PLATHINIUM

PLASMA THIN FILM INTERNATIONAL UNION MEETING

Abstract book

11 - 15 September 2023 - Antibes, French Riviera

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PLATHINIUM

PLASMA THIN FILM INTERNATIONAL UNION MEETING

ORAL PRESENTATIONS

- Tuesday 12 September
- Wednesday 13 September
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PL1 ● Plasma-surface interactions of atomic-layer processing toward sub-nm node semiconductor devices

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The most advanced generation of semiconductor devices that are already in mass production (as of early 2023) is said to be 3nm technology node devices. The actual sizes of the smallest transistors used in such devices may vary among the chip producers and can be larger than 3nm, but they are still smaller than the smallest pattern sizes that the lithography processes can create. Such structures are typically formed by self-aligned double and quadruple patterning (SADP/SAQP) processes, where atomic-layer deposition (ALD) and plasma etching are used. For ALD, as the surface temperature during the processes is often required to be sufficiently low, plasma-enhanced ALD (PE-ALD) is also widely used. In this way, plasma technologies are the driving force for the most advanced semiconductor manufacturing processes. As the mass production of the next generation of semiconductor devices, i.e., 2nm node devices, is already in sight and new and complex device structures such as those for gate-all-around field effect transistors (GAA-FETs) need to be mass-produced, highly innovative plasma processing techniques with atomic-scale accuracy must be developed expeditiously and cost-effectively. For this purpose, a large part of the conventional try-and-error approach for process development must be replaced with more logical approaches based on a better understanding of the fundamental mechanisms of surface processing. In this presentation, recent analyses of plasma-material interactions based on atomic-scale numerical simulations and surface reaction experiments will be presented with plasma-enhance atomic-layer etching (PE-ALE) of Si and SiN with halogen and hydrofluorocarbon surface modification,[1,2] thermal ALE of Ni by oxidation and formation of metal complexes,[3] and PE-ALD of SiN with chlorosilane precursors and nitrogen/hydrogen plasmas[4], as examples of the most challenging atomic-layer processes.[5] The need for a process-oriented database of surface reactions will be also emphasized.

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SURF1-O1-019 ● Gas- and plasma-surface interactions in cryogenic conditions: a *quasi in situ* XPS study on Si substrates

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Plasma processing and nanofabrication at low temperatures, typically from –80 to –140 °C, have exhibited significant benefits over their room/high temperature counterparts, in several fields of science and technology. For instance, cryogenic silicon etching using SF_6/O_2 plasmas has provided high aspect ratio structures and controllable sidewall profiles in devices [1]. This was attributed to the formation of a SiO_xF_y passivation layer that only occurs in cooled surfaces [2]. Low temperatures are also interesting to obtain low-energy and amorphous phases during sputter deposition of oxide thin films [3], due to the low mobility of the condensate species. Nonetheless, the physicochemical mechanisms in cryogenic conditions, *i.e.*, the species concerned and their surface mobility, residence times, reactivity, and adsorption rates, are still far from being identified and understood. Therefore, to advance our knowledge on some of these issues, we performed a detailed X-ray Photoelectron Spectroscopy (XPS) study on the uppermost layers of Si/SiO_2 cooled surfaces, under vacuum and O_2 and fluorinated plasmas. One of the main advantages of our facility is that the sample can be transferred in vacuum at low temperature from the processing reactor to the XPS analysis chamber (*quasi in situ* condition). This is very helpful, since most of the species involved in the cryogenic process desorb if the sample is brought to the room temperature (RT) during analysis.

It was found that, under high vacuum level ($p = 10^{-6}$ mbar), the chemical state of the Si surface remains practically unchanged from RT to –120 °C. However, for lower temperatures, water physisorption becomes a major issue. The thickness of the H_2O layer and its concentration on the Si surface increase exponentially as temperature decreases, following an inverse Arrhenius law. Physisorbed fluorine can also be detected from –100 °C, although less markedly. Both molecules desorb when the sample is heated up to RT, which attests the physical nature of the adsorption/desorption mechanism. These results demonstrate the impact of the residual gases present in the plasma reactors and are powerful to stablish the limits in the ranges of operation in cryogenic etching and deposition. In addition, the interaction of O_2 and fluorinated plasmas with the cooled surfaces is addressed.

Thanks/Acknowledgement
We acknowledge the project EmergenceINC-CNRS Opera.

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SURF1-O2-034 ● Selective cryoetching plasma process of Si_3N_4

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Selective etching of Si_3N_4 is a key issue for some applications in today's nanofabrication technology. For example, spacers of Si_3N_4 in CMOS have to be etched with a very high accuracy without etching any atomic layer of silicon at the interface. Many different approaches have been investigated to control the process at the atomic layer scale [1,2]. In this paper, we show that cryogenic etching could be a good candidate to reach this achievement.

Cryogenic etch processes are usually used to deeply etch silicon. In this particular process, the substrate is cooled to a very low temperature (typically -100°C) in order to form a passivation layer [3]. So far most of experiments have been performed in SF_6/O_2 plasma to form an SiO_xF_y layer at the vertical trench sidewalls. Here, we propose to use a mixture of CHF_3/Ar in an inductively coupled plasma reactor to etch selectively Si_3N_4.

2x2 cm² SiO_2, Si_3N_4 and p-Si samples were glued on a 150 mm diameter silicon carrier wafer. The ICP injected power was 800W. CHF_3 and Ar flows were 30 and 70 sccm respectively. The process was performed at a pressure of 1 Pa. Temperature and bias voltage were varied.

In figure 1, we show the etched thickness obtained with a bias voltage of -60V versus temperature. Negative values correspond to deposition regime. A process window appears between -120°C and -60°C where Si_3N_4 is etched while deposition occurs on p-Si and SiO_2.

In situ characterization was also performed. The results will be discussed to explain the involved chemical and physical mechanisms.

Thanks/Acknowledgement
We thank Tokyo Electron Limited for their support. This work is supported by CERTeM 5.0 and by the French National Research Agency (ANR PSICRYO project - 20-CE24-0014).

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Etched thickness of SiO_2, Si_3N_4 and p-Si versus T

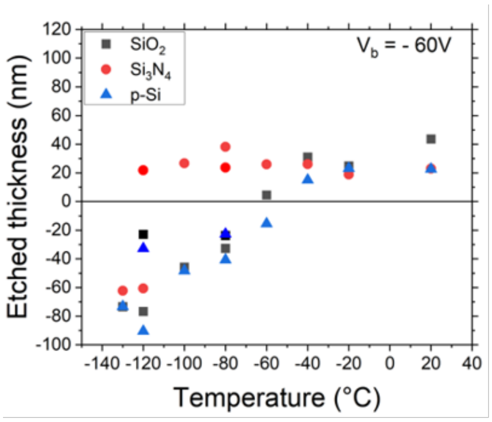

Fig. 1 : Etched thickness of SiO_2, Si_3N_4 and p-Si versus temperature at a bias voltage of -60V after 1 min of CHF_3/Ar plasma

SURF1-O3-049 ● Photoresist removal in MEMS fabrication process with HDRF®, optimized chemistry by adding hydrogen radical in oxygen process

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In this work, we introduce a unique inductively coupled downstream plasma multi sources configuration to generate High Density Radical Flux (HDRF®) used for MEMS fabrication, Photoresist striping, Sacrificial layer removal (Fig.1), Descum, and Surface activation. We optimize the chemistry of process based on oxygen plasma, by adding a source of hydrogen radicals, to raise the etch rate of hard bake or coated photoresist, and replace wet process by single multistep dry process, working below bake temperature.

The photoresist removal process, in its dry form, uses an oxygen plasma where the O* radicals generated will chemically etching to strip away resin present on a substrate. A direct plasma can thus cause damage by ion bombardment on the substrate's surface and the electric fields which develop on the surface due to the formation of the sheath can affect the sensitive structures. SU8 is polymer used as a resin to manufacture mechanical elements with a high aspect ratio in the structures of MEMS type devices [1]. The polymer removal rate is strongly influenced by the etchant gas used. The radicals generated by HDRF® remove the polymer even from deep [2], narrow trenches with a large aspect ratio (> 40:1) like in plasma dicing [3] after Bosh process.

The advanced HDRF® technology developed by Plasma-Therm, where plasma is only generated and existing outside the process chamber [2], offers photoresist removal with unparalleled precision and control to avoid damage to exposed surfaces. We observe an important etch rate, over 4µm/min for SU8, below 90°C. This safety cleaning process is essential in microelectronics and industry like micro and nano mechanical systems for the frontend and backend industry.

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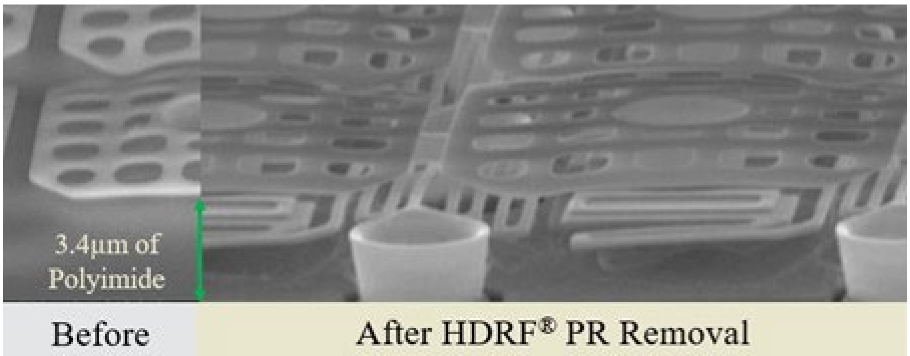

Photoresist removal in MEMS 3D structures

SURF1-O4-108 ● Effects of the substitution of Ar by Kr in ALE process of GaN

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Surface defects introduced by etching steps during device fabrication process are currently a major limitation in the advancement of GaN technology. In GaN based micro-LEDs, reduction of light efficiency due to non-radiative recombination related to surface-sidewall etch defects is frequently reported.To reduce or controlled these etch related defects, Atomic Layer Etching (ALE) is an attractive substitution to conventional Reactive Ion Etching (RIE). ALE is a cyclic etching process by which monolayers of material can be removed sequentially by combining separate, self-limiting, reaction steps. A common approach for ALE of GaN relies on the separation of the synergistic effect at the basis of the Cl_2-based RIE process. In that case, the first half-reaction consists in the adsorption of Cl-based species (Cl radicals or Cl_2). The removal of the modified layer(s) is achieved by ionic bombardment predominantly from an Ar plasma.
In this work, we report the benefits of substituting Ar by Kr on the surface quality of GaN and the emission properties of GaN with an embedded single InGaN quantum well.Cl_2/Kr ALE processes show a self-limiting etching characteristics allowing a controlled EPC at 5.2 Å equivalent to almost two GaN monolayers for a wide ion energy window around 7 eV, also called the ALE window. Surface characterizations by SEM and AFM show improvement of surface roughness after etching [1]. Implementation of the Cl_2/Kr ALE to GaN layer with embedded InGaN quantum well allow to reduce the non-radiative dead layer thickness to less than 200 nm, down from 450 nm, see Figure 1. By contrast Cl_2/Ar ALE processes do not display a self-limiting behavior, in agreement with other reports [2].This work provides a simple and an easily implementable solution for improving the surface quality (roughness and stoichiometry) of GaN after plasma processing.

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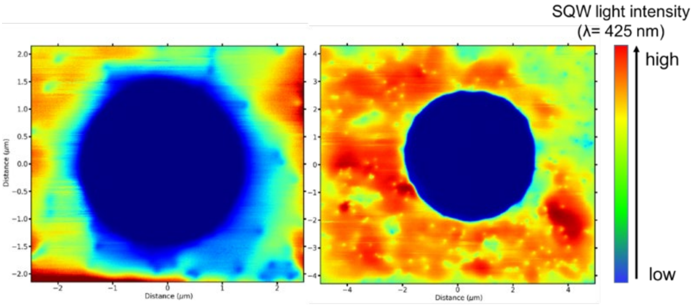

InGaN Single Quantum Well light intensity

SURF1-O5-081 ● Impact of temperature towards the reduction of C_4F_8 passivating gas-flow during Bosch processing

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Bosch processing is a technique widely used in the semiconductor industry since the last 30 years towards the deep etching of silicon notably for applications such as MEMS devices. It is based on the regular repetition of an etching step using SF_6 plasma followed by a passivating step with C_4F_8 plasma to ensure anisotropic profiles. However, the main drawback of this process is the use of a fluorocarbonated C_4F_8 plasma which tends to accumulate in the form of a polymeric deposit on the reactor sidewalls at ambient temperatures [1].
As a result, different pathways are studied to extend process stability and reduce the occurrence of reactor sidewall cleanings. In comparison, cryogenic processes present the advantage of low chamber wall contamination as the reactive species mainly deposit on the cooled substrate surface due to its cryogenic temperature. However, there is no significant data in the scientific literature which attests of the impact of performing Bosch process at cryogenic temperatures and its general temperature dependence.

