this has also enabled flexibly changing the waveform shape to tailor the ion energy distribution (IED), incidentally modifying other plasma behavior. Etching depends not only on the IED, but also on the plasma chemistry and the electron energy and angular distributions at the wafer. In order to leverage these emerging capabilities, a detailed understanding of the effect of waveform tailoring on each of these is required.
In this study, simulations and fast camera imaging of a capacitively coupled plasma with waveform tailoring are used to investigate the plasma dynamics in response to these tailored waveforms. Modern semiconductor processes, especially those used to produce high aspect ratio features, are approaching such low pressure and high voltage that fluid approximations fail and a fully kinetic approach is required. Therefore a particle-in-cell Monte Carlo collision (PIC/MCC) model, EDIPIC [1] was used to simulate the plasma dynamics in a reactor with tailored voltage waveforms. A dual frequency capacitively coupled plasma at 5-10 mTorr of Ar is modeled with a range of conditions. The results of these simulations, with varying conditions such as waveform shape, operating pressure and voltage amplitudes are analyzed in detail.
The IEDs and electron energy distributions will be discussed, along with their implications for etching (wafer side) and erosion (upper electrode). The role of secondary electron emission was also explored by varying yields and for incident electrons and ions. For example, time resolved ion energy distributions for varying ion-induced secondary electron yields are shown in Figure 1. Fast camera imaging in the sheath also provides insight into the plasma dynamics, especially the role of high frequency in the sheath dynamics.

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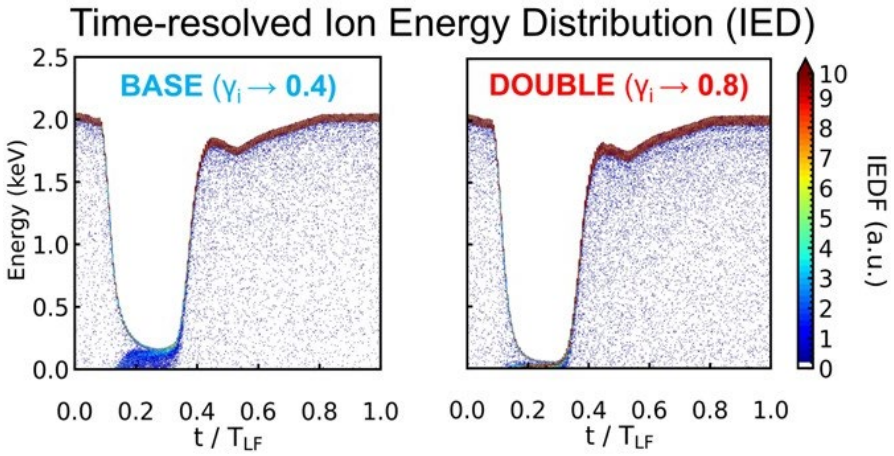

Time resolved ion energy distributions.

PLATH00121

EROSION RESISTANT PVD COATINGS ON CFRP SUBSTRATES

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Environmental challenges and European regulations push aircraft manufacturers to increase the efficiency of engines and to reduce the weight of the whole aircraft. Carbon-fiber reinforced polymers (CFRP) rose as a solution on the CFM LEAP engine to reduce the weight of the engine as the compressor fan blades, the outlet guide vane (OGV) and other elements are made of CFRP. Nevertheless, this material is vulnerable to the erosive conditions that the aircraft encounters during service. Right now, some of these elements are coated with polyurethane to reduce the erosion and increase the lifetime of the elements, but this material is targeted by REACh regulations and its substitution is a challenge for manufacturers.
To address this problem, some research has been done to coat CFRP substrates via PVD techniques with erosion resistant coatings like TiN in combination with metallic coatings like titanium, aluminum and chromium. These studies used mainly magnetron sputtering technique with laboratory scale coaters.
This study presents an original approach that combines magnetron sputtering and arc evaporation on an industrial scale Oerlikon Surface Solutions coater. Arc evaporation without filter has the reputation of coating at high temperatures (> 400°C), but it will be shown that it is possible to coat CFRP components via this process.

Trying to modify arc evaporation processes to reduce the substrate temperature during the coating can result in a dramatical loss on deposition rate and mechanical properties of the layer.
In this talk we will share a strategy to mitigate the loss of mechanical properties (H > 18GPa) while keeping an acceptable deposition rate (>1µm/h) and substrate temperature below 180 °C, which is a critical temperature for CFRP.
An extensive set of parameters is tested and their influence on deposition rate, substrate temperature and mechanical properties of the coating is reported.
The resulting arc evaporated coating is compared to a magnetron sputtered version of the same material done in the same machine. Finally, we will share some erosion test results done on this coating/CFRP system.

PLATH00067

EXTRAORDINARY OXIDATION BEHAVIOR OF W-Zr THIN-FILM METALLIC GLASSES: A ROUTE FOR TAILORING FUNCTIONAL PROPERTIES OF W-Zr-O FILMS

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Thin-film metallic glasses (TFMGs) represent a unique class of metallic amorphous films that combine the exceptional properties of bulk metallic glasses with the advantages of thin-film fabrication. As oxidation is a critical factor that directly impacts the long-term performance and durability of materials, understanding of the oxidation behavior of TFMGs is essential. The oxidation kinetics of TFMGs typically obey the parabolic rate law below their crystallization temperature. This behavior is characteristic of a diffusion-controlled process, where the transport of ionic species occurs through an oxide surface scale acting as a barrier. However, our recent investigations (10.1016/j.jallcom.2022.166599) have revealed that W-Zr TFMGs prepared by magnetron-sputter deposition deviate from this standard oxidation behavior, suggesting different oxidation mechanisms for these materials.
Therefore, the oxidation behavior of W-Zr TFMGs with 32, 48 and 61 at.% Zr was comprehensively studied. The films were sputter-deposited onto unheated, unbiased substrates in argon using two unbalanced magnetrons equipped with W and Zr targets. The investigation focuses on the effect of the annealing temperature (up to 600°C) on the oxidation process, oxygen saturation, structure evolution, and their subsequent impact on electrical, optical and mechanical properties.
The findings revealed that controlled oxidation transforms W-Zr TFMGs into amorphous ceramic W-Zr-O films with substoichiometric compositions and dense and compact amorphous structures. This is a consequence of a unique oxidation process that leads to a gradual incorporation of oxygen across the film volume due to thermodynamics factors. A higher Zr content promotes O diffusion into the amorphous structure and enhances its depth uniformity. As O saturation increases, the films become more optically transparent and less electrically conductive. The relationship between the extinction coefficient and the electrical resistivity highlights the versatility of the W-Zr-O films, enabling their tailoring for desirable combinations of optical transparency (extinction coefficient: 0.28–1.06) and electrical conductivity (resistivity: 1.7–95.7 × 10^{-4} Ω·cm). The films also exhibit remarkable hardness values ranging from 16.0 to 17.5 GPa, which surpass those of most electrically conductive and optically transparent coatings. These exceptional properties demonstrate the potential of W-Zr-O films in advanced optoelectronic and protective applications.

Thanks/Acknowledgement
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PLATH00047

DEVELOPMENT AND OPTIMIZATION OF CrN COATINGS FOR ENHANCED TOOL PERFORMANCE IN CRYOGENIC MACHINING OF Ti_6Al_4V

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Cryogenic machining has emerged as a sustainable alternative to conventional cutting fluids, reducing environmental impact while enhancing cooling efficiency at the tool-workpiece interface [1]. This study focuses on the development of protective coatings for cutting tools used in the cryogenic machining of Ti6Al4V titanium alloy. Ti6Al4V is widely employed due to its excellent mechanical properties and corrosion resistance; however, its poor machinability resulting from low thermal conductivity, high hardness at elevated temperatures, and strong chemical reactivity with the cutting tool presents significant challenges [2].
Various coatings are applied to tungsten carbide tools due to their excellent mechanical and tribological properties to improve their machining performance [3,4,5]. The present study reports the enhancement of mechanical and tribological properties of CrN coatings deposited using high power impulse magnetron sputtering (HiPIMS) technique. Several deposition parameters, such as the nitrogen flow rate, target duty cycle, target bias voltage, and the synchronization of the bias pulse (T_{on}) with the target were optimized to enhance film adhesion and density, thereby improving the tool performance.
Microstructural and morphological characterization as well as phase identification were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). Nanoindentation results revealed a maximum hardness of 33.2 GPa and an elastic modulus of 317 GPa at Ton = 110 µs. Tribological tests, conducted with a rotary tribometer, showed a friction coefficient ranging from 0.51 to 0.53 for all coatings, with a minimum wear volume of 1.13×10^{-5} mm³/Nm obtained for Ton = 210 µs. Moreover, coatings deposited at Ton = 210 µs and 310 µs exhibited superior adhesion strength, with critical loads (LC3) of 3.23 N and 3.33 N, respectively.
The CrN coating deposited at Ton = 210 µs showed the best balance between mechanical and tribological properties, confirming the important role of bias pulse synchronization in optimizing the performance of HiPIMS deposited coatings.

Thanks/Acknowledgement
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PLATH00083

ENHANCED MORPHOLOGY AND FERROELECTRIC PROPERTIES OF $Sc_{0.3}Al_{0.7}N$ SPUTTERRED THIN FILMS VIA A COMPOSITIONALLY GRADED LAYERS

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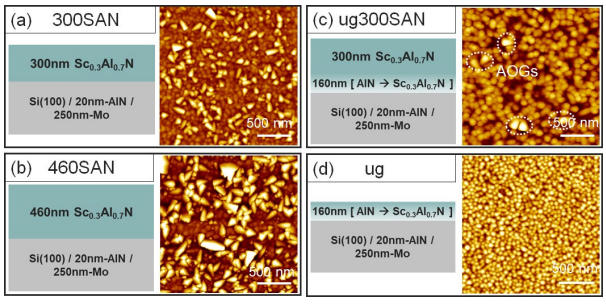
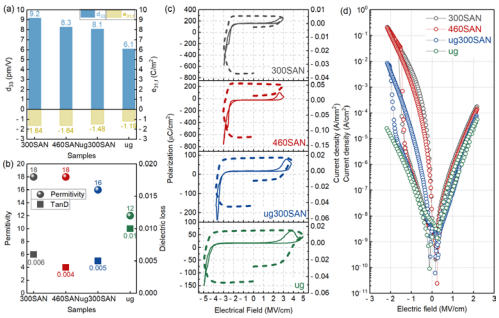
The significant enhancement in piezoelectric properties reported in 2009 and the discovery of ferroelectricity in 2019 for $Sc_XAl_{1-X}N$ alloy thin films, have drawn increasing attention not only from industry for technological-mature device applications such as RF and MEMS devices, but also from academia for fundamental understanding of unconventional ferroelectricity in wurtzite thin films. High Sc-content (≥ 30 %) $Sc_XAl_{1-X}N$ thin films are particularly valuable for MEMS and memory applications due to their higher piezoelectric coefficients, improved electromechanical coupling factor, and lower coercive fields. However, growth of high Sc-content thin films requires significant effort for the process optimization to reduce abnormally oriented grains (AOGs) and leakage currents, both of which degrade piezoelectric and ferroelectric properties. Here, we demonstrate that a compositionally graded ScAlN thin film (ugSAN), with a linear Sc concentration gradient from 0 to 30%, acts as a buffer layer that significantly suppress the number of AOGs in an over-grown $Sc_{0.3}Al_{0.7}N$ layer to approximately 1.9%, compared to the 15–38% observed in regular $Sc_{0.3}Al_{0.7}N$ thin films, without requiring additional process optimization (Figure 1). Additionally, the 10-50nm AlScN layer in the ugSAN, with lower Sc-content and wider bandgap (~ 6 eV) compared to $Sc_{0.3}Al_{0.7}N$ layer (~ 3.4 eV, *Appl. Phys. Lett. 102, 112103 (2013)*), can enhance the conduction band offset and the Schottky barrier height to the metal electrode, or. As a result, leakage current is remarkably suppressed by more than one order of magnitude for the film using the graded layer, leading in a proper ferroelectric switching. This work provides an unambiguous and effortless approach to facilitate the growth of high Sc-content ScAlN thin films, thereby fostering their integration into MEMS device applications.



Thin film configurations and their AFM images



Dielectric, piezo/ferroelectric properties

PLATH00131

CONTROL OF THE STRUCTURE OF TiN SULFIDE THIN FILMS

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Tin sulfide (SnS) is a p-type semiconducting material with a band gap of approx. 1.3 eV. This compound is a promising material for thermoelectric applications, as an alternative to SnSe with the same crystallographic phase Pbnm but with no critical chemical elements [1]. Indeed SnS may crystallize in various structures, the orthorhombic phase (Hertzenbergite, α-SnS,) being the most stable one. Other structures are also reported in the literature, such as the π-SnS one that crystallizes in a cubic structure (P213) [2].
In the present work, SnS thin films have been deposited using pulsed-DC magnetron sputtering of a tin sulfide target. The effect of the experimental deposition conditions (total pressure and substrate temperature) to the structure, the microstructure, the composition and the functional properties has been studied.
The deposition total pressure strongly influences the structure of SnS thin films. The use of low pressure (0.5 Pa) favors the growth of the metastable cubic phase. A columnar microstructure with stacking faults has been evidenced by high resolution transmission electron microscopy for the films deposited at low pressure. Deposition at high pressure (1.5 Pa) induces the synthesis of the orthorhombic phase, the most stable phase. At intermediate pressure, the films are biphased: cubic + orthorhombic. The electrical properties of the films are strongly influenced by their structure. On one hand, the orthorhombic phase exhibits a high electrical resistivity that strongly decreases the transport properties. On the other hand, the cubic phase shows a low electrical resistivity that improves the film properties.
The cubic structure being a metastable one, this phase is not obtained anymore when the films are deposited on a heated substrate. For temperature lower than 100 °C, the orthorhombic phase is the only one detected by X-ray diffraction and Raman spectroscopy. The film microstructure becomes porous when the SnS films are deposited at a temperature higher than the ambient one. Such a porous microstructure has a negative impact on the electrical properties and therefore the thermoelectric properties.

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PLATH00115

SYNTHESIS OF METAL DOPED DIAMOND-LIKE CARBON FILMS BY MAGNETRON SPUTTERING

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The diamond-like carbon (DLC) films are known for their unique properties such as high hardness, wear resistance, chemical inertness, and low coefficient of friction. Various metals (Ti, Cr, Ni, Ag, Zr, Mo, W, etc.) and nonmetals (Si, N, O, F) are used to change the microstructure and improve the properties of the diamond-like carbon films [1,2].
Mo-DLC, Ni/Cr-DLC and Ag/Ti-DLC thin films were deposited on Si (100) substrates by direct current magnetron sputtering. The graphite, molybdenum, silver-titanium and nickel-chromium cathodes were used. The arc currents were fixed at 0.5 A and 0.25 A for the Mo and Ag/Ti targets. The temperature of formation was changed by increase the distance between the substrate and target from 4 cm to 8 cm, when Mo-DLC films were formed. The metals content in the DLC films was changed by increasing the opening of a shield mounted above the magnetron target. The elemental composition, surface morphology, water contact angle, microstructure, bonding type, nano-hardness and friction forces of the Mo-DLC, Ni/Cr-DLC, and Ag/Ti-DLC films were investigated by energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and MTS-Agilent G200 nanoindenter. The EDS results indicated that the increase in the metal content enhanced the oxygen concentration in the DLC films. The highest concentrations of the oxygen were obtained for Ag/Ti-DLC films. Raman spectroscopy and XPS data revealed an increase of sp^2 carbon bonding with higher metal dopant concentrations. The increase of the deposition temperature led to the graphitization of the Mo-DLC films. The friction coefficient of the Mo-doped DLC films depended on the structure and composition of the films. The nano-hardness and the Young's modulus of the Mo-DLC, Ni/Cr-DLC and Ag/Ti-DLC films was enhanced with addition of low amount of metals. However, the type of used metal also affected the nano-hardness of the doped DLC films. The increase of the Ag/Ti concentration in the films resulted in the enhanced friction coefficients, correlating with increase surface roughness. The nano-friction coefficient of the doped DLC films strongly depended on the type of used metals.

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PLATH00057

THE EFFECT OF ION POTENTIAL ENERGY ON THIN FILM CRYSTALLINITY IN PULSED FILTERED CATHODIC ARC DEPOSITION

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Filtered pulsed cathodic arc plasma is known for deposition of dense and often well-adherent thin films. These film properties are in large part due to multiply charged ions delivering significant kinetic and potential energies. The role of ion potential energy in film formation remains under-explored, since the enhancement of charge states in cathodic arcs is coupled with an increase of ion flux and ion kinetic energies, hence it is difficult to parse the individual effects. In this work, the effect of ion potential energy on crystallinity of thin films is studied, while the mean ion kinetic energies are kept unchanged. Two deposition scenarios are considered: non-reactive deposition of metallic V-Al and reactive deposition of compound V-Al-N films. For V-Al plasma and thin films, the impact of metal ion potential energy is clearly demonstrated. In the V-Al-N case, in addition to metal ions, activated (namely, ionized, dissociated, and excited) nitrogen species are shown to be a significant factor that enables the crystalline growth of the metastable cubic phase.

PLATH00070

ASSISTING PLASMA DIAGNOSTICS WITH ARTIFICIAL INTELLIGENCE METHODS: TRENDS AND APPLICATIONS IN NON-EQUILIBRIUM PLASMAS OPERATING FROM MODERATE-TO-ATMOSPHERIC PRESSURES

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Recent studies have demonstrated that Artificial Intelligence (AI) methods—ranging from unsupervised techniques, like principal component analysis, to supervised algorithms such as multilayer perceptron neural networks—can rapidly and accurately extract key plasma parameters from complex diagnostic data (e.g., optical emission spectra and imaging data) [1]. These approaches not only streamline the interpretation of diagnostics but also enable even real-time monitoring of plasma quantities such as electron temperature and density, providing valuable feedback for process development and control.
In this work (Fig.1), representative state-of-the-art AI frameworks that integrate with conventional plasma diagnostic tools will be discussed as well as their applications in diverse fields including materials processing, plasma medicine, and environmental remediation. Specific applications will be discussed on the use of AI algorithms to study two types of plasmas based on their optical emission spectra, an Atmospheric Pressure Surface Dielectric Barrier Discharge [2] and a Micro-Hollow Cathode Discharge [3]. It will be shown how AI can assist plasma diagnostics, improving parameter estimation accuracy (e.g., applied voltage, temperature), and uncovering hidden correlations within large diagnostic datasets (e.g., power deposition modes and plasma uniformity)—paving the way for more robust, adaptive, and intelligent plasma systems.

Thanks/Acknowledgement
SPECTRON (ANR-23-CE51-0004-01), Labex SEAM (ANR-10-LABX-0096; ANR-18-IDEX-0001)

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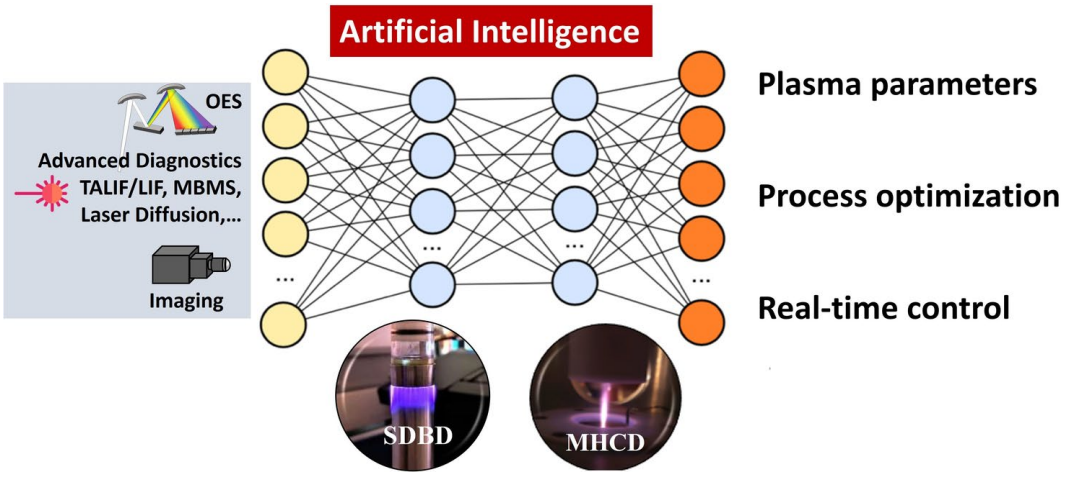

Integration of AI with plasma diagnostics

PLATH00019

M-SECOND PULSE AND RF COUPLING IN AN APPJ

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The challenge of obtaining a diffused discharge in open air can be faced with several approaches from RF jets to nanopulses. We already showed that a possibility is offered by coupling two frequencies respectively in the kHz (LF) and MHz (RF) ranges [1]. This dual frequency configuration allows to expose a dielectric substrate to a RF plasma in the Ω regime and to ignite the γ phase only in selected fractions of the LF and RF period. The advantage of the configuration is linked to the control of the ion-surface interaction and to the low sensitivity to substrate distance. However, the discharge is not stable.
Here, substituting the LF with a micropulse generator we show the stabilization of the discharge which gives further insight in the plasma-substrate interaction control and discharge characteristics.
The jet is a 6mm alumina tube with two outer ring electrodes. The upstream electrode is connected to a micropulse power supply, while the other to a 27 MHz RF generator. Ar gas is flown inside the tube and a silica slide substrate is placed at 5mm from the outlet.
The ICCD images of the micropulse coupled with the RF at different stages show light emission also tens of μs after the pulse (Fig. 1). Focusing close to the substrate, the single photons are counted and their modulation at 27 and 54 MHz is extracted, representing respectively the γ and Ω regimes. These regimes switch depending on the μ-pulse electrode voltage. A 2D model developed in COMSOL fully agree with this presentation highlighting the γ phase ignition as a function of the sheath voltage in front of the substrate.
The optical emission spectroscopy shows that the plasma density does not change as a function of the RF power, however it increases the number of filaments and slowly the gas temperature. The results therefore highlight that the substitution of the LF with the microsecond power supply allows to stabilize the discharge, enabling its use for a dose control.

Thanks/Acknowledgement
CloudVeneto is acknowledged for the use of computing and storage facilities.
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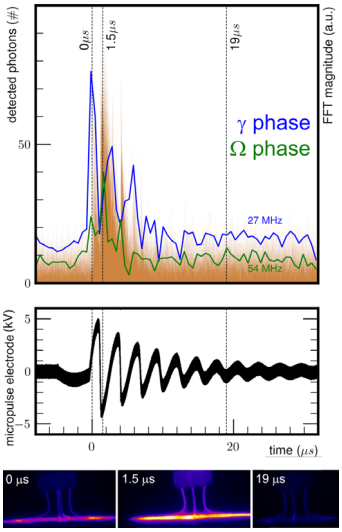

μpulse+RF coupling optical emission time resolved.

PLATH00024

COMPARATIVE ANALYSIS OF ns- AND ps-TALIF DIAGNOSTICS OF ATOMIC OXYGEN GENERATED WITH A PLASMA JET DRIVEN BY A TAILORED VOLTAGE WAVEFORM

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Atomic oxygen (AO) generated by non-thermal atmospheric pressure plasma is the key species for application in contactless cleaning of heat sensitive objects. The generation pathway of AO has been investigated with different diagnostics. In this study, we compared measurements of AO spatial density distribution obtained via nanosecond two-photon absorption laser-induced fluorescence (ns-TALIF, using dye laser and ICCD camera) and picosecond TALIF (ps-TALIF, using solid-state optical parametric generator (OPG) and streak camera). The temperature and density distribution of the quenchers in the effluent were determined from independent CFD simulations validated by additional experiments with identical jet source and conditions. AO was generated in the plasma jet driven by tailored voltage waveforms which superimposed the base frequency (f_0 = 13.56 MHz) and the second harmonic (f_1 = 27.12 MHz). Experiments were independently conducted with the following varying parameters: gas flow rate, operational electric power, and relative phases of the harmonics. Results from ns- and ps-TALIF show good consistency; the introduction of harmonics in the driving waveform enhances both density and lifetime of oxygen atoms at relatively high operational powers (≥7 W). In particular, when the relative phase of the second harmonic is shifted from 90° to 270°, the oxygen atoms density in the far field (≥10 mm from the outlet) more than doubles. These observations are attributed to the establishment of a DC bias between the electrodes due to the tailored waveforms, which modifies the electron energy and thus enhances oxygen dissociation. Notably, on the one hand, ps-TALIF demonstrates a better time-related calculation at atmospheric pressure for the quenching coefficient, where the sub-10 ps laser pulse greatly limits the depletion of laser-excited state, and the high temporal-resolution ($\Delta\tau \geq 1$ ps) of streak camera allows captures as brief as 50 ps. On the other hand, ns-TALIF exhibits better signal-to-noise ratio (≥ 10 dB) in spatial profiling applications, particularly in low-density regions (< 10^{22} m^{-3}). These characteristics suggest different uses for ps-TALIF and ns-TALIF: time-resolved kinetics and high-sensitivity spatial mapping studies, respectively.

Thanks/Acknowledgement

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PLATH00093

DESCRIPTION OF H-ATOM ABSOLUTE DENSITIES AND SUB-ns DECAY TIMES IN A PULSED MICROTUBE PLASMA JET USING ps-TALIF AND A STREAK CAMERA

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The use of ns-TALIF in atmospheric pressure plasmas shows ineffectiveness for resolving the laser-excited states effective lifetime (τ). This is due to strong collisional quenching of fluorescent states which can decrease τ down to ~100s ps. A solution is to employ ps-TALIF with typical laser pulses as small as few ps [1]. Compared to ns-TALIF, in ps-TALIF the two-photon excitation is significantly faster than the fluorescence decay. This makes it perfect for directly resolving decay times of different reactive atoms (H, N, O, …) in atmospheric pressure plasmas. To measure such small decay times, detectors with exceptional temporal resolution are necessary. Streak cameras, with a temporal resolution as low as a few ps [2,3], are perfect solutions in this case. However, the implementation of ps-TALIF and streak camera diagnostics needs specific precautions.
This work presents a ps-TALIF and streak camera diagnostic platform for the direct measurement of atomic decay times in atmospheric pressure plasmas. The capacity of the system is showcased through the exemplary measurement of the τ and absolute density of H-atoms in a pulsed microtube helium plasma jet (MHPJ). The τ of (50–400 ps) and density (1014–5.5×1014 cm-3) of H-atoms depend on the distance from the tube exit. At its smaller time range (TR=100 ps), the streak achieves its highest time resolution (~1 ps), thus allowing a direct measurement of the laser pulse (Fig.1). However, the TR should be increased to 5–10 ns when capturing TALIF, which is distorted by the streak's instrumental function [3]. Therefore, a methodology is proposed to remove this distortion and extract the actual TALIF signals.

Thanks/Acknowledgement
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SESAME DIAGPLAS

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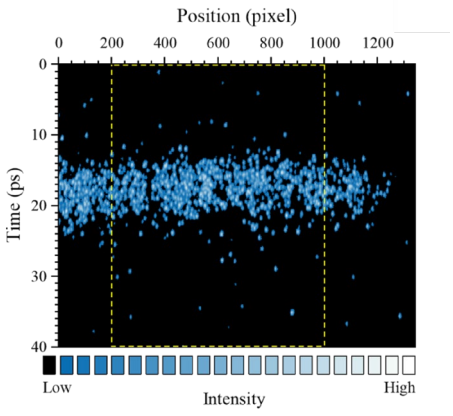
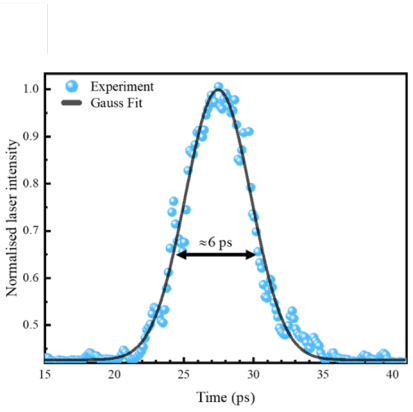


Streak image of the laser pulse profile 205.08 nm



reconstructed laser pulse temporal profil

PLATH00082

UNRAVELING NO PRODUCTION IN N_2–O_2 PLASMAS WITH 0D KINETIC MODELING AND EXPERIMENTAL VALIDATION

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Driven by the importance of nitrogen fixation for fertilizer production, we studied the mechanisms of nitric oxide (NO) formation in N2-O2 plasmas, comparing experimental data with modeling results. The experiments used radiofrequency (13.56 MHz) plasma discharges at 5 mbar pressure, with oxygen concentrations ranging from pure N2 to air-like mixtures (see figure 1). Power levels ranged from 40 to 120 W, with a constant mass flow rate of 100 sccm. On the modeling side, we solved the Boltzmann equation for electrons and rate balance equations to describe heavy species kinetics, including vibrational processes [1]. To account for ground state NO(X) generation at the reactor wall, we combine the volume chemistry with a mesoscopic description of the surface, taking into account adsorption sites and various elementary surface phenomena. Comparisons between experiments and modeling demonstrate very good agreement, extending beyond NO(X) formation to encompass other species in the plasma such as N2O(X) and atomic nitrogen N(4S). Noteworthy findings include (i) the pivotal role of surface mechanisms in NO(X) production, particularly at low oxygen content values; (ii) the significance of describing the postdischarge phase, where depletion of plasma species occurs at different time scales; and (iii) the importance of electronically excited states (e.g., O2(b)) in elucidating NO(X) formation dynamics. This work makes an important step toward formulating a reaction mechanism for N2 and N2–O2 plasmas applied to nitrogen fixation, covering both volume and surface mechanisms, and lays a robust foundation for future research, particularly in the presence of catalysts [2].

Thanks/Acknowledgement

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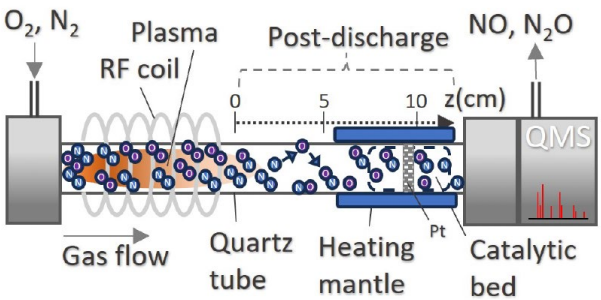

RF plasma setup used to convert N_2-O_2 into NO

PLATH00097

TIME-RESOLVED BAYESIAN ANALYSIS OF LOW-PRESSURE MISTY PLASMAS USING A COLLISIONAL-RADIATIVE MODEL COUPLED TO OPTICAL EMISSION SPECTROSCOPY

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Optical emission spectroscopy (OES) is widely used for non-invasive, real-time plasma characterisation. OES data is often coupled with sophisticated collisional-radiative modelling (CRM) to get in-depth insight on the fundamental properties of the plasma. The CRM comes with a number of adjustable parameters, whose values must provide the best agreement between the measured and simulated spectra. This work presents an OES/CRM method with a twist: the search for the best-matching spectrum is framed in terms of probability, to take full advantage of the principles of Bayesian inference. Some of the tools provided by Bayesian analysis are illustrated in the specific case of OES/CRM diagnostics. Both experimental and modelling uncertainties are taken into account in a rigorous mathematical framework, and results are expressed as probability distributions rather than single error-minimizing values. Time-resolved data is used to define proper prior distributions. The question of model selection is addressed through the estimation of the Bayesian evidence of each candidate CRM, so that the Bayes factor can be used as a quantitative metric to filter out superfluous adjustable parameters. Low-pressure “misty” plasmas, in which liquid droplets are injected as aerosols, are used as an adequate case study: they are complex in nature, subject to time-dependent changes, and require non-invasive diagnostics as they are usually employed for thin film deposition. Results include the temporal evolution of the electron temperature, electron density, and quenching frequency of metastable species during the pulsed injection of liquids in an argon plasma, all extracted from OES measurements.

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PLATH00099

TRANSIENT BEHAVIOR OF CHARGED PARTICLES IN PULSE-MODULATED INDUCTIVELY COUPLED Cl_2 DISCHARGE

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Recently, a new plasma etching technique called transient-assisted plasma etching (TAPE) has been proposed, in which both the discharge source power and gas flow are pulse-modulated to control the ion-to-neutral flux ratio reaching the substrate. Since the gas flow is simultaneously modulated, the transient behavior of charged particles becomes more complex than in cases where only the source power is modulated, as their creation and loss processes are coupled with neutral gases. In this study, we investigated the transient behavior of charged particles in pulse-modulated inductively coupled Cl_2 discharge under low-frequency modulation, which is applicable to TAPE, across various discharge conditions (source power, pulsing frequency, and pressure). We employed the Fourier cutoff probe[2] for electron density measurements and a quadrupole mass spectrometer with an electrostatic energy analyzer[3] for ion flux measurements. The results show that electron and ion densities exhibit well-modulated behavior during pulsing. It indicates that the pulse modulation period is shorter than the inverse of the effective generation and loss rates of charged particles. A simple particle balance model was used to analyze this transient behavior. This study contributes to the optimization of TAPE processing and enhances the understanding of the underlying etching mechanisms.

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FUNDAMENTAL DIAGNOSTICS AND MODELING OF STREAMER DISCHARGE AND ITS APPLICATION FOR CANCER TREATMENT

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Streamer discharge is a representative form of cold plasma generated in ambient air. To elucidate its radical production and reaction mechanisms, we have employed various laser diagnostics. However, the random branching and filamentary nature of streamer discharges poses challenges for laser spectroscopy, as the random discharge filament does not always intersect the laser-irradiated region. To address this problem, we developed a single-filament streamer discharge system composed of a single, unbranched filament [1]. This setup enables precise laser spectroscopic measurements and allows comparison with two-dimensional simulations, as the discharge is pseudo-two-dimensional, similar to the computational model.

In this study, we present laser spectroscopic diagnostics of single-filament streamer discharges. These include measurements of the electron energy distribution function and negative charged particles (electrons and negative ions) using laser Thomson scattering [2]; electron density using a dual-wavelength Talbot interferometer system; electric field vectors via electric-field-induced second harmonic generation (E-FISH); and radical species densities using laser-induced fluorescence (LIF) and two-photon absorption LIF (TALIF). We also compare these experimental results with two-dimensional simulation data for validation [1].

Beyond fundamental studies, streamer discharge has promising applications, including cancer treatment. Previous studies have demonstrated that streamer discharge treatment of tumors in mice can induce antitumor immune responses, resulting in an *abscopal effect*—a systemic therapeutic effect at sites distant from the treated tumor [3]. Remarkably, this effect has been observed even when only normal tissue, distant from the tumor site, is treated [4]. Furthermore, applying streamer discharge to tumor-resected sites in mice suppresses tumor recurrence [5]. When combined with immune checkpoint inhibitors (ICIs), the treatment exhibits a synergistic antitumor effect in mouse models. These therapeutic applications of streamer discharge, along with experimental evidence supporting its efficacy, will also be presented.

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PLATH00055

REACTIVE SPUTTERING ONTO IONIC LIQUID, A NEW PROCESS TO SYNTHESIZE COMPOUND NANOPARTICLES

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Nanoparticles (NPs) are nowadays extensively studied because of their unique properties which can be exploited in various fields, such as catalysis, optics, electronics, and medicine. Among the different chemical routes able to synthesize them, the sputtering onto a liquid is an original method to obtain NPs with a mean diameter lower than 10 nm and with very sharp size distribution. It also presents the advantage to form NPs without any side-product.
Up to now, this technique was mainly used to form metallic NPs. In this study, we investigate the possibility to synthesis compound NPs using this process in reactive mode. Hence, we sputtered a pure Bismuth target applying a radiofrequency power onto ionic liquids into inert (Ar) and reactive atmospheres ($Ar/O_2/CF_4$). Non-reactive sputtering in pure Argon plasma onto $[C_1C_4Im][NTf_2]$ liquid produces spherical, crystallized and well-dispersed pure Bismuth NPs of 4–6 nm in diameter. Introducing O_2 and CF_4 gases enables to form crystallized Bi-oxyfluoride NPs with mean size around 8 nm and presenting photocatalytic activity. Surprisingly, the NPs composition obtained in reactive mode may differ from the thin film ones, deposited in the same time. The processes involved to control the NPs composition were then investigated by exploring the effect of various ionic liquids (changing their anionic or cationic parts) with different physical properties (surface tension, viscosity…). The composition of nanoparticles is analysed by XPS, XRD and Raman spectroscopy; whereas size distribution and dispersion properties are determined from microscopy. In parallel, the influence of the liquid presence into the reactor on the plasma itself is explored by optical emission spectroscopy to draw a general scheme elucidating the formation of Bi-based compounds NP by sputtering onto a liquid in reactive mode.
Moreover, controlling the NPs composition paves the way for their use in photocatalysis. Hence, metallic NPs is associated with semiconductor to enhance its light absorption thanks to plasmonic effect; while the high specific surface aera of Bismuth oxyfluoride NPs allow to improve its photocatalytic performances. Both systems are tested for water remediation and CO_2 photoconversion.

PLATH00058

SPUTTERING OF SILVER ONTO SILICONE OILS: NANOPARTICLE FORMATION AND MASS TRANSFER INTO THE BULK SOLUTION

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Nanoparticles (NPs) synthesis by low-pressure plasma-based sputtering of metal atoms onto liquid substrates offers several advantages [1]. Three scenarios are described for the formation mechanism by sputtering onto liquid: (1) nucleation occurs at the surface then particle diffuse and formed NPs in liquid (2) both processes occurs at the liquid surface (3) all step occurs in the liquid[2]. However, NP formation mechanism is not well understood. In particular, influence of liquid viscosity, as well as kinetic energy of metal atoms interacting with the liquid surface, deserve detailed investigations. To better understand these relatively complex phenomena, operando absorption spectrophotometry has been set up [3] and used to record time- and space-resolved spectra of the liquid into which the sputtered metal atoms are incorporated.
Using a silver target and silicone oils, we studied the liquid viscosity effect, sputtering power, and type of sputtering plasma. In particular, we compared the NPs formation when using a DC magnetron sputtering (DCMS) discharge and a bipolar high-power impulse magnetron sputtering (BHiPIMS) plasma. With BHiPIMS, kinetic energy of metallic species is increased from a few eV up to 300 eV. [4]
This study shows that diffusion is slower as viscosity increases but it increases linearly with applied power due to a combination of liquid heating and the concentration gradient created. Moreover, NPs diffusion in liquid is faster if metal atoms are sputtered with BHiPIMS plasma as the atoms have a higher kinetic energy in BHiPIMS and penetrate deeper into the liquid sub-surface region. These effects affect the nanoparticle formation mechanism. It has been found that, with viscosity, nanoparticle formation can switch from one scenario to another, sputtering power affects nucleation rate and sputtering regime also affects the way nanoparticles form.