In this research study, an identical set of Bosch process parameters were performed at different temperatures to evaluate the evolution of the etching profile.
The study was carried out using a cryogenic ICP reactor equipped with in-situ ellipsometry and in-situ mass spectrometry diagnostics to characterize the thickness and desorption properties of the CF_x passivation layer in relation to the substrate temperature. The tests were performed on Si coupons with a patterned 1µm thick layer of SiO_2 hard-mask which were glued on SiO_2 4” carrier wafers using a specific thermal glue.
It will be shown that Bosch process is effectively temperature dependent and that the necessary C_4F_8 gas flow can be significantly reduced at cryogenic temperatures towards the obtention of anisotropic profiles. Additional observations concerning Bosch processing in relation to the temperature will also be presented.

Thanks/Acknowledgement
This research project is supported by the CERTeM 2020 platform, which provides most of the equipment and funded by the European Union (FEDER fund) as well as the French National Research Agency (ANR PSICRYO fund).

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DEPO1-O1-015 ● Properties of a new TiTaZrHfW(-N) refractory high entropy film deposited by reactive DC pulsed magnetron sputtering.

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In the last decades, refractory high entropy thin films have attracted more attention due to their superior properties at high temperatures. Besides the thermal stability, these new materials present good mechanical properties at high temperatures, which is interesting compared to conventional alloys. TiTaZrHfW(-N) films are deposited by reactive magnetron sputtering in various argon/nitrogen atmospheres. Optical emission spectroscopy is performed to analyze the target poisoning conditions and optimize the deposition parameters. The nitrogen flow rate ratio RN=FN2/(FN2+FAr) is varied from 0 to 29%. XRD analyses show a phase transition from amorphous to B1(NaCl) single phased films once the nitrogen is added. For all nitrides, an out-of-plane {111} preferential orientation is observed, except for RN = 9%, for which it changes to {200}. The morphology of the films changes from compact to columnar when the nitrogen ratio exceeds 5%. The hardness and Young's modulus are also studied and present evolution with maximum values, 29 GPa and 257 GPa for RN= 9% respectively. All nitrides show good thermal stability under vacuum at 800 °C for three hours, compared to nitrogen-free metallic film, for which phase transition occurs. Nitrides show improved oxidation resistance compared to that of metallic film.

Thanks/Acknowledgement
The authors gratefully thank the funding support of Le Conseil Départemental de l'Aube (CD10), University of Technology of Troyes (UTT) and le Groupement d'Intérêt Public Haute-Marne – GIP52.

DEPO1-O2-045 ● Chemical and physical properties of gold-boron Laser Mégajoule target components coated by sputtering physical vapor deposition

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The laser targets experimented on the Laser Megajoule (LMJ) facility of the French CEA (Commissariat à l'Energie Atomique et aux Energies Alternatives) are made with micrometric to millimetric components of various materials with very different chemical and physical properties [1, 2]. Most of the laser targets are made of a gold conversion hohlraum with a capsule containing gaseous deuterium at the centre. The purpose of the conversion hohlraum is to convert the UV laser light to X-Rays. Because of their shape, some laser targets require a micrometric-thick Au/B coating on the inner surface of the hohlraum (Fig. 1) with a boron concentration of 40 at. % in order to limit laser backscatter by decreasing the Brillouin backscattering. In order to achieve the laser experiments, the Au/B layer has to be characterized in terms of both stoichiometry and chemical environment.

Several Au/B coatings were deposited by Sputtering Physical Vapor Deposition (PVD) onto silicon and aluminum substrates. The influence of the main PVD parameters (Au and B sputter powers, cathode-substrate distance, work pressure) onto the Au/B composition and homogeneity were studied in order to adjust the stoichiometry to 40 at. % of boron. Because of the very low Z of boron, the alloyed coatings were analyzed using microbeam technics such as X-Ray Photoelectron Spectrometry (XPS) and Secondary Ion Mass Spectrometry (SIMS) as boron was not detected using Energy Dispersive X-Ray Spectroscopy (EDS) neither Rutherford Backscattering Spectroscopy (RBS). Those microbeam analyses were performed onto both flat and 3D surfaces.

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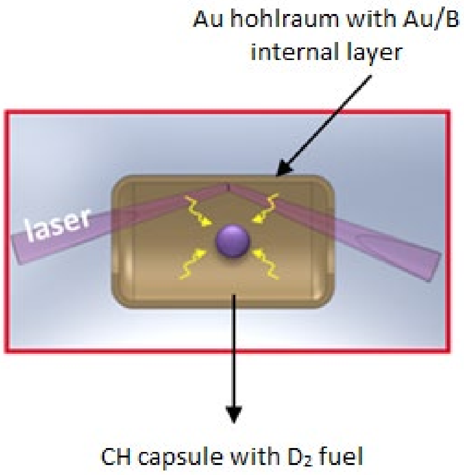

Au/B conversion hohlraum with a CH capsule

DEPO1-O3-150 ● PVD coating on metallic powders: an innovative metallurgical process

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Production of metal parts by powder metallurgy using the Spark Plasma Sintering (SPS) process, allows obtaining a fine and homogeneous microstructure with a chemical composition close to that of the initial powder. If the metallic powder is beforehand coated with a film composed by another alloying element, one can expect a local change of the bulk composition.

In this work, AISI 316L stainless steel powders were covered with a pure chromium PVD coating before sintering. The aim is to convert a part of the austenitic steel to ferritic one and obtain a duplex steel with a biphasic microstructure at the scale of the powder particles.

1 µm of pure chromium is deposited by DC magnetron sputtering on each 316L powder particles with a granulometry range of 63-90 µm in diameter. The coated powder is then sintered by SPS and a final thermal treatment is performed to convert the sigma phase to ferrite. The powder (uncoated and coated) and the sintered samples are characterized by SEM, TEM, EDS, EBSD, and XRD.

In addition, PVD simulation were performed with SIMTRA [1] for the transport and NASCAM [2] for the growth and the microstructure is compared to the experimental one.

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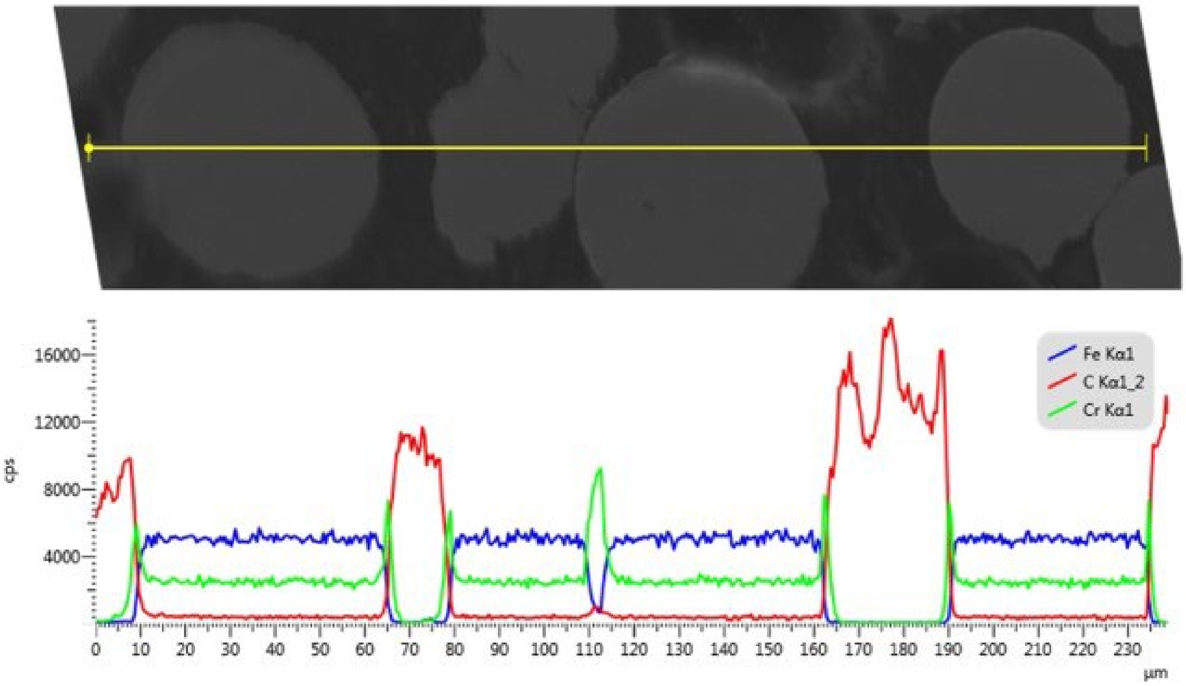

EDS profiles of coated powders

DEPO1-O4-051 ● Group III-Nitride semiconductor materials made by low temperature plasma based Atomic Layer Deposition

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In the last few decades, there has been a phenomenal rise and progress in the field of III–Nitride semiconductors. Now, the materials group III-N is changing the path of high-performance integrated circuits (IC) technology in high power and high frequency regimes and has received much attention due to its wide and direct bandgap, high electron mobility and high breakdown electrical field.

III-N semiconductors are largely present in the industry, through chemical vapor deposition (CVD) techniques such as Metalorganic vapour-phase epitaxy (MOVPE). Those deposition techniques use conventionally the reaction of ammonia (NH3) with industrially relevant precursors such as trimethylaluminum (TMA), trimethylgallium (TMG) or trimethylindium (TMI) at high temperatures (750-900 °C) [1]. Plasma-assisted Atomic Layer Deposition (PA ALD) is becoming a trustworthy alternative to the standard CVD deposition techniques, and it appears as a solution for highly conformal coating and low temperature processing as two important assets to tackle growth temperatures of the nitride films not interfering with CMOS circuitry.

This work is based on the optimization and engineering of the plasma ALD of c-axis highly oriented aluminium nitride (AlN) films we proposed [2]. The pathway was further extended to facilitate low temperature (<450 °C) deposition of other III-N materials, such as GaN and InN semiconductors with wide and small bandgap respectively. In this work we utilized a gas mixture of H2/Ar/N2 as nitrogen precursor for nitride thin films initiated by a plasma source. The mix of Ar and H2 allows both to stabilize the plasma phase and to induce an optimized reducing of the ligands of the organometallic precursors reducing the carbon contaminants measured in the materials. We observed by XPS stoichiometric III-N films with no detectable carbon contaminants and also a low level (<5%) of oxygen contaminants in the nitride films. The XRD and TEM analysis confirm privileged hexagonal crystalline structure of the thin film below 100 nm thickness.

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DEPO1-O5-115 ● Engineering multifunctional thin films by plasma copolymerization

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Plasma polymerization is a vapor-phase surface functionalization process consisting of the synthesis and deposition of functional polymer coatings. Using plasma polymerization, surface functionality and mechanical properties of plasma polymers can be controlled [1]. Effectively, a judicious choice of the precursor and careful control of the plasma conditions are essential for tailoring the surface functionality. In this direction, our group has studied the deposition kinetics and mechanisms during low-pressure plasma deposition processes for different precursors at different operating conditions. For instance, plasma polymerization of maleic anhydride (MA) allows the preparation of thin polymer films with different degrees of crosslinking and density of functional groups, depending on the selected deposition conditions [2]. Similarly, by changing some operating parameters of the low-pressure plasma polymerization process, thin films of poly (hydroxyethyl methacrylate), P(HEMA), with different viscoelastic properties can be prepared [3].

Furthermore, it is also possible to create multifunctional polymer thin films via plasma copolymerization by combining the properties of two or more precursors as shown in Figure 1. Physicochemical properties of polymeric products can be adjusted by plasma copolymerization, which can enhance the performance and application range of thin films. Plasma copolymerization of HEMA and MA is investigated by examining key copolymerization parameters (precursor feed ratio) and plasma process conditions (such as pressure and duty cycle). Further assessment of the nanocoating's physicochemical properties is conducted under those processing conditions.

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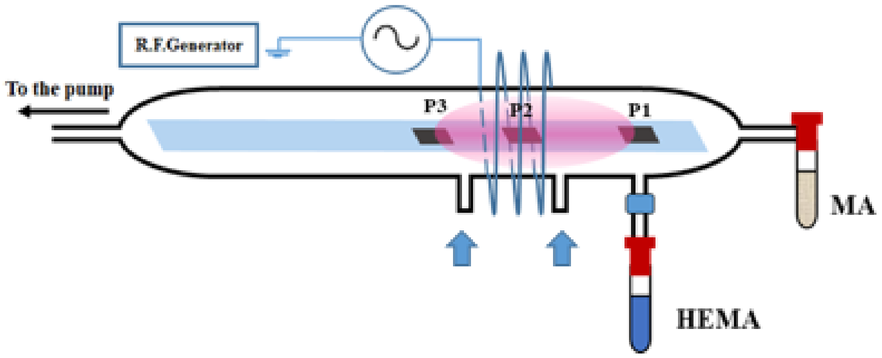

Scheme of the reactor for plasma copolymerization

PL2 ● Electrical characterization of barrier discharges: linking fundamentals and applications

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Barrier Discharges (BDs) are frequently considered plasma sources in both industrial applications and fundamental research. They are a simple and robust method for generating distinctly non-thermal plasmas at atmospheric pressure [1]. Despite its wide application in industry (e.g. ozone generation, surface activation, air cleaning, plasma medicine, surface modification), there are still many open scientific questions. The diagnostic and simulation are challenging due to the transient character and small scale of this usually filamentary plasmas. Fast imaging and spectroscopy, laser diagnostics and surface charge/field measurements give insights in the fundamentals of these plasmas, such as the physics and chemistry of single microdischarges or the mechanisms for the generation of diffuse BDs. However, the electrical characterization is always a mandatory task as this allows the determination of the plasma power and the evaluation of plasma chemical performance [].
Although the principles were described as early as the 1940s by Manley; and further developed in the 1980s by Kogelschatz, Neiger and others, there is still a flurry of publication activity on this subject today. This is due to ever new discharge geometries driven by the manifold application options, the use of novel high voltage supplies and materials and a deeper view on the phenomena [3]. The lecture intends to give an introduction to the physics of BDs, which become more and more attractive for surface modification, e.g. plasma-assisted chemical vapour deposition at atmospheric pressure. Then, the principles of electrical characterization will be explained. The determination of operation parameters such as the discharge voltage and power is based on equivalent circuits (see figure 1), which will be briefly determined and discussed for some selected examples.

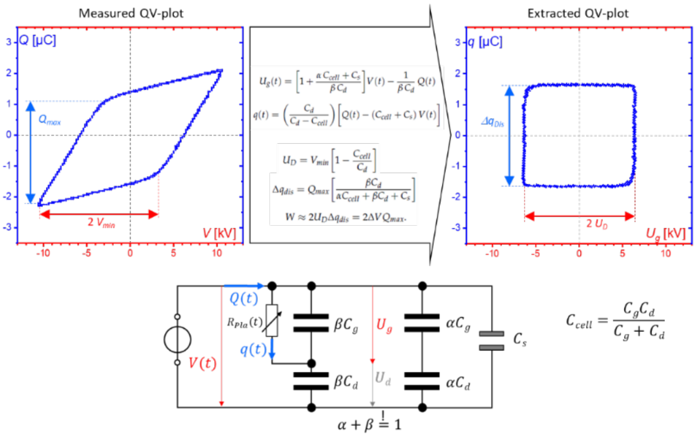

Figure 1: Typical charge-voltage plot of a BD (left). Based on the equivalent circuit shown in the bottom, distinct discharge parameters are determined (right).

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SOUR1-O1-048 ● Self-organization of HiPIMS plasma investigated by high-speed camera

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Studies of magnetron discharges in the last decade showed that magnetron plasma is not azimuthally homogenous instead it is localized in dense regions called spokes. These plasma structures typically have a triangular shape and exhibit periodic or quasi-periodic patterns that rotate with velocities of several km/s. The presence of spokes was observed in different operational regimes of magnetron sputtering: DC magnetron sputtering [1], high power impulse magnetron sputtering (HiPIMS) [2] and RF magnetron sputtering [3].

In this work, we used a high-speed camera to study HiPIMS discharges from the front- and side-view perspective and related the spoke patterns to the recorded discharge current waveforms. The discharges were investigated using a 3-inch magnetron with an aluminum target for a range of pressures (0.25-2 Pa) and peak discharge currents (10-400 A). Experiments reveal that plasma self-organization evolves through several stages with increasing discharge current. In the initial stage, from gas breakdown to the current of ~25 A, plasma forms spoke patterns similar to those observed in the DCMS regime, which rotate opposite to the direction of electron drift. After this stage, reorganization of plasma occurs (typically in the range 25-50 A). In this stage, spoke patterns are highly irregular and spoke rotation is chaotic. Some spokes rotate in the direction of electron drift while others rotate in the opposite direction, at the same time some spokes merge or split. This stage is followed by the formation of regular spoke patterns with a well-defined triangular shape. Spokes rotate in the same direction as drifting electrons (i.e., E×B direction). With further increase in current, spokes increase in size until at the highest currents (around ~400 A) plasma begins to appear azimuthally homogenous. The observed plasma stages were reproducible for all investigated pressures. Furthermore, the self-organization and plasma evolution was remarkably similar when the current waveforms were comparable from pulse to pulse.

Thanks/Acknowledgement
Research was financially supported by the Slovenian Research Agency (project J2-2509).

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SOUR1-O2-084 ● Angular distribution of ions and neutrals in High Power Impulse Magnetron Sputtering of Titanium

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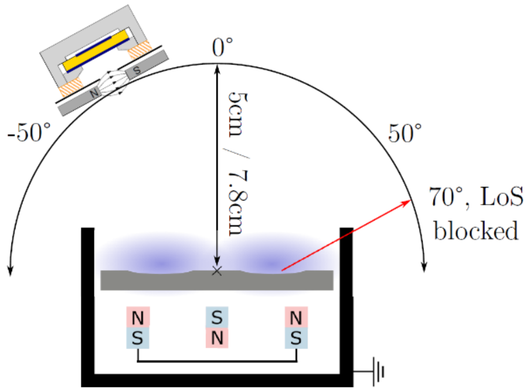
In high power impulse magnetron sputtering (HiPIMS) a large fraction of the film-forming material can become ionized. This is desirable for many applications, since it has been shown to lead to denser films, better adhesion, and improved coverage of complex substrates when combined with substrate biasing. However, this also introduces new challenges in the optimization of the deposition process and especially the uniformity of the coating thickness and properties. Unlike in non-ionized physical vapour deposition (PVD), not only the total deposition rate, but also the composition of the arriving flux in terms of ions and neutrals is generally position-dependent. The latter is usually characterized by the ionized flux fraction, which is the ratio of the ion flux compared to the total flux arriving at a given substrate position. The ionized flux fraction has previously been measured for a number of different target materials and process conditions. However, while measurements exist in different positions, so far, no systematic studies have been performed looking into the exact angular distribution of the ion and neutral fluxes.

To address this challenge, we employed a charge-selective quartz crystal microbalance (QCM) to separately record the total and neutral deposition rates on a semicircle centred on the target centre in titanium HiPIMS discharges. A schematic depiction of the measurement setup is shown in Figure 1.

It was found, that both ions and neutrals display the characteristic heart-shaped pattern previously seen for dc magnetron sputtering of titanium, however with noticeably more pronounced lobes. Moreover, the angular variation in the neutral flux is larger than in the ion flux, which results in the ionized flux fraction peaking above the target centre and decreasing towards the sides. Additionally, the effects of pulse length, peak current density, and process pressure on the obtained ion and neutral flux distributions have been analysed, yielding new insights and opening up new optimization pathways.



PROC1-O1-163 ● A Comparison between simulation & experimental results of a low-pressure Argon plasma generated by ECR

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An effective fluid model was developed and used to simulate a low-pressure argon plasma. The presented model describes a 2D axisymmetric dipolar microwave plasma source that is maintained through the resonant heating of electrons, a process known as electron cyclotron resonance (ECR). This model has facilitated a significant understanding of the interplay between microwave propagation, power density, plasma generation, and species transport. The simulated source, which comprises a solid-state microwave generator and a compact microwave launcher with coaxial geometry, is attached to the Top flange (Figure 1).

In parallel experimental investigations have been realized. Our experimental device consists of a vacuum chamber with a diameter of 46 cm and a height of 26 cm (Figure 2). This study was carried out in pure argon. The plasma was excited by a commercial microwave ECR source, Aura Wave from Sairem (Décines-Charpieu, France) which is powered by a solid-state operating at 2.5 GHz up to 200 W. The Optical emission spectroscopy characterization has been carried out using a high-resolution monochromator Princeton Instrument HRS-750 coupled to an ICCD camera, Princeton Instrument Pi-Max-4. Measurements have been realized to obtain 2D emission distributions of the plasma. These results will be presented and the plasma characteristics (gas temperature and electron density) calculated from the optical spectra.

Finally, experimental and simulation results will be compared as a function of the argon pressure and the injected power.

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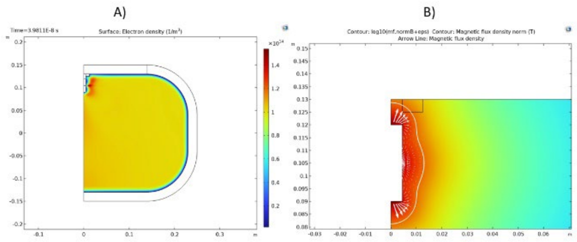
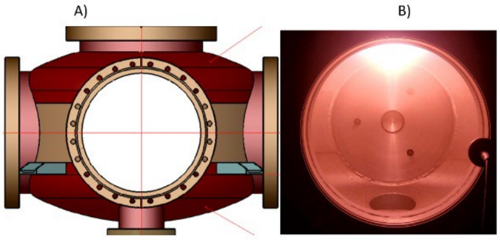


Simulation Results A) Electron density (1/m3) B) M



Experimental Results A) Vacuum chamber B) Plasma D

PROC2-K1-088 ● Studying the transport of atoms sputtered from a compound NbC target in HiPIMS discharges: plasma diagnostics and modelling

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Transition metal carbides are refractory materials possessing extremely high melting temperatures, outstanding mechanical strength, excellent electrical conductivity, and good chemical stability. Non-reactive high-power impulse magnetron sputtering (HiPIMS) of NbC films from a single compound target is an attractive deposition method because of its simplicity and scalability. The film composition (C/Nb ratio), microstructure and, consequently, mechanical properties can be controlled by varying the power density in the pulse [1].

This presentation focuses on explaining the observed change in the composition ranging from C-rich films to stoichiometric NbC films corresponding to an increase in the pulse-averaged power density (realized by shortening the pulse length) [1]. The Nb and C atoms sputtered from the target are under the influence of multiple processes that together affect their transport towards the substrate (including the sputtering rate and angular distribution, scattering off the process gas atoms, ionization in the high-density plasma and return of ions onto the target or loss of ions to chamber walls). These processes are expected to be manifested differently for Nb and C due to their disparate elemental properties, such as atomic mass and ionization potential.

To untangle the influence of the above-mentioned plasma processes on the transport of atoms in the discharge and, eventually, on the C/Nb ratio in the films, we use several plasma diagnostics techniques and modelling approaches. We measure Nb^+ and C^+ fluxes at the substrate position by energy-resolved mass spectroscopy and evaluate the ratios of Nb and C neutral and ion species at various positions in the discharge by optical emission spectroscopy. Using a pathway discharge model and particle-based Monte Carlo simulations, we analyse the ionization and return probabilities of Nb^+ and C^+ ions and their effect on the sputtering process and, consequently, the film composition. The aim of this presentation is to provide a general understanding applicable to magnetron sputtering of various multi-component targets.