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PLATH00030

FORMATION OF Ru CATALYTIC NANOPARTICLES ONTO POLYETHYLENE GLYCOL BY PLASMA SPUTTERING

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Development of metallic nanoparticles (NPs) materials with high catalytic and electrocatalytic potential by using innovative methods is essential for hydrogen storage. For this application, we synthesized Ru metal NPs in polyethylene glycol (PEG) by the sputtering on liquid (SoL) method, which is a favorable technique for the synthesis of ultra-pure NPs, halfway between the physical and chemical methods. Therefore, this process does not require an additional stabilisation step, while still being capable of synthesising NPs of controlled size, shape and purity.
The initial step of this study focuses on the diagnostic of the plasma phase by means of optical emission spectroscopy (OES). This allows for highlighting particularly the plasma/liquid interactions by showing the presence of excited species originating from the liquid, such as OH and Hα. Line emissions of excited Ru and Ar are also observed. Then, the PEG+NPs solution was characterized by various methods in order to verify the presence of nanoparticles and to determine their characteristics such as their morphology, concentration, size and size distribution as a function of the plasma generating power, the amount of liquid and the temperature of the latter. UV-Vis-NIR spectroscopy shows metallic or semi-metallic behaviour of the PEG+NPs solution, with the amount of NPs depending on the sputtering conditions. The main results of HRTEM and SAXS analysis show that the Ru NPs have a diameter of 2-5nm, but can aggregate to form larger particles during or after deposition, depending on both the sputtering conditions and the liquid characteristics.

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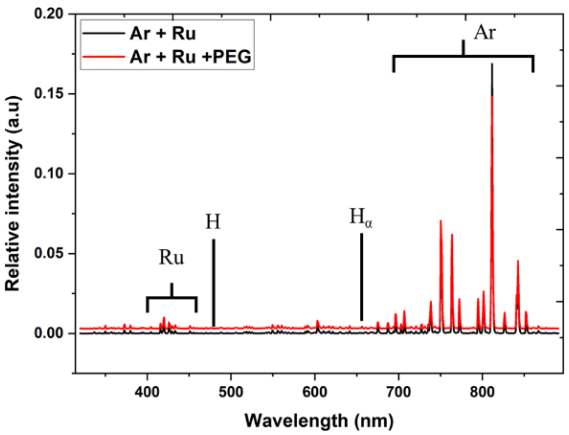
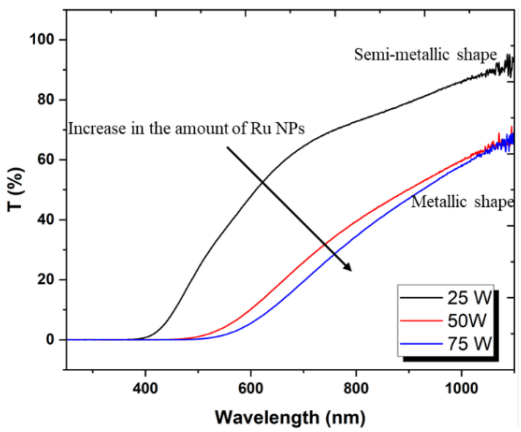


OES Spectra of Ar+Ru and Ar+Ru + PEG plasma



Transmittance of PEG+Ru NPs depending on the plasma

PLATH00080

DEPOSITION OF $ZnGa_2O_4$ THIN FILMS BY REACTIVE CO-SPUTTERING OF LIQUID GALLIUM

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Thin films of Ga_2O_3 and $ZnGa_2O_4$ are of technological interest due to their applications in wide bandgap electronic and optoelectronic devices. We have developed a method for reactive liquid magnetron sputter deposition of gallium oxide thin films [1]. In this study, we report the deposition amorphous and crystalline thin films of Ga_2O_3 [2] and $ZnGa_2O_4$ [3] by reactive pulsed direct current magnetron sputtering from a liquid gallium target onto fused quartz and c plane sapphire substrates, where the temperature of the substrate is varied from RT to 800°C. Non-stoichiometric $ZnGa_2O_4$ thin films, covering a wide range of Ga:Zn atomic ratios (≈ 0.3 – 5.7), were deposited by co-sputtering solid Zn traget next to liquid Ga target. The composition was controlled by varying the sputtering power of the Zn target and monitoring the process with plasma optical emission spectroscopy. Composition analysis shows no traces of impurities and a slight oxygen deficiency in the films. The static deposition rate of Ga2O3 (up to 37 nm/min at RT on f-quartz and 5 nm/min at 800 °C on c-sapphire) is two to five times higher than the rates reported in the literature for radio frequency sputtering. When deposited onto unheated substrates, the films are X-ray amorphous. Well-defined X-ray diffraction peaks of β-Ga_2O_3 begin to appear at a substrate temperature of 500°C, and $ZnGa_2O_4$ peaks at 300°C. Electron microscopy images reveal a dense and void-free microstructure. The thin films are highly transparent in the visible light range (≈ 84%) and the optical band-gap varies between approximately 3.9 eV and 5.1 eV, depending on the amount of Zn in the composition.

Thanks/Acknowledgement
This study was funded by ERDF project No. 1.1.1.1/20/A/057 “Functional ultrawide bandgap gallium oxide and zinc gallate thin films and novel deposition technologies”. Financial support was provided by the Project “Smart Windows for Zero Energy Buildings” (SWEB) GA nr. 101087367.

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PLATH00048

METAL OXIDE REDUCTION USING INLINE OPENAIR-PLASMA PROCESS IN COMBINATION WITH THIN FILM DEPOSITION TO ENHANCE ADHESION AND IMPROVE DURABILITY IN ELECTRONICS

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Traditional cleaning methods often rely on hazardous concentrated acids like citric or formic acid, which pose environmental risks. Additionally, residual traces from these methods can lead to surface reoxidation and adhesion loss over time. This study introduces an eco-friendly alternative using atmospheric pressure plasma generated from a forming gas mixture (N2/H2) operating at low temperatures and with high processing speeds.
The experiments utilized the REDOX-Tool, a plasma treatment system integrated into a tunnel setup for continuous processing and presented in figure 1. The tool operates in a nitrogen environment to prevent oxidation and consists of three sections. Samples are placed on a conveyor belt, preheated to 100–150°C, and then exposed to a reducing plasma generated by an RD2005 plasma source. The plasma gas, a mixture of 5% hydrogen and 95% nitrogen, directly reduces metal oxides. Finally, samples are cooled in a nitrogen environment to minimize reoxidation.
X-ray photoelectron spectroscopy (XPS) was used to analyze the reduction of metal oxides on the surface. Results showed a significant decrease in copper oxide (CuO) and an increase in metallic copper (Cu(0)) peaks, confirming effective surface reduction, consistent with prior studies [1]–[3].
This plasma-based method successfully reduces copper oxide surfaces and shows promise for treating other metals like tin (Sn) and nickel (Ni), commonly used in semiconductor and electronics manufacturing. When combined with plasma-based thin film deposition of protective coatings, it enhances adhesion and prevents delamination, particularly during aging. The environmentally friendly nature of this process makes it a viable alternative to traditional chemical cleaning methods in electronics manufacturing.

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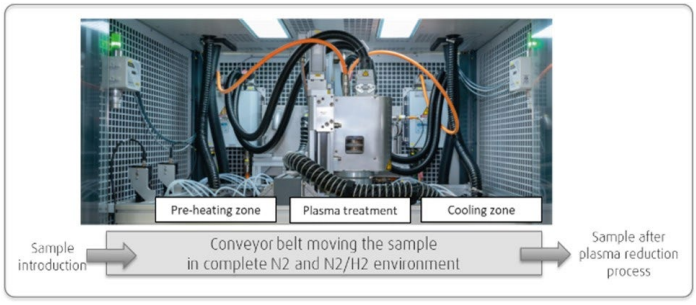

Illustration of the REDOX-Tool

PLATH00015

PUSHING THE LIMITS OF MAGNETRON SPUTTERING FOR INNOVATIVE SOLUTIONS

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Physical Vapor Deposition (PVD) technologies, particularly magnetron sputtering, have consistently proven their versatility in diverse industrial applications. However, as the demand for advanced materials grows, the boundaries of these methods are continually being tested to address complex challenges. This presentation focuses on two cutting-edge areas where magnetron sputtering is being pushed to its limits: coating powders and small objects, and depositing exceptionally thick coatings (10 to 100 µm) for specialized applications.
Our company, a pioneer in challenging PVD solutions, has developed a reputation for tackling intricate coating challenges with innovative approaches. By combining in-depth material science expertise and state-of-the-art deposition techniques, we deliver tailored solutions for industries ranging from energy to medical engineering.
The first part of the talk will highlight advancements in coating powders and small objects using magnetron sputtering. Achieving uniform and functional coatings on irregular geometries presents significant technical hurdles, including managing line-of-sight deposition and optimizing process parameters for consistent quality. Through case studies, we will explore solutions such as substrate handling and process customization, enabling successful deposition on complex shapes, from various size and geometries.
In the second section, we will delve into the development of very thick coatings (10 to 100 µm), which push the conventional limits of PVD technologies. These coatings are designed for demanding applications requiring enhanced durability, wear resistance, or thermal protection. The discussion will include strategies for managing residual stresses, maintaining adhesion, and ensuring structural integrity during the deposition process. Real-world examples will illustrate how these thick coatings have been successfully applied to address specific industrial needs.
This presentation aims to provide valuable insights into the capabilities of magnetron sputtering, showcasing its potential to solve challenging problems in modern material science. By pushing the boundaries of what is achievable, we can unlock new possibilities for PVD coatings in innovative applications.

PLATH00006

UNRAVELLING THE MECHANISMS BEHIND DISLOCATION DENSITY REDUCTION IN TUNGSTEN-DOPED SINGLE-CRYSTAL DIAMOND: A SYNCHROTRON X-RAY INVESTIGATION

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Due to its high breakdown field, high thermal conductivity and large carrier mobility, diamond is considered as the ultimate semiconductor material for high-power applications.
Single crystal diamond layers are commonly synthesized by homoepitaxy using Microwave Plasma Enhanced Chemical Vapor Deposition (MPCVD) and doped in situ with boron acceptors. Nevertheless, the presence of dislocations in the active layer has been shown to strongly degrade the performance of the diamond-based power devices [1]. Thus, extensive efforts have been made to reduce the propagation of dislocations within the crystal. The deposition of a W-doped diamond layer (using Hot Filament CVD (HFCVD) [1] or MWCVD coupled with W(CO)6 sublimation [2]) has been reported to reduce the density of dislocations emerging at the surface. Up to date, the mechanisms behind this crystalline quality improvement remain debated.
To unveil this phenomenon, W-doped diamond layers have been synthesised by tuning both thickness and doping levels using HFCVD and a home-made adaptation of the MWCVD process developed by DIAMFAB. **A decrease of one order of magnitude of the emerging dislocations density of has been observed** for most samples using molten salt selective etching (Fig. 1). Four 10 µm thick HFCVD and MWCVD W-doped layers have then been subjected to an extensive study by X-ray diffraction topography and X-ray fluorescence at the ESRF synchrotron. It appears that **some dislocations are deflected at the interface between the substrate and the W-doped layer** (Fig. 2). The influence of W-doping on the propagation of the dislocations will be discussed.

Thanks/Acknowledgement
We would like to acknowledge Marina Gutierrez, Gonzalo Alba and Daniel Araujo from Cadiz university (UCa) for their help and support with the Transmission Electron Microscopy (TEM) measurements.

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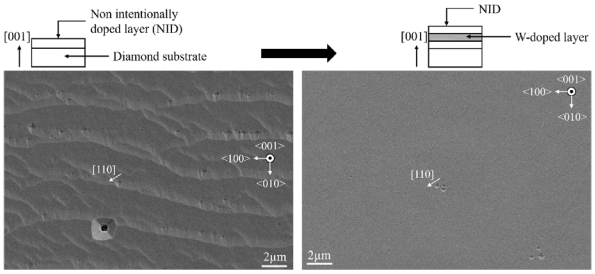

Fig 1. SEM images of the selective etching

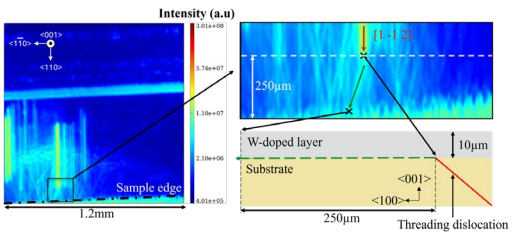

Fig 2. X-Ray diffraction weak beam image

PLATH00139

ANALYSIS AND MONITORING OF PROTECTIVE COATINGS: ADVANCES IN LECO'S GLOW DISCHARGE SPECTROSCOPY (GDS)

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Corrosion is a pervasive problem that significantly impacts the integrity and service life of metal structures. Various corrosion protection techniques are used to prevent this. A crucial aspect is the analysis and monitoring of protective coatings on metals. This is where LECO's Glow Discharge Spectroscopy (GDS) plays a crucial role. Mr. Stefan Böhm, Product Manager for GDS in the European Field Service, will present the possibilities for testing corrosion protection and explain how LECO's GDS technology is used to analyze thin coatings.
In addition to its primary function, LECO's GDS technology offers advanced features for detecting and quantifying trace elements in protective coatings. This ensures that the coatings meet strict quality standards and provide optimal corrosion protection. The versatility of GDS enables comprehensive analysis in various industries, including automotive, aerospace, and marine applications.
Furthermore, recent advances in GDS technology have made it an indispensable tool for researchers and engineers working on innovative corrosion protection solutions. The integration of GDS with other analytical techniques improves the overall understanding of coating performance and durability.
The presentation will also include case studies demonstrating the successful application of GDS in real-world scenarios, highlighting its impact on extending the service life of metal structures and reducing maintenance costs. Participants will gain valuable insights into the practical aspects of using GDS for corrosion protection analysis and monitoring.

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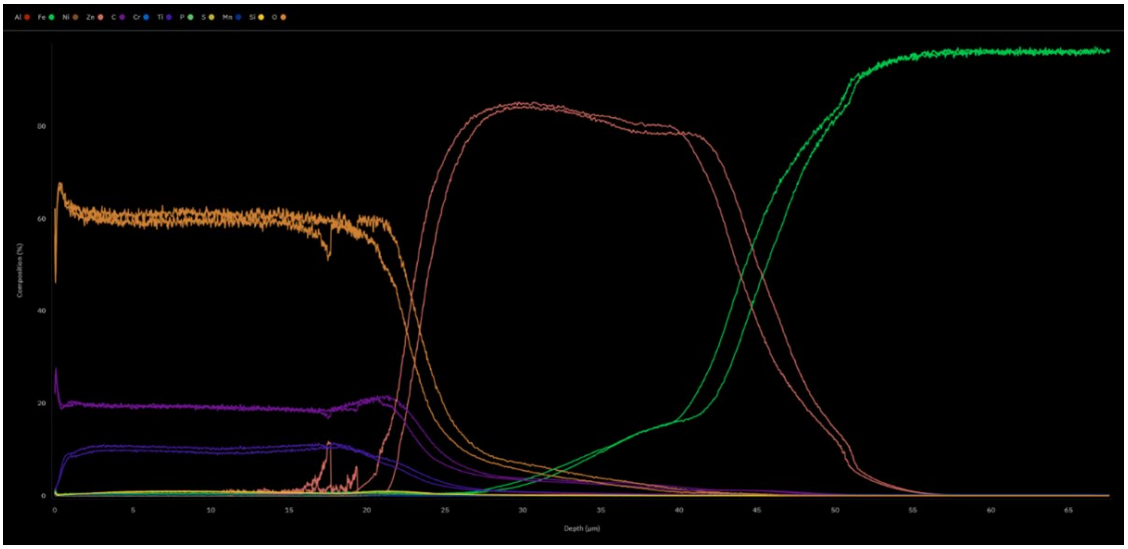

Figure 1 shows an example of a metal structure analyzed using LECO's GDS technology. The image shows a coated metal. The first layer consists of oxygen, titanium, and carbon, corresponding to a white paint approximately 25 µm thick. This is followed by a 25 µm thick zinc layer to protect the metal.

PLASMA TECHNOLOGIES ADVANCING BIOMEDICINE AND SUSTAINABILITY

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When powered by renewable electricity, plasma processing technologies requiring minimal amounts of gaseous reactants and generating minimal waste can provide sustainable solutions to many materials and chemical processing needs. Here we present plasma processes that enable the creation of bio instructive and biomimetic surfaces for wide ranging applications in biomedicine, eliminating the need for multi-step wet chemical treatments.

Materials used in biomedicine are selected according to bulk properties, such as mechanical, electrical and optical, required for particular in-vivo and in-vitro applications. However, their surfaces almost always provide suboptimum biological microenvironments and do not promote the desired biological responses. In addition, they are often formed into geometries that are not appropriate for traditional line-of-sight low pressure plasma treatment modalities. Here, we will describe sustainable and readily scalable low temperature plasma surface modification processes, that enable resilient and tailorable biofunctionalization on all surfaces of complex, including microporous, fibrous or hollow-fiber-based, structures.

As cell behavior is directed by biochemical signals and local stiffness, our strategy is to immobilize biomolecules and hydrogels onto the cell contacting surfaces. Typical time scales of cell culture and tissue integration necessitate covalent immobilization to prevent biomolecule desorption and exchange with molecules in the aqueous environment. Energetic ion implantation into carbon-based surfaces or surface coatings creates buried radicals whose unpaired electrons migrate to the surface. At the surface these highly reactive radicals form covalent bonds with proximate molecules [1]. This basic strategy is extended to plasma synthesized nanoparticles and applied via capacitive coupling within the internal porosity of scaffolds and to microparticles in a packed bed configuration [2]. For structures created by 3D bioprinting which is not compatible with low pressures, we developed instead a localized atmospheric pressure plasma treatment to generate and covalently bond reactive groups to the surface which then react with side chain groups present on the surface of biomolecules [3]. A combination of these plasma activation processes is applied to microfluidics for organ-on-chip applications [4].

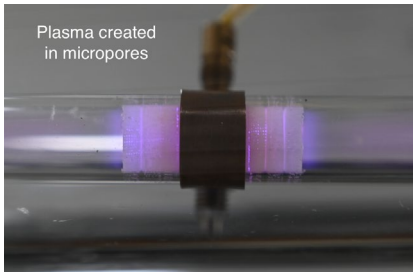

***Fig. 1**. Plasma treatment of scaffold for expansion of stem cells. Optimization of pressure as well as electrode size and location enables plasma within the micropores.*

The reported plasma treatments were found to activate a range of materials and structures for spontaneous, reagent-free, covalent functionalisation with bioactive, cell-signaling molecules and hydrogels. Functional molecules that can be immobilized to create tailored, bio instructive cell microenvironments include, but are not limited to, oligonucleotides, enzymes, peptides, aptamers, cytokines, antibodies, cell-adhesion extra-cellular matrix molecules and histological dyes. The covalent immobilization occurs on contact via radicals or reactive groups on the plasma activated surfaces. Subsequent laser annealing can add conducting tracks allowing stimulation of electroactive cells without sacrificing optical transparency. Controlled application of the functional molecules via droplet dispensing or contact printing enables the immobilization of biomolecular and hydrogel patterns onto the plasma activated surfaces.

Together these processes create a toolbox for fabricating bespoke biomimetic microenvironments that provide exquisite control in cell culture and tissue engineering. Commercialization is underway with expected impacts in personalized medicine, controlled tissue-integration, medical and environmental diagnostics, biosensing and nanomedicine.

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PLATH00004

PLASMA DEPOSITION IN NON-EQUILIBRIUM CONDITIONS

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In an electrically excited plasma, energy supplying and energy dissipating processes are typically dominant over energy exchange processes. The plasma thus is in a non-equilibrium state with high electron temperature and low gas temperature. In a low pressure plasma, electron impact excitation is the predominant way to transfer energy to molecules, whereby several inelastic collisions during the residence time of a molecule in the plasma result in an average energy uptake per molecule, the specific energy input [1]. In this case, thermodynamic principles can still be applied governing the plasma chemistry in the gas phase, empasizing the role of entropy changes [2].
Different examples are presented considering plasma polymer film growth in siloxane- and hydrocarbon-based plasmas as well as metal oxides for catalysts. Since film growth also involves plasma-surface interaction, methods are introduced to reduce its impact to obtain a more defined film chemistry [3]. Thus, surface functionalization can be tailored yielding various applications. The presented examples have been scaled up, demonstrating their industrial feasibility.

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PLATH00040

ATMOSPHERIC-PRESSURE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF SIZE AGENTS ON GLASS FIBERS FOR GLASS-REINFORCED PLASTICS

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Glass-reinforced plastics are a widely employed class of materials which consist in glass fibers embedded in a polymer matrix. Such reinforcing fibers provide to the composite material improved mechanical properties such as stiffness, while at the same time preserving its overall light weight. In the current state-of-the-art, the adhesion at the resulting glass-polymer interface and the protection thus afforded are provided by a size agent consisting of a size agent, i.e. an aqueous dispersion, oftentimes silane-based. The main limitations of such approach, which severely reduce the performances of the composite material, are caused by the very small fraction of fibers actually coated by such size agent, once it dries up [1]. In the present work, a complement to (or possibly a partial substitute of) the size agent is deposited on the fibers by means of an atmospheric pressure Plasma Enhanced Chemical Vapor Deposition (PECVD) process. The latter is carried out with a commercially available plasma torch, with air and/or nitrogen as feeding gas and several organosilanes as possible precursors. The aim is to produce a thin film rich of adhesion-promoting functional groups on the fibers surface.
The plasma source has been characterized over a wide range of operating parameters by emission spectroscopy, high-speed and thermal camera measurements, while the resulting thin films have been characterized via IR-spectroscopy, AFM and REM imaging. Their adhesion properties on glass plates and single fibers have been tested by means of pull-off and pull-out tests, respectively. The composition of the waste gases has also been determined by means of gas chromatographical methods.
Numerical gas simulations have been furthermore carried out with the aim optimize the PECVD setup and the design of a closed reaction chamber operating with multiple plasma sources, able to be fully integrated in an industrial in-line deposition step while at the same time obeying the required health regulations [2]. The resulting thin films show an increase of pull-off and pull-out force of up to 30% and more than 80%, respectively [2-4], even at high winding speeds of the fibers. The strong improvement over the state-of-the art offers promising perspective for the branching to non-glass fibers, too.

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PLATH00092

PLASMA POLYMER THIN FILMS AS ADHESION PRIMERS IN COMPOSITE/ELASTOMER ASSEMBLY: CONTROLLING ADHESION PERFORMANCE THROUGH DEPOSITION PARAMETERS

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Plasma polymerization has been recognized as an efficient process to engineer polymer thin films that serve as adhesion primers particularly in metal/elastomer assemblies [1] [2] [3]. A common approach involves depositing plasma polymers containing functional groups onto the metallic substrate. These groups then react with the elastomer during the crosslinking stage. However, the impact of the thin film deposition parameters on adhesion performance between the two materials remains underexplored.

This study aims to extend the understanding of the relationship between the operating parameters of plasma polymerization, the chemical and physical properties of the synthesized polymer thin film and the adhesion performance for assemblies made of a composite polymer material and an elastomer.

More precisely, thin polymers films containing anhydride groups were deposited onto the composite substrate using low-pressure RF plasma polymerization. These films were then modified via vapor-phase aminolysis to graft alkene groups, which subsequently reacted with EPDM (ethylene propylene diene monomer) rubber, forming covalent bonds between the coated substrate and the rubber during crosslinking. The influence of key operating plasma polymerization parameters such as generator power, duty cycle and deposition time on adhesion properties was systematically evaluated. Beyond the plasma polymer deposition step post-functionalization was also studied. Thin film properties were thoroughly characterized by FTIR and XPS spectroscopies, contact angle measurements, AFM and profilometry. Adhesion performance was quantified through 90° peel tests, complemented by detailed failure pattern analyses. This comprehensive investigation into the structure-property relationships of plasma polymers as adhesion primers has provided a clear understanding of the adhesion mechanisms at play. Consequently, it ensures durable cohesion in the fabricated composite-elastomer assemblies.

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PLATH00109

PLASMA POLYMER FILM AS AN INTERLAYER TO IMPROVE POLYMER-METAL COMPOSITES DISASSEMBLY AND RECYCLING EFFICIENCY

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Metal coatings on polymers are widely used in industries such as electronics, automotive, and packaging for their conductivity, barrier properties, and aesthetics. While strong adhesion between metal and polymer is typically beneficial, it poses a significant challenge for recycling. The separation of these layers is highly challenging (e.g., mechanical cleaning, burning, dissolving) and costly, often resulting in the disposal of such waste causing considerable environmental impact.
In this context, this study explores the use of plasma polymer films (PPF) as intermediate layers between metals and polymers to improve the recyclability. The PPF would ensure a strong adhesion with the metallic layer (i.e., Al) while weakening the interface with the polymer when exposed to a stimulus (e.g., heating).
The PPFs are synthesized from a gas mixture of C2H4 and CO2, known to generate PPF with a high content of carboxylic acid and alcohol functional groups1 ensuring a strong interaction with aluminum coatings2. The analysis of the XPS data reveals an increase in the OH and COOH concentration with the CO2 content in the gas mixture and the power. For extreme conditions, this also results in intense etching. Similarly, the cross-linking density also increases correlating the evolution of the glass transition temperature of the PPF. The latter property is crucial as it governs the behavior of the PPF when exposed to a thermal stimulus.

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PLATH00110

STUDY OF THE CHEMICAL AND TEXTURAL PROPERTIES OF 2-VINYLPYRIDINE-BASED PLASMA POLYMERS

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The objective of this study is to synthesize and characterize the 3D and chemical structure of ion conducting thin films prepared by plasma polymerization in the context of water electrolysis and fuel cell applications. Plasma polymerization is widely recognized for its ability to produce highly cross-linked thin films that exhibit particularly appealing chemical, mechanical, and thermal resistance. Notably, the chemical and textural properties of these films can be precisely controlled by varying precursor materials and synthesis parameters [1] [2]. Furthermore, plasma polymerization allows the deposition of thin layers on a broad spectrum of substrate, making it a highly advantageous technique for electrochemical applications using membrane-electrode assemblies.

Ion conducting plasma polymers are, just like conventional ion-exchange polymers, formed of a matrix providing structural and mechanical stability with active sites ensuring ionic conduction. Such features can be achieved by a mixture of two different precursors, as seen in plasma co-polymerization, using for example styrene as matrix building block and trifluoromethane sulfonic acid as source of ionic sites [3]. More relevantly, classical plasma polymerization using a single precursor providing required properties enables to simplify and better control the deposition process [4] [5]. In this study, 2-vinylpyridine (2VP) was chosen as the single monomer for several reasons. First, the vinyl group, which is inherently labile, promotes polymerization and cross-linking without disrupting the pyridine ring. Indeed, the pyridine ring should be preserved, as it serves as a spacer to ensure enough free volume in the material for transport purpose. Second, upon chemical post-quaternization, the pyridine ring converts into a pyridinium function acting as a cationic site.

2VP plasma polymers were deposited onto silicium wafers using a capacitively-coupled radio-frequency reactor equipped with a pulsed vaporization injector. XPS and TOF-SIMS analyses demonstrated in-depth homogeneous layers containing vinylpyridinium functions. GISAXS and ellipsometry techniques revealed that the materials have a density comparable to conventional polymers. Functionally, the ionic conduction observed through the thin films proved to be competitive versus state-of-the-art commercial materials, suggesting the potential of these thin films for electrochemical applications.

Thanks/Acknowledgement
We thank Biophy Research (Eurofins) for XPS and TOF-SIMS analyses.

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PLATH00020

IMPACT OF SURFACE CHEMISTRY ON THE MORPHOLOGY OF PLASMA POLYMERS

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The production of polymer thin films via plasma polymerisation is long-established. Beyond thin films, studies have demonstrated that nanostructures can spontaneously form on a surface during plasma polymerization. Experimentally, the prevalence of either nanostructures or thin films can be adjusted by various parameters, including plasma deposition conditions (power, duty cycle, frequency)[1] or the surface chemistry of the substrate[2]. The fundamental mechanisms governing the formation and growth of plasma polymers remains largely unexplored and, nowadays, it is still not possible to quantify the influence of the many variables involved in structure formation. Therefore, it is essential to isolate the role of each of these variables in order to better understand the formation and growth processes of plasma polymers. This work aims to carefully isolate the effect of surface chemistry on the formation of nanostructures or thin films for citronellal plasma polymers coatings. Citronellal was selected as a precursors as preliminary studies have shown that, under identical plasma conditions, the morphology of its plasma polymers varies depending on the surface chemistry. To precisely control the surface chemistry, our selected strategy explores the use of monolayers as model surfaces. Firstly, reactive self-assembled monolayers were generated and subsequently post-functionalised using photochemistry via a maskless lithography system. This approach allows for the creation of either fully post-functionalised or chemically patterned surfaces. Once well characterised, these surfaces with distinct chemistries are subjected to plasma deposition. The resulting citronellal plasma-polymer coatings are then analysed, especially by AFM, to establish correlations between the surface chemistry of the substrate and the morphology and growth characteristics of the plasma polymer.

Thanks/Acknowledgement
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PLATH00039

FORMATION OF RADICALS IN AMINE PLASMA POLYMER THIN FILMS AND THEIR POTENTIAL FOR COVALENT BINDING OF BIOMOLECULES

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Even though synthetic polymers are promising materials for bioapplications, poor biocompatibility hampers their applicability. Introducing polar groups to such material through coating by a thin plasma polymer (PP) film increases the surface free energy and makes the polymer hydrophilic. This facilitates immobilization of proteins or enzymes, as well as cell attachment and growth. Our previous publications showed that coating polycaprolactone nanofibers with amine or carboxyl PPs with bound platelet-rich plasma highly improves cell viability [1,2]. Immobilization of biomolecules is often mediated by chemical coupling through a linker to avoid nonspecific binding. However, recent studies [3,4] have shown that the deposition of amine PPs using enhanced ion bombardment produces many free radicals capable of covalently binding biomolecules to the PP surface without losing functionality. In this work, we proved abundant, long-lived radicals even for amine PPs prepared by a typical low-pressure plasma polymerization (with no additional ion bombardment). Although the radical density was the highest directly after the deposition, PPs preserved 60% of the original radical amount after 3 months of storage. The decrease was attributed to radical recombination in bulk or their diffusion to the PP surface, followed by reactions with adsorbed molecules. Interestingly, the radical density does not scale with the average discharge power but with the on-time power, and the deposition rate is similar during the off-time and on-time. It means that the radicals in the material grown during the off-time are created in the on-time because of the ion penetration effect. Finally, as proof of concept, we demonstrated a radical-assisted direct immobilization of a biomolecule, bovine serum albumin, to amine PP-coated quartz crystal microbalances.

Thanks/Acknowledgement
This research has been supported by the Czech Science Foundation (24-12321S). CzechNanoLab Research Infrastructure supported by MEYS CR (LM2023051) is also acknowledged.

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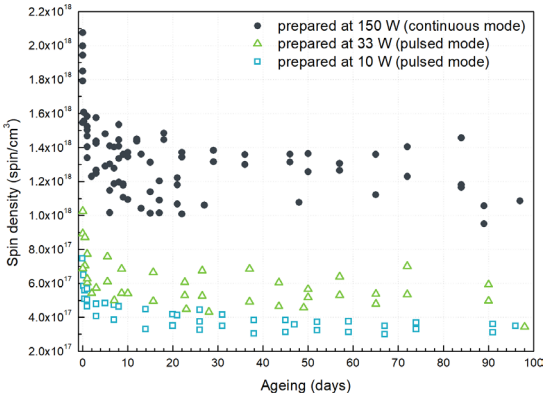

Radical lifespan in amine plasma polymers

PLATH00033

IN-SITU XRD INVESTIGATIONS DURING NITRIDING OF DUPLEX STEEL

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Nitriding of austenitic stainless steel is nowadays an established process. There, the formation of expanded austenite with a lattice expansion of up to 12% and with an incorporated nitrogen content of up to 30 at.% is observed. Similarly, stainless duplex steels can be nitrided or nitrocarburized. There, the austenite-ferrite matrix quite often is transformed into an expanded austenite phase for processing temperatures around 400 °C. For higher temperature beyond 450 °C, a final state consisting of CrN precipitates in an Fe-Ni matrix is reached. However, no details on the time evolution of both phase formation and diffusion is available for duplex steel – in contrast to austenitic stainless steel.
Now, in-situ XRD investigations during nitriding combined with in-situ XRD investigations during ion beam sputtering of the modified layer are presented to elucidate details. Before the nitriding experiment, ESBD and EDX mapping was performed to correlate the local composition (Fe-Cr-Ni content) with the phase formation (austenite vs. ferrite). During nitriding, the initial nitrogen diffusion is accessible from the decreasing XRD intensity of the underlying substrate. Thus, a much faster nitrogen diffusion is observed for the ferritic grains compared to the austenitic ones, yet no formation of expanded ferrite is observed by XRD with only expanded austenite being visible without any ferrite. As the increased nitrogen content is stabilizing the austenitic phase, a transition from ferrite towards austenite with increasing nitrogen incorporation is postulated. For longer times, ex-situ SIMS yields a time-averaged diffusion which indicates an inverse parabolic growth law with a thermal activation energy of around 1 eV.
More detailed information on the layered structure is obtained by combining results of sputter etching for depth-resolved (integrated) phase information with local EBSD data from a cross-section of a nitrided sample. At the same time, the onset of CrN precipitation is shifted towards lower temperatures by about 20 K compared to pure austenitic stainless steel. This is presumably caused by the microstructure of the duplex steel containing smaller grains and more defects or grain boundaries.

PLATH00029

REDUCTION OF OXIDES USING AN ELECTRON CYCLOTRON WAVE RESONANCE Ar/H_2 PLASMA - TOWARDS H_2O PRODUCTION ON THE MOON

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Space travel is currently limited by the need to bring all required resources and consumables from Earth. Use of resources found in space has the potential to transform space exploration. Oxygen is found on the Moon bound in the lunar soil. Lunar soil, or regolith, is mainly composed of inorganic oxides such as SiO2, MgO, CaO, TiO2, FeO, in the form of minerals such as silicates and ilmenite, (Landis, 2007). Lunar regolith comprises approximately 40-45% wt oxygen.
Reduction using hydrogen has been investigated for many years, however it is limited by low oxygen yields. H2 plasma processes, on the other hand, provide atomic H, which is very efficient for metal oxide reduction. In this work, we investigate the use of an Electron Cyclotron Wave Resonance (ECWR) plasma source to produce H2 based plasma for oxide reduction. ECWR plasmas are of particular interest as they provide a high dissociation rate of diatomic gases (Weiler, 1998).
This work focuses on the plasma-oxide interaction with the aim of understanding the mechanisms to give future paths for optimisation of the process to increase the oxygen yield. TiO2, Fe2O3 and Fe2TiO5 thin films are synthetised using PVD and then exposed to H2 based plasma. Samples are investigated using FTIR, XRD, TEM (EELS) and SIMS. Plasma time exposure and substrate temperature are explored. TEM observations of the oxide layers show a gradual composition and structural change which are used to propose a mechanism for deoxidation of these layers.
Experimental results demonstrate the high importance of the presence of atomic H, as well as the strong influence of the temperature on the reduction kinetics. We demonstrate increase in (energy) efficiency of ECWR H2 plasma over traditional H2 gas thermal reduction. Presented experimental findings will contribute to the development of hydrogen-based processes to support a permanent human presence on the Moon.

Thanks/Acknowledgement
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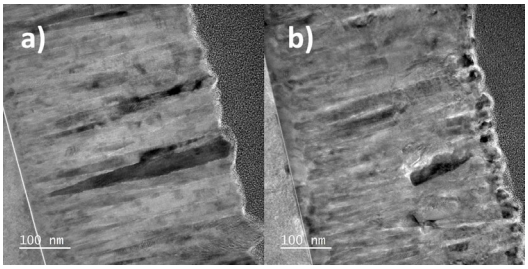

STEM - before and after H2 low temp plasma

PLATH00001

TRANSIENT SIGNALS MEASUREMENT CAPABILITY FOR THE ANALYSIS OF THIN FILMS AND SURFACES REACTIVITY

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Surface and Interface studies require the use of complementary analytical techniques as each instrumentation provides partial results only based on the interaction of the investigated material with a probing medium [1].
Coupling of techniques is sometimes possible – for example elemental and molecular information at different depths could be achieved by coupling Glow Discharge Optical Emission Spectrometry (GD-OES) and Raman Spectrometry [2,3].
When transient signals are of interest, ultra-fast acquisition techniques are required.
This is the case with Glow Discharge Optical Emission Spectrometry when nanometric layers are of interest. It is also true for people studying in real time the reactivity of surfaces, gas formation and elemental dissolution by coupling an electrochemical cell to an ICP-OES – the AESEC technique (Atomic Emission Spectroelectrochemistry) [4].
Recent patented developments offer more possibilities for transient signals analysis with new capabilities to measure all elements simultaneously, from Hydrogen (and Deuterium) to Uranium, at high acquisition rate. This includes new, innovative, optical design and detection system.
We will illustrate the benefit of these new developments in GD OES and ICP OES by showing selected results on metallic parts for high temperature fuel cells, catalysts coated PEM membranes, fuel facing materials in Na fast reactors, perovskite solar cells, hydrated alumina films, batteries and DLC coatings on bipolar plates.

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PLATH00105

PLASMA-SURFACE CHARACTERIZATION DURING V_2O_3 THIN FILMS ETCHING IN SF_6/Ar PLASMA

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The growth of microelectronics has led to a new technology called artificial intelligence (AI). This technology uses a lot of information and memory devices to store and process it quickly. While the world is facing an unprecedented environmental crisis, the heavy reliance on memory devices raises challenges in terms of performance and environmental impact. Many researches are focused on developing new materials with this dual impact. A line of research that meets these requirements is inspired by the mammalian brain, which involves reproducing the interconnected network of neurons and synapses. So, Mott insulator materials, as V2O3, are capable of reproducing this electrical behavior of neurons.
To facilitate the interconnections between the different layers of the memory device, an etching process is necessary. Unfortunately, in the literature, most of the existing etching processes are wet etching [1], RIE reports are scarce [2] and the main existing are related to thermal ALE of VO2 [3]. Thus, many open questions still have to be addressed: which plasma chemistry to use to ensure the formation of volatile products, for which plasma conditions? What are the plasma-surface interaction mechanisms involved? The present work tries to answer these questions.
To address these challenges, etching experiments are carried out by using an ICP reactor equipped with two 13.56 MHz RF generators. Samples consist of 230 nm thick of V2O3 thin films deposited on SiO2/Si substrates by sputtering. We first focused on parametric studies by using in situ ellipsometry in SF6/Ar plasma and investigating the effect of varying plasma excitation power, pressure, gas mixture composition and RF sample bias on the etching rate. Then we characterize the chemical state of the surface using both in situ and ex situ XPS. AFM and SEM with EDX provide information on surface morphology and composition after RIE processes.
These studies show that V2O3 thin films can spontaneously be etched in SF6/Ar plasma with etching rate values up to 1 µm/min. Additionally, varying the sample bias suggests a non-conventional RIE behavior. To summarize, plasma diagnostics (OES, mass spectrometry) and surface characterization will be presented to gain better understanding of the etching mechanisms at play.