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PROC2-O2-082 ● Sputtered atom density – target heating correlation in hot magnetron sputtering discharge

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Hot magnetron sputtering (HMS) is a perspective way to increase the deposition rate as compared to the classical sputtering systems. In the HMS configuration, a target is thermally insulated from a water-cooled system. It allows a higher power density to be safely applied and lets the bombarding ions to heat the target up. Ultimately, when high temperatures are achieved, additional mechanisms start to contribute to the discharge behaviour: evaporation/sublimation of target atoms [1] or intense thermionic emission [2].

This work was aimed to evaluate the impact of the intense thermionic emission and high target temperatures on the behaviour of Nb sputtering species in the HMS system. For this purpose, laser-induced fluorescence (LIF) spectroscopy was used. Both ground state Nb neutrals and ions were monitored as a function of power in the range from 5 to 40 W/cm^2. Moreover, time-resolved 2D LIF-imaging of the magnetron discharge area was performed during the target heating interval (about 900 s).

Our results show that the density of ground state Nb neutrals saturates when the target temperature reaches 1600-2000 K. Afterwards, it starts decreasing as the applied power continues to grow. To the contrary, the density of Nb ions increases together with the target temperature, showing twice faster growth at 1900 K. Based on this, we can claim that the HMS of Nb target provides 2 times higher ionization degree as compared to classical magnetron system that may lead to a change of the deposited thin film properties.

Thanks/Acknowledgement
The work was supported by FNRS (National Fund for Scientific Research) under FRIA (Fund for Research training in Industry and Agriculture) grant FC 41423.

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PROC2-O3-169 ● Characterization of a helium micro-plasma jet by means of ps-TALIF and a streak camera

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Atmospheric pressure plasma jets (APPJ) present rich gas-phase chemistry, transient electric fields and electron densities, low gas temperatures, etc., which make them very promising in various novel applications such as ambient ionization mass spectrometry [1]. Due to their operation at atmospheric pressure, collisional quenching of generated reactive species becomes significant, and, in some cases (e.g., excited atomic hydrogen), the corresponding effective lifetimes may fall to sub-ns timescales [2]. In most published studies, classic optical diagnostics (such as nanosecond –ns– TALIF and ICCD cameras) are employed to understand the kinetics of reactive atoms in APPJ. However, precise measurements of their densities using ns-TALIF may become challenging at atmospheric and higher pressures [2]. In this case, the use of picosecond (ps) or femtosecond (fs) TALIF as well as ultrafast detectors for atomic density and lifetime determination is a better solution [2,3].
This work focuses on the investigation of a µs-pulsed microtube helium APPJ by means of ps-TALIF (laser: Ekspla®; pulse width: ~10 ps) and a streak camera (C1091005, Hamamatsu®; few ps time resolution). The achieved spatial resolution can be as low as 400 µm, while we were able to measure laser-excited H-atom lifetimes down to a few hundred ps (Figure 1). The obtained H-atom density and lifetime values depend on the distance from the tube exit and the APPJ parameters (voltage, helium flow rate, …). These results are supported by electrical and OES diagnostics. This study provides useful information for APPJ kinetic models while it helps in the optimisation of APPJ for novel applications [1].

Thanks/Acknowledgement
This work was funded by the ANR ULTRAMAP project (ANR-20-CE51-0020) and the IDF regional project SESAME DIAGPLAS.
C. Ansatassiou and J. Franzke acknowledge funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement No. 810686.

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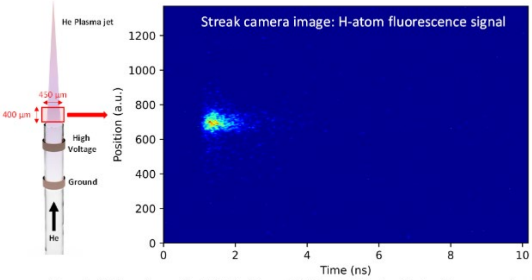

Figure 1. Helium plasma jet studied in this work (left) and indicative H-atom fluorescence signal recorded by the streak camera (right; the laser-plasma interaction volume is indicated with a red square).

He plasma jet (left) and ps-TALIF (right)

DEPO2-O1-058 ● Plasma polymer-metal composites: relations between chemical structure, topography and electrical properties

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Composites have attracted attention during the past decades because of their interesting properties unlike their individual elements. Among them, polymer-metal composites showed good optical and electrical properties. They are mostly synthesized by Plasma Enhanced Chemical Vapor Deposition (PECVD) using an organo-metallic precursor[1,2]. The electrical conductivity improvement of these materials has been achieved by the degradation of the organic matrix. This degradation can occur during the process by using a reactive gas[3] or after the synthesis by annealing the composites[4].
Our approach aims to elaborate in only one step polymer-metal composites with tunable electrical properties. To this end, an organo-metallic compound based on copper is used as precursor and is polymerized under different pulsed plasma conditions. All the obtained thin films show aggregates on their surface whose shape is spherical. The change in plasma on-time has no effect on the copper content but its increase decreases the number of aggregates and the retention of the monomer chemical structure. Less monomer fragmentation at high plasma off-time leads to the highest copper content. But the variation of plasma off-time has no effect on the number of aggregates. It can be concluded that the metallic proportion is not associated to the layer morphology but that the reactions occurring during plasma off-time favour the incorporation of copper in the thin film. The influence of the roughness and the chemical structure on the electrical conductivity was studied by four-point probe measurements.

Thanks/Acknowledgement
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DEPO2-O2-074 ● Double tube configuration of atmospheric pressure plasma Jjt for deposition of organic coatings in open air

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In the present article, results on double coaxial tube configuration of atmospheric pressure plasma jet (APPJ) are presented. Characterization and comparison were carried out for thin carbon films obtained from plasma polymerization of toluene in a single-tube and double-tube APPJ configurations. The effectiveness on minimizing the influence of ambient air during the deposition process was shown for a double tube APPJ, where Ar gas fed into the outer glass tube acting as a shielding gas. The inner tube consisted of SUS tube, which acted as the power electrode and was fed with a mixture of Ar gas with the precursor, i.e., toluene vapor, an organic precursor which does not contain any oxygen. The dynamics of gas flow and its dependence on composition was investigated with a Schlieren imaging system. The deposited thin plasma polymerized toluene films in single and double-tube APPJ configurations were analyzed and compared by FTIR spectroscopy and XPS. The results show clearly that the argon shielding gas protects to a great extent the diffusion of oxygen in the deposition zone(cf figure below), giving rise to polymers with much less oxygen incorporated in their structures. Such a configuration can be used for the deposition of plasma polymerized polymers such as PEG coatings, whose properties are very sensitive to the amount of oxygen incorporated in the structure which shifts from a cell and bacteria antifouling surface to a cell adhesive one. In a single tube configuration, the only parameter studied was the role of the gas flow rate in obtaining PEG coating with different properties[1].

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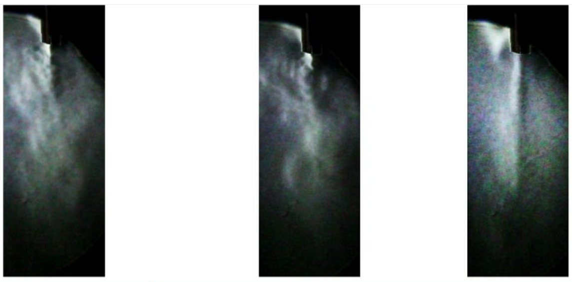

	Single Tube APPJ	Double Tube APPJ	
Outer tube	Argon 2slm + Precursor	Argon 2slm	Argon 2slm
Inner tube	N/A	Precursor + Argon 0.1slm	Precursor + Argon 0.5slm

Schlieren images for APPJ in single & double tube

DEPO2-O3-161 ● Environmentally-friendly plasma polymers to get durable water-repellent textile fabrics: a comprehensive study on coating structure-performance relationship

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The textile industries have been interested for long in water-repellent properties that can be added to their products. To achieve the desired performance, the currently most effective solutions involve fluorinated substances that are toxic and harmful to the environment. In this context, it is particularly relevant to develop new textile surface treatments leading to durable, superhydrophobic coatings without using perfluorinated compounds. Therefore, low-pressure plasma polymerization of hexamethyldisiloxane (HMDSO) has been investigated. Previous work has already shown the possibility of controlling the properties of plasma polymers using pulsed plasma polymerization, i.e. by temporally controlling the plasma species formed during deposition.[1] In this study, it was also proposed to spatially control the plasma species generated during plasma polymerization thanks to an original one meter-long plasma reactor allowing the treatment of textiles in the plasma discharge, in a pre-discharge zone or in a post-discharge zone.[2] In order to better understand the mechanisms of thin film growth, a macroscopic approach was chosen to describe the plasma polymerization allowing to correlate the deposition rate of the thin film to an apparent activation energy. In addition, the polymer films deposited on model substrates but also on a cotton fabrics were analyzed by FTIR, XPS, AFM, SEM-EDX and wettability. Numerous laundering cycles have also been performed to evaluate the durability of these coatings, which has been few described in the literature. The results after washing interestingly highlighted a significant dependence of the water-repellency property to a temporal parameter of the plasma discharge, which strongly influences the crosslinking rate of the deposited polymer. The relative position of the textile fabrics to the plasma discharge has also an impact on the durability of the coating, which may originate from different types of radicals that are formed at the substrate – thin film interface in the early stages of the deposition. These relationships between the operating conditions of plasma polymerization, the interface properties and the performances of the functionalized fabrics, but also the characterization methodology developed in this work, can undoubtedly serve the engineering of water-repellent, fluorinated-free coatings on fabrics with optimal durability.

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NANO1-K1-121 ● Investigation by TEM and XPS of the thermal stability of multi-layer solar selective absorber

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The solar energy resource is still relatively under-exploited although it could cover most of our energy needs. Beyond the development of photovoltaics, there is a worldwide challenge to deploy large-scale concentrated solar thermal power plants. To address this issue materials with high absorption in the visible, low emissivity and good temperature resistance are needed. To this end, multi-layer materials produced by plasma processes are developed in this study.

The absorbing active layer W-SiC:H is obtained by reactive magnetron sputtering from a W target and tetramethylsilane (TMS-Si$(CH_3)_4$) gaseous precursor diluted in Ar. The top anti-reflective layer is also deposited by reactive magnetron sputtering from a metallic tantalum target by controlling the oxygen and nitrogen flow rates in the plasma discharge.

XPS and TEM characterisations were carried out to get insight on the nature of the absorber and the anti-reflective top coating. Depending on the TMS proportion in the discharge, the quantity of Si introduced in the W-SiC:H material can be tuned. In dedicated conditions (8% TMS), W nanoparticles could be identified by coupling HAADF images, EDS mapping and High Resolution imaging.

In order to test for beneficial effect of plasmonic resonance on absorption, triple layers SiC:H/metallic W thin layer/SiC:H were also prepared. Upon annealing at 500°C in dried air for duration up to 48h, XPS profiles indicate that excepting a diffusion of oxygen from the surface in the upper SiC:H layer, the W interlayer acts as a blocking layer for oxidation. However after annealing for 96h, the triple layer is severely modified with segregation of the different species involved.

Finally, surface analysis by XPS accounts for the sensitivity of the absorber and antireflective layer toward oxygen when air exposed. However, this contamination layer is limited to the first nanometers.

Thanks/Acknowledgement
Acknowledgement for the financial support of the French Agence Nationale de la Recherche (ANR) through the project NANOPLAST ANR-19-CE08-0019.

NANO1-O2-140 ● Pulsed laser processes for the development of gold/silver nanocomposites for plasmonic applications

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This communication presents the synthesis and the development of metallic silver/gold nanocomposites with the purpose of enhancing the Surface Plasmon Resonance (SPR) effect. The excitation of the surface plasmon wave through the interaction of an optical beam, at the interface between a metal and a dielectric medium is particularly interesting for biosensing applications such as the detection of low molecular weight biological species in low concentration (under the pM scale) [1].

The silver/gold materials are developed using a pulsed laser ablation process consisting of free nanoparticles (NPs) generator coupled with a Pulsed Laser Deposition (PLD) set-up. The nanosecond KrF laser-PLD method is used to create thin films with controlled properties. For NPs generation, in a dedicated nucleation chamber, the pulsed plasma, produced by a Nd-YAG laser (532 nm) is quenched using high-pressure inert gas (helium), resulting in the in-flight synthesis of NPs at room temperature. This unique source allows the fabrication of nanoparticles with controlled size (< 5 nm) and narrow size distribution (FWHM < 0.5 nm).

By using separately, simultaneously or sequentially the NPs generator and/or the PLD, the system leads respectively to isolated NPs, NP-stacks, nanocomposite thin films with embedded NPs or multilayers NPs/thin films combination [2].

In this study, Au thin films, Au/Ag multilayers and Au/Ag-NPs composite materials with thickness of 45 to 50 nm are developed and their properties are investigated. Electrical and optical behavior are correlated with the microstructures and architectures. The plasmonic properties are particularly investigated by the study of the Goos-Hänchen (GH) effect which is highly sensitive to refractive index changes of the sensing interface, induced by the molecular binding of the biological samples. These results will allow the determination of the detection threshold for cancer biomarkers.

This work was partially supported by the LabEx å-lim ANR-10-LBX-0074–01, laboratory of excellence launched by the French Ministry of Higher Education and Research (https://www.unilim.fr/labex-sigma-lim) between the XLIM (https://www.xlim.fr) and IRCER (https://www.ircer.fr) Research Institutes.

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NANO1-O3-102 ● Influence of Cu nanoparticles addition on fracture properties of sputter deposited nanostructured refractory MoNbTaVW HEA coatings

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MoNbTaVW high-entropy alloy (HEA) falls into the group of refractory HEAs which are composed mainly of refractory metals. Such HEAs may find use in high-temperature applications due to the individual constituents' high melting temperatures and high-temperature strengths but on the other hand, they are also brittle which limits their applicability. The focus of this work is to ingeniously incorporate ductile phase in form of Cu nanoparticles into the brittle matrix constituted by MoNbTaVW HEA with the aim to improve the fracture properties of that high-entropy alloy.

Reference MoNbTaWV coating was deposited by non-reactive dc magnetron sputtering using a laboratory-scale system equipped with one equiatomic MoNbTaVW target. To investigate the effect of Cu nanoparticles on fracture properties of the nanostructured MoNbTaWV/Cu coatings, alternating magnetron sputter deposition from the Cu target was incorporated into the process to embody Cu nanoparticles into the MoNbTaVW coatings. Three MoNbTaWV/Cu coatings with various Cu nanoparticle concentrations over the coating thickness were synthesized. To further enhance the fracture properties, the confocal arrangement was utilized to grow a nanostructured MoNbTaWV/Cu coating with a two-dimensional chevron-like microstructure consisting of 12 sublayers with individual thicknesses of 250 nm.

MoNbTaWV/(Cu) coatings exclusively exhibited a single-phase body-centered cubic structure with a preferred (110) orientation. Due to the relatively low concentration of Cu nanoparticles no peaks stemming from the Cu phase were revealed by X-ray diffraction. The effect of sophisticated nanostructure design together with Cu nanoparticle addition on fracture properties of MoNbTaWV/(Cu) coatings was investigated. The fracture toughness was determined by the in-situ bending of microcantilever beam specimens in a scanning electron microscope equipped with a nanoindenter. Subsequently, SEM was conducted to observe the fracture planes of the beams after the bending experiments for correlation with measured fracture toughness values.

This work demonstrated that such a sequential deposition approach allowed for the synthesis of MoNbTaWV/Cu coatings having tailored Cu nanoparticles concentration over the coating thickness leading to optimized fracture properties.

ITEC1-O1-006 ● A plasma for multidimensional elemental and molecular analysis of surfaces & interfaces

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Surface and Interface studies require the use of complementary analytical techniques as each instrumentation provides results based on the interaction of the investigated material with a probing medium [1].

Obtaining elemental and molecular information for different probing size and depth is especially crucial for materials characterization and processes optimization.

HORIBA offers a Platform with multiple instruments able to tackle these complex analytical challenges. At the center of this platform is a pulsed RF Glow Discharge Instrument that relies on a GD Plasma to sputter a representative area of a material and provides fast elemental depth profile with nanometer resolution.

The unique characteristics of this Plasma have been studied in length (by electrical and optical methods and also in practice by combined measurements with XPS) and will be summarized (operating parameters, erosion rate measured in real time, structural integrity, surface damage etc) [2, 3].

We will then show that this GD Plasma can be used to prepare samples for SEM studies [4] and we will illustrate the benefits of coupling the GD instrument with micro XRF and Raman microscopy to obtain elemental & molecular information at various depths with micrometer lateral resolution on selected results on metallic parts for high temperature fuel cells, perovskite solar cells, hydratation of anodic films and DCL coatings on bipolar plates [5,6,7].

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ITEC1-O2-009 ● Advanced Patterning – Ion Beam Etching for Nano Structuring

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Nowadays, the demands in micro- and nano-scale structuring are getting higher and higher. Ion beam etching (IBE) can play a crucial role when it comes to meeting the increasing requirements. We like to show the impact of IBE for nano structuring using two applications as examples.

Modern high-precision spintronic devices ranging from angular position sensors in automotive industry to read-out sensors in hard-disk-drive industry often exploit the tunnel-magneto-resistance effect (TMR). Compared to giant-magneto-resistance sensors, the TMR has a higher thermal stability and increased signal output while decreasing the sensor's power consumption. However, the multilayer composition of the TMR sensor leads to issues regarding the etching, which is essential for electrical contacting of the sensor. Classical dry-etching methods are limited due to their poor reactivity of magnetic materials like CoFe, CoPt or NiFe. Additionally, the required reactive gas can lead to after-corrosion of the sensor electrodes. The ion beam milling process applies bombardment by argon ions and thereby allows to remove all materials used in the TMR stack in contrast to chemical etching. Additionally, the dry-etching with inert gas like argon, suppresses any after-corrosion effects, which would lead to an increased metal resistivity.

The production of slanted surface relief gratings (SRG) for applications such as augmented reality (AR) devices has recently gained more and more interest. In order to fabricate lightweight near eye displays, SRGs are used for coupling the light from the light source into the waveguide and out of the waveguide towards the eye. To suppress higher diffraction orders, and thus maximize the light yield, the gratings for AR devices are often slanted. The production of those gratings is realized by a pattern transfer of a masked substrate. By using ion beam etching the substrate can be freely tilted within the ion beam. This leads to excellent etching results for common slant angles of 45, but also for angles up to 60 (from substrate normal). In order to enhance the etching rate and control the selectivity between different materials, reactive gases, such as CHF3, O2 or SF6 are introduced in the process. The so-called reactive ion beam etching (RIBE) allows to influence the design of the gratings further. By changing ion energy and ion beam current density, the ratio between anisotropic and isotropic etch behavior can be influenced and by this the design of side wall parallelism and bottom shape for the gratings is possible.

ITEC1-O3-172 ● Advanced retarding field energy analyzer for accurate measurement of ion energy and flux in plasma-assisted thin film deposition tools

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Plasma-assisted technologies have been used historically in the fabrication of thin films composed of metallic, semiconductor, ceramic, and polymer, etc. for various end-use applications. The advent of sputtering, HiPIMS, and plasma-assisted Atomic Layer Deposition/Etching (ALD/ALE) techniques have extended the role of plasma manifold[1-3]. It is seen that ion energy distribution function (IEDF) and ion flux reaching the electrode are the key drivers to govern the kinetics of any physical or chemical process occurring near or on the top of the electrode. These electrodes are either grounded or floating but can also be driven by some DC/AC/RF bias (pulsed or continuous) to enable the control of the ion energy and ion flux. Additionally, other process variables such as the plasma gas mixture, pressure, delivered power, reactor design, and type of plasma source also affect the IEDF and hence change the deposited film properties.

To give insights into the key drivers of film properties from a plasma perspective, Impedans presents a family of retarding field energy analyzers (RFEAs) to study the impact of energetic ions bombarding samples under various plasma and substrate biasing conditions[4]. The SEMION RFEA measures the ion energies, ion flux, and bias voltage in situ. A special version of the RFEA known as SEMION pDC, reports time-resolved measurements of these parameters. While an advanced RFEA with integrated Quartz Crystal Microbalance (QCM) known as Quantum measures live deposition/etching rates along with the absolute contribution of neutrals or ions towards the process in addition to the basic information about ion energy, flux, and bias voltages. This talk will review these novel technologies and their field applications supported by various published results[5-8].

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ITEC1-O4-151 ● How to identify the optimal plasma treatment length for different surfaces

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Good adhesion between two surfaces is a key characteristic for products in many industries. Typically, the polarity of a surface increases when it gets treated with plasma, which leads to a better adhesion with most adhesives. However, when a surface is plasma-treated for too long, it starts disintegrating, which diminishes its adhesive properties. Thus, finding the optimal plasma treatment length is essential to optimise manufacturing processes and product quality.

To analyse the chemical changes through plasma treatment at the surface quantitatively, one can measure the contact angle between a water drop and the surface. The longer the plasma treatment, the smaller the contact angle becomes, i.e., the drop of water spreads more fully on the surface. However, if the plasma treatment time passes a certain point, the contact angle plateaus, and no further insight can be gleaned from such measurements.

To quantify the exact point at which the optimal plasma treatment length is reached, another measurement technique needs to be utilised. A suitable one is the measurement of the adhesive force using a force tensiometer with an additional camera like a DCAT with an UpVideo module from DataPhysics Instruments. In addition, 3D-profiles of the sample surfaces can be generated to gain more insight in the disintegration processes at the surface.

In our work, we could show that the adhesive force rose with longer treatment times and then reached a maximum before declining. The maximum in adhesive force could be linked to the beginning of surface disintegration as observed in the 3D-profile. With those measurement techniques combined, it was therefore possible to define the optimum plasma treatment length for different polymeric substance surfaces. All three measurement procedures (contact angle measurements, adhesive force measurements, 3D-profile) were carried out for a paraffin-coated polyethylene film and a substrate with a thick polyfluorinated coating

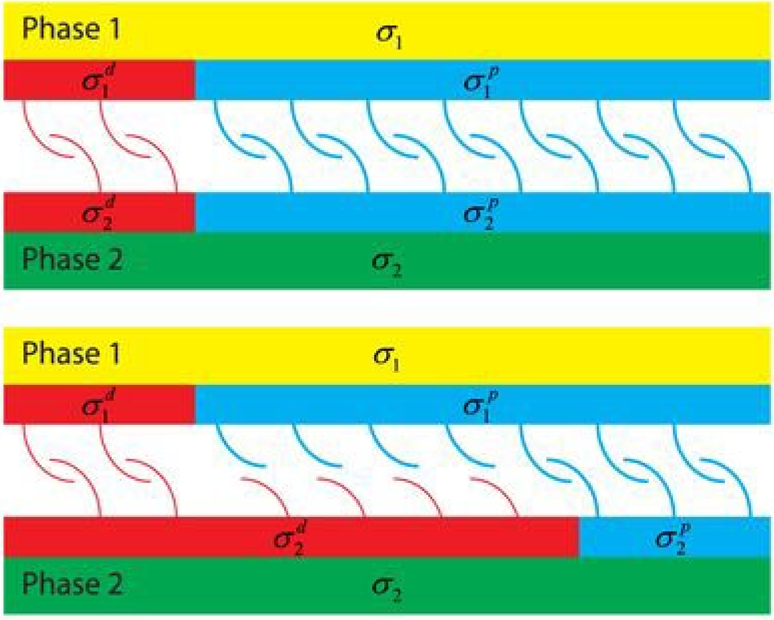

Figure 1: Activating surfaces with plasma treatment

PL3 ● Nonthermal plasma synthesis of photonic silicon nanocrystals

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Chemically reactive nonthermal plasmas at low pressure are an interesting medium for the growth of nanocrystals. Molecular precursors are dissociated by electron impact reactions and the resulting molecular fragments and radicals, many of them charged, nucleate to form clusters and nanocrystals. Energetic surface reactions heat these initial clusters to temperatures that exceed the gas temperature by hundreds of Kelvin.[1] This enables plasmas to form crystalline nanoparticles even of materials with very high melting points. In this presentation, we will discuss the plasma synthesis of silicon quantum dots with diameters on the order of ~3 nm for luminescent applications as well as the synthesis of larger silicon nanocrystals, 60-200 nm in diameter, that show interesting scattering behaviors. We also discuss how the temporary trapping of nanoparticles in the plasma contributes to the very narrow size distributions observed in both cases.[2]

Plasma-synthesized silicon quantum dots have shown good luminescence properties with photoluminescence quantum yields of up to 60%. One application of luminescent silicon quantum dots is in luminescent solar concentrators (LSCs), semitransparent waveguides that are doped with silicon quantum dots.[3] The silicon dots absorb solar radiation primarily in the blue range of the spectrum and reemit it in the near-infrared. Waveguiding concentrates this radiation on small solar cells that can be edge or surface mounted. We discuss results of a numerical model that investigates the application of silicon LSCs to greenhouses and demonstrate that LSC roof panels have the ability to enable net-zero-energy greenhouses in certain climates.[4]

We also discuss recent progress in the plasma synthesis of larger, highly monodisperse silicon nanocrystals with diameters of 60-200 nm.[5] These nanocrystals exhibit intriguing optical scattering through overlapping electric and magnetic dipole modes. We show that ensembles of silicon nanocrystals produced by plasmas show scattering behavior that is essentially consistent with single particle scattering models due to their very narrow size distribution.