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PLATH00122

SENSING ENHANCEMENT OF CHEMIRESISTIVE GAS SENSORS BY SURFACE FUNCTIONALIZATION

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The sensitive, repeatable, reliable, and selective detection of various hazardous gases at an early stage has become increasingly important in daily living places as well as modern industrial factories. The aims of gas sensors include safety both in industry and at home, health care, defense of terror or chemical warfare, and environment monitoring. Various types of gas sensors have been developed and employed. Gas sensors can be classified according to mainly materials used and sensing principles operated. Chemiresesistive type gas sensors have been widely used. They have a simple sensing mechanism in which a change of resistance is measured as exterior environment is changing; that is, resistance change of the senor materials by adsorption and desorption of gaseous species. The materials used for such type of gas sensors are usually semiconducting metal oxides. The merits of chemiresistive-type gas sensors are easy fabrication, low cost, adaptability to nanostructures, and potential possibility of attaining extremely high sensing performances. However, to fulfill their practical application, several sensing properties need to be further improved; higher selectivity to a target gas, more stable sensing signal for a long time period, humidity resistance, and less temperature dependency, and selective detection, etc. For the purpose of improving such sensing performances, considerable research and developments have been made up to the present. Surface functionalization based on thin film growth has emerged as an effective strategy to enhance sensor performance by modifying the surface properties of the sensing material. This study explores different functionalization techniques, including noble metal nanoparticle decoration, metal oxide heterojunctions, and organic ligand modifications, to improve gas adsorption, charge transfer, and catalytic activity. Experimental results demonstrate significant enhancements in response magnitude, detection limits, and long-term stability. These findings provide insights into optimizing chemiresistive sensors for high-performance gas detection in diverse environmental conditions.

PLATH00111

DEFECT-ENGINEERED V_2O_5/TiO_2 THIN FILMS DEPOSITED BY DC SPUTTERING FOR IMPROVED CARBOFURAN DEGRADATION

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Vanadium pentoxide (V_2O_5) thin films, known for their favorable band gap for visible light harvesting, were investigated for the photocatalytic degradation of Carbofuran. Carbofuran is a potent neurotoxic insecticide which is baned in most first world countries, but still very used and present in waste water in developing countries.
The inherent fast recombination rates of photogenerated charge carriers in pristine V2O5 limit their efficiency. To address this, we synthesized V_2O_5 thin films and TiO_2/V_2O_5 multilayer thin films, further modified by nitrogen doping. These modifications were implemented to enhance the photocatalytic performance by mitigating charge carrier recombination and extending the visible light absorption.
The synthesis involved DC reactive sputtering of Ti and V targets in oxygen atmosphere, followed by controlled nitrogen doping during annealing in reactive atmosphere. Comprehensive characterization was performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and UV-visible spectroscopy. These techniques were utilized to analyze the structural, morphological, compositional, and optical properties of the synthesized materials.
Photocatalytic degradation experiments demonstrated that nitrogen-doped V_2O_5 and nitrogen-doped TiO_2/V_2O_5 films exhibited significantly improved degradation of Carbofuran under visible light irradiation compared to undoped counterparts. The results highlight the crucial role of defect engineering and heterostructure formation in enhancing the photocatalytic activity of V_2O_5-based materials. This study provides valuable insights into the design of efficient photocatalysts for environmental remediation applications, emphasizing the importance of manipulating oxygen vacancies and heterojunctions to optimize photocatalytic performance.

Thanks/Acknowledgement
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PLATH00026

CLEANING PROCESS OF 3D AND DELICATE HETEROGENEOUS STRUCTURES WITH HDRF®, OPTIMIZE CHEMISTRY WITH REMOTE PLASMA, FOR MICROELECTRONICS' AND MEDICAL APPLICATIONS

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In this work, we introduce different applications of our unique Inductively Coupled Downstream Plasma multi-sources configuration design to generate **H**igh **D**ensity **R**adical **F**lux (HDRF®) used for MEMS fabrication, Descum, and Surface activation. The HDRF® process is optimized using the right chemistry needs to generate etchant species that interact with product to clean, raise the etch rate [1,2], and could replace wet process with single multistep dry process.
The organic dry-cleaning process is usually made with oxygen radicals to strip away photoresists or organic residues present on a substrate. Direct plasma by ion bombardment can cause damage on the substrate's surface sensitive structures, especially heterogeneous structure with metal part subjected of sputtering. Some medical parts like stents or dental implants with 3D structure are good candidates for transfer Microelectronics' Photoresist Striping process and warranty cleaning through all 3D structures, and surface activation. The radicals generated by HDRF® remove the polymer, even from deep [3], narrow structures with a large aspect-ratio like in plasma dicing [4] after Bosh process.
The advanced HDRF® offers organic etching with unparalleled precision and control to avoid damage to exposed surfaces. We applied processes on lithography mask without issue on the metal parts, at low temperature (<120°C). Within the French national program called **TSIAS** (**T**raitements de **S**urfaces **I**nnovants pour **A**pplications à la **S**anté) with partnership of cleaning industry, we realized dental implants cleaning (Fig.1) and surface activation with HDRF©. All our safety cleaning processes are essential in the microelectronics industry, 3D structure cleaning for the frontend and backend or medical industry.

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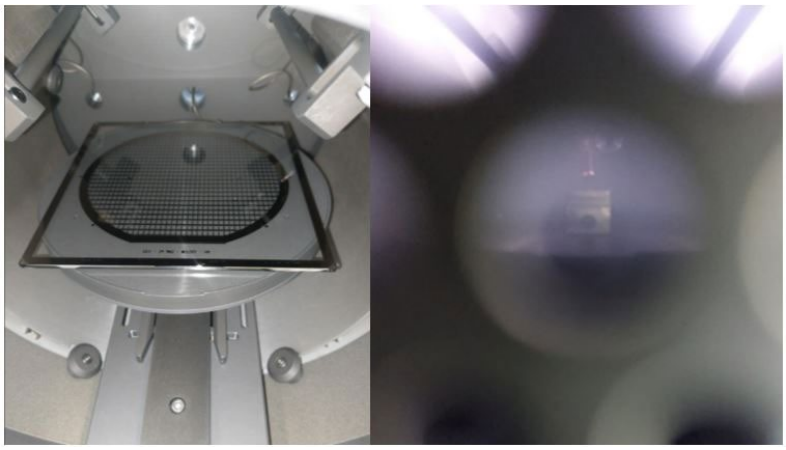

Lithography Mask & Dental implants HDRF cleaning

TACKLING LITHIUM-ION BATTERY CHALLENGES WITH PVD TECHNOLOGIES

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Lithium-ion batteries (LiBs) have become essential components in a wide range of energy systems and are expected to continue experiencing robust growth, powering everything from electronics to electric vehicles and large-scale grid storage. As the demand for higher-performing, longer-lasting, and safer energy storage systems intensifies, the materials science community faces challenges to innovate beyond traditional approaches.
This talk explores how thin film deposition techniques, particularly Physical Vapor Deposition (PVD), are unlocking new pathways to address persistent challenges in LiB technology. While conventional synthesis methods such as solid-state reactions and hydrothermal routes have brought us far, they often struggle to provide the electrical conductivity, interfacial stability, and corrosion resistance required by next-generation devices. PVD, by contrast, offers control over film composition, thickness, and microstructure, enabling the design of tailored surface coatings and functional layers that directly enhance battery performance.
From conformal oxide coatings that stabilize cathode–electrolyte interfaces to silicon-based anode films that accommodate volume changes and suppress degradation, thin films are proving indispensable in overcoming mechanical, chemical, and electrochemical limitations. These engineered layers not only extend battery lifespan but also open new possibilities to innovative LiBs architectures.
This plenary lecture emphasizes the interdisciplinary collaboration needed across surface science, electrochemistry, and materials engineering to fully harness the potential of thin films. By integrating advanced PVD techniques into battery development workflows, we can accelerate the transition toward more durable, scalable, and high-performance energy storage solutions.

KEYWORDS:
Lithium-Ion Batteries, Energy Storage, Battery Challenges, Thin Films Technologies, Nanostructured Films, Electrode Design, Interface Engineering, Electrochemical Stability

PLATH00007

ENHANCING CORROSION RESISTANCE OF MAGNESIUM ALLOYS WITH PLASMA TREATMENT AND ELECTROSPUN BIODEGRADABLE POLYMER COATINGS

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Traditional metallic orthopedic implants, such as stainless steel and titanium alloys, are non-degradable and often require removal due to complications like toxic ion release and immune reactions. Magnesium (Mg) alloys offer a promising alternative with biocompatibility and controlled biodegradability, but their rapid corrosion leads to mechanical failure, hydrogen evolution, and pH disturbances. Electrospun biodegradable polymeric coatings serve as protective barriers that slow degradation while enhancing cell adhesion and drug delivery; electrospinning creates ECM-like 3D fibrous membranes that promote better tissue integration than dip-coating. Plasma activating the Mg substrate further improves polymer coating adhesion by increasing hydrophilicity and incorporating functional groups, and combining electrospun coatings with plasma treatment significantly enhances corrosion resistance and biocompatibility. In this study, a low-temperature atmospheric-pressure plasma source, Diffuse Coplanar Surface Barrier Discharge (DCSBD), was used to both functionalize Polyhydroxybutyrate (PHB) powder and modify the Mg substrate. The PHB powder was treated with DCSBD before preparing the electrospinning solution, while polished Mg substrates received a short-time DCSBD treatment to improve coating adhesion. The final samples were characterized by SEM/EDX, ATR-FTIR, LCM, EIS, WCA, and SFE. When evaluated in Simulated Body Fluid (SBF) for seven days, the coated Mg exhibited a marked reduction in hydrogen gas evolution and pH fluctuations compared to untreated and plasma-treated bare Mg. The electrospun nanofiber barrier effectively slowed the reaction between magnesium and oxygen, and notably, the two-step plasma-treated sample demonstrated the lowest hydrogen release, consistent with improvements in corrosion rate and pH stability.

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PLATH00114

ELUCIDATING THE GROWTH MECHANISM OF FUNCTIONNALIZED PLASMA POLYMER FILMS USING COMPLEX GEOMETRY SUBSTRATES AT VARIOUS SUBSTRATE TEMPERATURES

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Plasma polymerization has become a well-established method for the synthesis of solid organic thin films referred to as plasma polymer films (PPF). However, the underlying growth mechanism remains partly unsolved, notably due to the limited methods available for evaluating microscopic properties and processes such as the impact of bombarding ions and the sticking coefficient of the film-forming species. Nevertheless, recent studies have highlighted the use of complex geometry substrates such as “cavities” and “undercuts” to achieve a better understanding of the growth mechanism of PPF at a molecular level.[1]
In this context, this work further investigates this approach while incorporating the use of an emergent synthesis parameter in the field, namely the substrate temperature (Ts) governing the adsorption/desorption equilibrium.[2] As a case study, allyl-alcohol is used as a precursor for plasma polymerization on undercut substrates.
By means of AFM characterization-based techniques including Peak Force Quantitative Nanomechanical Mapping, the mechanical behavior of PPF deposited on undercut substrates is evaluated and found to be similar to those obtained on plane substrates (i.e. a few GPa). However, the oxygen content drastically decreases (up to 6%) as the coating would reach deeper into the 3D structure, as highlighted by XPS. Similarly, ToF-SIMS experiments indicate a decrease in the cross-linking degree for the PPF deposited in the undercut as compared to 2D-deposited ones. Those observations are explained by the uneven diffusion of various reactive species as well as the limited ionic bombardment in undercut substrates resulting in gradient PPF properties.
Additionally, the deposition profile on 3D substrates allowed for the determination of the surface loss probability (β) of the film-forming species as a function of Ts. These results reveals a decrease in β with Ts and are discussed in regard to molecular dynamics simulations.
The whole set of our data provide new insights into the growth mechanism of plasma polymer films while paving the way for new experimental and theoretical methods to probe the microscopic processes involved in plasma polymerization.

Thanks/Acknowledgement
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PLATH00124

PLASMA-INDUCED PHYSICOCHEMICAL AND TOPOGRAPHICAL SURFACE MODIFICATIONS FOR ENHANCED POLYMER ADHESION

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As polymer and composite materials compete with metal alloys in the challenges of lightweight design and environmental sustainability, the low surface energy of polymers continues to drive ongoing developments aimed at improving adhesion, particularly through the use of dry and versatile processes such as cold plasmas [1].
We have previously shown that surface activation and/or texturing mechanisms enhance the adhesion of thermoplastics using lasers or plasmas, either under atmospheric or low-pressure conditions [2]. However, this increase in adhesion could be limited by thermomechanical degradation of the polymer.
We demonstrate that even in the case of a high-performance thermoplastic like polyetheretherketone (PEEK), which offers a wide thermal usage range (between -100°C and 150°C) and high fracture resistance (≈100 MPa), changes in local crystallinity can occur under plasma exposure. A significant correlation is observed between the local degree of crystallinity, assessed through micro-Raman spectroscopy, and the local mechanical properties within the PEEK cross-section, obtained by nanoindentation [3]. Furthermore, Scanning Electron Microscopy (SEM) supports these findings by illustrating the density and evolution of spherulitic structures. Tensile mechanical tests evaluate the influence of local crystallinity variations on the overall mechanical behavior.
Electron Cyclotron Resonance (ECR) plasma in various oxidative atmospheres was used to both functionalize and texture the PEEK surfaces. The results enhance our understanding of the effects of plasma treatment on crystallinity and the surface mechanical properties of the polymer, while preserving its integrity and optimizing its adhesion performance.

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PLATH00113

UNDERSTANDING BACKSCATTERED IONS IN HiPIMS PLASMAS

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High-Power Impulse Magnetron Sputtering (HiPIMS) has gained significant attention because of its superior film quality, enhanced ionization, and precise control over deposition parameters. A key process influencing HiPIMS discharges is the backscattering of ions from the target, often referred to as the ”backscattered ion wind”. These ions play a crucial role in discharge behavior affecting the neutral gas density, and therefore, the ionization rate and film growth, and film growth mechanisms. Although argon is commonly used in HiPIMS discharges, interest in lighter gases such as helium has grown because of their unique plasma properties, including higher electron temperatures and enhanced ionization rates.

This work investigates the energy distribution of backscattered ions in HiPIMS plasmas using Monte Carlo simulations based on SRIM calculations and the role played by the hor backscattered gas species in the HiPIMS discharge. We analyze helium, argon, and molybdenum ions impinging on a molybdenum target at different incident energies. Our study quantifies the fraction of ions that backscatter, their energy spectrum, and their potential impact on sputtering efficiency and secondary electron emission.
Figures 1 (a) and (b) illustrate the energy distributions of the ions backscattered for 1keV and 0.8keV, respectively, of the incident ion energies. The results reveal distinct backscattering behaviors depending on ion mass. Light elements such as helium exhibit a broad energy distribution, with a significant part retaining a large fraction of their initial ion energy, leading to enhanced gas recycling within the plasma. In contrast, argon ions display a lower energy tail (maximum energy devided by 2 with respect to He) as a result of their higher mass and greater momentum transfer during collisions. Additionally, these findings show there is a flux of fast neutral atoms coming back from the target to the ionization region, which significantly impacts impact the discharge dynamics, such as gas rarefaction and ionization. Plasma results obtained from the Ionization Region Model will be also presented and discussed. Plasma results obtained from the Ionization Region Model will be also presented and discussed.

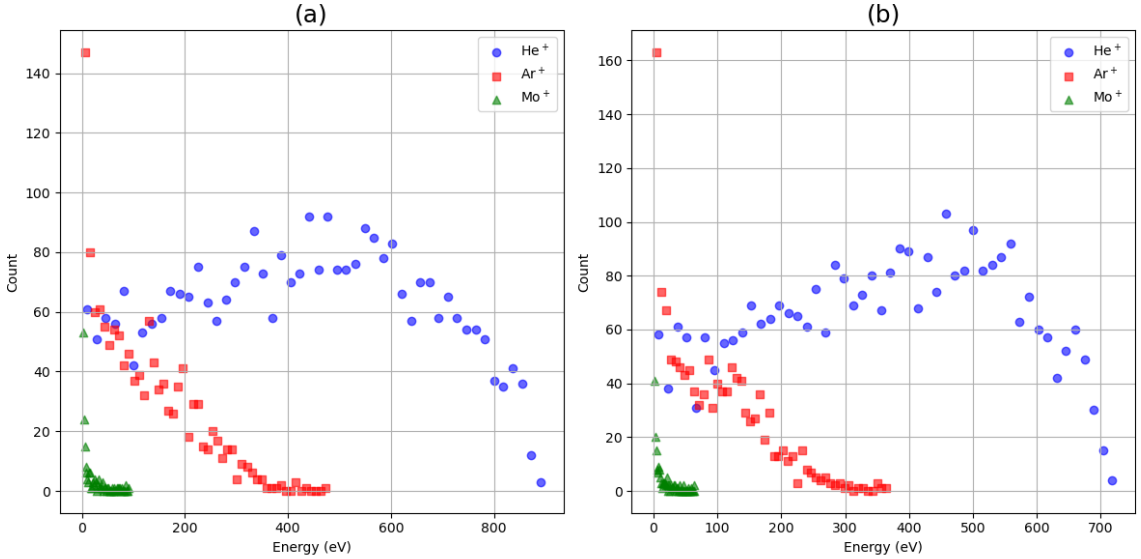

Figure 1 : Energy distributions of backscattered ions on a Molybdenum target.
(a): 1keV incident ions, (b): 0.8keV incident ions

Energy distributions of backscattered ions

PLATH00054

ENHANCING ENERGY FLUX TO INSULATING SURFACES USING UNIPOLAR AND BIPOLAR HiPIMS PULSE CONFIGURATIONS

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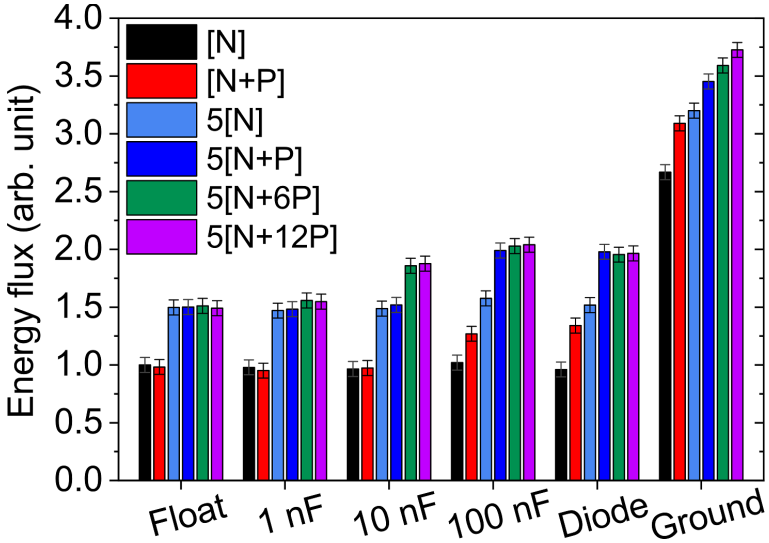
High-power impulse magnetron sputtering (HiPIMS) is an advanced thin film deposition technique, delivering high target power in short pulses, increasing ionization compared to conventional DC sputtering. However, many ions still have low energy, so substrate biasing is often used to enhance energy transfer to the growing film. For insulating surfaces where direct biasing is impossible, bipolar HiPIMS (alternating negative and positive pulses with floating substrate) offers a partial solution. However, rapid charging of insulated surfaces limits energy transfer. This study aims to optimize bipolar HiPIMS pulse configurations to explore the potential enhancement of energy transfer even for insulating surfaces.
Experiments were conducted using a magnetron with a Ti target powered by a DC source and a bipolar HiPIMS pulsing unit. Various pulse configurations (unipolar, bipolar, chopped unipolar, and chopped bipolar HiPIMS) were applied under unbalanced magnetic fields with the same average power. In-situ ion mass and energy spectrometry (MS) analyses were employed, and total energy flux to a substrate was measured using a passive thermal probe at a floating and ground potential. Moreover, the depositions on insulating substrates or films with various capacitances were simulated by connecting a defined external capacitor between the probe and the ground. Finally, Ti films were deposited on a floating substrate holder for structural analysis.
Thermal probe measurements confirm that chopped unipolar pulses enhance the energy flux to the substrate compared to standard HiPIMS. Bipolar HiPIMS introduces a high-energy peak in the IEDF; for chopped bipolar configurations, this peak broadens, and the high-energy tail is enhanced. For chopped bipolar configurations, the energy flux increase varies with substrate capacitance (Fig. 1). For low capacitance, ion acceleration occurs only at the start of each positive pulse before the substrate surface is fully charged, providing a slight increase in energy flux. For medium capacitance, chopping the positive pulse amplifies the increase of energy flux due to longer charging time and substrate neutralization during pulse off-times. Finally, with high capacitance, ion acceleration is sustained throughout the positive pulse regardless of its length, as for a grounded substrate. These effects were also verified by analyzing the deposited film properties.



Energy flux normalized to [N] at float potential.

PLATH00037

EXPLORING IONIZED METAL FLUX FRACTION IN MAGNETRON SPUTTERING: INSIGHTS FROM LABORATORY AND INDUSTRIAL APPLICATIONS

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In magnetron sputtering, atoms are ejected from the target and may become ionized before reaching the substrate. This effect is especially prominent in techniques such as Ionized Physical Vapor Deposition (IPVD) and High Power Impulse Magnetron Sputtering (HiPIMS). The Ionized Metal Flux Fraction (IMFF) in the non-reactive sputtering of metallic targets is defined as the ratio of metal ions to the total flux of metal ions and metal neutrals. This study presents IMFF measurements conducted in both laboratory and industrial environments for single-element Ti, Al, and Cr targets, as well as compound AlCr and TiAl targets. IMFFs of individual metals in the case of HiPIMS sputtering from single-element targets are compared to those of an alloy target being sputtered. Innovative strategies to maximize IMFF are explored while maintaining high deposition rates, including HiPIMS with pulse packaging and high-power sputtering using movable magnets (commercialized as focused magnetron sputtering, F-type sputtering, by Platit). Furthermore, the influence of increased IMFF on the properties of the resulting coatings is discussed.

PLATH00042

HEXAGONAL BORON NITRIDE DEPOSITION USING MICRO-PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION (µPECVD) BASED ON A MICRO HOLLOW CATHODE DISCHARGE (MHCD)

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Micro-hollow cathode discharges (MHCD) are microplasma sources consisting of a dielectric material (e.g., alumina) glued between two molybdenum electrodes, thus forming a "sandwich" structure with a central hole of a few hundred micrometers in diameter. The MHCD serves as an effective source for N_2 dissociation and has been proposed as a promising technology for the deposition of hexagonal boron nitride (h-BN) over large surface (~5 cm) substrates [1]. However, more work is necessary to improve the properties and quality of the deposited h-BN films. The primary objective of this work is to investigate various deposition conditions of h-BN using a MHCD driven by a negative pulsed high voltage. The operating gas is a N_2/Ar mixture, and different substrates are used for depositing h-BN such as silicon or sapphire. These are placed on a holder which is positively polarized (≈200 V DC) and heated (≥800 K) (Fig 1a). The MHCD is installed in the junction between two chambers: a high-pressure chamber at 30 mbar and a low-pressure deposition chamber at 1 mbar. The gas mixture is introduced into the high-pressure chamber and passes into the low-pressure chamber through the hole. The boron precursor, boron tribromide (BBr_3), is directly injected into the deposition chamber along with hydrogen [2]. The biased holder makes the plasma generated in the MHCD to extend toward the substrate. The plasma emission is studied using ICCD imaging, electrical measurements and emission spectroscopy. The deposits are analysed using Raman spectroscopy, SEM, XPS and AFM to determine key parameters such as the thickness and grain size of the deposited h-BN. The Raman spectroscopy shows the signal of h-BN around 1366 cm^{-1} that varies in intensity with the deposition time. The thickness of the h-BN films has been probed with AFM (fig 1b) and depending on the deposition time it varies from 50nm to 200nm. XPS allows us to determine the B/N ratio that is near 1:1 and SEM showed surface state of substrates.

Thanks/Acknowledgement
PlasBoNG (ANR-20-CE09-0003), Labex SEAM (ANR-10-LABX-0096;ANR-18-IDEX-0001), SPECTRON (ANR-23-CE51-0004-01)

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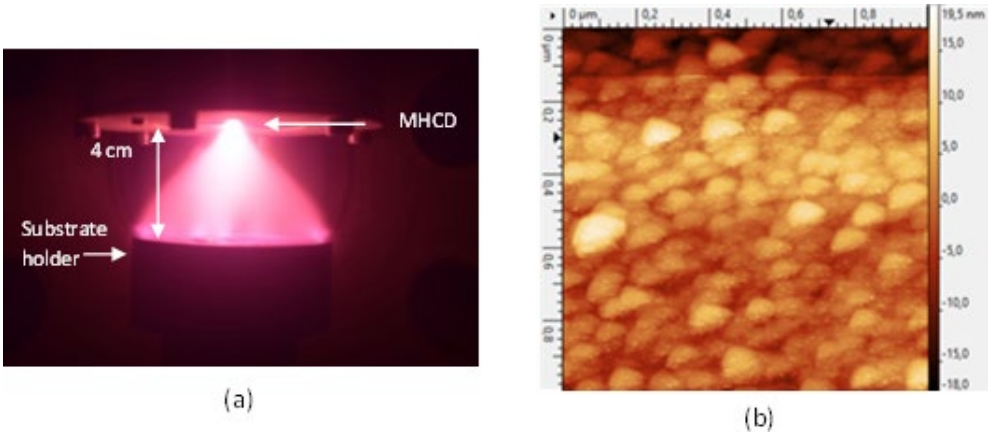

a) Photograph of the plasma b) AFM image of h-BN

PLATH00116

PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION OF SION OPTICAL THIN FILMS AND NANO-LAMINATES

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The ability to form dielectrics whose linear refractive index and nonlinear properties can be tailored facilitates the fabrication of optical devices in the form of optical coatings [1-3] or photonics integrated circuits [4-5]. Plasma-Enhanced Chemical Vapor Deposition (PECVD) techniques are often used to that extent as they allow to reach high deposition rates and can be performed at sufficiently low temperatures to be compatible with CMOS processes and even with the coating of organic compounds.
Here, we report a method to create optical thin films and nano-laminates of mixed compounds of silica (SiO_x), silicon nitride (SiN_y) and amorphous silicon (a-Si) by Inductive-Coupled-Plasma PECVD and demonstrate their use to fabricate anti-reflective coatings, optical mirrors, as well as birefringent structures.
SiO_x (respectively SiN_y) layers are deposited using a gas mixture constituted of SiH_4 and N_2O (resp. SiH_4 and N_2O and N_2). Intermediate compositions between SiO_2 and Si_3N_4 were obtained by varying the flux of N_2O while keeping all other parameters constant. To create silicon-rich SiN layers, the approach relied on the adjustment of the ICP RF power (up to 750W). Ex-situ variable-angle spectroscopic ellipsometric characterization of the produced layers was carried out and revealed that the refractive index at the wavelength of 790 nm can be tuned from 1.48 to 2.78+i0.007 as shown on Fig. 1.
Subsequently, the operation of the equipment in pulsed regime was investigated to create nanolaminates of adjustable refractive index and anisotropy with the specific objective to produce layers whose refractive indexes are matched to Z-cut LiNbO3 to ease the on-chip integration of optical devices exploiting the latter material.

Thanks/Acknowledgement
This work was supported by the ANR SCOPOL project (ANR-22-CE09-0019), by OPALE the joint laboratory between LAAS-CNRS and Essilor-Luxottica, and by the LAAS-CNRS micro and nanotechnologies platform, a member of the Renatech French national network.

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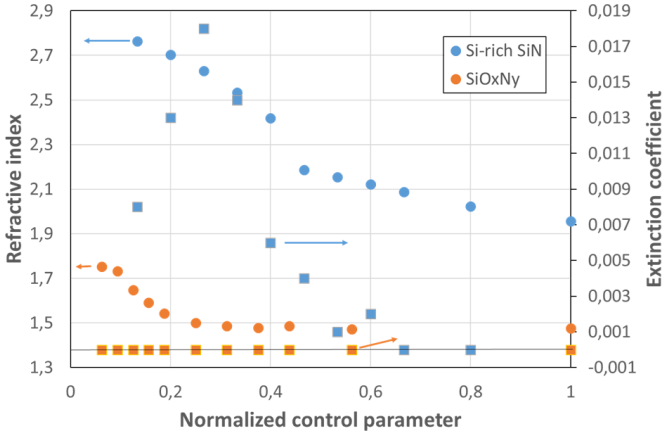

Refractive index of the produced SiON layers

PLATH00051

PACKAGING SOLUTIONS WITH PLASMA TECHNOLOGY FOR ENHANCING GASES BARRIER PROPERTIES

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Innovations in food packaging are driven by the need to improve aesthetics, design, and technical properties for optimal food preservation. With increasing legislation demanding sustainability standards in the plastic and food sectors, there has been a significant shift towards biopolymers and bio-based materials, with gum rosin resin derivatives emerging as a promising solution. Biopolymers, valued for their biodegradability and positive environmental impact, must undergo functional enhancements to comply with evolving industry regulations and reduce food waste, ensuring sustainability and performance standards are met.

Plasma treatments can be used to achieve functional barrier layers that reduce permeability to gases and humidity, increasing the shelf life of packaged products. The growing demand to reduce the use of hazardous chemicals and solvents values the plasma approach as a positive alternative for surface treatments of plastics

This work explores plasma technology as a key enabler for improving gas barrier properties using three technical methods: (i) atmospheric plasma pre-treatment for surface cleaning and activation before spray coating using water-based formulation, (ii) atmospheric plasma-assisted coating with an HMDSO-based precursor, and (iii) PVD sputtering with aluminum target.

The results show that incorporating gum rosin resin derivatives into biopolymers significantly enhances water vapor and oxygen barrier properties. Plasma pre-treatments and assisted coatings further improved these properties, reducing WVTR and OTR by more than 70% compared to the original substrate. They also enhanced adhesion, cross-linking, and densification, reducing permeability.

This study highlights plasma-assisted functionalization as a strategy for improving biopolymer-based food packaging. Integrating plasma technologies significantly enhances barrier performance while meeting the increasing demand for sustainable, eco-friendly, and biodegradable packaging solutions.

Thanks/Acknowledgement
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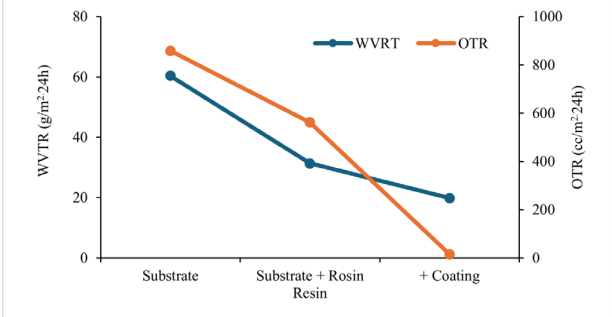

Barrier Performance of Coated Substrate

PLATH00120

ATMOSPHERIC PRESSURE PLASMA-ASSISTED DEPOSITION OF ZINC-BASED COATINGS FOR AGRICULTURE APPLICATIONS

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Bacterial soft rot is a major global plant disease affecting crops causing an estimated 15–30% annual yield loss in agricultural production. This disease impacts a wide range of crops, including potato, dragon fruit, cabbage, cucumber, and tomato. *Erwinia carotovora* subsp. *Carotovora*, a Gram-negative pectolytic bacterium of the Pectobacteriaceae family, is a key causal agent of soft rot. *Erwinia carotovora* spreads via irrigation water, manual transmission, and crop transport, persisting on weeds and plant debris leading to complication in the disease management.
Currently, several strategies are used to prevent soft rot disease, including crop rotation, chemical treatments and antibiotics. However, these methods are costly, environmentally harmful, contribute to bacterial resistance, and can possess potential health risks. Moreover, growing environmental sustainability concerns, highlighted by initiatives like the European Green Deal, emphasize the need for eco-friendly alternatives to nowadays used chemical treatments. One promising solution is seed coating, which enhances seed handling, protection, germination, and rooting.
In this context, nano-agrochemicals, such as ZnO nanoparticles (ZnO NPs) and alike and the use of innovative technologies like Atmospheric Pressure Plasma (APP) processes, offer sustainable alternatives. [1] APP is a cost-effective, scalable technology that enhances seed decontamination and growth, providing a viable solution for eco-friendly seed coatings. [2] Correspondingly, this research proposes the use of Aerosol Assisted Atmospheric pressure plasma jet (AA-APPJ) deposition to prepare polyethylene glycol (PEG)-like coatings embedding ZnO NPs or other zinc derivatives on model polyethylene (PE) substrates leveraging its antibacterial properties as an alternative to chemical treatments and antibiotics. The antimicrobial efficacy of these plasma-polymerized PEG-ZnO coatings against *Erwinia carotovora* demonstrates a robust antibacterial effect, both when ZnO NPs (10–30 nm) and when zinc acetate dihydrate is co-polymerized with the PEG precursor (2% weight).
Preliminary results suggest that AA-APPJ is a promising novel tool for seed coating. Ongoing work aims to optimize the deposition of nanocomposite films containing zinc on *Cucumis melo* var. *agrestis* seeds.

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PLATH00061

TiO_xC_Y ORGANOMETALLIC MULTILAYERS FOR TITANIUM DENTAL IMPLANTS: THE ROLE OF CARBON IN PROMOTING OSSEOINTEGRATION

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Titanium, along with its alloys, is a biocompatible material widely employed in biomedical applications. Specifically, its use in dental implants is widespread due to its mechanical, chemical and biological properties [1]. The wettability of the implant is crucial for accelerating osseointegration mechanisms, as external surfaces of the implant with low hydrophilicity do not promote contact between the metal part of the implant and the cells, leading to poor osseointegration and, therefore, implant failure [2]. The implant body, or screw, is the part of the dental implant that is inserted into the jawbone. The metal must integrate with the bone, making the creation of hydrophilic surfaces necessary for optimal bonding.

In this work, TiO_xC_y multilayers were deposited on $Ti_{90}Al_6V_4$ foils using Plasma Enhanced Chemical Vapor Deposition (PECVD) technique. The layers have been prepared varying the flow and proportion of the gases (Ar, O_2), the power, and the deposition time producing changes in the chemical composition of the films, and consequently in their hydrophilicity, deposition rate and thickness. The idea is to produce a TiO_2 like layer on the metal side, by using an oxygen rich plasma, and a TiO_xC_y layer rich in carbon on the bone side, by using an Ar rich plasma. The characterization of the coatings was conducted using X-ray photoelectron spectroscopy (XPS), contact angle and profilometry analyses to study the chemical composition, the hydrophilic character of the surface and the thickness.

The results indicate a TiO_xC_y multilayer with a low carbon concentration near the $Ti_{90}Al_6V_4$ substrate and with a carbon gradient towards the surface, varying from mineral (low C) to organic (high C), because carbon-rich TiO_xC_y layers could induce favorable cell adhesion and improve osseointegration.

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PLATH00021

DIAGNOSTIC OF DC ARC PLASMAS IN AERONAUTIC ARC FAULT CONDITIONS: APPLICATION TO DETECTION

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Detecting electric arc faults is a major challenge for the electrification of transportation systems, particularly in the aeronautics sector, as well as for the broader use of DC power supplies. The ignition of a DC arc plasma in an electrical system can have serious consequences, releasing substantial energy and potentially leading to electrical fires. To address this issue, promising detection methods leverage machine learning to identify arc plasma formation within extensive cable networks, such as those found in aircraft. However, these approaches require large, high-quality databases that are difficult to construct and validate. Therefore, improving database reliability through a deeper physical understanding of arc behavior or by prioritizing hybrid detection methods is essential. Our approach focuses on the strong signal disturbances observed in electrical measurements following arc plasma ignition. By implementing advanced plasma diagnostic techniques such as fast-camera stereoscopy, optical emission spectroscopy, and electrical measurements, we aim to deepen our understanding of arc plasma behavior under aeronautical fault conditions. This will be achieved through the identification of key descriptors and their correlation with plasma dynamics, paving the way for more accurate and reliable arc fault detection methods.
This approach already enables the correlation of electrical fluctuations with plasma-surface interaction phenomena. The surface of materials in contact with the arc foot undergoes intense energy exchange. The interface between the arc plasma and the electrode is predominantly composed of liquid metal, resulting in specific behaviors that can release material into the plasma and generate detectable electrical disturbances. In this presentation, the correlation between droplet ejection and current peaks will be discussed, along with a deeper understanding of this phenomenon achieved through object-tracking methods [1]. The signature of molten metal bubble explosions has also been identified, and we will demonstrate how it could be utilized for arc fault detection in aeronautic conditions using an initial detection algorithm approach. Finally, the dynamics of arc plasma will be examined through fast-camera stereoscopy, with 3D reconstruction of recorded sequences (figure 1) providing valuable insights into the arc's electrical signature and its connection to plasma-electrode interface phenomena.

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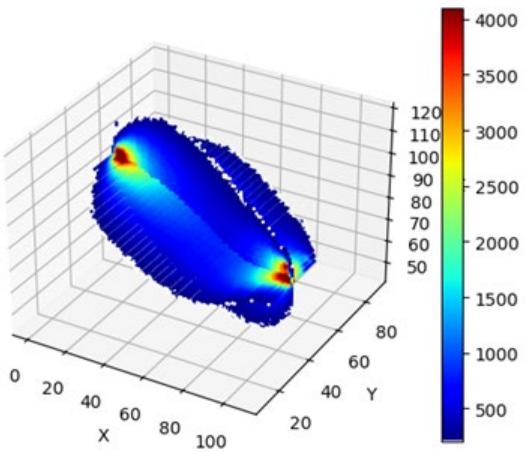

3-dimensional reconstruction of an arc plasma

PLATH00088

PLASMA PROCESSING OF MONOLAYER GRAPHENE EXPLORED WITH NUMERICAL SIMULATIONS

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The first successful synthesis of monolayer graphene in 2004 motivated tremendous research efforts for the discovery and tailoring of new 2D materials for nowadays applications. In that mindset, processes with atomic-level control combined with a low substrate temperature are required. Low-pressure plasmas alter the surface through excited species impact while keeping substrate temperature relatively low. Monolayer graphene exposure to very low energy ions (<15 eV) leads to the fast generation of defects despite the strict threshold for defect generation estimated at 18-22 eV[1,2].
Numerical simulations can provide great insight into graphene modifications by ion irradiation. Molecular Dynamics (MD) simulations shed light on the influence of low-energy ion irradiation. Furthermore, the effect of ion neutralization upon the surface by sub-threshold energy ions can be mimicked. As ion neutralization occurs at a larger distance than impact, graphene is locally altered right before ion collision with the surface. However, MD simulations are inherently inadapted for such study as electron dynamics are involved during ion neutralization. To properly investigate this phenomenon, first-principle simulations are necessary. The code FPSEID21 enables Ehrenfest MD simulations with forces determined by Time-Dependent Density Functional Theory calculations that can be run to further study sub-threshold ion's interactions with graphene.
From those investigations, a fundamental understanding of plasma interactions with monolayer graphene is reached. Those results provide significant insight for the modification of other 2D materials such as MoS2 which are also sensible to very-low energy ions irradiation[3].

Thanks/Acknowledgement
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PLATH00028

DC PLASMA-INDUCTED PHASE AND MORPHOLOGICAL EVOLUTION OF PtSn AND PtRuSn NANOPARTICLES PRODUCED IN A MAGNETRON-BASED GAS AGGREGATION SOURCE

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Bimetallic platinum-tin (PtSn) and trimetallic platinum-ruthenium-tin (PtRuSn) nanoparticles (NPs) were grown in a cluster beam source equipped with in-plane multi-magnetrons inside the gas aggregation source (GAS) [1]. The growth parameters were controlled by varying the power applied to the targets and evaluated by recording the in situ mass distribution curves measured by a quadrupole mass spectrometer (in situ-QMS) (Figure 1b) located in a low-pressure chamber connected to the GAS through a hole. The QMS is then replaced by a biased substrate holder in front of which a DC glow discharge (or secondary plasma, SP) is ignited at +50 V (Figure 1a). In comparison with depositions without the SP, the NPs are able to grow in this SP leading to morphological changes from densely packed NPs to sponges as observed by Scanning Electron Microscopy (SEM) (Figure 1c) and Grazing-Incidence Small-Angle X-ray Scattering (GISAXS). X-ray diffraction (XRD) revealed that PtSn clusters without the influence of SP exhibit an alloy phase (A1), whereas an ordered intermetallic Pt_3Sn ($L1_2$) phase is obtained with the SP. The presence of the SP also influenced their atomic composition, as energy-dispersive spectroscopy (EDS) indicated a decrease in the Pt content for PtSn. The NPs with varying Pt, Ru and Sn composition were synthesised in GAS and introduced into the SP to examine SP's effect on phase and morphology evolution. These findings offer valuable insights into how SP induces phase transitions and stabilizes specific phases depending on the elemental composition.

Thanks/Acknowledgement
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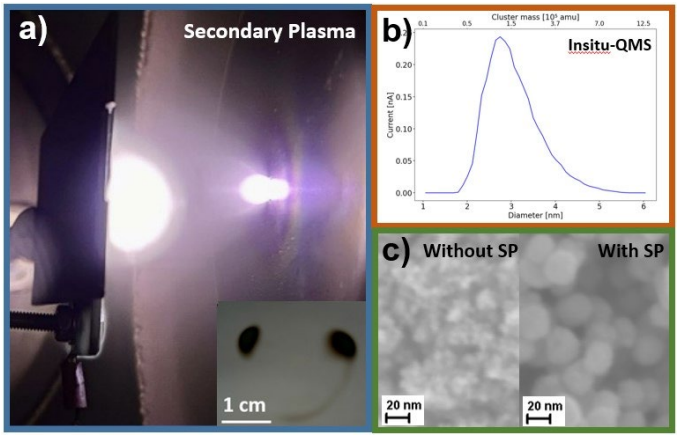

Plasma exiting from the GAS through the hole and s

PLATH00076

THERMALLY-INDUCED MICROSTRUCTURAL EVOLUTION IN NANOPARTICLE-BASED CuO, WO_3 AND CuO-WO_3 THIN FILMS FOR HYDROGEN GAS SENSING

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This work aims to improve conductometric gas sensing by incorporating nanostructures into the sensing material, enhancing interaction with target gases. Metal oxide semiconductors (MOS) are highly sensitive to oxidizing and reducing gases, with composite MOS systems further benefiting from heterojunctions that improve sensitivity. Our focus is to develop advanced hydrogen gas sensors using composite nanoparticle-based thin films of p-CuO and n-WO_3, and study the effects of annealing on these films, to understand the effect of heat treatment on nanoparticle (NP) microstructure and, consequently, gas sensing performance.
The CuO, WO_3 NP-based thin films, and their composite were synthesized using a magnetron-based gas aggregation source, with the composite consisting of alternating monolayers (10 nm in diameter) of CuO and WO_3 NPs. Samples were annealed at temperatures from 200 to 400°C in synthetic air to investigate the effects of annealing on their microstructure using extensive characterisation techniques such as XRD, SEM, XPS, and Raman spectroscopy. Significant changes in particle size and crystallinity were observed in CuO, while WO_3 and the composite samples exhibited slower microstructural evolution, even at elevated temperatures. Notably, at 400°C, the composite crystallized into a novel phase and is being investigated via DFT simulations. The annealed samples were evaluated for their conductometric gas sensing properties towards H_2 using an in-house built four-point probe measurement setup. The impact of annealing on gas sensing performance of the prepared NP-based films was however not pronounced, likely due to the competing influences of evolving microstructural features. Additionally, in a separate study, we tuned the CuO to WO_3 ratio to optimize nano p–n heterojunction formation within the composite, successfully enhancing the H2 gas sensing response.
This study highlights the crucial role of thermal treatment in influencing NP microstructure, offering insights into stabilizing and tuning NP-based thin films for enhanced gas sensing. Additionally, the optimized ratio of CuO and WO_3 NPs within the composite improved H_2 sensing performance by promoting optimal p–n heterojunction formation, demonstrating that precise compositional control can significantly boost the sensitivity of nanostructured systems. Together, these findings provide a strong foundation for advancing MOS-based sensor technologies in applications demanding high sensitivity and robust response.

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PLATH00086

NOVEL NANOCOMPOSITE THIN FILMS BY PULSED LASER PROCESSES FOR PLASMONIC BASED SENSING OF CANCER MARKERS

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This communication presents the development by pulsed laser deposition processes, of a novel nanocomposite thin film architecture as a highly sensitive plasmonic platform for rapid and early-stage disease diagnosis. The bio-detection principle is based on surface plasmon polaritons (SPP) existing at the interface between a metallic thin film and a dielectric, aiming to achieve high sensitivities and detect small analytes in very low concentrations (lower than fM concentration).

Nanocomposite thin films are deposited on a glass substrate and are constituted of an ultra-thin (12 nm) Al2O3 matrix with embedded silver nanoparticles (diameter 2.3 nm), covered by a 48 nm gold layer. This architecture, combining localized surface plasmon resonance (LSPR) in nanoparticles with propagating SPR that exists in the gold film in a single material, can result in enhanced sensitivities.

These plasmonic nanocomposites were made in a single reactor coupling two laser processes and developed by our group [1]. The well-known Pulsed Laser Deposition (PLD) method enables the deposition of thin films (Al2O3 matrix and gold upper layer) with high quality and offers the possibility to manage accurately their thicknesses. The associated free cluster generator developed for nanoparticles (NPs) synthesis with a diameter in the range 1-10 nm with quasi-monodisperse size distribution is used for silver NPs fabrication.

A specific detection method based on lateral position shift of the reflected wave, known as Goos-Hänchen (GH) shift applied to this highly performing material results in high detection levels, with an ultra-high sensitivity up to 3.3×108 nm.RIU-1. The detection of cancer markers in sub-attomole concentrations was achieved, demonstrating the excellent potentials of the architecture for sensing with the highest detection level ever reached [2]. It is important to emphasize that these fully biocompatible sensors do not require functionalization before detection tests, making them easier to use compared to other platforms.

Thanks/Acknowledgement

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PLATH00052

SATURATED PLASMONIC COLOURS FOR IDENTITY SECURITY FEATURES OBTAINED BY MAGNETRON SPUTTERING AND LASER TREATMENT

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Plasmonic colors from Ag nanoparticles leverage localized surface plasmon resonance (LSPR) for high-resolution, durable security features. Their tunability enables dynamic, enhancing anti-counterfeiting measures[1]. We aim at inscribing a large gamut of saturated colors to personalize ID documents thanks to laser treatment. To achieve that, we deposit Ag metallic nanoparticles (Ag:NPs) by magnetron sputtering in a resonant cavity of TiO_2 over an Ag mirror to exalt the absorption of the LSPR. The Ag:NPs' shape, size, and distribution are modified with laser treatment[2] to tune the plasmonic colors and provide new security features. The thin films are deposited in a semi-industrial magnetron sputtering chamber, from Ti, Si, and Ag targets. A specific protection layer was developed over each Ag deposition to protect Ag from O_2 oxidation and to maximize reflectance outside the extinction band (Figure, left). Depending on the nanopulsed laser parameters used, various hues from magenta are obtained (Figure, right). First SEM observations showed Ag:NPs with sizes from 10 to 100 nm over a porous TiO_2 structure, which gives us this complementarity property. Characterizations by SEM-FIB and AFM have also been performed to investigate the morphological changes in relation to the laser treatment.

Thanks/Acknowledgement

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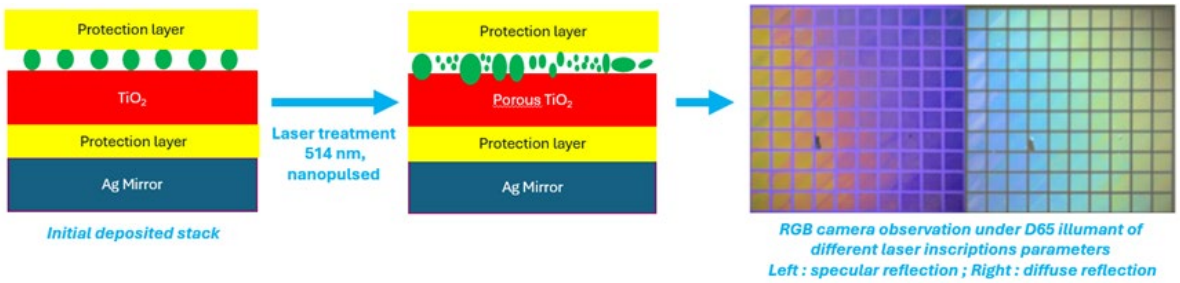

Figure

PLASMA-CATALYST INTERACTION MECHANISMS FOR CO_2 RECYCLING AND MOLECULE CONVERSION

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Plasma catalysis offers a promising avenue for creating energy-efficient CO_2 recycling processes. By activating CO_2 through dissociation or vibrational and electronic excitation, plasma can enhance the yield of desired products, while the catalyst can enhance the selectivity in processes such as methanation, methanol synthesis, and DRM. However, the direct dissociation of CO_2 by plasma is not always energy-efficient, and the role of CO_2's excited states and dissociation products remains unclear [1].

Advancing plasma catalysis research requires tools that enable precise quantitative comparisons of data across different research groups. One possibility to study these complex systems is to establish standards and databases, similar to practices in conventional catalysis, for instance, but adapted to the specificities of plasmas. In this vein, the PIONEER European project has initiated a database focused on CO_2 conversion performance through plasma catalysis [2]. However, the lack of fundamental understanding of the plasma-catalyst interaction makes it difficult to define the most relevant parameters for meaningful comparisons between various plasma-catalytic systems. Moreover, the catalysts typically used in plasma catalysis are often those developed for thermal catalysis, which may not be optimal for efficiently using the short-lived species generated by plasma. To maximize the benefits of cold plasma, it is crucial to separate the chemical kinetics of the gas phase from surface processes and understand how plasma can alter the catalyst itself, necessitating *in situ* measurements.

In this study, various low-pressure plasma reactor configurations were employed to validate step-by-step kinetic models of plasmas, particularly for CO_2/H_2 and CO_2/CH_4 systems. Batch reactors with pulsed radiofrequency sources were used to constrain the characteristic times of the primary chemical reactions. Once the gas phase kinetics are understood, the same plasma sources can be used to assess their impact on catalytic surfaces. In particular, simple materials known for their oxygen mobility, such as CeO_2 and YSZ pellets, were exposed directly to plasma to conduct time-resolved infrared absorption and *in situ* Raman measurements. These measurements allowed the study of carbonate formation on the material surfaces and the creation of oxygen vacancies within the materials. The combination of detailed characterization of the plasma kinetics and the surface evolution in a single system proves to be a powerful approach to understanding the microscopic mechanisms of the plasma-catalyst interaction.

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PLATH00135

ENHANCING CO_2 PLASMA CONVERSION BY IN-SITU OXYGEN REMOVAL USING A SOLID OXIDE ELECTRICOCHEMICAL CELL (SOEC)

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Hybrid plasma-solid oxide electrochemical cell (SOEC) systems have shown promise in CO_2 splitting processes [1,2]. They might provide future solutions for power-to-X schemes, i.e. renewable electricity driven chemical conversion processes such as the generation of syngas from H_2O/CO_2 for methanol production and synthetic fuels. But also it might provide solutions for in situ resource utilization in Mars expeditions to produce oxygen from Marsian atmospheric CO_2. In this contribution, we investigate key factors affecting oxygen production in a plasma-assisted SOEC with CO_2 feed gas, focusing on reducing operating temperatures of the SOEC, leveraging SOEC materials lifetime. Using a symmetric LSM | YSZ | LSM SOEC, experiments show that a He-CO_2 glow discharge reaches up to 90% conversion. Under oxygen pumping conditions, the plasma-SOEC system achieves a higher CO_2 conversion rate than plasma-only processes, demonstrating a true synergistic effect. Plasma improves the surface-limiting step of CO_2 electrolysis, i.e., shifting from dissociative adsorption of CO_2 towards oxygen surface adsorption reactions, enhancing energy efficiency. Additionally, oxygen removal via SOEC shifts CO_2 plasma splitting equilibrium, increasing gas conversion rates, while CO_2 plasma avoids CO oxidation on the LSM electrode, further boosting SOEC oxygen pumping performance.

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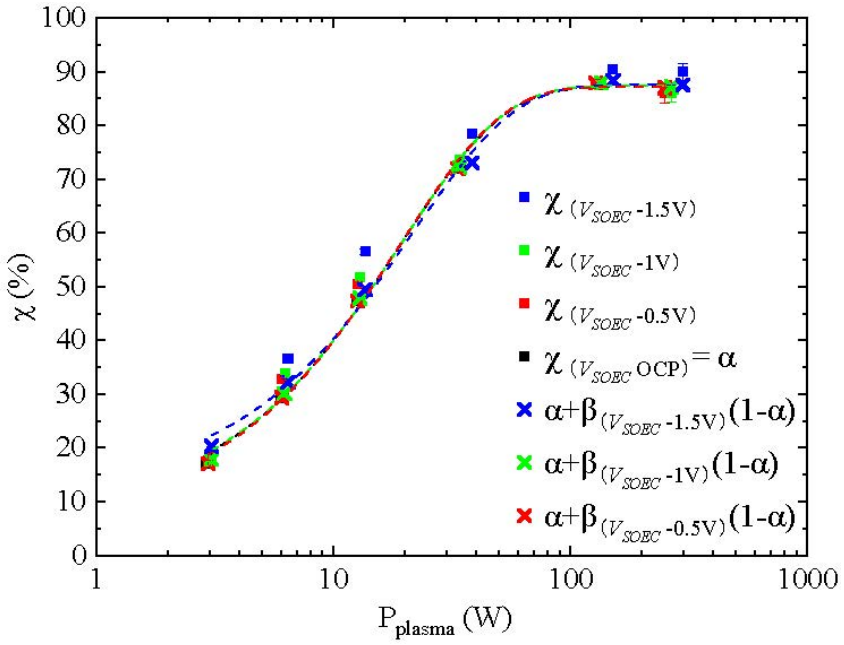

CO_2 conversion vs. plasma power

PLATH00034

EXPLORING THE POTENTIAL OF A PULSED THERMIONIC VACUUM ARC AS METAL ION PROPULSION SYSTEM

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The development of efficient and versatile space propulsion systems remains crucial for advancing space exploration and satellite operations in an increasingly complex space environment. This study reports on a novel approach to metal ion thruster development using Pulsed Thermionic Vacuum Arc (PTVA) technology, offering advantages in cost, lifespan, size, and versatility while eliminating the need for acceleration grids.
The experimental investigation was conducted under high and ultra-high vacuum conditions, making it particularly relevant for space applications. Anode-plasma potential and potential gradients between anode-plasma and vessel walls were measured using an emissive probe. A magnetic deflection ion energy analyzer was employed to assess ion energy distribution functions.
Results demonstrate that this technology achieves thrust and specific impulse levels surpassing traditional systems such as the Xenon Ion Propulsion System and Stationary Plasma Hall Thruster [1]. Key findings include the observation of consistent anode-plasma potential near the anode potential and the formation of a sharp potential drop between the anode-plasma and vessel walls. The analysis revealed quasi-monoenergetic ion energy distributions strongly correlated with the anode-plasma potential, which can be fully controlled through various operational parameters, including arc current/voltage, pulse configuration, thermionic filament current, and the set-up design. Furthermore, the study identified that the total anode current serves as an effective indicator of the plasma ionization degree. Both ion energy and ionization degree are key factors in evaluating the thruster's performance in terms of thrust force and specific impulse.
This comprehensive investigation demonstrates that PTVA-based metal ion thrusters represent a promising advancement in space propulsion technology. The system's ability to independently control thrust and specific impulse generation, combined with its superior performance metrics compared to classical systems, makes it an attractive solution for diverse space mission requirements. The flexibility in operational parameter adjustment enables customized propulsion solutions, marking a significant step forward in spacecraft propulsion system development.

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PLATH00125

STUDY OF CH_4 PYROLYSIS IN A PLANAR ATMOSPHERIC GLIDING ARC DISCHARGE

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Plasma-based reforming for hydrocarbon feedstocks such as CH_4 into H_2 and carbon-based by-products is being extensively investigated in our environmental context. In this work, a home-made planar DC constant-current 'warm' gliding arc discharge is tested for the pyrolysis of CH_4 at atmospheric pressure. Our objective is to better understand the CH_4 pyrolysis mechanism in such discharges.
The impact of the fixed current (I_D), the total gas flow (Φ, 5-15 L min-1) and the CH_4 content (Φ_{CH4} =10-50% in Ar) on the process conversion rate (χ), product selectivity and total energy cost (EC) were evaluated. Gas chromatography and FTIR spectroscopy were implemented to respectively quantify H_2 and C_2H_2 as the primary gaseous products. Optical Emission Spectroscopy (OES) was further implemented to evaluate the gas temperature reached in the arc. In addition, we specifically investigated the effects of I_D and Φ_{CH4} on the generated carbon materials properties that where evaluated by Raman spectroscopy and electron microscopy.
Two discharge regimes were identified in our experimental window, which differs by the plasma energy density. A turquoise flame was typically obtained at low values of the energy density. In this condition, no carbon formation is observed (whatever Φ_{CH4} is) revealing a too low associated discharge power (P_D). When increasing I_D, the plasma features is strongly affected with the appearance of a yellow flame, associated with the production of incipient soot, expanding as a function of I_D. In these conditions, carbon is always generated. The maximum χ achieved reached 87.3%, for an EC of 23.7 kJ/LCH_4, as the operating conditions were set to optimize the flame temperature (maximum CH_4 dilution and I_D, minimum Φ_{CH4}). Just by lowering I_D, the EC could be reduced to 14.3 kJ/LCH_4 while maintaining χ above 84%.
Characterization of carbon products reveals the formation of two distinct types of nanomaterials: graphene nanoflakes (GNFs), predominantly synthesized at Φ_{CH4} = 10%, and carbon nanoparticles (CNPs), primarily generated at higher Φ_{CH4}. For CNPs, a comparative thermogravimetric analysis and derivative thermogravimetric study with commercial Carbon Black (CBs) reveals that the thermal stability and purity of CNPs improves with increasing P_D, shifting their properties closer to those of CBs.
This work demonstrate that in addition to the production of H_2, it is possible to control to a certain extent the features of the carbon-materials by-products in a GAD.

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PLATH00044

IMPACT OF SWIFT HEAVY IONS IRRADIATION ON THE MICROSTRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF SPUTTERED VANADIUM NITRIDE THIN FILMS FOR MICRO-SUPERCAPACITORS

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Microsupercapacitors are electrochemical energy storage devices expected to be deployed on large scale for Internet of Things applications. Current research deals with the development of new materials, such as pseudo-capacitive vanadium nitride (VN). This latter has attracted a great deal of attention due to its high electrical conductivity and high capacitance partly due to the multiple oxidation states of the vanadium cation.
VN thin film electrodes could be easily implemented in micro-devices by the use of plasma-assisted deposition such as magnetron sputtering. This method provide high flexibility for tuning the morphology and microstructure of pseudocapacitive films, allowing for the evaluation of the structure–property relationships of thin-film materials. Our recent works have highlighted the importance of controlling discharge and deposition parameters to optimize the electrochemical performance of VN thin films[1][2].
Here, VN thin film electrodes were prepared by reactive DC magnetron sputtering and then subjected to swift heavy ions irradiation, aiming at modifying the microstructure and create structural defects. We have used 129Xe19+ ions with energy 70.95 MeV at IRRSUD beamline of GANIL facility to irradiate 350 nm-thick VN thin films with dose up to 1014 ions·cm^{-2}. The microstructural, chemical and electrochemical properties of the films were studied by SEM, XRD, XPS, cyclic voltammetry and impedance spectroscopy before and after irradiation.
We reveal that ions irradiation induces densification, amorphization, and surface oxidation, favouring the formation of higher oxidation state vanadium oxides. Besides, ions irradiation induces a clear increase in the electrical conductivity of the films as a result of densification. These changes have strong impact on the electrochemical performance of VN electrodes. While as-deposited VN shows superior capacity at low cycling rates due to its porous and crystalline microstructure, the irradiated VN electrodes demonstrate improved capacity retention and faster charge/discharge capabilities at high cycling rates.
This work emphasizes how to optimize the microstructure and chemical properties of VN thin films by adjusting plasma parameters, and reveal the impact of using swift heavy ion irradiation to achieve functional properties for energy storage applications.

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PLATH00084

PLASMA THIN FILMS FOR HIGH-FREQUENCY FILTERING SUPERCAPACITORS

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The increasing demand for miniaturized electronic devices with high power efficiency and energy density has driven the exponential growth of electrochemical capacitors. Currently, available electrochemical capacitors achieve peak performance under direct current (DC), primarily in low-frequency regions (below 1 Hz), due to their electrode architecture and configuration. As a result, the commercialization of electrochemical supercapacitors remains in its early stages. Their application in large-scale electricity systems is also limited by insufficient response to alternating current (AC).
Since most energy storage devices perform optimally under DC, designing a system capable of responding to AC power sources while efficiently converting AC to DC is crucial for consumer applications. Consequently, research interest in line-filtering supercapacitors has been increasing. The performance of these supercapacitors is significantly influenced by the design and architecture of the electrode material. Key factors include the electrical conductivity of the electrode material, minimal contact resistance between the active material and the current collector, an optimal thickness of 1–10 μm, and microstructural design. Directly depositing the active material onto the current collector without polymeric binders is essential for fabricating electrodes with these characteristics.
Among various deposition techniques, plasma-enhanced chemical vapor deposition (PECVD) stands out due to its ability to engineer nanostructures directly onto substrates with diverse morphologies, orientations, dimensions, and thicknesses. This paper highlights the advantages of plasma-based methods for the structure-controlled design and customization of carbon nanostructures as advanced electrodes in supercapacitors for AC-to-DC line-filtering applications. Plasma-deposited vertical carbon nanostructure electrodes achieved a capacitance of 430 μF in the high-frequency range (100 Hz) and exhibited a phase angle of approximately -80°. Additionally, a prismatic prototype was developed to evaluate the electrodes' stability and filtering efficiency in AC-to-DC conversion. The prototype demonstrated a capacitance of 12 mF at 100 Hz with long-term filtering stability exceeding three hours.
The exceptional filtering efficiency of supercapacitors made from plasma-engineered carbon nanostructures presents a paradigm shift, offering a potential alternative to conventional aluminum electrolytic capacitors for high-frequency applications.

Thanks/Acknowledgement
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PLATH00078

LANTHANUM NIOBIUM OXIDE THIN FILMS DEPOSITED VIA REACTIVE SPUTTERING FOR HIGH POWER MICRO-BATTERIES

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Recently, the emergence of a growing number of miniaturized electronic devices such as sensors for the internet of things (IOT), RFID tags, smarter cards or medical implants made it mandatory to develop new micro devices for electrical energy storage and delivery. Perovskite oxides have recently gained attention as promising electrode materials for high-power Li-ions micro-batteries due to their unique functional properties such as their oxidation states [1].
Here, we demonstrate a strategy to prepare La_xNbO_3 perovskite material thin films as an alternative negative electrode material to graphite and $Li_4Ti_5O_{12}$ anodes. Thin films were prepared by reactive co-sputtering of lanthanum and niobium targets in Ar-N2 atmosphere, followed by annealing in air at 1000°C. Targets powers and nitrogen flow were finely controlled to achieve the targeted $La_{0.33}NbO_3$ crystal phase with two third of vacancies on the A-site. The creation of vacancies channels in the perovskite film aims to allow lithium insertion and fast ionic diffusion in the material [2], [3], [4].
To achieve high electrochemical performance (energy and power), it is critical to have fine control over the composition, structural (microstructure, crystalline phase, orientations…) and mechanical properties of the thin film electrode. In this work, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) results are discussed for a series of thin films with various La/Nb ratios. Then, the electrochemical properties of perovskite oxide thin films were studied through cyclic voltammetry and galvanostatic cycling measurements in lithium containing electrolyte. A high capacity of 190 mAh/g is achieved at a low scan rate of 0.1 mV/s. At a faster scan rate of 2 mV/s, a capacity of 150 mAh/g was retained, indicating excellent rate performance suitable for high-power applications.

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PLATH00091

DIRECT INJECTION OF IRON ACETATE SOLUTIONS IN A LOW PRESSURE PLASMA TO PREPARE Fe_2O_3/TiO_2 NANOCOMPOSITE THIN FILMS

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Designing innovative materials that combine low toxicity, abundant elements (e.g. Fe and Ti), and promising photocatalytic properties is essential in building a sustainable future. This work presents a novel approach for the preparation of photocatalysts. We deposited a nanocomposite material composed of Fe_2O_3 nanoparticles embedded in a thin TiO_2 layer, with the objective of enabling the degradation of organic pollutants in both water and air.
TiO2 is a well-studied semiconductor with low fabrication cost, increasing the chance for widespread development on an industrial scale. The anatase variety of TiO2 is used in many energy-storage, photovoltaic and photocatalytic systems but one challenge to overcome is that TiO2 light absorption is limited to the UV region [1] . The current study aims to develop a hybrid process combining a RF plasma-enhanced chemical vapor deposition (PECVD) and injection of an iron salt solution allowing the controlled dispersion of Fe2O3 nanoparticles in a TiO2 matrix. Such nanocomposite is expected to evidence a synergetic effect between TiO2 and Fe2O3, extend the absorption spectrum of the material and improve the spatial photogenerated charge separation [2]. To optimize the preparation of the nanocomposite, the work has been divided in two steps: (1) evaluate the behaviour of an iron salt solution in an oxidizing plasma, (2) injection of a solution containing Fe nanoparticle precursor into an oxygen/titanium isopropoxide plasma.
In this preliminary phase (1), spin-coated films of an iron salt solution (Fe(CH3CO2)2xH2O in propylene glycol (PG)) were treated with a low-pressure O_2/Ar plasma (400 W, 3 mTorr) using a 13.56 MHz inductively coupled plasma (ICP) source. X-ray induced photoelectron spectroscopy (XPS) analysis confirmed promising oxidation states of iron: along the treatment steps, concentrations in oxidized iron Fe2+ and Fe3+ evolve. Building on these results, the iron salt solution (dissolved in PG and ethanol) was then directly injected into the O_2 plasma, enabling further characterization of the resulting thin films, solvent evaporation dynamics, and plasma-induced reaction kinetics (optical emission spectroscopy, pressure monitoring, ellipsometry). Photocatalyst properties of these thin films were investigated as well when injected on a TiO2 thin film.

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PLATH00106

AEROSOL ASSISTED ATMOSPHERIC PRESSURE PLASMA DEPOSITION OF HYBRID TiO_2-BASED PHOTOACTIVE NANOCOMPOSITE COATINGS FOR WATER REMEDIATION

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Nanocomposites have been a topic of increasing interest in the last decades because of their superior properties when compared to their single components. Among metal oxide nanocomposites, TiO_2-based ones are largely studied for environmental remediation applications (such as wastewater treatment, photodegradation of organic pollutants or antimicrobial activity). Indeed, NPs of TiO_2, an n-type semiconductor, show valuable photocatalytic properties, although affected by several drawbacks, such as a wide band gap of 3.2 eV that leads to a strong absorption in the UV region, thus requiring a high energy irradiation, and a fast electron-hole recombination rate. Noble metals nanoparticles, e.g. AgNPs, and carbon nanomaterials, e.g. reduced graphene oxide and fullerene, are often used as co-catalyst together with TiO_2 in order to reduce the electron-hole recombination time.
In this work, the deposition via Aerosol Assisted Plasma Deposition (AAPD) of three types of TiO_2-based nanocomposites coatings respectively with rGO, fullerene C_{60} and $AgNO_3$ in a hybrid siloxane matrix will be presented. This technique has been already used for the deposition of TiO_2 nanocomposites in siloxane matrix [1] as it allows to embed thermodegradable or scarcely volatile species, to deposit also on 3D structures and thermodegradable materials and to reduce chemicals and materials waste with respect to traditional methods of thin films deposition. Furthermore, the immobilization of photocatalysts onto a support can make them more suitable and technologically viable for environmental applications, as they can be more easily retrieved and recycled.
In the present study the coatings are deposited in a dielectric barrier discharge reactor, feeding the plasma with two aerosol generators: one is fed with TiO_2 NPs dispersed in a HMDSO/isopropyl alcohol mixture, and the other with a water dispersion (rGO or C_{60}) or a solution ($AgNO_3$) of the cocatalyst. The chemical composition and the morphology of the coatings have been characterized by means of FT-IR, EDX, profilometry, XPS, SEM and TEM analyses, evidencing the complex nature of the structure of these materials. The photocatalytic activity towards the degradation of methylene blue has been evaluated under UV light irradiation and rationalized. The recyclability of $TiO_2/AgNO_3$ nanocomposite coating, which was proven to be the best performing photocatalysts, was assessed over 3 cycles and even an improvement of the performances was found upon reuse; a post-operational characterization via XPS and ICP was carried out to better understand this result.

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PLATH00010

OPTIMISATION AND *IN SITU* CONTROL OF THE DEPOSITION OF NANOCOMPOSITE THIN FILMS IN LOW PRESSURE MISTY PLASMA

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Nanocomposite (NC) films consisting of nanoparticles embedded in a solid thin film matrix, have attracted growing interest as multifunctional coatings. Their high tunability have made them great candidates for various applications where innovative simultaneous properties are needed.

The approach retained for NC thin films deposition is a hybrid deposition process, combining a low pressure RF inductively coupled plasma and a pulsed injection of a colloidal solution (using a Direct Liquid Injector). Liquid droplets are used to deliver the nanoparticles to the substrate, which allows to protect them from the reactive plasma and from agglomeration. Ideally, the liquid solvent evaporates during transport, leaving nothing but the nanoparticles on the surface of the sample, which will be quickly covered by the continuous deposition of the matrix. This approach has previously been successfully developed for the deposition of NC films made of TiO_2 anatase nanoparticles embedded in a SiO2 matrix [1]. Plasma pressure measurement, time-resolved optical emission spectroscopy (TROES) and *in situ* real time spectroscopic ellipsometry are used to control the pulsed injection of the solution in the plasma and to investigate the NC film deposition kinetics.

Here, the same approach is carried out using a colloidal solution containing ZnO nanoparticles (dispersed in heptane with oleic acid and dodecylamine ligands [2]) injected in the low-pressure O_2/HMDSO plasma. Due to the low volatility of the ligands, a step of optimisation of the solution injection had to be achieved and was performed using pressure vs. time and TROES measurements which are very sensitive to any fault during the injection of the solution. Results relative to this optimisation step as well as on the plasma composition and NC growth kinetics obtained in optimized deposition conditions will be presented. Finally, NC films containing 5 nm in diameter ZnO nanoparticles in a SiO_2 matrix with a broad photoluminescence emission in the visible and the ZnO exciton emission peak in the UV were synthesized.

Thanks/Acknowledgement

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PLATH00069

METAL-DOPED DLC COATING BY PE-CVD COUPLED WITH PULSED LIQUID INJECTION

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The doping of Diamond Like Carbon (DLC) with a metallic element (Ti, Nb, Ni, Fe, Co …) is widely used because it makes it possible to increase or modify the properties of the carbon structure according to the desired properties. [1,2] The most commonly used techniques are PECVD or PVD in which the metal is produced by tearing atoms from a metal target either by sputtering, heating or a laser. In most processes, the carbon matrix is obtained by injecting gaseous carbon precursors, such as acetylene or methane, etc... [3,4]
In our study, the metal atoms are not extracted from a metal target, but are injected by organometallic precursors dissolved in a pentane solution. A hybrid process has been developed in our team, combining an RF plasma (PECVD) with a pulsed injection device (DLI or PDLI). Here we are interested in the incorporation of nickel atoms into a layer of DLC by injection of a pentane solution containing an organometallic precursor, nickelocene (NiCp2). [5]
The effect of several parameters will be studied, in particular the concentration of the precursor in the pentane solution, the plasma frequency and the pressure in the deposition chamber. In order to understand their impact on the atomic percentage of Ni that can be inserted with this method. The influence of Ni incorporation on the structure of the carbon matrix will also be studied.
Finally, we will examine the influence of the choice of precursor by comparing different organometallic precursors in order to improve the Ni concentration in the solution by having a better solubility in pentane. This optimisation aims to increase the nickel content in the initial solution, in order to improve the efficiency of the process compared with the use of $NiCp_2$, as well as to discuss the role of the precursor in the process and its potential insertion in the layer.

Thanks/Acknowledgement
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PLATH00041

GROWTH OF GOLD-PALLADIUM NANOALLOYS BY OBLIQUE ANGLE DEPOSITION: EXPLORATION OF THEIR STRUCTURE AND OPTICAL PROPERTIES

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Multimetallic nanoparticles (NPs) are currently attracting a great deal of interest in scientific research thanks to their unique physical and chemical properties, which can be applied in many fields such as optics, catalysis and biosensors. These properties are highly dependent on NP characteristics, including their structure (size, shape, composition) and their environment [1]. For example, the use of gold and palladium enables the combination of distinct characteristics inherent to each component, such as the plasmonic properties of gold and the reactivity effects of palladium, which makes these bimetallic NPs particularly attractive for many applications such as hydrogen detection [2]. In this study, we investigate Au_xPd_{1-x} NPs synthesized by electron beam evaporation on flat and nanorippled alumina surfaces, and the influence of deposition parameters on their optical properties and structure.
The NPs were produced in a unique deposition chamber that enables surface nanostructuration by ion-beam sputtering and the synthesis of monometallic and multimetallic NPs under oblique angle conditions, while allowing real-time monitoring of their growth via *in situ* optical spectroscopy (transmission and reflection). As shown in Fig. 1, we analyzed the evolution of the optical response during deposition of gold using different deposition incidence angles (α) and surface morphologies, as well as during palladium deposition on gold NPs. Our results show that the growth dynamics and the plasmonic properties are greatly influenced by deposition conditions. Real-time optical studies are complemented by *ex situ* transmission electron microscopy, confirming that the optical response of NPs is strongly correlated with their structural characteristics.

Thanks/Acknowledgement
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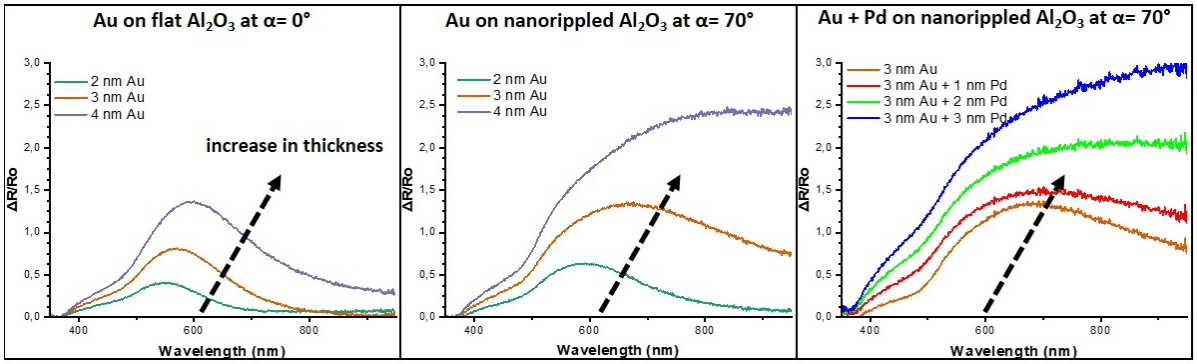

Fig1: Monitoring the optical response of NP growth

PLATH00018

OBLIQUE ANGLE CO-SPUTTERING OF NANOSTRUCTURED TI-W THIN FILMS: INFLUENCE OF DEPOSITION CURRENT ON STRUCTURE AND ELECTRICAL PROPERTIES

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In the present work, Ti-W thin films were deposited on glass and (100) silicon substrates by DC magnetron co-sputtering. Films were prepared by the glancing angle deposition method by fixing the deposition angle to 80° for both targets. Ti and W target currents, namely ITi and IW, were systematically and reversely changed from 0 mA to 300 mA, to tune the composition of the films. All other working parameters were kept constant. For all co-sputtering conditions, the deposition time was adjusted in order to get a film thickness close to 400 nm. A columnar microstructure was obtained with a Janus-like architecture as a function of the operating target currents. Different morphologies were observed between the two opposite sides of the columns. Surface and cross-section views of Ti-W thin films were observed by scanning electron microscopy (SEM). The chemical composition was determined by energy-dispersive X-ray spectroscopy (EDX). Evolution of the films crystallographic structure was also investigated by X-ray diffraction. Electronic transport properties of Ti-W films co-deposited on glass substrates were studied measuring DC electrical resistivity ρ as a function of the temperature T from 7 K to 300 K. The electron-phonon and electron-defect interactions were investigated from the ρ vs. T measurements and correlated with variations of the film's composition and structure. Ti and W atomic concentrations exhibited a symmetric evolution as a function of each target current. Using ITi/IW = 55/245 mA, films presented equimolar Ti and W concentrations. DC electrical resistivity vs. temperature was strongly influenced by the reverse change of target currents. These metallic-like behaviors are directly connected to the atomic concentration of elements in the films, grain size, phase occurrence and voided microstructure.