This work was supported by the Army Research Office MURI grant W911NF-18-1-0240.

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NANO2-O1-100 ● ZnO nanoparticles thin films and evolution of their photoluminescence under oxygen plasma treatment

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ZnO is a well-known wide band gap (3.37 eV at room temperature) semiconductor studied for its numerous applications such as optical devices and solar cells. In particular, ZnO exhibits emission properties from near UV to visible light. The main reported emission in the visible domain is observed in the green-yellow range, centered around 580 nm, and ascribed to O vacancies [1].
The goal of our study is to investigate the effect of plasma treatment on the photoluminescence of ZnO thin films. In this study, thin films of zinc oxide nanoparticles have been prepared by spin coating of colloidal solutions on silicon and quartz substrates. These solutions were composed of ZnO NPs of 5 nm in diameter prepared following an organometallic approach [2] dispersed in hexamethyldisiloxane and pentane solution in a 80-20 %vol. Characterization of the as-prepared samples before and after exposure to low pressure radiofrequency (13.56 MHz) inductively coupled O_2 plasma [3] by different methods such as X-Ray photoelectron Spectroscopy, Scanning Electron Microscopy, and spectrofluorimetry are performed in order to identify the effect of the plasma on the composition and the physical properties of the thin films. In addition, in situ ellipsometry was carried out during the plasma process to follow the evolutions of the optical index of the samples. Our interest is in understanding the effect of the plasma on the structural defects of ZnO NPs and how it affects its photoemission. We have shown, for example, that global emission of plasma-treated sample shifts from orange to white emission on CIE chromaticity diagram, which opens the way to the achievement of a device with white light emission.

Thanks/Acknowledgement
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NANO2-O2-075 ● Optical study of metallic nanoparticles generated by thin-layer ion irradiation

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When embedded in a dielectric matrix, metallic nanoparticles (NP) can trigger interesting optical properties. Electromagnetic waves induce collective electron oscillation in metals NP in a phenomenon called local surface plasmon resonance. This induces absorption peaks in the UV-visible light range. By varying the size or inter-distance of nanoparticles, it is possible to tune peak width and position as predicted by optical models.

In this work, NPs are generated by ions (He, N, Ar) irradiation of thin pre-deposited dielectric/Silver/dielectric layers. A low-cost 15-40kV ion source has been used to investigate the impact of beam current and energy on the optical response of the PVD layers stack. Basic information on the metal layer morphology can then be extracted by optical simulation based on Maxwell-Garnett or Bruggeman formalism(1).

These observations are then confronted with literature data. First, irradiation provokes de-wetting of the metallic layer into large colloids (2). Then, a second phenomenon occurs as ballistic mixing dissolves larger NPs (3). This double effect can be used for NP size control with beam parameters, which gives this technic a potential key advantage compared to other methods of production.

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NANO3-O1-073● Plasmonic Cu nanoparticles embedded in semiconductor heterostructures for photoconversion applications.

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Gold, silver and copper, are known for exhibiting quite interesting optical properties in the nanoscale. When the wavelength of an incident light source corresponds to the surface plasmon frequency of the nanomaterial, hot carriers are generated due to the Localized Surface Plasmon Resonance (LSPR) phenomenon [1]. Additionally, if a semiconductor is in contact with the metal, those carriers can be transferred to its conduction or valence band, contributing to the increase of its electron density and the photocurrent of a potential device [2, 3]. Some plasmonic metals like copper are abundant in the earth crust, not expensive and environmentally friendly. However, they are not as well studied as gold or silver. In this work, a reactive magnetron sputtering system coupled with a gas aggregation source (GAS) [4] is used to obtain plasmonic Cu nanoparticles and include them in semiconductor heterostructures for possible optoelectronic applications. By controlling the oxygen partial pressure in the sputtering chamber or the GAS particles flux, we were able to in-situ grow Cu nanoparticles into Cu_2O, CuO and ZnO matrices [5] and observe the resulting composites via high resolution microscopy. Moreover, we evidenced the surface plasmon bands corresponding to Cu particles by UV-Vis spectroscopy and ellipsometry measurements. In order to evaluate the impact of the LSPR in the photogeneration, we developed devices with Cu nanoparticles embedded in the different semiconductor matrices and at the p-n junction. The characterization of the devices using I−V and spectral response measurements showed an increase in the photocurrent density under light illumination as a consequence of the plasmonic particles excitation leading to hot carrier injection in the nearby semiconductors. Furthermore, we observed a dependence between the position of the Cu nanoparticles and the performance of the devices. These results showed the possibility of obtaining and controlling, through the sputtering technique, functional, non-toxic and low-cost plasmonic heterostructures for the enhancement of light harvesting in photocatalysis and photovoltaic applications.

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NANO3-O2-092 ● Development of a microwave microplasma process for the elaboration of nanodiamonds

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In this work, we present the conditions that can support the gas-phase formation of diamond nanoparticles (DNPs) in a MW micro-plasma torch with hydrogen-methane-Argon gas mixtures. The carbon nanostructures produced in our discharge were collected on a silicon substrate placed downstream the torch[1].

The Raman spectra of the deposit evolved with gas composition, pressure and power. Formation of DNPs was favorable at high power at pressure between 100 and 125 mbar for methane gas-composition between 4 to 7%. This was evidenced by the presence of diamond peaks at 1332 cm^{-1} (Fig.1) along with the presence of D and G bands at 1355 and 1598 cm^{-1}, respectively. Adding small quantities of Argon (up to 2%) supported the production of DNPs. However, the nanostructures become amorphous for larger concentrations of Argon and methane.

The micro-plasma was characterized using optical emission spectroscopy (OES). While the gas temperatures varied in the range 1000-1400 K, the electron density was nearly constant for the different conditions studied (about 2.10^{13} cm^{-3}). Similarly, the concentration of H-atom was estimated to be nearly constant 10^{16} cm^{-3}, indicating dissociation of Hydrogen through electron impact processes. The large population of atomic hydrogen produced in the plasma plays an essential role in stabilizing the diamond phase by saturating the dangling bonds of the carbon atoms on the surface and ensuring the etching of the non-diamond phases (sp^2 carbon) that are likely to co-deposit with diamond. This ensures a net predominance of sp^3 phase carbon (diamond). We also showed that the hydrocarbon chemistry leading to the formation of carbon nanostructures is strongly influenced by the gas temperature and the concentration of carbon radicals especially as C_2 and CH_3. In particular, larger NPs amounts in the deposit are correlated with larger concentration of CH_3 and C_2 in the plasmas, which is consistent with a DNPs production mechanism initiated by C_2 and CH_3. However, higher concentrations of hydrocarbon in the presence of acetylene favor formation of amorphous carbon. Further studies are being undertaken in order to identify the molecular growth pathways leading to the different carbon nanostructures.

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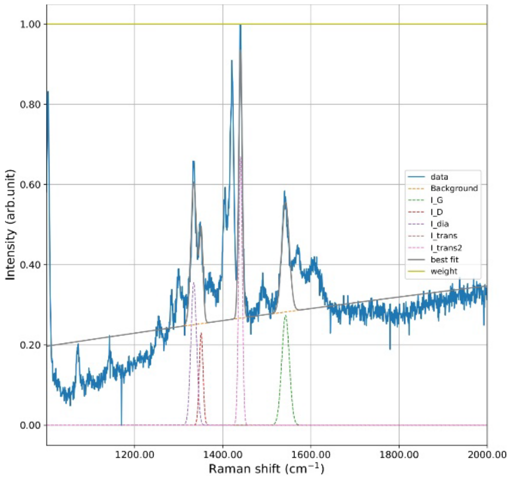

Raman spectra of diamond NPs collected

NANO3-O3-076 ● Dielectric barrier discharge in nitrogen for the realization of nanocomposite layers using multifrequency excitation and gold salt precursors

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This study aims to develop a low-cost, one-step process to deposit nanocomposite gold plasmonic thin films with well-controlled properties on large surface substrates. It is based on the association of a Dielectric Barrier Discharge (DBD) in nitrogen at atmospheric pressure associated with an aerosol of metallic salt dissolved in a solvent.

Thin film synthesis on large surfaces is a well-known process in the scientific community. However, associating the synthesis of thin layers with the insertion of nanoparticles in the matrix is unusual. Currently, no system allows the synthesis of nanoparticles and the matrix in one step to avoid the handling of the nanoparticles. This is the appeal of this study.

Here, the dissolved Au salts in the solvent are directly injected with nitrogen between the dielectrics of the DBD. The salts will be reduced directly by the plasma (electrons and excited species) to produce the nanoparticles. Nevertheless, this can also destabilize the discharge and change its regime. Therefore, a study of the influence of the aerosol on the discharge is essential to determine its operating regime.

The density of energetic species (electrons, metastables, ions) depends on the discharge regime [1]. A study of these species will help us to understand their effects on the formation of the Au/polymer nanocomposite.

The polymerization of the matrix and the reduction of salts requires higher plasma energy and, thus, higher excitation frequency. In contrast, the transport of the nanoparticles to the surface is related to the electrostatic forces and then requires a low excitation frequency. Then, the process needs a double excitation frequency [2]. The correlation between the discharge parameters and the characteristics of the deposited layers will be made by various ex-situ characterizations.

Thanks/Acknowledgement
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NANO3-O4-120 ● Synthesis of gold/polymer nanocomposites in an atmospheric pressure plasma

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Atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) is a low temperature process used for the growth of thin films. Unlike low-pressure PECVD, it does not require the use of vacuum systems and is suitable for the treatment of large surfaces. Another interesting aspect of working at atmospheric pressure is that liquids or colloidal solutions can be easily injected in the form of an aerosol into the plasma. This can lead for instance to the growth of nanocomposite thin films through proper selection of the precursors of the matrix and of the nanoparticles (NPs) embedded in it. One of the main benefits of this method is that NPs are not in any case directly manipulated, making the process safe by design.

In this work, the aerosol of a solution of a gold salt (i.e., NPs precursor) in isopropanol (i.e. polymerizable solvent acting as matrix precursor) is explored using a dielectric barrier discharge (DBD) [1]. The effect of the process parameters on the nanocomposite morphology, chemical composition and optical properties is studied. A previous study [2] using an aerosol of a colloidal solution of $TiO2$ NPs highlighted the benefits of alternating a high plasma frequency, responsible for the matrix polymerization, and a low one, to control the transport of NPs onto the substrate. In this research, both high and low frequencies are alternated; the low frequency is continuously applied while the higher is modulated. Furthermore, the aerosol formation and the evolution of the aerosol-droplet size is also characterized prior to plasma entrance.

Results show that two nanocomposites families can be deposited. The first one corresponds to plasmonic thin films. Measurements by absorption spectroscopy and atomic force microscopy indicate the presence of isolated gold NPs with plasmonic resonance peaks ranging from 540 to 750 nm depending on the process parameters. The thin films from the second family are characterized by a lower plasmonic absorption and a larger UV-Vis absorption of the matrix.

In the light of these results, it can be concluded that the injection in a DBD of an aerosol consisting of Au metallic salt in isopropanol can be considered a promising, single-step plasma process for the formation of Au NPs nanocomposites.

Thanks/Acknowledgement
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NANO3-O5-146 ● Au nanoparticles decoration of different TiO_2 nanostructures using atmospheric pressure cold plasma

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Herein, we present the possibility of using an atmospheric pressure Dielectric Barrier Discharge (DBD) plasma torch for gold (Au) nanoparticles (NPs) decoration of TiO_2 nanoparticles and nanotubes (NTs). Au NPs were synthesised using an aerosol of $HAuCl_4x3H_2O$ solution that was carried with an inert gas to the near post-discharge zone of plasma. The precursor containing droplets are considered to be micro-reactors for "in-flight" Au NPs synthesis as described by Maguire et al [1]. The experimental setup consisted of a vertically placed torch where the plasma was created between the inner quartz tube coated with Pt (carrying the precursor aerosol) and the outer plasma tube (covered by Al foil which is connected to the HV generator). Bellow the plasma torch the TiO_2 nanoparticles colloid was stirred to enable the homogeneous deposition of Au NPs on the surface of TiO_2. The colorization of the colloid from white to purple was an initial proof of a change due to Au NPs deposition. Another demonstration was the use of anodized TiO_2 NTs vertically aligned to Ti support [2]. The films were used as substrates for Au NPs deposition. The careful optimization of the parameters was done to ensure the uniform and profonde decoration of TiO_2 NTs. Using scanning and transmission electron microscopy (SEM and TEM) with energy dispersion spectroscopy (EDS) the chemical and morphological analyses were done. To demonstrate the effectiveness of the proposed method and its perspective we also provide the absorption spectra of the samples. The samples with Au NPs showed, indeed, the plasmon resonance peak in the region 500-600 nm [3], characteristic for Au NPs. The X-ray diffraction (XRD) was used to confirm that the deposit was pure metallic Au. The catalytic properties of synthesised Au decorated TiO_2 structures were also characterised to assess their practical application in energy and environmental.

Thanks/Acknowledgement
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DEPO1-O1-040 ● VN coatings for supercapacitor, an innovative approach to improve stability

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Vanadium nitride is a promising transition metal compound for use in electrochemical capacitors (ECs) with high supercapacitance, due to a dual contribution from double layer-type and a pseudo-capacitance mechanism.
However, the cyclability of VN is still low due to its oxidation and subsequent dissolution of the vanadium oxide in the electrolyte. Several approaches have been reported, such as the reduction of voltage window, but it limits the energy density.
Here, we proposed to tune the electrolyte composition to limit the oxide layer dissolution. Indeed, with the addition of V2O5 powder in the electrolyte, we are able to stabilize the oxide/oxynitride layer at the VN surface, instead of its dissolution, thanks to the chemical equilibrium shift of the VN dissolution reaction. With this innovative approach, the energy density is also increased.
VN coatings have been synthesize by reactive magnetron sputtering. Extensive films characterization, including XPS, XPS depth profile, SEM and XRD have been performed before and after electrochemical measurements, including cyclovoltammetry in pure KOH and V5+-containing KOH, in order to demonstrate the surface stabilization of the electrode. The communication will present the strategy, the film characterization and a model to explain it.

DEPO1-O2-065 ● Plasma-assisted segregation of self-grown catalytic nanoparticles in perovskites for H_2 production by photoelectrocatalysis

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Perovskite oxides (ABO_3) are promising materials that have been explored as electrode materials for fuel cells, electronic devices or heterogeneous photocatalysis. Their wide variety of properties can be attributed to the large structural and compositional flexibility of the perovskite structure. Recently, composite materials elaborated by integration of functional catalyst nanoparticles (NPs) on perovskite oxide supports have received rising attention. These structures are prepared by conventional deposition methods (vapour deposition, chemical impregnation, etc.). Although these techniques are applied widely, they offer limited control over the size, distribution and anchorage, not only during preparation but also during ageing. Therefore, an advanced approach is required to overcome these drawbacks. Segregation mechanism leading to in situ growth of catalytic NPs is an attractive approach for designing NPs on perovskite materials: catalytically active transition metals are incorporated by substitution on the B-site of perovskite oxide during synthesis and then the transition metals are segregated from the perovskite backbone as highly dispersed NPs, under reducing or oxidizing atmospheres [1-2]. Another strategy for promoting segregation is to start from A-site deficiency perovskites.

The use of afterglow plasma treatments could modify these segregation mechanisms and improve the control of the nanostructure design by moving the temperature window by about 100 K downward. This shift enables the development of higher stress levels and offers the possibility to tune segregation trends. In this study, the segregation of Cu was achieved from $La_{0.8}Fe_{1-x}Cu_x$ thin films deposited beforehand by magnetron co-sputtering and oxidized in a flowing microwave plasma process [3]. The growth of spherical CuO NPs with well-defined boundaries on the surface of perovskite films was observed by TEM analyses. Enhanced photocatalytic activity by adjusting stoichiometry, plasma oxidation conditions and film thickness was confirmed by H_2 photoproduction rate with a large increase (270 %) by comparison with a stoichiometric $LaFeO_3$ thin film [4,5]. The improvement in catalytic performances for these non-stoichiometric films composed of abundant, low cost and non-toxic elements, make them of high interest materials for photoelectrodes in water splitting systems.

Thanks/Acknowledgement
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DEPO4-O1-079 ● W/W-SiCH/TaO_xN_y solar selective absorber coatings for Concentrated Solar Power

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The improvement of solar technologies (PV, Concentrated Solar Power, PV/CSP hybridization) requires the design and elaboration of new materials solutions able to limit optical and thermal losses, but also to resist to damaging operating conditions, by using stable thin films with controlled spectrally selective properties.

Solar selective absorber coatings to improve the performance of CSP solar receivers in air, with a high transfer potential to industry, were developed in the ANR NANOPLAST project (nanoplast-project.cnrs.fr). These coatings are composed of: (i) a W/W-SiCH selective absorber deposited by reactive magnetron sputtering assisted by microwave sources involving a tungsten target in an argon/TetraMethylsilane (TMS) plasma and; (ii) a TaO_xN_y antireflective layer deposited by sputtering a tantalum target in an $Ar/O_2/N_2$ plasma.

The multilayered coatings and their constitutive monolayers were studied by various characterisation techniques (SEM, IBA, XPS, XRD, PDF and EPR) in order to investigate their physicochemical properties, microstructure and chemical composition, as-deposited and after aging at 500°C in air. The solar performance was simulated and optimized by optical modelling, based on the measurement of their optical indices by confronting ellipsometric spectroscopy and UV-Vis-NIR spectroscopy, and measured by spectrophotometry in the solar range. A deeper study of their thermal stability in air will be carried out using a thermal cycling ageing process to get closer to the real operating conditions of concentrated solar power receivers.

In the framework of the Selhysol project (supported by French Occitanie Region and University of Perpignan), similar absorber coatings are reoptimized by optical simulation and used for hybrid PV/CSP systems based on selective PV mirrors. The latter allow the absorption of the effective part of the solar spectrum by underlying PV cells while reflecting the remainder of the solar spectrum towards a CSP thermal absorber.

DEPO4-O2-148 ● PVD coatings for PEMFC bipolar plates functionalization

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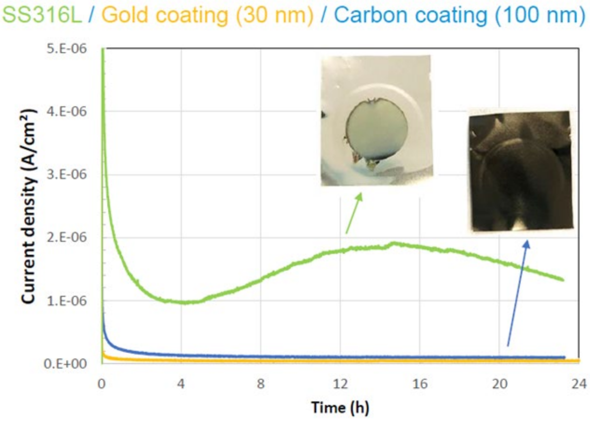
Polymer Electrolyte Membrane Fuel Cells, employing dihydrogen as fuel, are promising energy sources particularly for the automotive sector. In these electrochemical systems, bipolar plates enable to electrically connect the cells and represent 20-30% of the total cost of the system, for about 70% of its mass and volume.
Stainless steel is the most used materials for this component, but cannot meet the necessary high degree of performance (in terms of conductivity and corrosion resistance), and a surface treatment is necessary to enhance its surface properties. The goal of the treatment is double : to ensure an efficient protection against corrosion, avoiding electrolytic membrane contamination with metallic corrosion products; to optimise the electrical contact between the plate and the gas diffusion layer, guaranting low electrical losses. A high performance coating is therefore key to the durability and efficiency of the bipolar plates and consequently of the fuel cell stack itself.
PVD is a technique of choice to deposit highly adherent, conductive and corrosion resistant coatings. PVD gold coatings have long been the reference solution to fulfill the above mentioned requirements, and still today in heavy duty vehicules. Of course, treatment price is a sticking point for large volume commercialization, so alternative materials have been developed.
In this paper, we will review the deposition methods and present experimental results on the performance of PVD coatings of different materials : gold, ceramic, and carbon based layers.
Performance tests will focus on results of electrochemical ex-situ tests : coupons of coated stainless steel are solicited in corrosion conditions representative of the PEMFC bipolar plates environment : hot (80°C), acid, oxidant, and oxidative potential at the cathode, reductive at the anode. Beyond these basic tests, results to accelerated corrosion stress tests will also be presented, developed to simulate in a few hours the more detrimental conditions that can be encountered in the 7000 hours lifetime of the electrochemical system. Coating degradations mechanisms are evidenced by post-mortem coupons and plates analysis. Complementary to these corrosion tests, electrical contact resistance of the coated surface is also evaluated before and after corrosion sollicitation.



Potentiostatic corrosion current curves at 1V/NHE

DEPO4-O3-128 ● Characterization of $CuBi_2O_4$ thin films deposited by RF magnetron sputtering

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The ternary compound CuBi2O4 possesses an unusual crystal structure with stacks of square planar CuO4 groups linked to distorted trigonal BiO6 polyhedra, associated with very interesting electrical and antiferromagnetic properties [1]. In recent years, this p-type semiconductor has been identified as a promising material for its use in photocatalystis, photoelectrochemistry and the generation of hydrogen from water [2]. Up to now, all CuBi2O4 thin films reported were widely synthesized by electrodeposition, hydrothermal synthesis, sol gel method but there are only few publication about the use of the sputtering technique for its deposition.
In this work, we thus report the preparation of CuBi2O4 thin films which have been deposited by radio-frequency magnetron sputtering using a homemade CuBi2O4 ceramic target [3]. X-ray diffraction characterizations revealed an amourphous phase for as-deposited films. After air annealing at 450 °C for 12 hours, a polycristalline CuBi2O4 phase can been obtained. Raman spectroscopy confirmed the film phase apparent purity. The influence of the thickness on the structural properties of the films have been studied and we observed that all films treated at 450°C are crystallized. Atomic force microscopy shows a homogeneous polycristalline microstructure at the surface of the film. Optical measurements performed by UV-Vis-IR spectrophotometry indicate that these films have one of their optical band gaps in the visible region (Eg~1.5 eV) which makes them suitable as thin films solar absorption materials.