PLATHINIUM

PLASMA THIN FILM INTERNATIONAL UNION MEETING

POSTER PRESENTATIONS

- Session #1 - Tuesday 23 September
- Session #2 - Wednesday 24 September

PLATH00053

SLOW PULSED SPUTTERING ONTO LIQUID : IMPORTANCE OF SURFACE REFRESHMENT AND OF PLASMA HEATING

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The synthesis of nanoparticles (NPs) in liquids under vacuum has been generally considered as a curiosity. Most authors have been interested in understanding the importance of material nature and of the synthesis parameters on the NPs properties during sputtering onto liquid (SoL). Various NPs have been synthesized, ranging from conventional spherical NPs of noble metals to multimetallic NPs through ceramic donuts.
By pulsing the deposited material [1,2] and so limiting the quantity of material arriving at the surface in a given time, we have shown that it is also possible to control the solvation and the residence time of the Pt, Ag, PtAg NPs on the liquid surface. This mechanism of pulsed surface regeneration seem to limit the NPs growth and prevents their agglomeration, leading to smaller and more homogeneous NPs. Moreover, Pt NPs formed in polyethylene glycol were found to be smaller and better dispersed than those synthesized in visquous glycerol. We believe that the low surface tension and reduced viscosity promote the rapid solvation of newly formed NPs on the surface.The question regarding the location where the NPs growth takes place during SoL has been the subject of three main hypotheses [3] leading to the formation in the gas phase, on the liquid surface or in the liquid. In our study, the mean free path of the sputtered atoms is relatively large, and molecular dynamics simulation [4] clearly shows that growth do not occur in the liquid volume, indicating that growth occurs on the surface. But another hypothesis, never discussed in the literature, is the NPs formation in the gas phase at the liquid vicinity. When plasma bombards this surface, it causes localized heating, favoring the liquid evaporation (as we observed using a mass spectrometer) and generating a pressure gradient in the vicinity of the interface. In this transitional zone, nuclei could be formed before reaching the true surface and their incorporation into the liquid.
Finally this study highlights the importance of three scientific topics: the plasma – surface energy transfer, the recycling of the liquid surface and the characteristic of liquid-vacuum interface.

Thanks/Acknowledgement
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PLATH00128

THE INFLUENCE OF THE DISCHARGE PARAMETERS ON THE PHYSICOCHEMICAL PROPERTIES OF PLASMA ACTIVATED WATER

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The gliding arc discharge (GAD) plasma and spark arc discharge systems were produced for the generation of plasma-activated water (PAW). The air and air-nitrogen gases plasmas were used to produce PAW using the GAD. The flame-emission spectrometer was used to determine the composition of air and air-nitrogen plasmas. It was obtained that the N_2, N_2^+, N^+, NO and atomic oxygen species were the dominant particles in an air and air-nitrogen plasmas. The influence of the air plasma composition on the GAD plasma parameters (voltage, frequency, gas flow rate) were investigated. The results indicated that the increase in the voltage and reduction of the air flow rate enhanced the ionisation degree of the air and increased the concentration of NO, N_2^+ and N^+ particles in plasma. PAW was produced by exposing a 200 ml of deionized water, tap water, deionized water supplemented by salts to GAD for 5 min at various output voltages. Additionally, the tap water was treated with an air plasma at various durations. The spark discharge was produced in the water in air at atmospheric pressure. The 80 ml of different types of water were treated at various frequencies. The duration of treatment was 2 min, 4 min and 6 min. The electrical conductivity, pH, concentrations of NO_3^- and H_2O_2 in the generated PAW depended on the type of used water, the type of plasma discharge, treatment duration and the plasma discharge parameters. The increase of the output voltage and treatment time increased the NO_3^- concentration in PAW. The pH and electrical conductivity varied depending on the GAD plasma parameters and type of used waters. The increase of the discharge frequency from 20 kHz to 50 kHz and treatment duration enhanced the NO_3^- and H_2O_2 concentrations in tap water, when the discharge was produced in water. The highest H_2O_2 concentration (~32 mg/L) was produced in tap water, while the highest NO_3^- (150 mg/L) was in the deionized water. The effects of generated PAW on seed germination in vitro, and effects of seedling watering and leaf spraying with PAW on plant growth and leaf biochemical composition were compared in two lettuce cultivars - green 'Perl Gem' and red 'Chervanek' cultivated under different conditions.

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PLATH00146

EXFOLIATION AND FUNCTIONALIZATION OF GRAPHITE PARTICLES BY PULSED PLASMA DISCHARGES IN THE GAS-LIQUID PHASE

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Graphene-based materials exhibit exceptional electrical, mechanical, and physicochemical properties [1], but their production, specifically at a larger scale, remains a challenge. In this study, a new plasma technique is used to exfoliate and functionalize graphite particles by using pulsed discharges on the surface of a liquid, generating reactive chemical substances and shock waves. These, in turn, modify both the liquid environment and the graphitic material. Graphite exfoliation induces surface functionalization, while the treated graphite particles possess a relatively low defect density compared to those treated by traditional chemical or ultrasonication methods. The first electrode is a tip electrode made of 1 mm tungsten wire and is grounded. A graphite rod measuring 2 cm in diameter is connected to the high-voltage source at the bottom of the liquid beaker. The amplitude, frequency, and duty cycle of the high-voltage pulses are set at 6 kV, 6 kHz, and 0.6% respectively. A plasma discharge is initiated at the surface of demineralised water to treat the graphite particles in two distinct stages. First, a columnar nitrogen plasma is produced, which results in a strong acidification of the liquid by the formation of reactive nitrogen ions and the solvation of charged species in the plasma. The discharge current increases during this stage, and as the current approaches 2 A, the discharge becomes an arc/filamentary plasma that is dominated by water vapor and the electrical charges it produces. During this phase, the graphite particles are chemically modified due to the heat and shock waves generated by the plasma. Transmission electron microscopes (TEM) and scanning electron microscopes (SEM) are used to measure the lateral size of the particles before and after treatment, as shown in Fig. 1. X-ray diffraction and Raman spectroscopy are used to examine the thickness and structural configuration of the particles. Characterisation of the treated samples reveals partial exfoliation, with more than 75% reduction in particle thickness and the formation of a graphene-like turbostratic stacking. By changing the gas atmosphere as H2/Ar, O2/Ar and NH3, an even higher exfoliation yield is achieved, resulting in few-layers and multi-layers graphene mass production in controled continous process. In addition, depending on the gas composition, remarkable oxidation occurs at the particle surface, resulting in the presence of carbonyl and carboxyl functional groups.

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PLATH00147

ENHANCEMENT OF GRAIN QUALITY OF BREWER'S RICE CULTIVAR WITH PLASMA TREATMENT OF CARYOPSIS USING "SMART AGRICULTURE SYSTEM" BASED ON COLLECTED DATA

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Cold plasma has much attention to establish novel agricultural technologies, because it becomes difficult to ensure high-quality crops stably due to drastic climate changes. Our group has verified the enhancement of yield and quality by plasma treatment of the rice plants in an actual field [1,2]. Interestingly, the formation of white-core grains was activated. White core is important for producing Japanese rice wine due to insufficient starch crystallization in central of endosperm. In this study, we further focused on the grain-maturation process, and each caryopsis of brewer's rice cultivar, Yamadanishiki, were treated with pen-type plasma [3]. Seedlings planted in a paddy at Togo town, Aichi, were transplanted into pots on Aug 10, and thereafter grown in greenhouse. After start of flowering on Aug 31, flowering days of each caryopsis were checked, and they were individually treated with plasma at 1, 5, 10, or 15 days after flowering (DAF). After harvest in Oct, to evaluate grain qualities, the ratio of white-core grains to total number of grains was calculated. The ratios in grains treated at 10 and 15 DAFs were increased. Thus, plasma treatment of caryopsis improved the quality. Moreover, similar results were showed from investigations in laboratory. We constructed "Smart Agriculture System", composed of sensors and cameras in growth chambers and data management system, and set the temperature and daylight to simulate climate conditions at Togo town. The results demonstrate that the system is effective for construct of cultivation recipe using plasma by collecting data under various climate conditions. Furthermore, the results of the analysis of the interaction of the plasma and/or plasma-activated solution with the caryopsis surface to elucidate the mechanism of these results are also presented.

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PLATH00154

OPTIMIZING AMMONIA DECOMPOSITION FOR ENHANCED HYDROGEN PRODUCTION IN A NOVEL ROTATING GLIDING ARC REACTOR

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The growing demand for clean energy has intensified interest in hydrogen as a sustainable fuel, highlighting the need for efficient storage and transport methods. This study explores ammonia (NH_3) as a hydrogen carrier, owing to its high hydrogen density and existing infrastructure. Recent studies have highlighted the efficacy of plasma technologies in improving the decomposition of ammonia and its subsequent conversion to hydrogen. Among these, gliding arc reactors are considered a compelling option, as they combine thermal and non-thermal plasma characteristics, enabling efficient energy transfer to reactive species.

This study investigates the decomposition of ammonia in a novel rotating gliding arc reactor, with a particular focus on the influence of carrier gases (N_2 and Ar) on process efficiency. Key parameters analyzed include ammonia flow rate, power consumption, and hydrogen yield, intending to optimize operating conditions for enhanced hydrogen production. The reactor was driven by a sinusoidal voltage signal (6-10 kV, frequencies 50-900 Hz). The total gas flow rate was maintained at 10 L/min, while the ammonia flow was varied from 0.25 to 2.25 L/min to assess its effect on hydrogen yield and energy efficiency. Optical emission spectroscopy and mass spectrometry analyzed reaction dynamics to further optimize conditions for enhanced hydrogen production.

Figure 1 shows that ammonia concentration influences both hydrogen production and energy efficiency. In the nitrogen system, hydrogen yield peaked at 1 L/min, while in the argon system, it increased linearly up to 2.25 L/min. The percentage of decomposed ammonia decreased from 40% to 14% in the N_2 system, whereas it remained stable when Ar was used. Power consumption remained constant with N_2 but increased with ammonia flow in the Ar system, highlighting the importance of optimizing ammonia concentration to improve hydrogen output and overall efficiency.

Thus, ammonia is an effective hydrogen carrier, with nitrogen enabling higher decomposition rates and hydrogen yields compared to argon. Although increasing the ammonia flow rate enhanced hydrogen production, efficiency tended to plateau at higher flow levels. The Ar+NH_3 system exhibited lower power consumption, suggesting greater energy efficiency under certain operating conditions.

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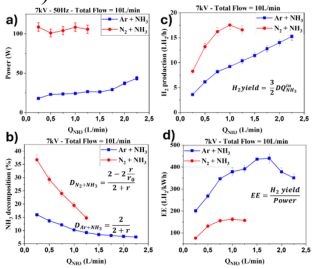

Electrical and production parameters

PLATH00160

LIQUID FLOW CONTROL IN A DUAL-FREQUENCY APPJ ON WATER SOLUTIONS

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Dual-frequency atmospheric pressure plasma jets (APPJs) offer a promising method for controlling ion flux and plasma propagation on surfaces [1]. However, its interactions with liquid and the fundamental mechanisms governing the induced liquid flow have not been investigated yet. We used a dual-frequency jet setup in a coaxial configuration with an upstream high-frequency electrode (17kHz) and a downstream radio-frequency electrode (27MHz)[1]. The resulting plasma is sustained mainly by the RF oscillations in an Ω regime, providing an ionisation through the plasma bulk with a frequency double than RF (54MHz). On the other side, the HF allows to control the sheath thickness even on the facing substrates, enabling the ignition of a γ regime due to secondary electrons with the modulation of the RF (27MHz). In Figure 1 is presented the HF electrode voltage and the charge collected on the liquid surface as a function of time and the number of photons detected. At 60µs a peak in the photon emission appears and correspond to the instant when the magnitude of the Fourier transform at 27MHz is higher than at 54MHz demonstrating that the γ regime can be ignited also on liquid surfaces. To characterise the electrohydrodynamic (EHD) forces and the electric field acting in the liquid, Particle Image Velocimetry (PIV) was performed using, at first polyethylene particles and then graphene oxide (GO) as particle tracers in solutions of varying conductivity, thereby avoiding surfactant-induced flow artefacts.
Most importantly, our research reveals a novel dual benefit: short-pulse HF signals coupled with RF provide typical electrical characteristics of the HF component while also achieving upward flow regimes that are identical to RF-only and lower compared to a non-pulse HF coupled with RF (Figure 2). Additionally, evaporation analysis was correlated to the RF power revealing possibilities for even finer flow control through lower RF power combined with a µ- or nanopulse generators.

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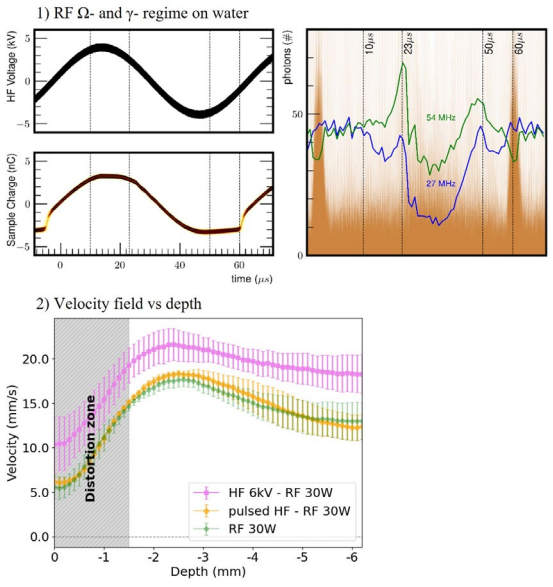

PLATH00170

FIXATION OF NITROGEN IN WATER WITH THE USE OF A MULTIPHASE PLASMA REACTOR

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Nitrogen fixation (N-fixation) plays a significant role in agricultural production. The current method of creating nitrogen-based fertilizers is the Haber–Bosch process. This process has a significant environmental impact. The use of small-scale localized production units, powered by renewable energy sources, may be an alternative [1]. The "heart" of this unit is a reactor of low-temperature plasmas, fixing nitrogen locally on the farm. In reality, N-fixation based on plasmas was one of the first methods used [2], but Haber-Bosch proved more energy efficient. In this work, nitrogen is fixed in water as nitrites (NO_2^-) and nitrates (NO_3^-) by a homemade and laboratory-scale, multiphase dielectric barrier discharge jet reactor operating in glow mode (Figure 1). Air is fed into the reactor at atmospheric pressure, and a continuous AC wave generator is powering the high voltage electrode. In Figure 2, the concentrations of NO_2^- and NO_3^- are portrayed versus the air feed. With the use of a secondary vessel, passive-N-fixation (without the use of extra power) can be achieved. For the case of 4 slm air feed, the energy consumption is 41 MJ/mol of fixed nitrogen. A parametric optimization study is performed to reduce the energy consumption by changing the volume of the secondary vessel, the process time, and the number of the diffuser's holes.

Thanks/Acknowledgement
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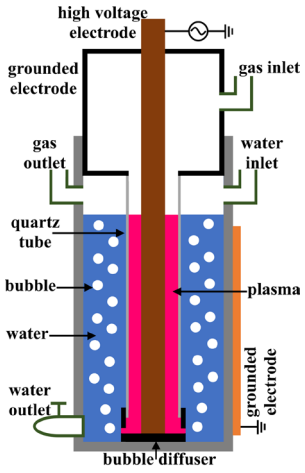
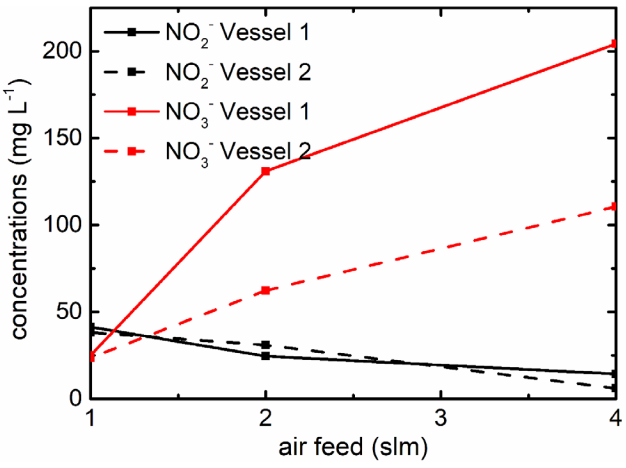


Multiphase dielectric barrier discharge reactor



Concentrations versus air feed at the inle

PLATH00013

ELABORATION OF 316L/Cu COMPOSITE ALLOY USING A HYBRID PVD/SPS PROCESS

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Powder metallurgy is an ideal field for developing advanced materials with complex geometries and compositions. Iron-based alloys produced through sintering often exhibit significant porosity. Adding small amounts of copper provides several benefits: it lowers the sintering temperature, eliminates pores due to its excellent wettability, reduces stress concentrations, and prevents microcrack formation. The localization of copper at the grain boundaries of steel powders enables the design of an alloy with a controlled microstructure, thus enhancing its mechanical performance (ductility, wear resistance, creep, and fatigue) as well as its resistance to corrosion and oxidation [1]. Several approaches can be employed: liquid copper infiltration into a compacted steel powder or the direct incorporation of copper into the steel powder before sintering as a binding agent. The innovative hybrid approach presented in this work, combines physical vapor deposition (PVD) and spark plasma sintering (SPS) processes. In this study, we investigate the development by SPS of a 316L alloy (particle size: 250-300 µm) with copper-enriched powder boundaries deposited by sputtering. Surface functionalization of the powders is performed using a custom-designed PVD chamber prototype (Fig. a) developed in-house with an original configuration [2]. This fabrication method ensures more precise control over the amount and distribution of copper at the powder grain boundaries, making it easier to achieve a more homogeneous material and enhanced optimization of its mechanical performance (fig. b). The influence of the copper layer thickness on the powders, regarding mechanical performance and the microstructure of the material after sintering, is analyzed. The mechanical behavior of the samples is evaluated using mechanical tests (tensile, compression, hardness…). The microstructure and phase identification are studied via SEM, EDS, and X-ray diffraction (XRD).

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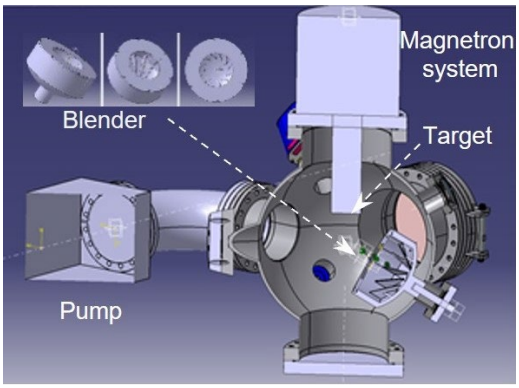

Fig 1. Diagram of the PVD deposit chamber

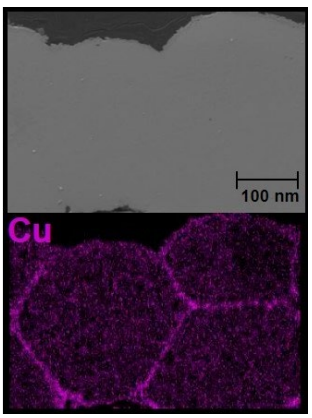

Fig 2. SEM image and Cu mapping after sintering

PLATH00027

DEVELOPMENT AND INVESTIGATION OF ADVANCED COATINGS FOR HIGH-TEMPERATURE APPLICATIONS

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Thermal barrier coatings (TBCs) are crucial for protecting components operating in extreme thermal conditions, particularly in the aerospace and energy sectors. These coatings improve energy efficiency and extend the lifespan of components by limiting the thermal load on the underlying materials.
Yttria-stabilized zirconia (YSZ) stands out for its low thermal conductivity, high phase stability, and remarkable resistance to thermal cycling.
The performance of TBCs is largely dependent on the stabilization of the metastable tetragonal phase (t') of zirconia, which provides excellent resistance to cracking due to phase transformation mechanisms induced by thermal stresses.
Additionally, the stability of this phase at high temperatures significantly enhances the thermal stability of the coatings, maintaining their insulating efficiency and structural integrity under prolonged thermal exposure.
This study aims to investigate the effects of oxygen and yttrium content on the microstructural, chemical, and thermomechanical properties of YSZ top coats deposited by magnetron sputtering.
In addition, the thermal stability of the coatings will be evaluated under high-temperature conditions, with tests conducted at temperatures representative of the intended operating environments, typically ranging from 1000°C to 1200°C.
SEM, EDS, and XRD analyses were used to examine the morphology, chemical composition, and crystalline structure, respectively.
The results aim to optimize the deposition process to enhance the performance and durability of TBCs in high-temperature applications and contribute to the advancement of high-temperature protective coatings

PLATH00050

DEPOSITION OF DIELECTRIC, AND METAL LAYER SOLUTION FOR TSV INTEGRATION, INNOVATIVE SEQUENTIAL PROCESS, APPLICATION OF LOW TEMPERATURE DEPOSITION

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The innovative “Fast Atomic Sequential Technology” (FAST®) [1], is a unique combination of deposition solutions that can be used in three distinguish modes: continuous mode, pulse-purge mode or pulse/sequential only mode FAST® fig.1, combined with dual frequency plasma generation. The FAST® technology manages separately, the pulsing position and duration of precursor, of reactant, and of RF (13,56 MHz) with or without Low Frequency (380kHz). This technology has been developed and proposed to answer the thick and conformal layer request of Through-Silicon Via (TSV) integration scheme [2]. A large library of precursor molecules already implemented in industry (for example: TDEAT for TiN, or TEOS for SiO2) can be applied because they can be in both: liquid state or gaseous state. The compromises of FAST® make it ideal for thick and conformal layers in TSV or photovoltaic devices.

Initially we developed sequential process based on Trisilylamine (SiH3)3N TSA to prevent carbon presence inside SiNx layer at low temperature and extended this recipe to deposit oxynitride or other dielectric layer before or after metal deposition (Cu, TiN). Carbon free precursors like TSA applied with our sequential deposition method would ensure better quality of film deposition. We compare SiNx deposition with BDEAS and TSA. Regarding optical index, we observed a better result at low temperature (below 250°C) with carbon free precursor, the optical index with TSA (~1.9 to 2.2) is closer to the usual value expected of Nitride layer than with SAM24 (~1.6 to 1.8). Different dielectric layers would be accessible at low temperature (150-250°C) that would have interest on TSV or Plasma Dicing [3]. The generation of different material based on carbon free precursor and our sequential method will be also discussed.

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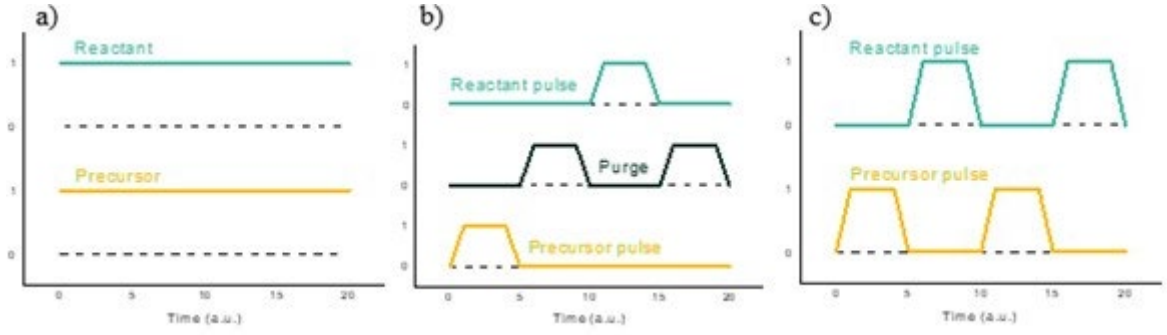

Fig.1: a) CVD mode, b) ALD mode, and c) FAST

PLATH00068

DEVELOPMENT OF HYDROGEN BARRIER THIN FILMS BASED ON SILICON CARBONITRIDE

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Hydrogen Permeation Barriers (HPBs) are essential for strategic applications such as hydrogen energy and nuclear fusion reactors that will help meet global energy challenges and reduce dependence on fossil fuels. However, traditional metallic materials such as steel do not meet the requirements for hydrogen resistance in acidic or hydrogen-rich environments. The development of new materials for these barriers is therefore critical. Silicon carbonitride thin films (SiCN) have excellent physical and chemical properties. Covalent materials derived from light elements such as silicon, carbon, and nitrogen appear to be promising candidates for these applications due to their exceptional properties, low mechanical stress, chemical inertia, and high electrical resistivity.
In our study, SiCN thin films were deposited by magnetron sputtering. The influence of process parameters (bias voltage, working pressure, etc.) was evaluated. The morphology, chemical composition and structure of the films as well as their hydrogen diffusion coefficient and permeability have been investigated using SEM, EDS, XRD and electrochemical permeability techniques, respectively.
In fact, the aim of this study is to investigate the properties of silicon carbonitride thin films and their potential as hydrogen barrier materials in aggressive environments, offering the possibility of sustainable solutions for the energy and industrial sectors. The results obtained show the beneficial role of silicon carbonitride thin films as hydrogen barrier in improving the performance of coated structures used for hydrogen energy applications.

PLATH00072

STUDY OF THE IMPACT OF DIFFERENT DIELECTRIC MATERIALS ON THE PERFORMANCE AND OPTICAL FEATURES OF A MICRO-HOLLOW CATHODE DISCHARGE (MHCD)

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Micro Hollow Cathode Discharge (MHCD) has been a promising microplasma source for the deposition of hexagonal boron nitride (h-BN) [1,2]. It has a low consumed power (typically few watts), relatively low gas temperature (≤800 K), and generates high-power density (up to 100 kW/cm³). These features enhance their potential for improving the dissociation of molecular nitrogen, which is attractive for the synthesis of large band gap nitrides such as h-BN [3].
However, h-BN growth over large surfaces on different substrates remains challenging, and a better understanding of the MHCD physics is essential to control the N-atom production (among others) and improve the properties of h-BN films. Our group synthesized h-BN over a SiO2/Si substrate (5 cm diameter) with an MHCD using alumina (Al2O3) as dielectric [2]. However, trace amounts of oxygen were found in the film lowering its quality [2]. Building on this foundation, the present study focuses on the effect of the dielectric material of a DC MHCD operating in N2/Ar gas mixtures (Fig.1a)—comparing aluminum nitride (AlN), alumina (Al_2O_3), sapphire, and Macor—on its endurance over time while also investigating key plasma features: morphology of the discharge expanding on the cathodic surface, emissive species generation, gas temperature, and electric current. Preliminary results (Fig.1b) indicate a difference in the discharge's intensity and cathodic expansion between using Al_2O_3 and AlN which is to be corroborated trough emission spectroscopy and image processing. Eventually the MHCD efficacy in producing N-atoms will be assessed using laser-based methods towards achieving h-BN deposition on large surface substrates (see, e.g., Fig.1c).

Thanks/Acknowledgement
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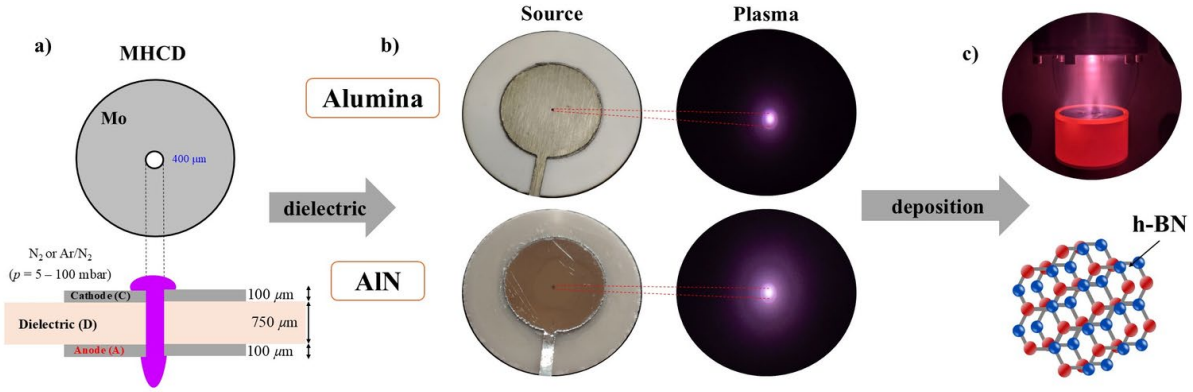

a) MHCD, b) Al2O3 and AlN MHCD, c) h-BN deposition

PLATH00140

ON THERMAL STABILITY AND OXIDATION BEHAVIOR OF METASTABLE W–Zr THIN-FILM ALLOYS

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Recently, we have successfully prepared W-Zr thin films in a very wide composition range and thoroughly investigated their as-deposited properties [1,2]. We showed that different metastable structures, including amorphous films with metallic glass features, supersaturated α-W(Zr) solid solutions, dual-phase glassy-crystalline structures, high-temperature β-Zr(W) and high-pressure ω-Zr(W) phases, can be prepared in the W-Zr system by dc magnetron co-sputtering on unheated and unbiased substrates. Since metastable structures are kinetically frozen structures out of the equilibrium, they tend to transit to the thermodynamically stable state. Such a process is more favorable at elevated temperature. Therefore, it is of key importance to have information about the high-temperature behavior of W–Zr films with the metastable structures. To address this, we investigated the thermal stability and oxidation behavior of metastable W–Zr thin-film alloys with up to 83 at.% Zr and focused on the effect of gradual substitution of Zr for W [3]. The experiments showed that a supersaturated α-W(Zr) solid solution structure of as-deposited W-rich films with up to 19 at.% Zr is highly thermally stable up to 1200°C in argon and the thermal stability of the W–Zr thin-film metallic glasses (33–83 at.% Zr) decreases with increasing Zr content. Nevertheless, the thermal stability of the W–Zr thin-film metallic glass with 33 at.% Zr reaches 1420°C, which is very high value for binary metallic glass. The annealing of W-rich films (0–24 at.% Zr) in air to 600°C leads to the formation of a protective surface oxide layer, which serves as a more effective oxygen diffusion barrier due to an increasing packing factor and amorphization with Zr addition. On the other hand, no protective surface oxide layer is grown during the annealing in air in the case of the W–Zr thin-film metallic glasses and the oxidation leads to the formation of compact, homogeneously oxidized substoichiometric W–Zr–O films with an amorphous structure and enhanced mechanical properties.

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PLATH00148

INFLUENCE OF SUBSTRATE BIAS ON THE PROPERTIES AND CONFORMALITY OF TiN THIN FILMS DEPOSITED BY HIGH POWER IMPULSE MAGNETRON SPUTTERING (HiPIMS)

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High Power Impulse Magnetron Sputtering (HiPIMS) is a physical vapor deposition technique that generates a dense plasma with a high degree of ionization of the sputtered species [1] ; compared to conventional Direct Current Magnetron Sputtering (DCMS), HiPIMS consists in very short (30–100 µs) and high-voltage (100–1000 V) pulses. We use HiPIMS discharges to deposit titanium nitride (TiN) thin films on three-dimensional (3D) substrates for micro-supercapacitor applications. HiPIMS should enhance ion flux, thus changing the thin-film microstructure [2].

In this study, we focus on how applying substrate bias influences the deposition process in HiPIMS and in DCMS. The substrate bias raises the incoming ion energy and narrows their directionality, which is expected to enhance conformality on 3D substrates and to impact the film properties [3], such as density, morphology and surface roughness. We systematically compare HiPIMS and DCMS processes as the substrate polarisation should have more impact on a more ionized plasma.

The TiN thin films are systematically analyzed using microstructural characterization techniques, including Grazing Incidence X-Ray Diffraction (GIXRD), Scanning Electron Microscopy (SEM), and profilometry for thickness measurement. Their functional properties are also evaluated: electrical resistivity via four-point probe measurements and electrochemical performance through cyclic voltametry.

Preliminary results show that HiPIMS yields a slower deposition rate but produces denser and more conductive TiN films, particularly when substrate bias is increased. In contrast, these effects are less pronounced with DCMS.

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PLATH00149

PLASMA-GROWN VERTICALLY ORIENTED GRAPHENE FOR SUPERCAPACITOR ELECTRODES

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Carbon nanowalls (CNWs), which are composed of vertically-oriented graphene sheets, are a good candidate for future supercapacitor electrodes because of their high surface area and high density of edges with defects. Therefore, CNW-coated stainless-steel disk substrates were prepared from a polymer to demonstrate the possibility of recycling waste plastic to produce advanced materials (scheme in Figure 1). CNWs were grown during plasma deposition of carbon-containing building blocks originating from melted polypropylene precursor in combination with inductively-coupled RF hydrogen plasma [1]. CNWs of different thicknesses and morphologies were formed by varying deposition times. The morphology and structure of deposited CNWs were thoroughly investigated using scanning electron microscopy and Raman spectroscopy. Significant variations in the structure and morphology were observed with increasing deposition time. The stainless-steel discs with CNWs served as electrodes that were used for assembling the capacitors. Their electrical characteristics were measured as well. It was found that variations in the structure and morphology of CNWs were reflected in the electrical properties of the assembled capacitors, as the shape of the CNWs` growth curve matched well with the variation of their specific capacity.

Thanks/Acknowledgement
The research was funded by the Slovenian Research Agency, project L2-50052.

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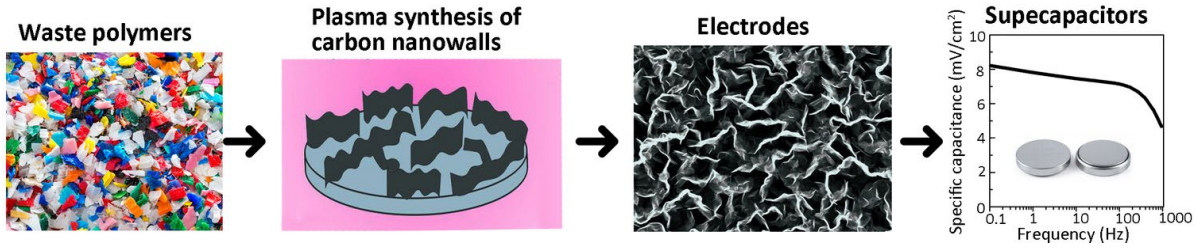

Scheme of the preparation of supercap electodes.

PLATH00158

UTILIZING GAS RAREFACTION TO OPTIMIZE PREFERENTIAL METAL ION ACCELERATION FOR EPITAXIAL AlN GROWTH ON SILICON(111)

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Utilizing synchronized substrate bias to selectively accelerate ions is a common approach for controlling the stoichiometry, structural quality, and microstructure of films grown by high-power impulse magnetron sputtering (HiPIMS)[1,2]. In this technique, the inherent temporal separation of metal- and gas-ion fluxes provides the ability to selectively accelerate metal ions towards the substrate. This effect stems from a combination of mechanisms, such as time-of-flight as well as gas rarefaction, and is more pronounced for metals with a high metal/gas-atom mass ratio[3,4]. However, light elements like aluminum exhibit limited temporal separation due to their lower mass, complicating ion selectivity. In this study, we investigate how working gas rarefaction can be utilized in HiPIMS discharges of light metals to enable more effective synchronization of substrate bias for preferential metal ion acceleration. We use energy- and time-dependent mass spectrometry to analyze the evolution of metal- and gas-ion fluxes during the synchronized HiPIMS deposition of AlN on Si(111). Our investigation reveals that by varying the HiPIMS pulse length from 10 to 50 µs, the arrival of Ar^+ ions at the substrate is progressively delayed without affecting the Al^+ ion dynamics. This provides a temporal separation between these two ionic species, allowing for selective Al^+ acceleration. As a result, AlN films exhibit enhanced epitaxial character, achieving narrow distribution of lattice orientation for the case of the pulse length of 50 µs. φ-scans confirm in-plane texture originating from epitaxy-like alignment with six-fold symmetry, and AFM measurements show smoother film surfaces. EDX analysis confirms that the chemical composition remains unchanged across different pulse lengths. These findings demonstrate that temporal ion separation can be intentionally introduced, enabling precise metal-ion acceleration for better control of AlN film growth.

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PLATH00161

AEROSOLS AS AN INNOVATING ROUTE FOR THIN FILM DEPOSITION BY PECVD

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Aerosol-assisted plasma process is an alternative to the classical gas and/or vapor plasma processes for thin films deposition1,2,3,4. It consists in injecting liquid droplets of solutions directly in the plasma. The main advantage of this innovative process deals with the possibility to use different precursors including liquid mixtures, solutions of reactive molecules, of nonvolatile compounds and/or of nanoparticles. Hence, it enables forming a wide range of materials from porous coatings to nanocomposites.
This paper aims to review the coatings obtained for different liquid mixtures in capacitively (CCP) and in inductively (ICP) coupled RF aerosol-assisted discharges in the few mTorr range. Especially, mixtures of pentane and hexamethyldisiloxane (HMDSO) are studied. In comparison with classical gas or vapor phase processes, the nebulization of liquid droplets in the plasma leads to singular film morphologies, deposition rates and chemical compositions. For example, Figure 1 shows a key role of the transport mechanisms, especially of the electrostatic confinement of the droplets in the plasma volume thus leading to coatings from droplet-like (in ICP) to homogeneous (in CCP) ones. As a consequence, the film composition characterized by XPS is directly controlled by the plasma-droplet interactions. Hence, from the same liquid mixture, it is possible to prepare a wide range of innovating materials, enabling to meet the needs of numerous applications (lighting, gas detection, surface protection…).

Thanks/Acknowledgement
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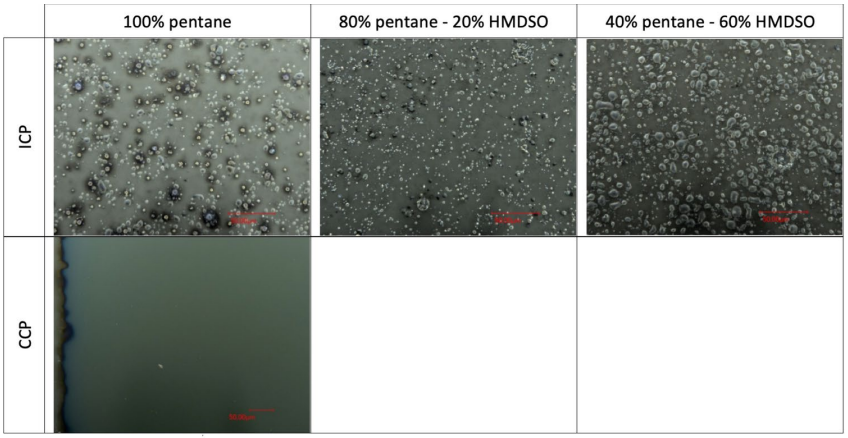

Figure 1

PLATH00162

Cu-SUBSTITUTION IN LANTHANUM-DEFICIENT $LaFeO_3$ PEROVSKITES FOR ENHANCED PHOTOELECTROCHEMICAL SOLAR HYDROGEN PRODUCTION

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Copper substitution in B-site of lanthanum-deficient perovskite thin films significantly improved their photocatalytic properties, particularly for hydrogen (H_2) production through photoelectrochemical (PEC) water splitting. Thin $La_{0.78}Cu_xFe_{1-x}O_y$ films were synthesized using magnetron co-sputtering, and the composition was finely adjusted by varying the power applied to the targets. La-deficient perovskites were found to promote surface segregation and agglomeration of copper oxide (CuO) following thermal annealing at 650 °C for 2 h. Highly dispersed CuO nanoparticles grew at the top surface, while copper remained present within the film (Fig. a: Cross-section STEM-HAADF micrography of $La_{0.78}Cu_{0.18}Fe_{0.82}O_y$ film oxidized in air at 650 °C for 2 h and the corresponding EDS maps). A detailed investigation was carried out to assess the influence of Cu-loading on the structural, morphological, optical and photoelectrochemical properties of the films. The $La_{0.78}Cu_{0.18}Fe_{0.82}O_y$ composition exhibited optimal performance, achieving a significant increase in H_2 production rates compared to undoped $LaFeO_3$ [1]. Under AM1.5G illumination (100 mW cm^{-2}), this film exhibited a H_2 production rate of 12.3 µmol h^{-1} cm^{-2} (Fig. b: H_2 production rates of FTO electrodes coated by $LaFeO_3$ and $La_{0.78}Cu_{0.18}Fe_{0.82}O_y$ thin films by light induced water splitting.), which is a 170% enhancement compared to undoped $LaFeO_3$ (4.5 µmol h^{-1} cm^{-2}) [2,3]. Additionally, the Cu-doped electrodes demonstrated stability, retaining a high activity (approximately 83%) after five reuse cycles. These results highlight the effectiveness of Cu-doped La-deficient $LaFeO_3$ films as a strategy for improving solar-driven H_2 production in PEC applications.

Thanks/Acknowledgement
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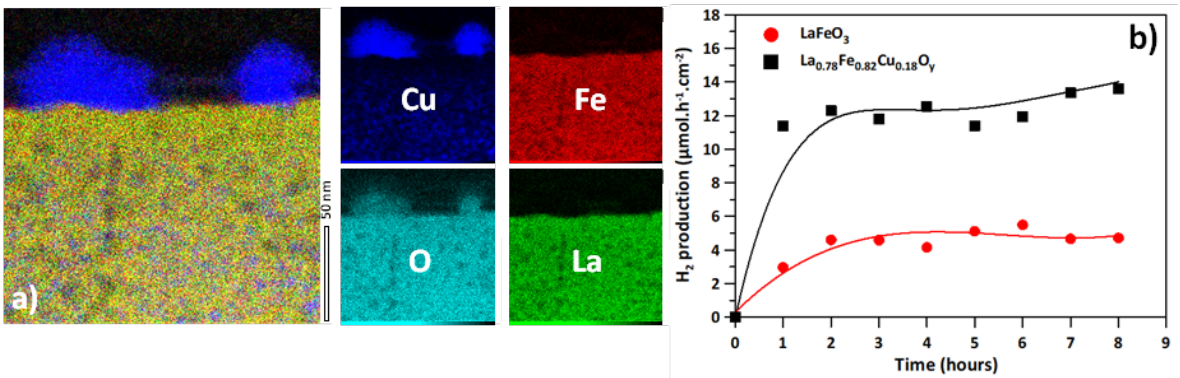

PLATH00168

Fe:CH THIN FILM DEPOSITION USING AN IRON ACETATE SOLUTION IN A DIELECTRIC BARRIER DISCHARGE

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Coupling solvents with plasmas is an effective way to produce a variety of materials, especially when the liquid is made of two components (solvent + nanoparticles): this association can result in formation of a nanocomposite thin film, which have been proven to have useful applications in medical aid, pollution control, photocatalysis, etc. Here, instead of using (toxic) preformed nanoparticles, a metallic salt is dissolved in a solvent mixture as a precursor of iron oxide particles. In this study, two methods are used to deposit organo-metallic thin films via a liquid precursor in a Dielectric Barrier Discharge (DBD) at the atmospheric pressure (750 mbar).
Firstly, a silicon substrate is coated with a solution made of iron salt (Fe(CH3COO) 2.H2O) in a mixture of propylene glycol (PG) and ethanol (EtOH). This coating is then subject to a plasma treatment in an N2/air environment and a plane-plane DBD configuration. The effect of the plasma on the iron salt is then characterized through XPS measurements: the oxidation state of the iron salt is determined by study of the Fe 2p peak and the composition of the carbon matrix is determined using the D parameter and through C 1s fitting.
Secondly, the same solution as previously mentioned is injected using a DLRI (Direct-Liquid Reactor-Injector), which allows the preparation of an aerosol upstream of the discharge zone, in the form of pulses in the same DBD configuration as for the first method. Again, the composition of the sample is assessed: using FTIR and XPS, we are able to compare both deposition methods.
More precisely, we notice the deposition of a vapor induced product during injections, which alters the chemistry of the resulting thin film. The optical coefficients of the carbon layers are determined by spectroscopic ellipsometry and the sp2/sp3 carbon ratio is deduced from the [MR1] decomposition of the CH band of the infrared spectrum. Compared to other carbon precursors (e.g. pentane), these results show a notable difference in chemical composition as well as material density throughout the amorphous hydrogenated carbon deposition, as confirmed by RBS/ERD analyses.

PLATH00062

FUNCTIONALIZED AMORPHOUS CARBON COATINGS FOR LOW SECONDARY ELECTRON YIELD AND CONTROLLED SURFACE RESISTANCE IN PARTICLE ACCELERATORS

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Amorphous carbon (a-C) thin films with low Secondary Electron Emission (SEY) are employed in particle accelerators to suppress electron multipacting and mitigate electron cloud formation—phenomena that can induce beam instabilities, pressure bursts, and excessive heat loads, compromising accelerator performance [1]. At CERN, over 500 meters of beamlines in the Super Proton Synchrotron (SPS) have been coated with a-C to reduce the SEY of stainless-steel vacuum chambers in critical focusing magnets [2]. Additionally, the ongoing HL-LHC project (2025–2027) involves coating more than 400 meters of copper beam screens in superconducting magnets using a-C films deposited by sputtering in argon.
Beyond metallic surfaces, a-C coatings have been recently explored for ceramic components in accelerators, where they help reduce SEY while maintaining a controlled surface resistance (1–10 MΩ) to dissipate charge without compromising insulation. However, achieving uniform and reproducible surface resistance is challenging due to the extremely thin films required (a few nanometers), which are comparable to the substrate's surface roughness. Additionally, film resistivity is highly sensitive to impurities in the argon discharge gas, further affecting consistency.
To address these challenges, we investigated hydrogen doping to increase the electrical resistivity of a-C films, allowing for greater thickness while keeping the surface resistance within specifications. However, hydrogen incorporation can also elevate SEY [3], requiring optimization to balance these effects.
This contribution presents the development of a deposition approach for functionalized a-C films, aimed at maximizing surface resistance reproducibility while minimizing SEY. Films were deposited in an Ar/D_2 atmosphere under varying power conditions to achieve thicknesses of 50–100 nm.

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PLATH00064

A LOW-TEMPERATURE SYNTHESIS OF STRONGLY THERMOCHROMIC VO_2-BASED COATINGS FOR ENERGY-SAVING SMART WINDOWS

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Vanadium dioxide (VO_2) exhibits a reversible phase transition from a low-temperature monoclinic VO_2 (M1) semiconducting phase to a high-temperature tetragonal VO_2 (R) metallic phase at a transition temperature of approximately 68°C for the bulk material. The automatic response to temperature and the abrupt decrease of infrared transmittance with almost the same luminous transmittance in the metallic state make VO_2-based coatings a promising candidate for thermochromic smart windows reducing the energy consumption of buildings. To meet the requirements for large-scale implementation on building glass, VO_2-based coatings should satisfy the following strict criteria simultaneously: a deposition temperature close to 300°C, a transition temperature close to 25°C, an integral luminous transmittance T_{lum} > 60%, a modulation of the solar energy transmittance ΔT_{sol} > 10%, long-term environmental stability, and a more appealing color than yellowish or brownish colors in transmission.

The paper deals with strongly thermochromic YSZ/W and Sr co-doped VO_2/SiO_2 coatings, where YSZ is Y-stabilized ZrO_2, prepared using a scalable sputter deposition technique on standard soda-lime glass at a low substrate temperature of 320°C and without any substrate bias voltage. The coatings exhibit a transition temperature of 22°C with an integral luminous transmittance T_{lum} = 63.7% (below the transition temperature) and 60.7% (above the transition temperature) and a modulation of the solar energy transmittance ΔT_{sol} = 11.2%. Such a combination of properties, together with the low deposition temperature, fulfill the requirements for large-scale implementation on building glass and have not yet been reported in the literature.

The fundamental principles of this technique, and the design, structure and optical properties of the thermochromic coatings are presented. Reactive high-power impulse magnetron sputtering with a pulsed O_2 flow feedback control allowed us to prepare crystalline VO_2 of the correct stoichiometry at a low deposition temperature. The W doping of VO_2 decreases the transition temperature to room temperature, while the Sr doping of VO_2 results in a significant increase in T_{lum}. An original design of a three-layer VO_2-based coating utilizing a second-order interference in two antireflection layers is used to maximize T_{lum} and ΔT_{sol} simultaneously. A compact crystalline structure of the bottom YSZ antireflection layer further improves the VO_2 crystallinity, while the top SiO_2 antireflection layer provides also the mechanical and environmental protection for the thermochromic VO_2-based layer.

Thanks/Acknowledgement
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PLATH00085

MAGNETRON DEPOSITION OF CHROMOGENIC THIN FILMS FOR SMART WINDOWS

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Chromogenic thin films are at the forefront of smart window development, which is expected to play a pivotal role in energy conservation for future buildings. Within the EU HORIZON project Smart Windows for Zero Energy Buildings, we have designed and fabricated innovative single- and multi-layered transition metal oxide (TMO), rare-earth metal oxide (REO), and oxy-hydride (REOH) thin films.
Building on our pioneering work initiated in the 1990s [1], we have resumed DC magnetron and HIPIMS deposition of chromogenic and multifunctional thin films:

(i) electrochromic ReO_3-WO_3 [2,3] and transparent conducting (TCO) WO_3/Cu/WO_3 [4];
(ii) photochromic rare-earth metal oxy-hydrides (REHO) Y-H-O [5];
(iii) thermochromic thin films, including doped VO_2 (WO_3, ReO_3).

Among these materials, REHO thin films represent a groundbreaking class of inorganic mixed-anion compounds with exceptional photochromic properties. Recent advancements have extended these investigations to photochromic Y-O-H systems and antibacterial (TCO) coatings like WO_3/Cu/WO_3, highlighting their potential for multifunctional applications.
Additionally, we have explored Reactive High-Power Impulse Magnetron Sputtering (R-HiPIMS) [5] and industrially scalable roll-to-roll (R2R) deposition, to enhance production efficiency. Large-area R2R deposition of YHO and WO3/Cu/WO3 has been explored to enable scalable production for smart windows and other optoelectronic devices. This work underscores the potential of advanced chromogenic materials to transform energy-efficient building technologies, offering a significant contribution to achieving zero-energy goals.

Thanks/Acknowledgement
Financial support was provided by the Project “Smart Windows for Zero Energy Buildings” (SWEB) GA nr. 101087367.

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PLATH00129

TRANSFORMING LEAK DETECTION IN VACUUM ENVIRONMENT WITH REMOTE PLASMA OPTICAL EMISSION SPECTROSCOPY

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Conventional helium leak detectors, which use mass filter technology, offer high sensitivity and currently dominate the leak detection market, making them the industry standard. However, the tracer gas that makes these tools effective, helium, also pose significant challenges due to rising costs and uncertainty regarding long-term supply. Furthermore, these high-performance leak detectors come with substantial production and maintenance expenses, and they are frequently deployed in scenarios where their sensitivity far exceeds what is truly necessary.
In this contribution, we present a leak detection method utilizing remote plasma optical emission spectroscopy (RPOES). This technique employs plasma-induced light emission to detect trace gases. The changes in gas trace plasma emission patterns could then be associated with leaks in real-time as a “marker/tracer” gas enters the detector’s plasma. This technique offers several advantages, including no need for helium as tracer gas, greater robustness, the ability to operate at real process pressures, and reduced maintenance requirements compared to traditional mass filter-based gas detection systems.
The benefits of this technique will be highlighted, along with case studies that demonstrate its effectiveness in identifying vacuum leaks across various industrial applications.

PLATH00171

NEW QCM-BASED DIAGNOSTIC FOR QUANTITATIVE TIME-RESOLVED MEASUREMENT OF THE ION FLUX IN HiPIMS

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High-power impulse magnetron sputtering (HiPIMS) plasmas exhibit rapid and complex dynamics, with plasma parameters evolving on microsecond timescales. Quantitatively resolving the temporal evolution of the depositing ion flux during the pulse period remains a significant yet challenging task for optimizing thin-film deposition processes. In this work, we present a novel method employing a magnetized quartz crystal microbalance (M-QCM) probe to achieve direct, high-resolution (microsecond-scale) measurements of the instantaneous ion flux of sputtered species contributing to film growth during HiPIMS discharges, a capability not previously reported to our knowledge. The technique is based on time-filtering the ion flux by applying a pulsed bias voltage to the probe with a controlled delay relative to the HiPIMS pulse. We describe the underlying principle of the method, demonstrate its versatility under a wide range of discharge conditions, and highlight its effectiveness in capturing dynamic processes within individual pulses. Finally, we discuss strategies for reconstructing the time-resolved ion flux from the measured data.

PLATH00036

OPEN-SOURCE MODELING OF GAS PHASE DYNAMICS IN INDUSTRIAL MAGNETRON SPUTTERING PROCESSES

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Magnetron sputtering offers compelling advantages in the production of thin films and coatings, including good adherence, good repeatability, high growth rates, and uniform and dense surfaces. However, the complexity and non-linearity of the underlying physical processes present challenges that must be understood to achieve precise control over coating properties. To gain detailed physical insight into these processes, particle-based numerical simulation tools for low-pressure plasmas are a well-suited simulation technique. They provide detailed physical insight into important industrial processes related to thin film deposition. A well-established method is the Direct Simulation Monte Carlo (DSMC) method, which accurately simulates the time evolution of a real 3D system in an acceptable computational time by approximating the collision integral of Boltzmann's equation using particle distribution functions.
In this work, we investigate the transport of the sputtered material in a vacuum chamber focusing on an industrial process using a TiO_2 target. For this purpose, the approach of Tonneau et al. [1] is implemented in the open-source simulation software PICLas [2], a parallel, three-dimensional PIC-MCC/DSMC solver developed in cooperation of two university institutes and the spin-off boltzplatz. Extensions are made in the area of gas phase distribution and sputtering rates, with a special focus on the modeling of the sputtering of particles. These methods will be investigated using an industrial coater and the results of the gas distribution in the coating chamber, the density at the target, and the particle impacts on the substrate will be discussed.
These simulations can provide valuable insights for the optimization and control of magnetron sputtering processes in industrial applications, contributing to improved efficiency and precision in the operation of the investigated industrial coater.

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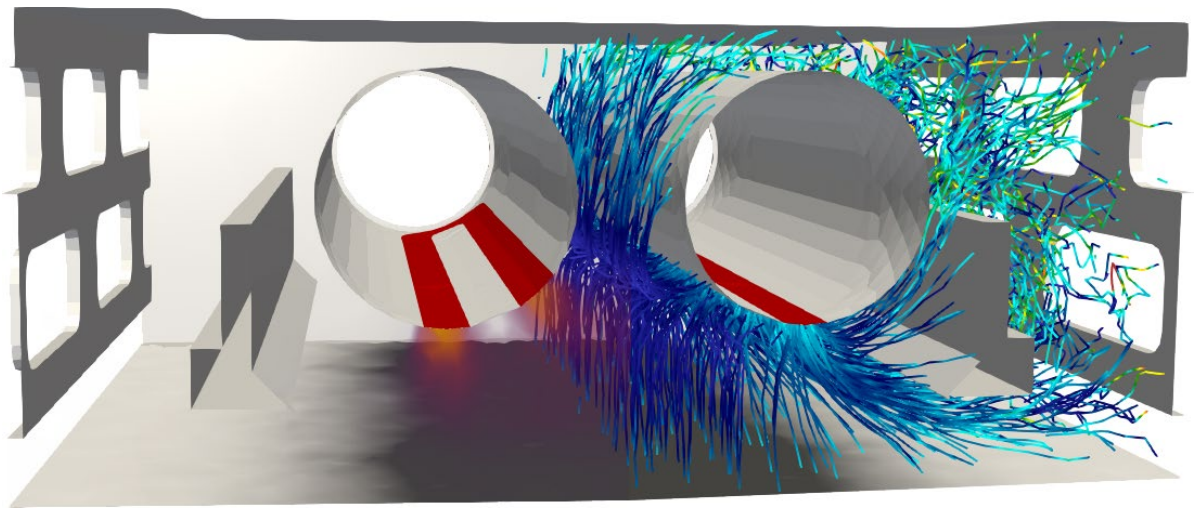

Simulated Ti distribution and impacts on substrate

PLATH00073

ROTATIONAL TEMPERATURE MEASUREMENTS OF $N_2(C)$, NO(A), AND OH(A) IN DIFFERENT MICRO HOLLOW CATHODE DISCHARGE CONFIGURATIONS USING OPTICAL EMISSION SPECTROSCOPY

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Micro Hollow Cathode Discharges (MHCDs) may be future technology for the synthesis of hexagonal boron nitride (h-BN) because they can dissociate molecular nitrogen while achieving relatively low h-BN deposition temperatures (typically ≤800 K) [1]. This work uses high resolution Optical Emission Spectroscopy (OES) to capture the spatial gradients of the gas temperature (T_{Gas}) in a DC-driven MHCD. T_{Gas} is estimated through the rotational temperature (T_{rot}) of $N_2(C)$, NO(A) and OH(A). The T_{rot} is determined by directly fitting the emission spectra of N_2(SPS), OH(A-X) and NO(A-X), which is cross-validated through the Boltzmann plot method. The MHCD is operated in three different regimes [2]: (i) plasma generated in the MHCD hole (Ø400 µm) and over an area of the cathodic surface (Fig.1a), (ii) plasma jet (Fig.1b) expanding in the low pressure chamber and impinging on a floating potential aluminum substrate holder, and (iii) micro cathode sustained discharge (MCSD) where the substrate holder from (ii) is biased by a positive DC voltage (Fig.1c). The different T_{rot} are measured under various discharge currents, pressures, and Ar/N_2 gas mixtures. The differences on the measured T_{rot} and their origins (e.g., energy transfer between N_2 and metastable argon, Ar($1s_3$/$1s_5$)) are shown and discussed. The results indicate that the T_{rot} are highly dependent on the pressure gradient, with values ranging from 600 K to 1200 K depending on the discharge conditions. These findings provide valuable insights into the thermal dynamics of microplasmas, essential for applications in material synthesis.

Thanks/Acknowledgement
SPECTRON (ANR-23-CE51-0004-01), Labex SEAM (ANR-10-LABX-0096; ANR-18-IDEX-0001)

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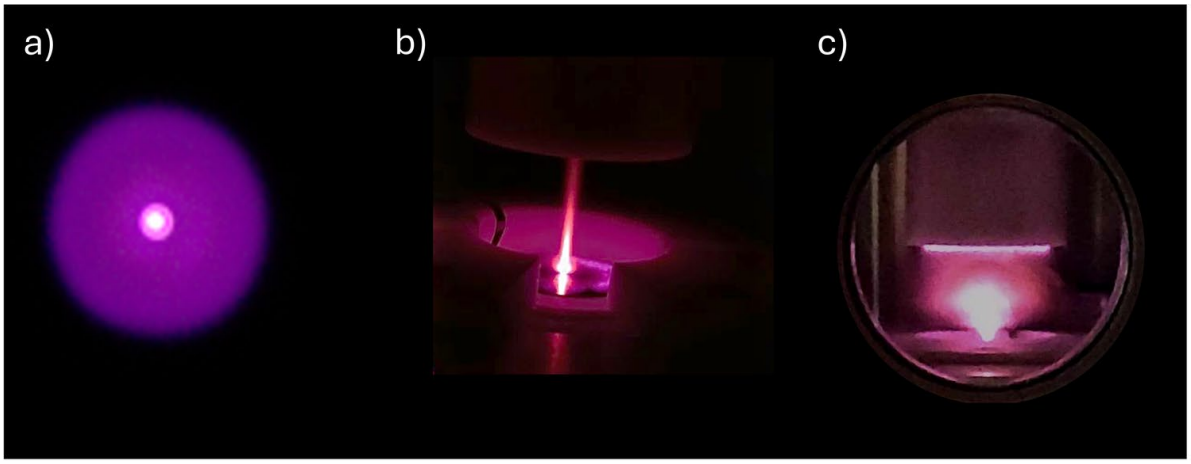

Three different MHCD setups presented in this work

PLATH00081

ASSESSING ACTINOMETRY AND LINE RATIO TECHNIQUES FOR SPECIES DENSITIES AND ELECTRIC FIELD DETERMINATION IN DC GLOW DISCHARGES

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For the optimal utilization of low-temperature plasmas, a clear understanding of discharge processes and the underlying physics is essential. Therefore, it is crucial to probe discharge parameters such as gas or vibrational temperatures, species densities, ionization degrees, and electron temperatures. Accurate measurement of these quantities enables better control and optimization of plasma-based processes. While many techniques are available for measuring these quantities, such as electric field induced second harmonic generation for electric field determination or two-photon laser induced fluorescence for species concentration, their complexity limits their practicality in many discharge operations and reactor geometries. In response to these challenges, a novel method combining actinometry-based approaches with the Boltzmann solver LoKI-B is proposed for determining plasma species densities and reduced electric fields in DC glow discharges. This system was selected for its reproducibility, homogeneity in the positive column, which enables easy measurement of the electric field, and its straightforward ability to vary electron density by simply controlling the current. The method has been applied to several case studies, including O2 and CO2 plasmas with admixtures of argon and xenon. The results were compared against measurements of the electric field using electrostatic probes and atomic oxygen density using cavity ringdown spectroscopy (CRDS), allowing the line ratio method to be benchmarked against independent measurements. Using the line ratio method with corresponding xenon and argon line intensities, the reduced electric field is estimated accurately. The calculated values are in good agreement with direct measurements, both in absolute value and in trends with pressure and current. The sensitivity of the method to the densities of O(3P) and O2(a) was tested by varying these values in the calculations by 50-150%. It was found that the calculated E/N is only weakly sensitive to these input values, with a difference of less than 7%. This indicates that the method can provide a reasonable estimation of the reduced electric field even without actively probing the discharge composition. The results were validated for E/N values ranging from 50 to 80 Td.

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PLATH00094

TWO DIMENSIONAL DISTRIBUTION OF ATOMIC NITROGEN ABSOLUTE DENSITY IN THREE DC MHCD

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Molecular nitrogen is a convenient precursor of atomic nitrogen used in low-to-moderate pressure plasmas for nitride deposition [1,2]. However, N_2 is hard to dissociate due to its strong triple bond. Micro hollow cathode discharges (MHCDs) can achieve efficient N_2 dissociation for the deposition of hexagonal boron nitride (h-BN) [1]. h-BN is a large band-gap material and a perfect substrate for graphene, being ideal for applications in electronics and photonics. Although the feasibility of its synthesis with MHCD has been achieved, the properties of the deposited films are not optimised and an improvement of the current MHCD technology is needed.

In this work, we investigate the N-atom production in a DC MHCD operated in the normal regime. The discharge current is set to 1.6 mA, and the plasma is ignited in a 20%Ar / 80% N_2 gas mixture. Nanosecond two-photon absorption laser induced fluorescence (ns-TALIF) is used to perform 2D mappings of the N-atoms in the low pressure chamber, which is typically used for h-BN deposition. An aluminum substrate, acting as a third electrode (second anode), is placed further away from the MHCD to emulate a substrate holder. The spatial density of N-atoms is measured in three MHCD configurations. First, we study an MHCD having the same pressure (50 mbar) on both sides of the anode/cathode electrodes and the N-atoms simply diffuse in three dimensions from the MHCD. The maximal density is found at the hole's axis, close to the MHCD. However, using a pressure differential, thus creating a plasma jet, an unexpected N-atoms distribution is measured with maximum densities away from the jet axis. This behavior cannot be explained by the TALIF measurements. Then, as a simplified approach, we studied the role of the gas flow pattern. Compressible gas flow simulations show a correlation between the jet width and the radial distribution of the N-atoms at different axial distances from the gap. Finally, a DC positive voltage is applied to the third electrode (second anode), which ignites a micro cathode sustained discharge (MCSD). Due to the pressure differential, two stable working regimes are revealed depending on the current distribution between the two anodes. The MCSD enables an homogenization of the density along the surface of the substrate, which is suitable for nitride deposition applications.

Thanks/Acknowledgement
Projects DESYNIB (ANR-16-CE08-0004) and SPECTRON (ANR-23-CE51-0004-01).

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PLATH00095

ANALYSIS OF SPUTTERED SPECIES TRANSPORT IN HIGH POWER IMPULSE MAGNETRON SPUTTERING (HiPIMS) DISCHARGE EMPLOYING MAGNETIZED QCM PROBE

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Among the numerous advantages of the high-power impulse magnetron sputtering (HiPIMS) technique, the most important is the enhanced ionization degree of sputtered species contributing to the film growth. Consequently, the quality of deposited thin films is highly improved [1].
However, the optimization process is challenging due to the complexity associated with the transport of the sputtered species, ionized or neutrals. The limited knowledge available on the spatial distribution of these species when operating a HiPIMS discharge makes the quantitative prediction of any deposition feature particularly difficult.
We investigated the influence of experimentally controllable quantities, such as gas pressure and target current density, on the transport of sputtered titanium in non-reactive (argon) HiPIMS, namely on the behavior of metal atoms and metal ion fluxes intercepting the substrate. Systematic quantitative measurements were carried out using a modified quartz crystal balance (QCM) equipped with an electron magnetic filter (M-QCM) [2, 3], which scanned the plasma discharge axially in a plane parallel to the target surface and radially along the target diameter. The magnetron source, whose central and outer magnets could be varied relatively, enabled us to enrich our study with various magnetic field mappings.
Hence, the 2D spatial distribution of the ionized flux fraction (IFF) and the total flux of titanium sputtered particles (deposition rate) have been evaluated by biasing the M-QCM. In addition, the wide range of investigated parameters gives precious hints to predict and optimize the flux of sputtered species based on complete mapping of the IFF of sputtered particles for different magnetic field configurations, as depicted in Fig. 1.
Depending on the desired objectives, the results can be used to define strategic substrate positions for the deposition processes.

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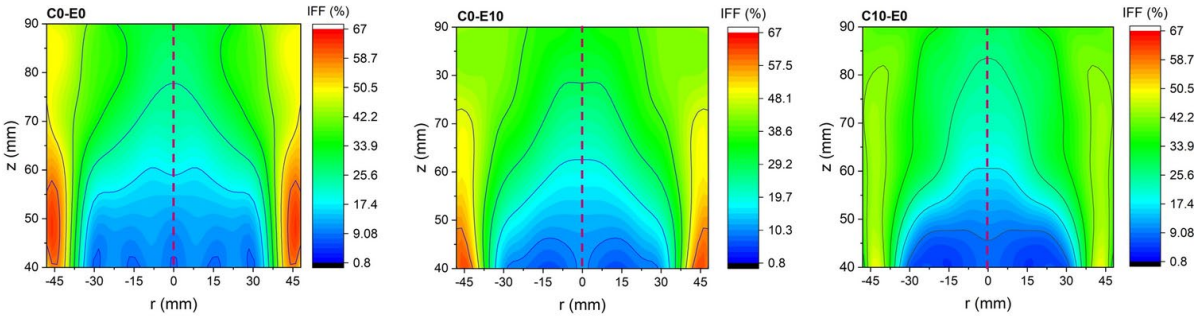

2D maps of the ionized flux fraction distribution

PLATH00101

PLASMA-SURFACE INTERACTIONS IN CO_2 GLOW DISCHARGES

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Heterogeneous surface kinetics plays an important role in most plasma processes, where surfaces interact either with active discharges or their afterglows. In plasmas for CO_2 conversion, adsorption and recombination of atomic oxygen on reactor surfaces determine the gas composition and the availability of O for dissociation and recombination reactions ($CO_2 + O \rightarrow CO + O_2$; $CO + O + M \rightarrow CO_2 + M$). Measurements in the positive column of oxygen-containing glow discharges in a Pyrex tube of 10 mm inner radius, for wall temperatures between -20ºC and 50ºC (50ºC in the figure), highlighted that the loss frequencies of O (υ_{loss}) and estimated wall recombination probabilities are significantly lower in CO_2 plasmas than in O_2 plasmas [1]. Although O recombination in O_2 plasma was recently described [2,3], the difference with respect to CO_2 plasma is poorly understood. Here we employ global modelling with surface kinetics to describe O loss in CO_2 plasmas and highlight the relevant mechanisms [4,5]. The newly developed model describes the experimental dependence of the atomic oxygen loss frequency on pressure, current, gas temperature and wall temperature and allows to identify the most important recombination mechanisms. The results suggest that partial CO passivation of chemisorption sites can justify the lower recombination in CO_2 than O_2. Moreover, the simulations highlight that source and loss volume processes are non-negligible in the analysis of O loss frequency. Figure 1 shows that the simulated O loss frequency follows the trend from experiment and highlights the contributions of the major surface recombination processes to the O loss frequency.

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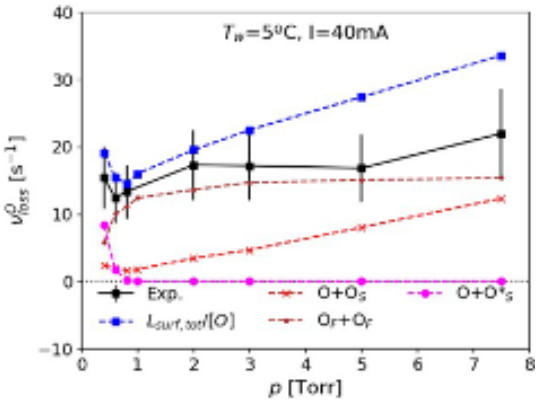

PLATH00153

STUDY OF THE PLASMA PYROLYSIS OF METHANE IN A ROTATING GLIDING ARC FOR CARBON BLACK SYNTHESIS

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Non-thermal plasmas offer a promising pathway for CO_2-free methane (CH_4) conversion to hydrogen and carbon materials through the so-called plasma pyrolysis process. In this study, we specifically investigate through extensive plasma diagnostics the plasma pyrolysis of CH_4 in a rotating gliding arc (RGA) reactor as a function of important experimental parameters such as: the CH_4 content in CH_4/N_2 and CH_4/Ar gas mixtures, the applied power, the flow rate, and the operating pressures. Our aim is to provide a comprehensive understanding of the CH_4 conversion process (including the carbon material synthesis mechanisms) by investigating the correlation between plasma properties and the carbonated products features. .
Optical emission spectroscopy (OES) shows that by increasing the CH_4 content and the applied power shift the plasma from non-equilibrium toward thermal equilibrium ($T_{rot} \approx T_{vib} \approx 4700 \pm 200$ K). More specifically, it is shown that low specific energy inputs (SEI < 3 kJ/L) allow for maintaining non-equilibrium, promoting electron-impact dissociation and, as a consequence, inducing the generation of graphene-like carbon flakes while higher SEIs favor thermal equilibrium and the formation of amorphous carbon black material. A maximum CH_4 conversion of 95% is achieved for dilute CH4 (5% CH4 in feed gas) at lower energy costs than conventional gliding arc or dielectric barrier discharge (DBD) systems [1–3].
The use of N_2 enhances the plasma stability and contributes to the vibrational excitation of CH_4 through metastable collisions, while Ar facilitates efficient dissociation through energy transfer from excited states. Furthermore, increasing reactor pressure reduces CH_4 conversion due to shorter mean free paths, therefore pormote the production of C balck.
These findings highlight how controlling plasma properties can allow to tune the carbon material selectivity , supporting efficient carbon production with minimal energy use and zero CO_2 emissions.

Thanks/Acknowledgement
This research was supported by the "Pyrocarb" project with funding from the Walloon Government (Win2Wal, Belgium) and Phillips Carbon Black Limited (PCBL).

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PLATH00157

TIME-RESOLVED MEASUREMENTS OF SECONDARY ELECTRON EMISSION DURING ION BOMBARDMENT

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Magnetron sputter deposition of compounds is a highly dynamic and variable process where the deposition rate, energy flux and chemical composition can change drastically. The underlying parameter is the dependence of the secondary electron emission yield on the ion energy but especially on the target composition. Typically, oxides exhibit a higher yield, thus reducing the target voltage (at constant current density) and hence the sputter rate as well as increasing the tendency towards target poisoning.
However, it is nearly impossible to obtain quantitative results in a conventional magnetron sputter discharge as plasma generation and ion bombardment are intrinsically entwined. Using a different experimental setup where the plasma generation is separated from the production of the ion flux to the target, it is possible to elucidate more detailed information on the secondary electron generation. Here, an ECR low pressure plasma discharge is combined with a target where independent high voltage pulses are applied. At the same time, the plasma sheath accelerating the ions from the plasma towards the target accelerate the emitted secondary electrons during their transit into the bulk plasma.
Time-resolved Langmuir probe and optical emission spectroscopy (OES) measurements with a time resolution of microseconds show indirect effects of the interaction of generated secondary electrons with the background gas: additional ionisations, an increased plasma density and the de-excitation of energetic plasma electrons within less than 50 µs. As the plasma density is low enough for the majority of secondary electrons to transit the plasma without interaction, they can be detected with a passive thermal probe near the wall of the vacuum chamber due to their high kinetic energy of a few keV. Hence, on a time scale of minutes it is possible to follow target oxidation/reduction processes during oxygen and argon ion bombardment as well as direct comparison of the electron yield ratio for oxidic vs metallic surfaces for different metals. Furthermore, the influence of changes in the surface topography and morphology can be correlated with variations in the secondary electron yield.

PLATH00167

DEVELOPING A MODELING FRAMEWORK FOR PLASMA ASSISTED SOLVOLYSIS OF FIBER REINFORCED POLYMERS

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Fiber reinforced polymers (FRPs) are utilized to high-end applications (e.g., automotive, wind energy sector) due to their superior properties (mechanical, corrosive, and thermal resistance). An important issue of the composite industry is the limited lifetime of FRPs. New strategies for dealing with these types of waste are needed. Conventional processes (thermal, chemical, mechanical) have not yet reached the ideal standards (energy efficiency, environmentally friendly). Plasma assisted solvolysis (PAS) of FRPs is a promising alternative for fast recycling processes at mild operating conditions.
PAS is implemented by an atmospheric pressure plasma (APP) reactor fed with Ar (see Figure 1). Plasma is produced between the high voltage electrode and the liquid surface (Figure 1). The bubbles formed by flow carry the plasma produced reactive species into the liquid phase inducing chemical kinetics assisting the matrix dissolution (by oxidative species) of the FRPs. The aim is the development of a modeling framework for PAS of FRPs. The modeling framework consists of 3 models: a) a global model for the filamentary plasma phase (plasma model), b) a global model for the bubble and liquid kinetics taking into account mass transfer across the bubble – liquid interface (bubble – liquid model), and c) a reaction-diffusion model in 2D (or 3D) for the dissolution of the FRP (FRP dissolution model).
Results from the plasma and dissolution models will be presented. In particular, the effect of the power density profiles (filaments' power and duration) on the densities of plasma produced species is investigated. Additionally, the effect of the type and the concentration of the oxidative species in the remaining mass of the FRP is demonstrated. The modeling framework will contribute to the optimization of PAS and could be adapted to alternate plasma – liquid systems (e.g., liquid waste and liquid fertilizers).

Thanks/Acknowledgement
The research project is implemented in the framework of H.F.R.I call "Basic research Financing (Horizontal support of all Sciences)" under the National Recovery and Resilience Plan "Greece 2.0" funded by the European Union – NextGenerationEU (H.F.R.I. Project Number: 15231)

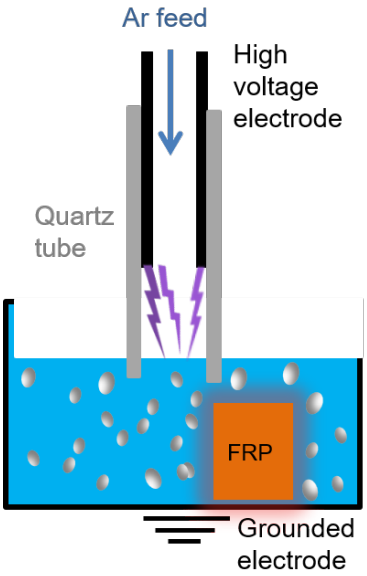

Figure 1. APP reactor for PAS of FRPs

PLATH00002

INFLUENCING THE PROPERTIES OF TiN AND (Ti,Al)N HARD COATINGS BY MODIFYING THEIR COMPOSITION AND STRUCTURAL DESIGN

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In general, for a certain compound, developed in the form of a coating, the properties can be modified, most of the time, by varying the composition (of the constituent elements ratio); for a certain established composition, the properties can be also influenced by modifying the structural design.
This study investigated the impact of the composition and nanostructure design of titanium nitride (TiN) and, particulary of titanium-aluminium nitride (Ti,Al)N coatings on their optical, electrical, thermal, mechanical and tribological properties. The impact of the composition (variation of N for TiN coatings and Al for (Ti,Al)N coatings) was studied only for the normal structural growth coatings. The growth designs of the coatings (normal, inclined and zig-zag) were tailored using conventional sputtering and GLancing Angle Deposition (GLAD) geometries. The results showed the potential to modify the properties of coatings by adjusting their nanostructure design, rather than changing their composition. TiN coatings prepared by GLAD, revealed wider and more significant variations in optical and electrical properties, while the thermal properties seemed to be more affected by the structural changes promoted by the N content in the films [1]. GLAD geometries resulted in the reduction of the film's reflectivity, and colour coordinates, as well as an increase and electrical conductivity. In general, the same tendencies were observed in the case of (Ti,Al)N type coatings.
For both cases, the mechanical and tribological properties were shown to be strongly depended on the roughness and porosity of the coatings. As the deposition configuration changed from regular to inclined and to zig-zag growth, surface porosity and roughness increased, inducing a systematic decrease in all Hardness, Young's modulus, friction coefficient, wear rates and resistance to scratch. However, it was shown, that the obtained values fit within the literature reported values and ensure a good applicability and are suitable for the intended use of such coatings in different applications, allowing the use of a single coating system, where the growing design allows the tailoring of the coating response according to the required responses.

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PLATH00011

HEA THIN FILMS AS PROTECTIVE BARRIER AGAINST CARBON DIFFUSION DURING SPS

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The production of metal parts by powder metallurgy using the Spark Plasma Sintering (SPS) process, results in a fine and homogeneous microstructure with a chemical composition close to that of the initial powder. In this process, the sintering is performed by the simultaneous application of a pulsed current, making it possible to heat the powder, and of a uniaxial pressure. The powder is isolated from direct contact with the graphite tooling (mould, punches) by a sheet of graphite.
A major drawback of this process, in the case of the sintering of metallic powders, is carbon contamination, which leads to the formation of highly carburized layers on the surface or even to the diffusion of carbon at the grain boundaries deeper in the part. In a previous study, the effectiveness of a titanium coating, deposited by magnetron sputtering onto the graphite sheet, as a carbon diffusion barrier during the sintering of pure iron, was demonstrated [1].
In this work, the potential of HEA thin films as a carbon diffusion barrier is investigated. A Ti-Ta-Zr-Hf-W equimolar target (8” in diameter) is used in pure argon and argon- nitrogen mixture atmospheres to deposit a 2 µm thick coating on graphite sheets, glass, and silicon. The coated graphite sheets are used in the sintering of iron powder, while the other samples are analyzed for film characterization (XRD, SEM, EDS). Compared to the previously tested films, the HEA thin films presents the best behavior as diffusion barrier and as antisticking coating.

Thanks/Acknowledgement
This study is part of the ANR OEDIPUS project (ANR-23-CE08-0028).

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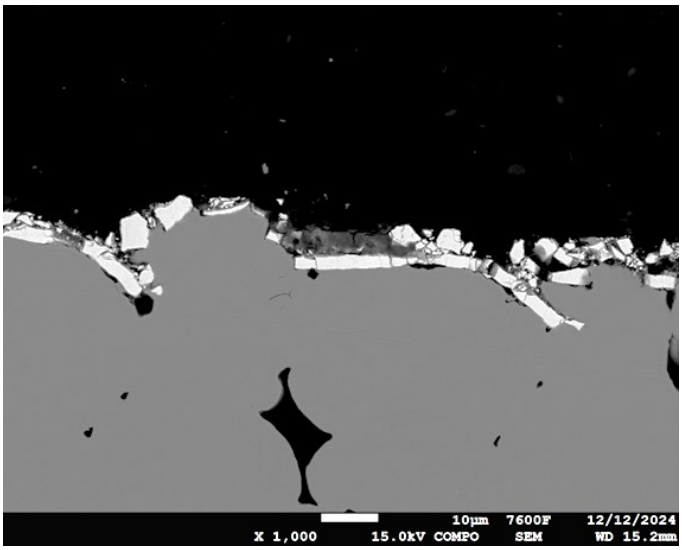

Sintered iron sample with the coated carbon foil

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PLATH00014

THERMODYNAMIC MODELING AND EXPERIMENTAL INVESTIGATION OF Ti PVD COATINGS AS PROTECTIVE BARRIERS AGAINST CARBON DIFFUSION DURING SPS

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The fabrication of metallic parts through powder metallurgy techniques, such as spark plasma sintering (SPS), represents a relevant alternative to conventional manufacturing processes. This technique enables the production of dense, high-performance materials with excellent mechanical properties in a single step. The powder is placed into a mold and densified through Joule heating and uniaxial pressure (Fig.1). One of the main challenges of the SPS process is the carbon diffusion from graphite tools and/or graphite foils in contact with the sintered powder. If carburization is not prevented, it can degrade material properties and lead to composition gradients at the surface [1]. In this study, titanium coatings (thicknesses ranging from 0.5 to 2 µm), deposited via PVD on graphite foils in contact with pure iron powder, proved to be effective in preventing carburization during sintering (1050 °C - 10 min - 70 MPa). However, coating thickness is a key parameter: a minimum thickness of approximately 1 µm is required for effective protection. The coating's stability and elemental diffusion at the coating/substrate interface were carefully analyzed using SEM-EDS and complemented by phase identification through XRD.Thermodynamic simulations using DICTRA (ThermoCalc®) confirmed the experimental findings (fig.2), enabling the prediction of optimal thicknesses and the selection of new elements (Ti, Zr, Hf, Ta, W) as diffusion barriers against carbon, due to their ability to form carbides with low carbon diffusion coefficients. This study is part of the ANR OEDIPUS project (ANR-23-CE08-0028).

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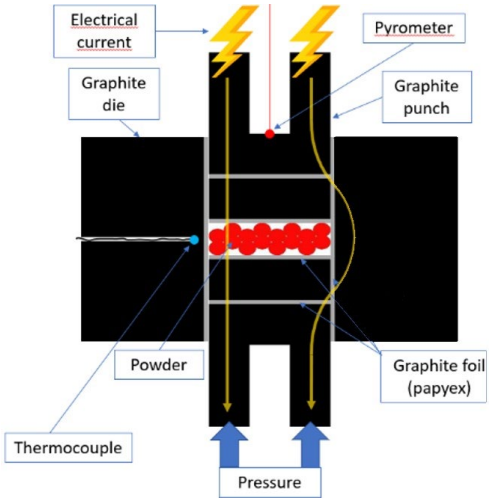

Fig.1 Diagram of SPS process

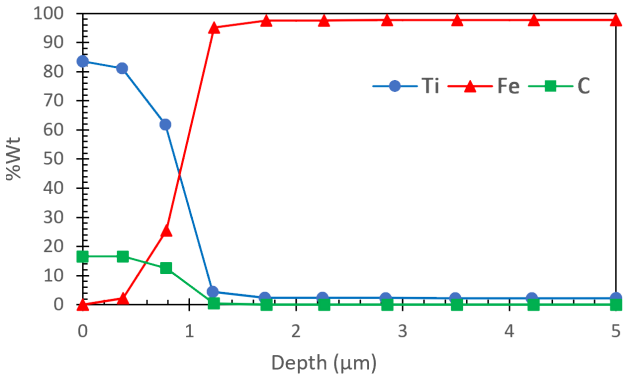

Fig.2 Simulation of a 1 µm thick Ti film at 1000°C

PLATH00066

NANOSTRUCTURING OF BISMUTH OXYFLUORIDE THIN FILMS BY OBLIQUE ANGLE DEPOSITION FOR CO_2 PHOTOCONVERSION

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Industrial decarbonization requires increased electrification and enhanced process efficiency. However, sectors such as metallurgy and cement production will continue to generate CO_2 emissions, making it essential to develop strategies for converting CO_2 into valuable products. Photoconversion of CO_2 from industrial flue gases offers a promising dual benefit: reducing emissions while generating high-value molecules for energy and chemical applications. Among the photocatalysts investigated, TiO_2 remains the benchmark material for CO_2 reduction. However, previous research has highlighted the potential of bismuth oxyfluoride (BiOxFy) based materials in heterojunction with metallic bismuth, synthesized via reactive sputtering in a single step. These thin film photocatalysts have demonstrated a CO_2 photoreduction efficiency of 25 µmol/h/g, comparable to that of commercial TiO_2, while exhibiting a significantly higher CO selectivity of 90%.

The objective of this study is to further enhance these materials performance by nanostructuring the thin films using the Oblique Angle Deposition (OAD) technique. This approach increases porosity and surface area in contact with CO2, but also reduces the distance for photogenerated charge to reach the surface, thereby improving photocatalytic efficiency.

The coatings were fabricated using reactive magnetron sputtering under OAD conditions, employing a 99.99% pure bismuth target in a reactive $Ar/O_2/CF_4$ atmosphere at a controlled pressure. Angle > 60°. The scanning electron microscopy (SEM) is used to investigate the film morphology in its thickness and evaluates the angle of tilted rods, depending on incident angle during deposition in OAD. These results are confronted to porosity and surface area determined using BET analysis. Furthermore, optical properties are characterized through ellipsometry and UV-Visible spectroscopy to evaluate structural modifications induced by substrate tilting during deposition. X-ray diffraction (XRD) and Raman spectroscopy are employed to confirm that expected BiO0.5F2 crystalline phases is maintained in OAD condition.

The film photocatalytic performances are first assessed through the photodegradation of methyl orange at ICCF, providing insight into the films' reactivity under light irradiation. Subsequent CO_2 photocatalytic reduction tests will be conducted at IFPEN to evaluate their ability to convert CO_2 into valuable chemical products, including carbon monoxide (CO) and hydrogen (H_2). This study aims to demonstrate that OAD nanostructuring is a promising route to enhance the efficiency of BiOxFy based photocatalysts, paving the way for more effective industrial applications in CO_2 valorization.

PLATH00134

DISCRIMINATING BETWEEN MORPHOLOGICAL AND CHEMICAL EFFECTS ON THE ANTIBACTERIAL PROPERTIES OF METAL THIN FILMS THROUGH LASER SURFACE STRUCTURING

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Surface transfer of microbes is one of the main routes of transmission of infectious diseases in critical applications including the healthcare environment [1]. Therefore, surfaces that reduce microbial residence time and viability and thus, the likelihood of pathogen transfer, are of great interest. In order to reduce bacterial transfer, research on antimicrobial materials has been done and is ongoing. Among them, sputtered alloy thin films composed of one or more bactericidal elements such as copper, zinc or silver … have shown promising results [2].
The mechanisms of action of surfaces on bacteria are well known: non-adhesion, killing by release of an active substance, physical killing by membrane damage and photocatalytic damage. They depend on the surface chemistry, morphology, roughness, local mechanical properties, porosity, etc. Although standard protocols have been developed to quantify the antibacterial activity of surfaces under controled conditions, they do not allow for the determination of the main mechanisms involved. Recent studies have successfully attempted to combine different protocols and complementary analyses such as the measurements of released ions, in order to decorrelate each mechanism [3].
This work contributes to the understanding of the antibacterial activity of CuZn-based thin films deposited by magnetron sputtering. In order to control the chemistry and morphology separately, ultrashort pulsed-laser structuring of the film, or of the substrate prior to deposition, was carried out. The laser treatment conditions have been set in order to induce the formation of nanostructures (LIPSS: laser induced periodic surface structure) or of spikes (micron-scale structures). Film characterisics were determined by conventional analyses: scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy etc. The ion release capacity was measured by ICP-OES and the wettability was evaluated by contact angle measurements. The antibacterial properties were investigated using different protocols adapted from standards used for non-porous surfaces.

Thanks/Acknowledgement
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PLATH00142

NANOSTRUCTURE ENGINEERING AND PROPERTIES ENHANCEMENT OF Cu-BASED FILMS BY Zr AND Ta ALLOYING

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Nanocrystalline Cu films exhibit unique mechanical properties due to the increased surface area of grain boundaries. However, this structural state creates excess free energy leading to low thermal stability. Our study addresses this challenge through targeted alloying of magnetron sputtered Cu films with low content of Zr and Ta. The mutual immiscibility and large atomic size mismatch between Cu and Zr or Ta have the potential to influence grain boundary chemistry and structure implying grain boundary engineering approach.
Nanocrystalline Cu-rich Cu-Zr and Cu-Ta films were deposited from two separate targets of the base metal (Cu) and alloying element (Zr or Ta) under identical technological conditions with a fine composition variation. The effects of Zr and Ta alloying on the structure, surface, mechanical, and electrical properties were investigated using X-ray diffraction, electron microscopy, atomic force microscopy, indentation, and the four-point probe method. Additionally, non-equilibrium atomic-scale growth simulations of Cu-rich Cu-Zr and Cu-Ta films were conducted to provide information not achievable experimentally.
The results show that alloying with Zr and Ta significantly influences the microstructure and anisotropy of the films, which leads to a notable structural refinement and a reduction of the average grain size from 220 nm in unalloyed Cu to below 100 nm with Zr or Ta alloying. A systematic investigation shows that during film deposition, a redistribution of alloying atoms occurs between the grain interior and grain boundaries resulting in the formation of a complex microstructure. As a result, the alloyed films exhibit hardness values between 3.2 and 4.2 GPa, exceeding the 2.5 GPa measured for the unalloyed Cu film. The electrical resistivity increases with increasing content of the alloying elements, primarily due to electron scattering by solute atoms and additional scattering at the grain boundaries. However, the as-deposited alloyed Cu films exhibit a favorable combination of hardness and electrical conductivity that is comparable to or better than reported values in literature.
Our findings demonstrate that precise alloying with Zr and Ta, combined with non-equilibrium conditions of magnetron sputter deposition, is an effective approach for modifying the structural state of the Cu films, optimizing their mechanical, electrical, and surface properties, and offer insights that can be applied to other comparable binary systems in the development of nanocrystalline metallic films.

Thanks/Acknowledgement
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PLATH00151

ATOMIC LAYER DEPOSITION OF ZnO ON FULLERENE: COMPARING THERMAL AND PLASMA-ENHANCED APPROACHES TOWARDS A PHOTOACTIVE NANOCOMPOSITE

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ZnO is a low-cost, environmentally friendly n-type semiconductor, known for its excellent photoactivity due to its wide band gap (3.37 eV), which enables strong absorption in the UV region. However, its photocatalytic efficiency is significantly limited by the rapid recombination of photogenerated electron–hole pairs. To overcome this drawback, ZnO has been frequently combined with carbon-based nanomaterials (CNMs), which serve as effective cocatalysts by acting as electron sinks, thanks to their extended conjugated π-networks of carbon atoms and favorable work function.
While ZnO/CNMs nanocomposites are typically prepared using wet chemical methods that involve the use of organic solvents and generate chemical waste, Atomic Layer Deposition (ALD) offers a dry, precise, and potentially more sustainable alternative. In this work, we report the fabrication of ZnO/C_{60} nanocomposites via thermal ALD (t-ALD) and plasma-enhanced ALD (PE-ALD), and compare the chemical, morphological, and photocatalytic properties of the resulting nanocomposites.
Going into detail, X-ray diffraction (XRD) confirms the crystalline nature of the deposited ZnO, while X-ray photoelectron spectroscopy (XPS) demonstrates stoichiometric ZnO growth in both deposition approaches. Scanning electron microscopy (SEM) reveals conformal coating on both the top of the surface and the internal pores of the fullerene powder. Notably, PE-ALD results in ZnO deposition confined to the walls of the most superficial pores, whereas t-ALD achieves coverage of deeper pores as well. X-ray fluorescence (XRF) analysis quantifies a two-fold higher Zn content in the t-ALD sample compared to the PE-ALD one.
The photocatalytic performance of the nanocomposites was evaluated by monitoring the degradation of methylene blue under UV irradiation. The t-ALD ZnO/C_{60} nanocomposite exhibited superior photocatalytic activity ($54 \pm 12\%$) compared to the PE-ALD counterpart ($33 \pm 10\%$), in line with the higher ZnO loading. However, the deposition of ZnO was not uniform across the powder batch, thus leading to a high relative error on the MB degradation percentage determined.
These findings suggest that optimizing the ALD process—particularly through the design of reactors tailored for powder substrates—could further enhance the uniformity and, hence, the performance of the resulting photocatalysts. This will be the focus of future investigations.

Thanks/Acknowledgement
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PLATH00159

RECYCLABLE THIN COATINGS DEPOSITED BY MEAN OF PLASMA-ASSISTED TECHNIQUES ON POLYMER FOILS FOR FOOD PACKAGING APPLICATIONS

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Plastic waste is one of the most pressing environmental challenges, particularly due to the widespread use of multilayer polymer films in food packaging. These materials combine different polymers to achieve barrier performance but complicate recycling. A promising alternative is the application of thin plasma-assisted coatings on single-layer polymers, which can deliver comparable barrier properties while maintaining recyclability.
In this work, two deposition methods were compared: Plasma-Assisted Chemical Vapor Deposition (PA-CVD), using a bipolar DC pulsed discharge with acetylene and HMDSO precursors, and Magnetron Sputtering Physical Vapor Deposition (MS-PVD), employed to deposit carbon and silicon coatings. Polypropylene, polyethylene, and polyethylene terephthalate films with a thickness of 20 µm were used as substrates. Coatings were characterized by FTIR, Raman spectroscopy, SEM, and surface free energy (SFE) analysis, while barrier performance was assessed via water vapor transmission rate (WVTR) and oxygen transmission rate (OTR). Additionally, melt flow rate (MFR) measurements were carried out to evaluate whether the coatings affect the processability of the polymers during recycling.
Si-based coatings exhibited a strong Si–O–Si band at ~1050 cm^{-1} in FTIR spectra, while those deposited from HMDSO also showed a double peak at 840 cm^{-1} and 800 cm^{-1} associated with Si–CH_3 groups, which resulted in the lowest surface free energy (20 mN/m) and hydrophobic behavior. C-based coatings displayed C=C vibrations near 1600 cm^{-1} in the IR spectrum and a graphite-like Raman response with a G band at 1580 cm^{-1}, accompanied by a higher SFE of ~45 mN/m. SEM analysis revealed coating thicknesses ranging from 20 to 150 nm. In terms of barrier performance, PA-CVD coatings did not significantly affect WVTR, whereas MS-PVD coatings reduced water permeation by up to 60% with carbon and by as much as 90% with thin silicon layers. For oxygen, MS-PVD coatings decreased permeation by nearly one order of magnitude. Overall, these plasma-assisted coatings provided barrier properties comparable to those of multilayer packaging based on EVOH films. MFR measurements indicated that the coatings did not significantly alter the melt flow behavior of the polymers, confirming their recyclability.

Thanks/Acknowledgement
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PLATH00163

A NEW SOLUTION TO REMOVE MACRO-PARTICLES DURING REACTIVE METAL NITRIDE ARC PHYSICAL VAPOUR DEPOSITION

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Arc PVD is a widely used and convenient method to create hard, wear resistant and decorative layers based upon metal nitrides. The arc discharge operates at low voltage and high currents which creates very high levels of metal ions within the vapour flux. This high level of ionisation ensures well adhered and dense coating structures, and ensures the process is ‘robust’ and suited to industrial production. In addition, the cost of the power supplies and sources are much lower than competing techniques such as sputtering and the more recent hipims type of power mode. The major downside to the ARC PVD method is an unwanted ‘side-effect’ of the process which results in a rough coating with large amounts of ‘macro-particles’, which in effect are defects and detract from the coating appearance and performance. The reduction of the number of macro-particles has been the main area of focus over the last 20 years, however, no convenient method is able to remove the problem. It has been shown that using a ‘u’ shaped magnetic filter to guide the metal ions and remove the macro-particles can result in smooth defect free layers. However the rate is reduced by over 80% and the area of coverage of the coating flux is much smaller. Consequently magnetic filtering is used only in niche applications.
This poster will present a new type of arc source that produces smooth defect free metal nitride coatings by the ARC PVD method. The arc source does not require any filtering method and is 125mm in target diameter, hence there is no loss in very high rates normally associated with ARC PVD. As with normal ARC methods the ionisation of the metal is very high, so the coatings are very hard and dense. Data will be presented for the TiN and TiAlN coating systems in the form of coating rates, defect counts, surface roughness, hardness and wear resistance. The method opens up the potential for ARC PVD to compete effectively with more recent Hipims sputter-based hard coating methods.

PLATH00164

DEPOSITION AND CHARACTERISATION OF NITRIDE THIN FILMS FOR DATA-DRIVEN OPTIMISATION OF OXIDATION RESISTANCE

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Artificial intelligence technologies open up a new perspective in materials science through a data-driven approach. Their use in the synthesis of inorganic thin films by physical vapour deposition (PVD) is rather scarce, especially in magnetron sputtering.
In a recent work [1], the authors compiled a database of reactive DC magnetron sputtered TiN coatings based on a large number of reports available in the literature (281). Machine learning algorithms were trained on the database entries from independent authors to establish a relationship between coating hardness and experimental deposition settings. Even though the trained algorithm was then applied to the inverse design problem, an important remark of this work is that some important information is missing in the literature... Another article [2] describes the closed-loop optimisation of epitaxial titanium nitride (TiN) thin film growth combined with a Bayesian machine learning technique to reduce the required number growth experiments. This strategy does not rely on external data-driven screening and is therefore a cheap and simple method that could allow continuous autogenous self-improvement of systems by increasing the number of experimental results.
Our aim is to apply such a strategy to nitride thin films with complex compositions instead of TiN. The films are deposited on a silicon substrate by reactive magnetron sputtering in a small reactor with three independent sources in a confocal configuration. Their structure, composition and microstructure are characterised by XRD and SEM-EDS before and after annealing at different temperatures. First results for binary and ternary nitrides based on tantalum, aluminium and chromium are presented, as well as the experimental conditions proposed by the algorithm to optimise the oxidation resistance.

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PLATH00173

PLASMA DEPOSITION OF III-V SEMICONDUCTORS: SPUTTERING AND RPVPE APPROACHES

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We are exploring plasma-based approaches to synthesize III-V thin films with lower cost and temperature requirements than traditional methods such as MOCVD or MBE [1]. These processes, although widely used, typically demand high growth temperatures between 600 and 1000 °C and large flows of toxic, expensive gases. Such conditions not only raise production costs but also generate strong thermal stress during hetero-epitaxy, often leading to defects that compromise material quality. These drawbacks hinder the broader adoption of III-V semiconductors.

To address these challenges, we have designed two complementary plasma reactors: reactive sputtering for GaN deposition [2] and Remote Plasma Vapour Phase Epitaxy (RPVPE) for GaAs growth [3]. Both techniques offer more energy-efficient and environmentally sustainable routes compared to conventional epitaxy.

With reactive sputtering, we demonstrate the ability to deposit polycrystalline GaN directly on silicon substrates at room temperature as evidenced by transmission electron microscopy (Figure 1.a). This highlights the potential of plasma-assisted processes for integrating GaN with temperature-sensitive substrates.

For GaAs, we employ RPVPE at only 500 °C to obtain high-quality homoepitaxial layers as evidenced by cross-sectional SEM images that reveal excellent crystalline quality, comparable to films grown at much higher temperatures (Figure 1.b).

In addition to film characterization, we are also investigating the plasma using spectroscopic tools. These analyses provide valuable insights into the interactions between reactive species and growing surfaces, guiding further optimization of growth conditions.

This research demonstrates that plasma-assisted techniques can open new opportunities for III-V integration at reduced energy and material costs.

Thanks/Acknowledgement
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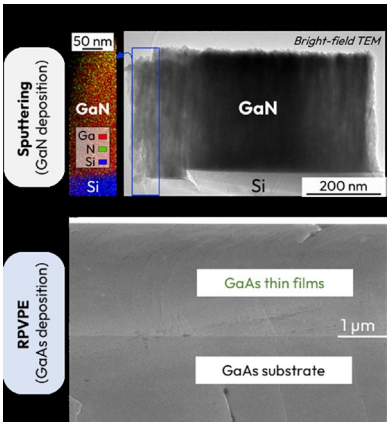

Figure 1. Typical images of the III-V growth.

PLATH00043

INFLUENCE OF DISCHARGE PARAMETERS ON THE PROPERTIES OF TiO_2 FILMS GROWN BY REACTIVE BIPOLAR HiPIMS DISCHARGES

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TiO_2 coatings were deposited onto glass substrates using reactive Bipolar High Power Impulse Magnetron Sputtering (BP-HiPIMS) without external heating or bias voltage in an Ar/O_2 atmosphere. The study focuses on exploring the influence of average power, peak current and positive pulse voltage on the crystalline structure of the deposited coatings. For this purpose, TiO_2 coatings were deposited at three different average power densities (2 W/cm^2, 3.5 W/cm^2 and 5 W/cm^2), two different peak current densities (0.5 A/cm^2 and 1 A/cm^2) and two different positive pulse voltages (100 V and 190 V). The general trend observed in this study was that increasing one or several of these parameters leads to an increase in coating crystallinity. For the lowest values, the coating was X-ray amorphous. By increasing the power density, peak current and/or positive pulse voltage, a transition into the rutile phase was observed, with crystallite sizes of ~ 5 nm. Furthermore, an evolution of the crystalline structure with coating thickness was observed, where the coating crystallinity increased as the coating was growing, without any change in the sputtering parameters.

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PLATH00127

MULTISOURCE DEPOSITION CONDITIONS PREDICTION TOWARDS REQUIRED COMPOSITION OF THIN FILMS

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The development of new materials is partially focused on tracing the influence of composition on studied functional properties of the materials. In the case of thin films, a multisource deposition is one of the beneficial techniques for preparing a series of samples with varying compositions. Recently, a simplified calculation model required only basic physicochemical constants (i.e. molar masses and densities) of the studied materials along with reduced number of trial depositions to cover basic instrument characteristics (tool-constants) was developed [1]. Previously, the developed calculation model was applied to the two source depositions of amorphous tellurides (GaSb + GaTe and GaSb + Te co-depositions [1]) and to amorphous selenides ($GeSe_2$ + Bi_2Se_3 co-depositions [2]).
Currently the above-mentioned calculation model is adopted and experimentally verified for the multisource depositions of amorphous sulfides within the GeS_2-Ga_2S_3-Sb_2S_3 pseudoternary system. The thin films were deposited by radiofrequency (RF) magnetron sputtering. Within the aim of the presented work the prepared thin films are characterized namely by means of Energy Dispersive X-Ray Analysis coupled with Scanning Electron Microscope (SEM-EDX) to determine the chemical composition and by Variable Angle Spectroscopic Ellipsometry (VASE) and profilometry to establish film thickness.
The presented model is found to be suitable for preparation of co-sputtered thin films in wide compositional range. In terms of composition, the accuracy of presented model is similar to the compositional deviations observed for single source depositions of binary compounds and close to the SEM-EDX technique accuracy, typically up to ~ 2 %at (and up to ~ 4 %at at worst) (Fig 1.). For the thickness, the accuracy of the model is mostly dependent on availability of co-sputtering thin film density data and typically vary up to ~ 10 %.

Thanks/Acknowledgement
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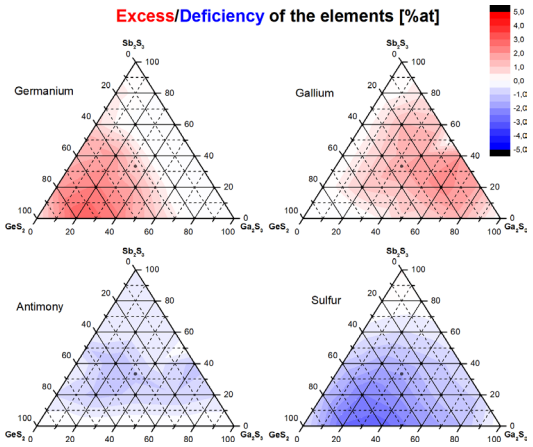

Compositional deviations of particular elements.

PLATH00009

PURE AMMONIA MICROWAVE DISCHARGES: A GLOBAL MODEL

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Ammonia is a hydrogen vector that can be synthesized and cracked to facilitate the transportation of H_2. Thermal processes assisted by catalysts are usually employed in that purpose, as their energy cost is the lowest of all. Thermal cracking of NH_3 requires a relatively long cold start duration, and plasma technology can be considered as an assisting tool—or an alternative. The microwave-assisted process is also an on-site rapid NH_3 decomposition method with higher decomposition ratio without catalyst and dilution. Such a process could also be used in plasma-assisted ammonia combustion.
In this work, we provide a global model describing the interaction of a pure ammonia discharge with microwaves, leading to the heating of the medium to temperatures around 2500 K in the selected conditions (typically 450 W, 40-200 mbar, 1-10 slm).
The propagation of the microwaves in the system defined by successive zones of distinct permittivity values leads to the development of a standing wave which deposits energy in absorbing media. This amount of energy is calculated and used as a heat source to define the flow conditions, leading to a temperature distribution in the volume of the reactor tube. The multiphysics problem is then relatively simple as it does not require to implement a feedback loop between the Navier-Stokes equations and the Maxwell equations. The COMSOL Multiphysics Software was used to solve the numerical problem.
Experimental results show that, regardless of the conditions tested, the electron temperature consistently remains around 0.5 ± 0.1 eV. The positions of the stub and the short-circuit piston used for impedance matching were accurately measured and associated with the selected experimental conditions to define the reflected power and therefore the absorbed power for a given incident power. The geometry and volume of the plasma were determined by image analysis for an average electron density measured by microwave interferometry.
Without any strong assumptions, it is possible to reproduce the values of the electron densities with an accuracy generally less than a factor of 2, which is very satisfactory. Nevertheless, in one condition (at 200 mbar, 10 slm) the calculation result is beyond this threshold compared with the experimental data. This is attributed to a new but unidentified physical phenomenon at high pressure. Deeper investigations are needed to understand the origin of this behavior. This illustrates the specificity of pure ammonia plasmas.

PLATH00017

RATE COEFFICIENTS OF THE N + H + M(Ar, N_2) → NH + M RECOMBINATION REACTION IN FLOWING AFTERGLOWS OF MICROWAVE PLASMAS

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Microwave flowing afterglows of N2, N2/H2 and Ar/N2/H2 gas mixtures were investigated by Optical Emission Spectroscopy (OES) at gas pressures between 1 to 10 Torr and flow rates between 0.5 and 2.0 slpm, the microwave power being set to 100 W. Absolute densities of nitrogen active species ([N2(X,v>13)], [N2(A)], [N(2D)]) present in the afterglows were deduced from band intensity ratios and a calibration of the absolute N-atom density by the NO titration method.
In parallel, absolute N and H atom densities were obtained by TALIF as shown in Fig.1, showing a good agreement for the N atom density [1].
In M = N2/≤5%H2 mixtures, a simple kinetic model was built, allowing relying the [H], [NH] and [NH(A)] densities through reactions :

N + H + N2 → NH + N2	(a)	ka
N + NH → H + N2	(b)	kb = 5 10-11 cm3 s-1
H + NH → N + H2	(c)	kc = 3 10-11 cm3 s-1
N2(X,v>13) + NH → NH(A) + N2	(d)	kd

The kd rate coefficient was assumed to be 5 10-11 cm3s-1, similar to the ones of the N2(X,v>13) + N2(A) [2] and N2(X,v>13) + N2+ reactions [3].
A value of 10-33 cm6s-1 was chosen for the ka rate coefficient, as estimated in [4]. Using the NH(A,v'=0) → NH(X,v'=0) band intensity (I336nm), it was then found similar values of the H atom densities or given by TALIF measurements [1].
When extended to the Ar/1.5%(N2/5%H2) mixtures, the same kinetic model conduces to a H2 dissociation degree ([H]/2[H2]0) higher than 1. Assuming the dissociation degree equal to unity in the Ar/1.5%(N2-5% H2), the ka recombination rate increases to 2.5 10-33 cm6s-1. TALIF measurements of N and H atoms densities in Ar-N2-H2 gas mixtures are currently in progress.

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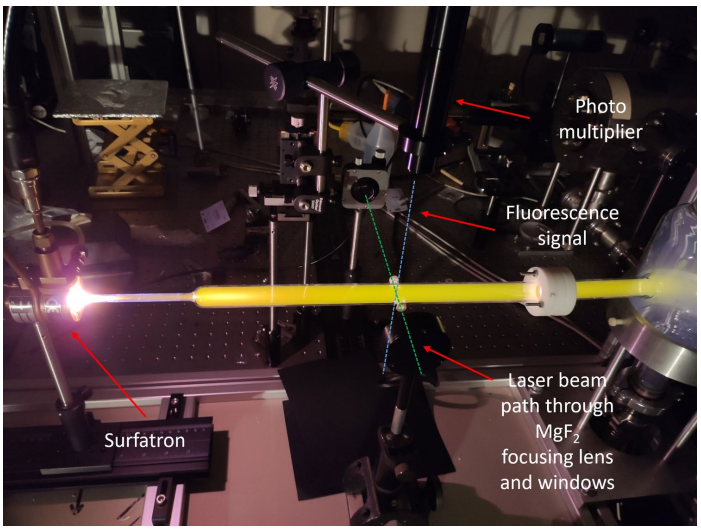

Fig.1 - Picture of the the microwave flowing after

PLATH00059

EXPERIMENTAL INVESTIGATIONS ON THE IMPACT OF GAS FLOW ON THE PROPAGATION DYNAMICS OF A PULSED-DRIVEN µM-SCALE PLASMA JET

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Micrometric-scale atmospheric pressure plasma jets (µm–APPJ) can be useful tools in analytical chemistry for the selective detection of trace amounts of drugs, explosives, biomarkers, etc. [1]. However, the comprehensive understanding of their physics towards enhancing their efficiency, is still scarce. Particularly, their small dimensions impose a challenge for optical diagnostics to probe key local quantities such as fluid properties (e.g., temperature), plasma electron density, electric field strength, etc. [2].
Combining Schlieren photography with ICCD imaging allows to provide a characterisation of the gas flow effect on a µm–APPJ (Fig.1). This device is made of a hollow stainless steel microneedle electrode (200 µm) inserted into a quartz capillary tube and subjected to positive high-voltage pulses (10 kV amplitude, 10 kHz frequency, 200 ns pulse width). Helium gas flows through the needle (flow rate: 0.1–1 slm), traverses the tube, and emerges as a jet in the surrounding air. Schlieren photography reveals impact of the gas flow on the discharge propagation outside the microtube (Fig.2a). Smaller flow rates studied (0.3–0.5 slm) favor the formation of a straighter collimated gas jet. The jet's local properties change with the ignition of the plasma, with a more rapid spreading revealed for Q_{He} 0.5 slm compared to the gas only case (Fig.2a). At Q_{He} =1 slm, the gas jet alone is broad compared to Q_{He}=0.5 slm, the plasma influence being smaller. Single-shot ICCD images (Fig.2b) reveal noticeable discharge branching in the regions where the flow-induced perturbations start to appear. At larger time scales the accumulation of the intensity of the different branches results in average emission profiles which resemble those of the Schlieren images captured at similar time scales.

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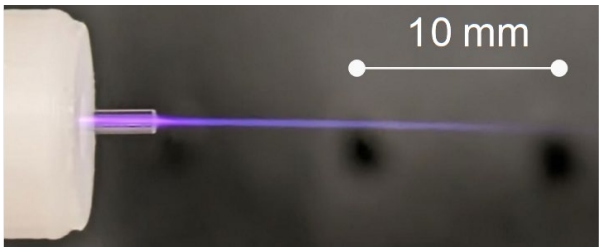
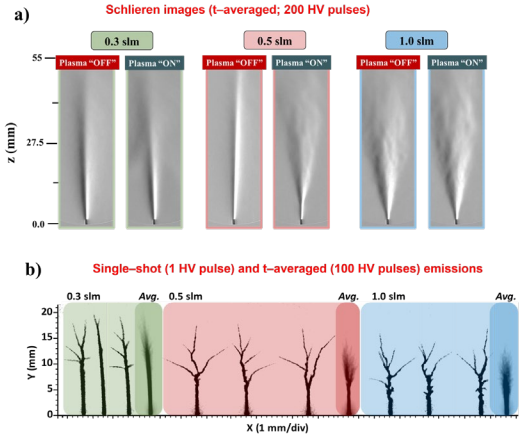


(a) Indicative photo of the µm-APPJ (QHe=0.3 slm)



(b) Schlieren images (c) ICCD images

PLATH00098

MODELLING N_2-H_2 FOR AMMONIA PRODUCTION

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This work reports a detailed study of nitrogen-hydrogen plasmas, including modelling and diagnostics analyses. For this purpose, we consider cylindrical DC glow discharges with no-catalytic walls, produced in N_2-H_2 gas mixtures at different pressures, currents and H_2 concentrations.
Experimental diagnostics include electrical measurements of the reduced electric field E/N (where E is the electric field and N is the gas density), in addition to FTIR and mass spectrometry measurements of the partial pressure of ammonia and the relative concentrations of the main ion species.
Simulations are based on coupled solutions of the electron Boltzmann equation (EBE), written under the two-term approximation [1], with the chemical rate-balance equations of a kinetic scheme for nitrogen-hydrogen plasmas [2,3], which considers the main heavy-species N_2(X,v=0-44), H_2(X,v=0-14), NH_3, N(^{4}S), H(^{1}S), in addition to: 13 electronic excited states (6 for N_2, 2 for N and 5 for H); positive ions N^+, N_2^+, N_3^+, N_4^+, H^+, H_2^+, H_3^+, N_2H^+, NH^+, NH_2^+, NH_3^+ and NH_4^+; negative ions H^- and NH_2^-; surface species H(S,F), N(S,F), NH(S), NH_2(S), physically (F) or chemically (S) adsorbed on the wall; and other molecules and radicals. The surface kinetics include different mechanisms, namely physical adsorption/desorption, chemical adsorption, surface transport, and Eley-Rideal and Langmuir–Hinshelwood recombination processes [4].
The model is numerically solved using the LisbOn KInetics (LoKI) simulation tool [1,5], composed by the EBE solver LoKI-B and the Chemical solver LoKI-C, which are coupled via a series of convergence cycles, ensuring a self-consistent solution for the electron energy distribution function, the species densities, and the reduced electric field, for a given pressure, mixture composition and discharge current.
Modelling results follow qualitatively the experimental values obtained for E/N, being overestimated at low concentrations of H_2. Simulations show that surface mechanisms are essential to correctly predict the measured concentrations of ammonia, although some discrepancies are still observed for larger amounts of H_2 in the mixture. These different aspects describing N_2-H_2 plasmas will be presented at the conference.

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PLATH00100

ION ENERGY DISTRIBUTION FUNCTION MEASUREMENT IN HYBRID HiPIMS WITH CARBON TARGET

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The deposition system, which is a combination of HiPIMS and deliberately ignited cathodic arc discharge with different ignition times and durations, was investigated [1]. The experiments were performed on a planar magnetron with an unbalanced magnetic field with a pure carbon target at a pressure of 1.4 Pa in an argon environment. Ion energy distribution function (IEDF) measurements were performed for Ar^{+}, Ar^{++}, C^{+} and C^{++} ions. Compared to the hybrid modes, the IEDF in the HiPIMS mode shows a significantly higher population of Ar^{+}, Ar^{++} and C^{+} ions. The situation changes dramatically in the case of C^{++}, which is present in the plasma substantially longer in the hybrid HiPIMS modes than in HiPIMS.
This study was carried out to investigate the possibility of DLC (Diamond-like Carbon) film formation. The formation of this type of film, with a predominance of sp^3 bonds in carbon [2, 3], requires significant energy to be injected into the substrate. Therefore, ions such as Ar^{++} and C^{++} are of most interest to us. The carbon ion (C^{++}) has a lower mass compared to argon ion (Ar^{++}), which allows it to accelerate more efficiently in the electric field. Figure 1a shows the clear dominance of the Ar^{++} ion intensity in the HiPIMS compared to the hybrid HiPIMS mode. On the other hand, C^{++} ions dominate in the flux on a substrate when the HiC-ARC HiPIMS mode is applied (Fig. 1b).

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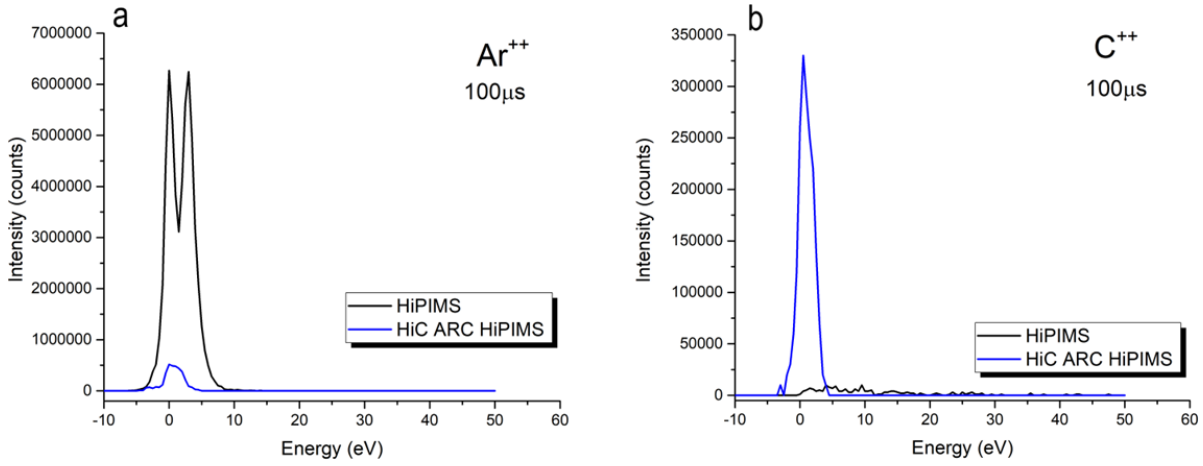

Figure 1. The IEDF curves of Ar++ (a) and C++ (b)

PLATH00126

OPTIMIZING ECR PLASMA ASHING FOR HIGH YIELD DURING SPINTRONIC SENSOR FABRICATION ON 200MM WAFERS

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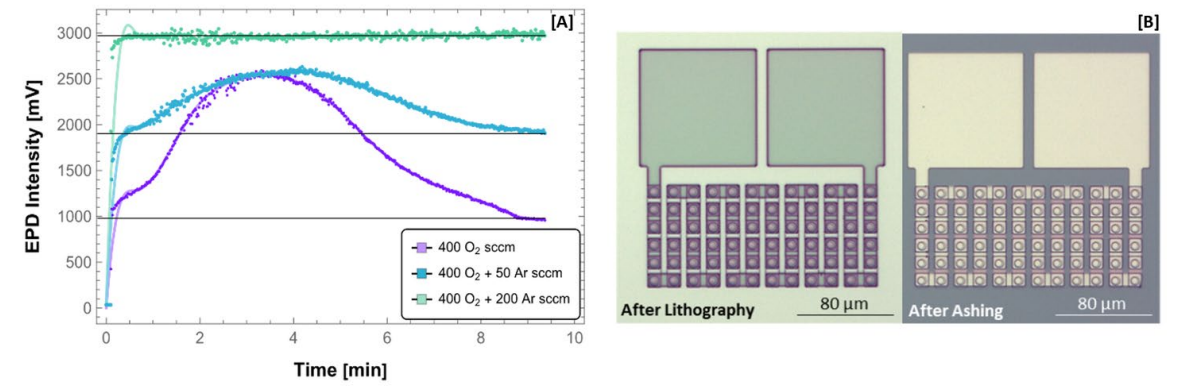
In this work, we demonstrate how oxygen ashing enhances efficiency and throughput in Tunneling Magnetoresistance (TMR) sensor fabrication on 200 mm wafers. The system used is a GIGAbatch 380M (PVA TePla) Electron Cyclotron Resonance (ECR) reactor with an Ar/O_2 plasma process for nano-micro patterned photoresist removal.
The ashing step is critical, removing photoresist after spintronic etching processes, including Ar^+ Ion Beam Milling (Nordiko N3600) and Reactive Ion Etching (RIE) in an inductively coupled plasma (ICP) reactor using CF_4/H_2 and $BCl_3/Cl_2/HBr/O_2$ chemistries (SPTS Omega® C2L). Effective ashing ensures clean surfaces for deposition, essential for device performance. Wafers are patterned with resist structures of various geometries, with feature sizes from 80 µm to 2 µm.
To define optimal conditions, we explored pressures from 0.8–1.1 mbar, microwave power from 600–1000 W, and O_2 (400–800 sccm) and Ar (0–200 sccm) flows. These parameters were adjusted to maintain uniform plasma and maximize throughput in batches of up to 6 wafers. Endpoint detection (EPD) based on emission spectroscopy was used to stop the process, and the impact of wafer count and spacing on ashing time was analyzed.
Figure 1-[A] shows the effect of plasma composition on the EPD signal for 800 W microwave power, 1.1 mbar, and different O_2/Ar ratios. A pure O_2 plasma (400 sccm) gave the best signal-to-noise ratio, with an endpoint criterion of 65% signal fall and a slope of 4 mV/min. Figure 1-[B] shows a TMR sensor in the contact definition step, lithography, and after RIE with $BCl_3/Cl_2/HBr/O_2$ and ashing under the specified parameters and EPD criteria.

Thanks/Acknowledgement
The authors acknowledge BASE (UIDB/0536/2020) Programs.



EPD Analysis and TMR sensor after ashing

PLATH00137

ENHANCING SURFACE EMISSION IN MICRO-GAP ATMOSPHERIC DISCHARGE VIA HARMONIC EXCITATION

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Enhancement of surface emission in micro-gap atmospheric dielectric barrier discharges (DBD) is achieved experimentally via harmonic excitation. Optimizing plasma emission near the dielectric surface in view of ultraviolet plasma-on-chip sources (UV-POCS) is proposed as a possible route to overcome the lack of integrated ultraviolet sources compatible with photonic integrated circuits (PICs). Harmonic excitation, especially with 270° phase offset, amplifies peak gap voltages, redistributing power deposition and further enhancing emission at the dielectric surface. Experiments reveal the spatial selectivity of the emission enhancement effect (Figure 1), supported by 1D plasma model (Figure 2). These results highlight temporal electric field tailoring as a prospective strategy for enhancing surface emission and efficiently coupling UV plasma emission into PICs.

Thanks/Acknowledgement
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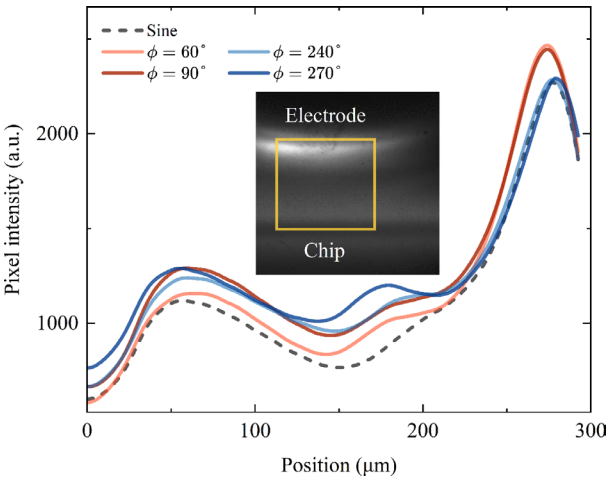
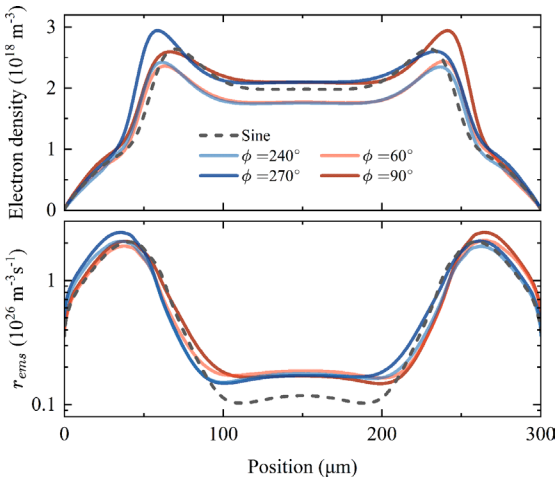


Emission profile's response to voltage waveform



Model-predicted electron density and emission rate

PLATH00156

SPECTROSCOPY STUDY OF THE LTE CONDITION IN THE LASER INDUCED BREAKDOWN USED FOR THE CHLORINE ION DETERMINATION IN BUILDING MATERIALS

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Laser-Induced Breakdown Spectroscopy (LIBS) has become a widely used technique for elemental analysis in numerous applications. In particular, the use of LIBS for analyzing construction materials has been the focus of many studies, as its ability to provide immediate results while preserving sample integrity makes it ideal for diagnosing the deterioration of buildings and structures [1]. In this context, it has been demonstrated that LIBS enables the detection and quantification of chlorine in mortars, thereby allowing for the estimation of the material's deterioration state [2–3]. These studies typically require prior calibration for each specific material composition, which must be performed individually.
In the present work, we propose a new method for estimating sample composition based on the intensity ratios of the Ca II 849.8 nm and Cl I 837.6 nm emission lines produced by the plasma generated upon laser impact. This method relies on the assumption that the plasma is in Local Thermodynamic Equilibrium (LTE).
To verify whether (and when) the LTE condition was satisfied, the temporal evolution of both electron density and plasma temperature was measured using Optical Emission Spectroscopy. This included analysis of Stark broadening of selected atomic lines and the use of the well-established Saha–Boltzmann plot. The results show that LTE is achieved at times greater than 3 µs after the laser pulse, at which point the McWhirter criterion is met. Under these conditions, the Saha–Boltzmann distribution of the plasma species is governed by a single temperature, which corresponds to the plasma temperature (Fig. 1).
These conditions are therefore suitable for determining chlorine content in construction materials. Furthermore, it was demonstrated that the signal-to-noise ratio of the emission lines is sufficient for reliable chlorine detection under the given experimental conditions.

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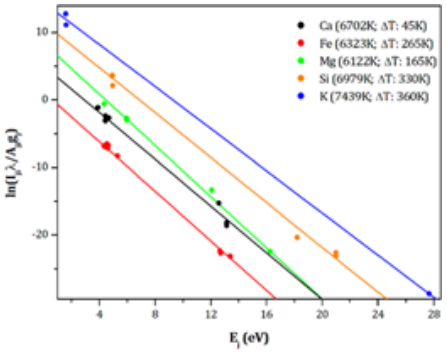

Saha-Boltzmann plot for different species

PLATH00165

TIA PLASMA CHARACTERIZATION BY OPTICAL EMISSION SPECTROSCOPY IN THE PRESENCE OF A SUBSTRATE

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The TIA (Torche à Injection Axiale) is a microwave plasma torch that generates microwave plasmas at atmospheric pressure in ambient air over a wide input power range (220 W to 1000 W). It is suitable for various applications including atmospheric pressure plasma enhanced chemical vapour deposition (AP-PECVD) processes [1]. In the present study, the TIA is employed for the deposition of titanium oxide thin films (TiO_2) from titanium tetraisopropoxide (TTIP) vapor using argon as plasma gas for photovoltaic and photocatalytic applications [2-3]. It has been shown that the microstructure of the thin films depends not only on operating conditions, but also on the nature of the substrate and on its position along the discharge axis.
The plasma is diagnosed using optical emission spectroscopy (OES), to study the effect of the substrate's presence and nature on the plasma parameters. This technique enables the measurement of electron temperature, gas temperature and electron density. It also gives information on how the plasma impacts thin films growth mechanism.
Spectroscopic analyses conducted under optimized deposition conditions (420 W microwave power and 17 slpm of argon flowrate) reveal excitation temperatures ranging from 7 000 K – 12 000 K along the plasma jet at various substrate distances and for different substrate natures (steel, silicon, alumina). Lateral profiles present off axis maxima which can be attributed to the dynamic filamentary nature of the plasma. Turbulent entrainment of air into the plasma plays a significant role in heating up the gas [4], resulting in gas temperatures of about 3 000 K – 3 500 K.

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PLATH00172

LINE-SPECIFIC RADIATION TRANSPORT SIMULATION IN SPATIALLY NON-UNIFORM ARGON PLASMAS FOR SELF-CONSISTENT COLLISIONAL-RADIATIVE MODELING

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Optical emission spectroscopy (OES), coupled with collisional-radiative modeling (CRM), is a common diagnostic method in the field of low-temperature plasmas. Although simple in appearance, especially experimentally, the OES/CRM diagnostic comprises subtle difficulties that are often overlooked or addressed using approximations that may not always be appropriate. One particularly challenging aspect is the description of the radiation trapping (or self-absorption) phenomenon, which is usually approximated using zero-dimensional “escape factors” (EF). The impact of the EF on the calculated spectrum is especially important as it is involved in the last calculation step as a product of the computed densities. However, the many existing definitions in the literature may yield conflicting results [1].
The long-term aim of this work is to develop a generalized radiation transport (RT) module that can eventually be included in larger, self-consistent, spatially-resolved CRMs. Here, we present the first development steps of this RT module. Radiation trapping is studied along the line of sight, considering an Ar capacitively coupled plasma in a cylindrical reactor. Escaping intensities are computed for typical density profiles, obtained from excited state-resolved 2D fluid simulations, and confronted with the EF-based results. It is shown that when absorption is significant, especially when the spatial distributions of emitting and absorbing species are different, the RT-computed values deviate from zero-dimensional approximations. In a plasma diagnostic context, such a contrast would lead to large systematic errors on the quantities of interest, which shows the need for a self-consistent description of radiative phenomena in CRMs. Future work includes the addition of the RT module to an existing one-dimensional CRM, so that collision, diffusion, and radiation processes can be solved self-consistently.

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PLATH00012

PHOTOLUMINESCENT ZnO-SiO_2 NANOCOMPOSITES PREPARED BY A HYBRID PROCESS COUPLING AEROSOL AND PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

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Due to their potential applications, white-light emitting materials have attracted extensive research interest. The covered fields of applications include information display, fluorescent sensors, and solid-state lighting. Among them zinc oxide with its photoluminescence characterized by two main bands: one related to excitons below 400 nm and a broad emission in the visible range could enable to obtain white light emission. In order to protect nanocrystalline phosphors such as ZnO nanoparticles (NPs) and keep their emission performance, a strategy is to embed them in a transparent matrix. Among the possible oxides fulfilling the specification, silica was identified as a suitable candidate thanks to its chemical stability and non-toxicity.
In this work, nanocomposite (NC) thin films are prepared by a hybrid process combining injection, at low pressure, of colloidal ZnO solution, forming an aerosol, in a Plasma Enhanced Chemical Vapor Deposition (PECVD) reactor. Hence this process is based on the use of misty plasma.
As a first step, in order to identify the impact of plasma treatment alone on the PL of ZnO NPs, films prepared by spin-coating are plasma treated in O_2 plasma and characterised. In a second step, ZnO colloidal solution dispersed in heptane are injected in the O_2 and hexamethyldisiloxane (HMDSO) plasma leading to NC. Complementary characterisations techniques were carried out in order to get insight in the structure of nanocomposites. The nanoparticles are concentrated in spots which are randomly distributed and are formed upon drying of solution droplets that reached the substrate after travelling through the plasma. Thanks to electron microscopies, we have demonstrated that the injected nanoparticles are indeed incorporated in the films as zinc oxide. XPS analysis showed that in the nanocomposite films, the zinc oxide nanoparticles are embedded in a silica matrix.
We also assess the photoluminescence emission of the films before and after plasma treatment, when prepared by the hybrid process and after aging. All the films are photoluminescent with two emissions: one in the visible range and the excitonic emission in the UV. The former is sensitive to the surrounding atmosphere for spin-coated films whereas the latter is enhanced for films prepared using misty plasmas. Finally, the silica matrix has demonstrated its effectiveness in protecting the nanoparticles from ageing and maintaining their optical emission.

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PLATH00087

PULSED LASER SOURCES FOR NANOMETER-SCALED COMPLEX MATERIALS AND DEVICES

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This communication reports on the development and synthesis of nanometer-scale complex architectures, including nanoparticles and thin films, fabricated using Pulsed Laser Deposition (PLD) combined with a free cluster generator. The association of the two technics results in the elaboration of various materials with a wide range of applications.
PLD facilitates the deposition of films with nanometer-scale thicknesses control, high density and crystallinity, ensuring congruent transfer from the target to the film. The synthesis of nanoparticles (NPs) is achieved using a free cluster generator developed by our group, based on Smalley's source principle. The pulsed plasma plume generated by a laser focused on a target is quenched in a nucleation chamber by a synchronized helium puff delivered through a controlled pulsed valve. This quenching process allows the formation of nuclei and the subsequent cluster growth. The NPs passed inside the PLD chamber through a nozzle designed to maintain their size and shape from the nucleation chamber. Using separately, simultaneously or sequentially the NPs generator and/or the PLD, leads to the synthesis of new nanomaterials with exotic properties, respectively NP-stacks, nanocomposite thin films with embedded NPs or NPs/thin film multilayers [1, 2].
This specific setup was used to synthetize complex structures including Au, Al2O3 thin films and Ag NPs. Monodisperse and crystallized metallic silver NPs (diameter 2.5 ± 0.5 nm) incorporated into the amorphous Al2O3 matrix exhibits optical absorption at a wavelength of 432 nm, consistent with Mie theory. This reactor provides contamination-free interfaces, with an accurate control over each layer. The growth at ambient temperature additionally avoids interdiffusion between the different material components.
These nanomaterials have a large set of applications particularly for electronics and optoelectronics, such as plasmonic based biosensors or solar cells, optical switching and modulation, transparent conductive films, microelectronic components as Metal-Insulator-Metal (MIM) capacitors, etc…

Thanks/Acknowledgement
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PLATH00032

STABILITY OF EXPANDED AUSTENITE DURING ANNEALING IN VACUUM

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Expanded austenite formed by inserting nitrogen into austenitic stainless steel is a very hard and wear resistant phase characterised by a lattice expansion of about 10% with a nitrogen content of 15 – 30 at.%. Using energetic nitrogen insertion, it is possible to form this phase between 350 and 500 °C. However, at higher temperatures, this metastable phase converts to CrN and an Fe-Ni phase. During nitriding, the process starts directly at the surface with a subsequent progression of the front between CrN and expanded austenite with time into the substrate. Thus, phase transition and diffusion are occurring simultaneously.
Here, in-situ X-ray diffraction has been used to investigate the stability of expanded austenite during annealing in vacuum for the austenitic stainless steel 316Ti, the super-austenitic stainless steel 904L, and the duplex steel 318LN. Time-of-flight secondary ion mass spectrometry before and after annealing yielded complementary information regarding nitrogen depth profiles and CrN precipitation using cluster analysis. The decay of expanded austenite during annealing was found to be thermally activated with an activation energy of 1.8 ± 0.3 eV, starting within five minutes at 550 °C and taking more than two hours below 450 °C. The decay occurs simultaneously throughout the whole nitrogen-containing zone—and not at the surface as during nitriding.
Nitrogen diffusion occurring in parallel slightly complicates the data analysis. This nitrogen diffusion has a lower activation energy than the decay. Hence, the time-temperature limit for operating hard and wear-resistant expanded austenite layers at elevated temperatures of up to 350 °C is given by this nitrogen diffusion, reducing the hardness, and not the decay into CrN.

PLATH00074

ATOMIC LAYER ETCHING OF SiO_2 USING CF_4 PLASMA IN DEPOSITION REGIME AT CRYOGENIC TEMPERATURE

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Plasma Atomic Layer Etching (ALE) is a sequential process using self-limiting steps to etch a material monolayer by monolayer. SiO_2 ALE is usually achieved at room temperature of the substrate by alternating a C_4F_8/Ar plasma, that deposits a thin fluorocarbon (FC) layer, and an Ar plasma with low energy ions to etch about one monolayer [1]. However, this also results in FC deposition on the reactor walls, which leads to process drifts and requires chamber cleaning [2]. This can be addressed by flowing C_4F_8 in gas phase and cooling the SiO_2 substrate at cryogenic temperature. C_4F_8 molecules are physisorbed only on the cooled surface and therefore, wall pollution is greatly reduced.
In this work, the C_4F_8 plasma is replaced by a CF_4 plasma and the substrate is cooled at cryogenic temperature. UV absorption spectroscopy is used to highlight a dramatically enhanced sticking of CF radicals on surfaces cooled at cryogenic temperature. This is correlated to the fact that a CF_4 plasma, usually in etching regime at room temperature switches to deposition regime by decreasing the substrate temperature. Therefore, the FC layer is deposited only on the cooled surfaces and the chamber walls remain polymer-free. Figure 1 shows that an ALE process using a CF_4 plasma enables sequential etching of SiO_2 cooled at cryogenic temperature. The etched amount per cycle increases as the substrate temperature decreases and reaches 0.4 nm/cycle at -130°C. This process exhibits a high synergy, close to 100%, if deposition during CF_4 plasma is well balanced with etching during the Ar removal step.

Thanks/Acknowledgement
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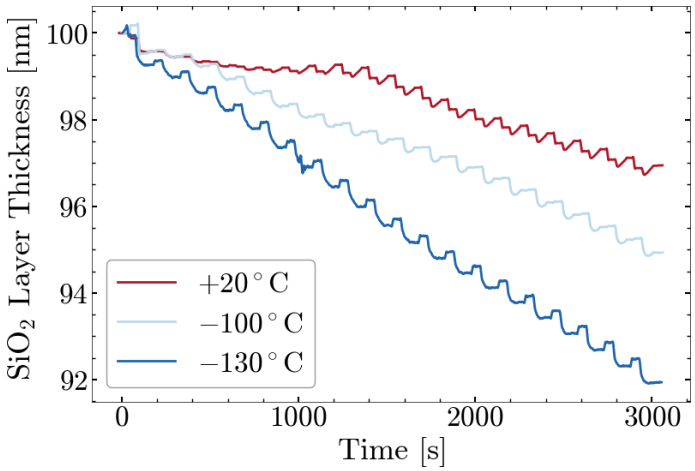

Fig1: SiO2 thickness versus time for 20 ALE cycles

PLATH00079

NOVEL ATMOSPHERIC-PRESSURE PLASMA CURING OF ANTI-CORROSION TRANSPARENT SILICON-BASED COATING

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Metal corrosion poses substantial risks to safety, economics, and the environment across industries and daily life, with associated costs estimated at 1-5% of each nation's Gross National Product. While conventional polymer coatings provide optical and protective benefits, they often fail in acidic or basic environments, allowing corrosive elements to penetrate and degrade the underlying metal. This has driven the development of advanced anti-corrosion coatings to extend product longevity.
Silicon-based polymers, e.g., Polysilazane (PSZ), offer exceptional chemical resistance, high-temperature stability, and flexibility. This research introduces a novel approach to crosslinking the PSZ coating on the flexible copper foil utilizing a low-temperature atmospheric-pressure plasma. The Multi-Hollow Surface Dielectric Barrier Discharge was used as a source of plasma and plasma-generated species for remote plasma curing of PSZ. The plasma-based curing approach can replace the standard long-time (up to 7 days) and high temperature (>150˚C) curing methods and significantly reduce the processing time to short curing times typically less than five minutes and thus enhance the productivity and energy efficiency.
The anti-corrosion performance of the coatings was comprehensively analyzed under repeated bending stress and in various environments (acidic, basic, and saline), using EIS. Additionally, the crosslinking process is thoroughly characterized through FTIR and XPS analyses. Hydrophobicity and adhesion are evaluated using surface-free energy measurements and adhesion tests. This study aims to advance the development of effective anti-corrosion coatings by providing insights into distinctive crosslinking mechanism enabled by low-temperature atmospheric-pressure plasma techniques.

Thanks/Acknowledgement
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PLATH00133

ENHANCING FIBER/MATRIX INTERFACE IN BIO-BASED COMPOSITES BY COLD PLASMA TREATMENT: A STEP TOWARDS BETTER FLUID SEALING

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Bio-based composites reinforced with plant fibers are a promising alternative to synthetic and petro-based materials, especially for applications such as fluid transport. This alternative is due to their light weight, cost-effectiveness, biodegradability and low environmental footprint.
However, the adhesion between the plant fibers and the polymer matrix is limited, which can compromise the final performance of the final product. Especially, the durability of materials used in fluid transport is conditioned by their permeability to the fluid. The presence of porosities at the fiber/matrix interface can alter the watertightness (i.e. sealing) functionality, promoting the development of fluid permeation pathways and subsequently causing its cracking [1].
This study aims to explore an eco-responsible way with the use of a physicochemical pretreatment of bio-resources fibers, i.e. by cold plasma. The compatibility quality between flax fibers and the thermoplastic polymer matrix is investigated. This process eliminates impurities such as the wax layer present on the fiber surface, while modifying their surface topography (***Fig1***) [2]. The fiber/matrix bonding area is improved while reducing the formation of porosities and adjusting the solidification stage of the polymer matrix at the interface.
By offering a clean and solvent-free process, this approach expects to optimize the performance of bio-based composites for fluid transport applications. This process can pave the way for sustainable and high-performance solutions in other sectors such as construction.

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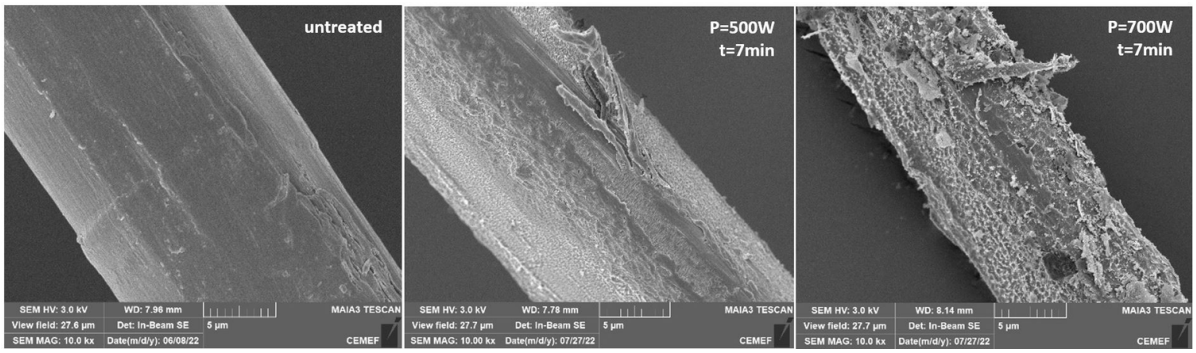

Fig1: SEM images of air plasma-treated flax fibers

PLATH00144

REGULATION OF PERIPHERAL PLASMA CHARACTERISTICS VIA ENGINEERED ALTERATIONS IN ELECTRODE SHIELDING MATERIALS UNDER A DIRECT CURRENT-BIASED POWER CONFIGURATION

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As the semiconductor industry advances toward further miniaturization, the need for high aspect ratio (HAR) structures has made dry etching techniques indispensable. However, achieving plasma uniformity—particularly at the wafer edge—remains challenging. This issue stems largely from limitations in the edge ring materials embedded in electrostatic chucks, which, as illustrated in Figure A, play a critical role in shaping the sheath potential and stabilizing plasma under DC-biased RF conditions. Quartz is widely used due to its transparency and dielectric properties, but its insufficient robustness in high-energy plasmas leads to unstable edge behavior, degraded etch control, and yield loss.[1,2]

To overcome these limitations, we propose a rectangular waveform biasing scheme with an independent edge electrode (Figure B) to actively control peripheral plasma conditions. Additionally, we introduce a silicon-based edge ring structure, redesigned to improve impedance matching between the center and edge regions of the chamber (Figure C). By targeting an impedance ratio of ~1.3, we investigated how modifications in ring thickness and contour influence plasma uniformity through both experiments and numerical simulations.

Our results show that the impedance ratio can be effectively tuned between 1.0 and 1.4, significantly enhancing edge plasma confinement and sheath formation—particularly under rectangular bias conditions. Simulations further revealed that the reengineered silicon ring improves the unidirectionality of ion flux, which is critical for achieving the anisotropic etching required for HAR structures. These improvements led to higher etching precision, greater yield, and extended component lifespan.

In conclusion, the combined optimization of ring material and geometry offers a promising strategy for stabilizing plasma behavior and improving reliability in advanced etching systems. This approach is particularly beneficial for next-generation platforms utilizing rectangular waveform DC biasing.

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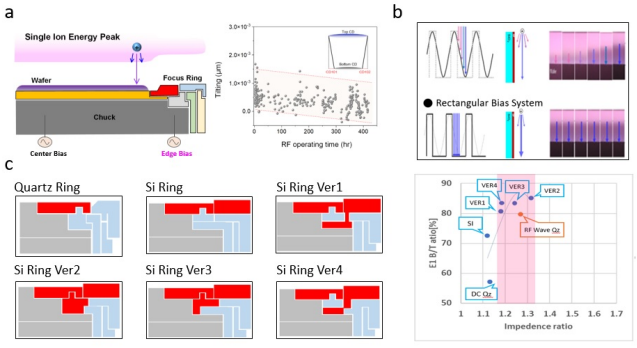

Figure 1. (a) Temporal Evolution of Measured Sidewall Inclination as a Function of Etching Duration (b) Comparison Between Conventional Sinusoidal RF Waveforms and Rectangular Bias Waveforms (c) Deformation Rates of Etched Profiles Under Various Impedance Modeling Conditions

PLATH00150

OPTIMIZING ACTIVE SCREEN PLASMA NITRIDING OF AISI 316L THROUGH ALTERNATIVE APPROACHES: REACTOR CONDITIONING AND ARGON ADDITION

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Since last decade, Active Screen Plasma Nitriding (ASPN) is an established industrial technique. However, nitriding steel alloys remains challenging due to their sensitivity to oxygen contamination, which hinders nitrogen diffusion [1]. In this work, for comparative reasons, a baseline process was defined, consisting of 30 minutes of cathodic bombardment of samples in Ar/H_2 plasma, followed by 7 hours of nitriding in N_2/H_2 plasma. Subsequently, two methods to enhance nitrogen diffusion depth in ASPN-treated AISI 316L were investigated: (1) 2-hour preliminary reactor conditioning before sample sputtering and (2) argon introduction during nitriding (N_2/H_2/Ar plasma).The processes maintained constant parameters: -650 V applied on active screen, -100 V sample holder bias, 1 mbar, 100 sccm total gas flow and 400°C treatment temperature - this low-temperature regime prevents chromium nitride formation while preserving the material's corrosion resistance properties and promoting expanded austenite (γ_N) formation for improved surface hardness [2]. Previous studies identified nitrous oxide (NO) as a plasma contamination indicator concerning the sensitivity of 316L to oxygen-containing species in the plasma [3]. Post-treatment characterization via optical microscopy (OM), glow-discharge optical emission spectroscopy (GDOES), and X-ray diffraction (XRD) confirmed γ_N phase formation in all cases, with both alternative methods resulting in higher nitrogen concentration and greater nitrided layer depth than the baseline mentioned. Plasma diagnostics results presents that argon introduction does not accelerate NO population reduction. Instead, it addition possibly enhances nitrogen solid diffusion by directly modifying plasma-surface interactions during nitriding. The proposed mechanism involves concurrent surface sputtering and nitrogen incorporation, where sputtering simultaneously: (1) heats the sample surface to promote diffusion, and (2) removes surface oxides, creating lattice vacancies for nitrogen incorporation - as demonstrated by GD-OES depth profiles (N and O) and supported by Scheuera, et al. [4]. Additionally, argon may further enhance nitriding efficiency through Penning ionization processes mediated by argon metastable states (Arm* ($^3P_2$,$^3P_0$), 11.55-11.72 eV), which serve as an energy reservoir for nitrogen dissociation and ionization [5]. However, comprehensive plasma diagnostics and mass spectroscopy are required to fully validate these mechanisms. This synergistic effect may promote nitrogen incorporation and diffusion, as evidenced by thicker nitrided layers. Notably, the N_2/H_2/Ar nitriding atmosphere demonstrated superior performance compared to pre-reactor conditioning approach, eliminating the requirement for a 2-hour pretreatment step.

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PLATH00166

PERFORMANCE OPTIMIZATION OF METALLIC BIPOLAR PLATES FOR PEMFCS BY POST-DISCHARGE PLASMA

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Proton Exchange Membrane Fuel Cells (PEMFCs) represent a key technology in the hydrogen sector. They convert hydrogen and oxygen into electricity through electrochemical reactions, operating silently and without pollutant emissions. Their high energy density and short refueling time, comparable to that of an internal combustion vehicle, make them a promising alternative for mobility applications.

To compete with current or emerging energy solutions, PEMFCs must meet strict requirements such as durability, high performance and low cost. A critical component of PEMFCs is the bipolar plate, which ensures current collection, gas distribution and separation, as well as water management. Different materials can be used, including graphite, graphite–polymer composites, or metals such as stainless steel, aluminum or titanium. Stainless steel plates offer a good compromise between mechanical strength and manufacturing cost, but their electrical conductivity needs to be improved.

Several approaches are used or under study, such as optimization of steel grades, deposition of protective coatings or thermochemical treatments. We are exploring this latter path through an oxidation process performed by post-discharge plasma. This treatment allows uniform surface coverage, even on complex geometries, and provides fine chemical selectivity thanks to the adjustment of the gas composition and the distance between the plasma and the samples.

Chemical and structural analyses (GDOES, SEM, TEM) were performed alongside Interfacial Contact Resistance (ICR) measurements to evaluate the influence of thermochemical parameters on surface composition and morphology. TEM observations showed that the post-discharge plasma treatment promoted the migration of iron atoms toward the surface, leading to a thin oxide layer (a few nanometers thick) covered with unevenly distributed oxide agglomerates.

Looking ahead, this plasma treatment could be combined with other surface modification processes such as nitriding, nitrocarburizing or ion implantation, to simultaneously target improved ICR and corrosion resistance, with the goal of a global optimization of bipolar plates for industrial PEMFC applications. Such treatment can reduce the ICR by more than 75 % compared with bare stainless steel, significantly enhancing bipolar plate performance.

PLATH00169

COMPARISON BETWEEN FILAMENTARY AND DIFFUSE DIELECTRIC BARRIER DISCHARGES AT ATMOSPHERIC PRESSURE FOR THE TREATMENT OF MONOLAYER GRAPHENE FILMS

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This work compares the treatment of monolayer graphene films by either diffuse or filamentary Dielectric Barrier Discharge (DBD) operated in N2 at atmospheric pressure. To control the discharge regime, the 1 kHz sinusoidal voltage waveform used for diffuse discharge formation is shifted to a square voltage waveform, while keeping all other parameters constant. Polycrystalline graphene films are first grown by chemical vapor deposition (CVD) and then exposed to the DBD for up to 30 000 cycles of the applied voltage (total treatment time of 30 s). Plasma-induced disordering is investigated by Hyperspectral Raman imaging. In the diffuse discharge regime, a progressive rise in defect density is observed with increasing treatment times, with a transition towards amorphous carbon after 30 s. However, graphene maintains its CVD growth structure with the presence of domains and grain boundaries. For short treatment times in the filamentary discharge regime, the highly localized energy transfers associated to the microdischarges lead to circular defective areas. The diameter of typical damaged zones from Raman imaging is ~40 µm , while the diameter of the zone in which atoms are clearly removed, as seen in Atomic Force Microscopy, is only ~2 µm . After 30 s of plasma treatment, an amorphous carbon sheet is formed with no evidence of grain boundaries remaining.

Thanks/Acknowledgement
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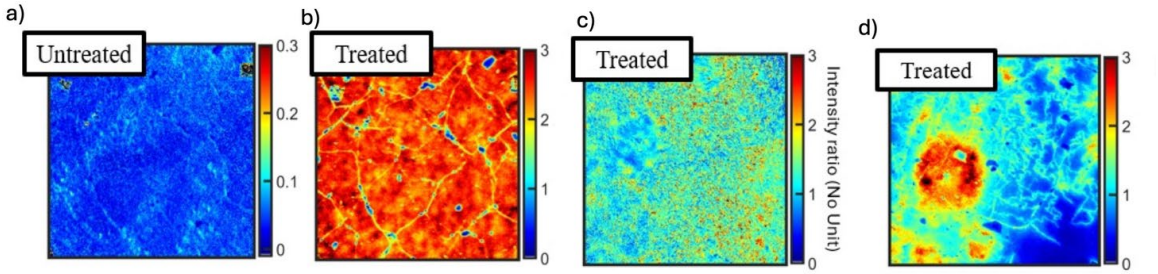

Figure : 130x130 µm² Raman mappings of I_D/I_G for the (a) untreated and (b-d) plasma-treated samples. The results are shown for the sample treated for 30 s by either b) diffuse DBD – 30 s, c) filamentary DBD – 30 s, and d) filamentary DBD – 1 s.