Thanks/Acknowledgement
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DEPO4-O4-166 ● High-rate reactive deposition of ultrawide bandgap Ga_2O_3 by liquid metal target sputtering

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We have developed a high-rate deposition of Ga_2O_3 thin films by liquid metal target sputtering. The thin films were deposited by reactive pulsed direct current magnetron sputtering from a gallium metal target in an Ar/O_2 atmosphere. As the melting temperature of gallium is 29.8°C, the target was in a liquid state during sputtering. To prevent the melted metal from flowing off the magnetron surface, a box-shaped stainless steel target container was used with 3-mm-high walls and a machined recess in the base plane. To prevent the liquid gallium from contracting into islands and leaving parts of the container base plate exposed to sputtering, the container surface was pre-coated with a wettability-promoting layer of carbon. The target was prepared by melting metallic gallium pellets and then cooling the container to allow the target to solidify before being placed onto the magnetron.

Amorphous and crystalline thin films of ultrawide bandgap Ga_2O_3 were deposited onto fused (f-) quartz and c plane (c-) sapphire substrates, where the temperature of the substrate is varied from room temperature (RT) to 800°C. The deposition rate (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 data given in the literature for radio frequency sputtering. Deposited onto unheated substrates, the films are X-ray amorphous. Well-defined X-ray diffraction peaks of β-Ga_2O_3 start to appear at a substrate temperature of 500°C. Films grown on c-sapphire at temperatures above 600°C are epitaxial. Composition analysis shows stoichiometry close to Ga_2O_3 and no traces of impurities. The optical properties of low absorptance (<1%) in the visible range and an optical band gap of approximately 5 eV are consistent with the data in the literature for Ga_2O_3 films produced by other deposition methods.

DEPO4-O5-124 ● Non-equilibrium synthesis of Si1-xMnx thin films for magnetic application

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Green and digital transition will change the consumption scheme of materials. It will require electronics to be based, more and more, on abundant raw materials such as copper, iron, aluminum, silicon or manganese. But using only abundant materials may be at the expenses of performances. Metastable materials propose a solution to that conflict. In this scenario, properties are reached by managing other parameters like non-stoichiometry and obtained phases. Different properties can be improved, by playing with those parameters and using the same set of elements.

In this work, it is studied the case of non-stoichiometric MnSi compound. Si1-xMnx ($x = 0.51$-0.53) have been reported to show a higher Curie temperature than its stoichiometric version, MnSi [1]. Since MnSi is a chemically-defined compound with extremely narrow composition domain (less than 0.1 at%) [2], non-stoichiometric Si1-xMnx should be synthesized via non-equilibrium processes. Magnetron Sputtering offers both the possibility for a fine tuning of the material composition (through target current control) and non-equilibrium conditions of synthesis.

TEM inspection and XRD measurements show that as-deposited films are nanocrystalline. Increase in crystal size is achieved by Rapid Thermal Annealing (RTA). As comparison, it was performed crystallization by picosecond laser irradiation; giving, in this case, enough energy for crystallization in a much shorter time. The magnetic state evolution with temperature is studied by Vibrating Sample Magnetometry (VSM). Films metastability is analyzed by comparing phase diagram, composition and XRD diffractograms.

It is found that crystallization dynamics, by RTA, is strongly affected by manganese diffusion. Low temperature annealing results in small crystal size while high temperature annealing results in bigger crystal size but also more pronounced diffusion of manganese out of the film. Crystallization by laser irradiation shows a weaker Mn diffusion in comparison with RTA. Films are confirmed to be ferromagnetic a low temperature. The evolution of the magnetic state with temperature depends on the crystallization history where the amount of Mn diffused play an important role.

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PL4 ● Plasma-assisted CO_2 recycling: investigation on volume and surface kinetic

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Instituto Superior Técnico, Lisbon (PT)

The development of green technologies that accelerate the transition towards a more sustainable and resilient world with zero net emissions by 2050 requires long-term and large-scale energy storage solutions. A promising and environmentally friendly solution to this problem relies on the development of a suitable energy storage scheme in which the excess of renewable power is used to convert feedstock of pollutant gases such as CO2 into chemical fuels. In this context, over the past years, non-thermal plasmas have gained much attention regarding CO2 decomposition due to their potential to activate CO2 at reduced energy cost, while exciting CO2 vibrations that efficiently contribute to overcome the dissociation barrier. This has led to a growing field of research aimed at combining renewable electricity with plasmas to convert pollutant gases into synthetic fuels for energy storage pathways.

In this talk, I will provide an overview of recent research associated to plasma-based conversion, while discussing different lines of investigation and current challenges related to plasma-surface interactions. More specifically, I will address: (i) the role of industrial gases on CO2 decomposition in a plasma environment, (ii) the impact of volume and surface kinetics on vibrational excitation and (iii) recent efforts targeted at developing plasma-based reaction mechanisms to account for the volume/surface production of value-added products in gas reforming applications. In all these situations, modelling studies, based on the coupling of the electron Boltzmann equation with a system of rate balance equations, are compared against experimental data obtained in different plasma reactors, including DC glow discharges and inductive coupled plasmas.

Acknowledgments
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PLACC1-O1-133 ● Interplay of transport, plasma concentration, and chemistry in microwave dischargesh

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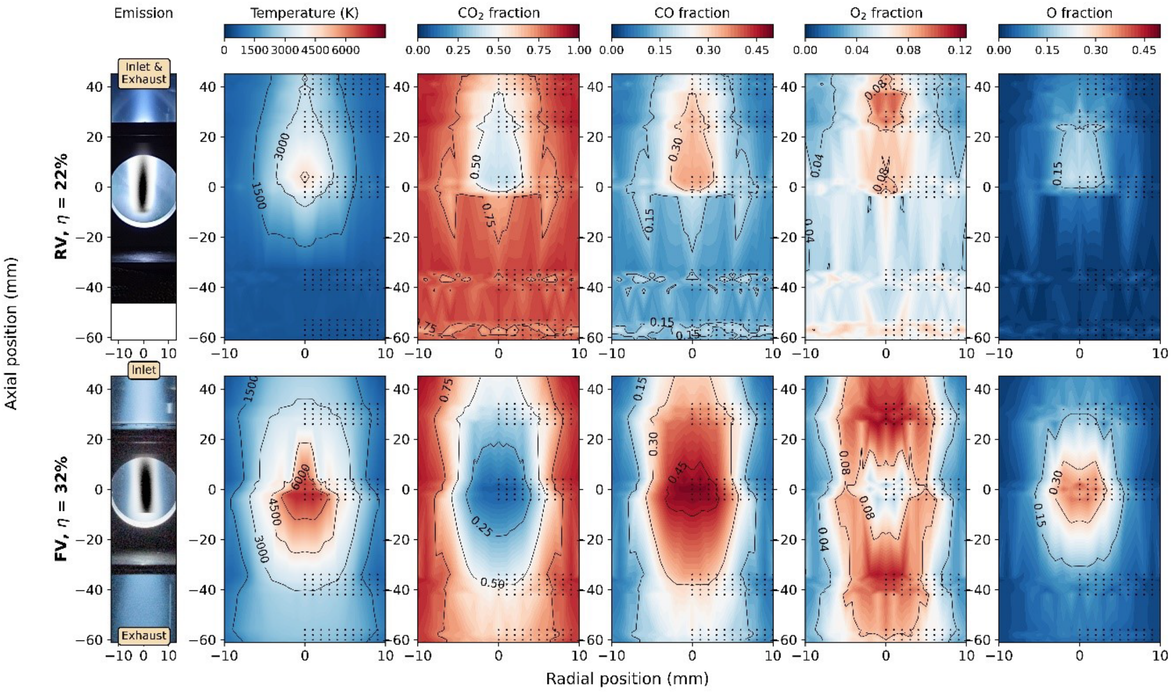
Microwave plasma is investigated as gas conversion technology for its compatibility with intermittent power sources and its promise in efficiency and selectivity, e.g. in dissociation of CO_2 or carbon coupling in CH_4. Understanding of transport and power density and their relation to plasma concentration are key for optimization of performance and scale up of the technology. In this work, we demonstrate the dominant phenomena at play in a comparison of CO_2 and CH_4 discharges in Forward Vortex (FV) and Reverse Vortex (RV) flow, involving maps of composition (CO_2, CO, O_2 and O) and temperature measured with Raman scattering.
Large differences in temperature and composition are observed. In CO_2, we measure temperatures below 4500 K in RV versus 6000 K in FV and consequently lower dissociation degrees in the plasma core for RV versus FV. In CH_4, the macroscopic production of soot is entirely suppressed. It will be shown how these observations correlate with measured global gas conversion performance.
In effect, a decoupling of core temperature and composition with power density is achieved, enabling concentrated plasma conditions at different gas temperature. Furthermore, the work shows that plasma concentration results from a balance between ambipolar diffusion and recombination. Such aspects underline the importance of gas flow geometry for reactor parameters and it will be sketched how these can play an important role in future reactor engineering and design, in particular in relation with ongoing R&D for electrification of process industry.



2D results of rotational Raman scattering.

PLACC1-O2-119 ● Plasma-assisted CO_2 hydrogenation over Ir/TiO_2 catalytic thin films in a DBD reactor

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Plasma-catalytic conversion of CO_2 to methane, the Sabatier reaction, is a promising process for mitigating the emission of CO_2 into air and storing the excess H2 generated from renewable energy. Thin catalytic coatings provide an effective route for plasma-catalysis synergy whereby activated plasma species are generated near catalytic sites, efficiently reducing activation energy for surface reactions. This work applies a Ir/TiO_2 coating for CO_2 hydrogenation to methane. The reaction was carried out in a tubular dielectric barrier discharge (DBD) reactor (ID 3.0 mm, OD 5.0 mm, length 250 mm), with a 1.2 µm Ir/TiO_2 layer deposited onto the inner wall. The catalyst was prepared by combustion-evaporation method reported elsewhere[1]. The catalyst was characterized with XRD, SEM/EDX, and gas conversion measurements of CO_2 hydrogenation under plasma conditions. The morphology of the catalysts was characterized by HRTEM. The Ir particle size was 2.5 ± 1.9 nm. The plasma was created with a power generator at a frequency of 68 kHz, and peak to peak voltage 5.6 kV. The CO_2 conversion and product yield were measured with a gas chromatograph. Different product distributions were obtained over TiO_2 and Ir/TiO_2 coatings (Figure 1). Over Ir/TiO_2, a CO_2 conversion of 35% was achieved with the energy efficiency (EE) of 1.6% which is in line with the state-of-the-art in the field. The results provide a good avenue for moving towards to other products through catalyst optimisation.

Thanks/Acknowledgement
ERC Synergy Grant Surface-Confined fast modulated plasma for process and energy intensification (SCOPE) from the European Commission with the Grant No. 810182.
We are grateful to Johnson Matthey for supplying materials for this research.

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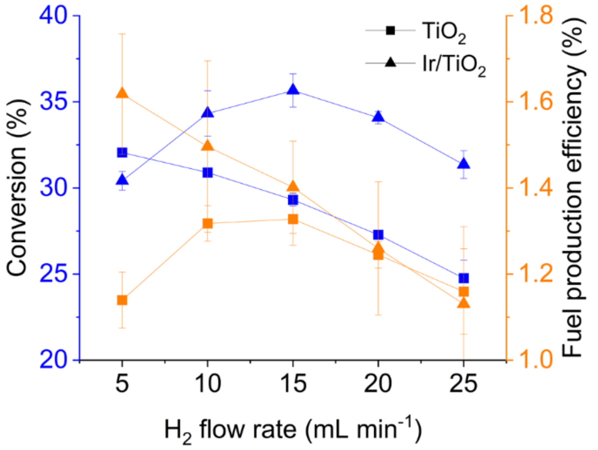

Conversion and fuel production efficiency

PLACC1-O3-173 ● Discharges in honeycomb monoliths and capillary tubes

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Atmospheric pressure plasmas generated by electrical discharges are often used for air pollution control. The common discharge types are corona and dielectric barrier discharges (DBD) generated in gases or on dielectric surfaces. They can be also generated inside cavities and pores of materials, such as foams, pellets, beads, or tubes [1]. It is very interesting from the point of view of plasma catalysis as the interaction of the plasma with (catalytic) materials can be utilized to enhance associated chemical processes. This contribution summarizes the results on generation of discharges in a single capillary tube, a bundle of capillary tubes as well as ceramic honeycomb monolith. Electrical and optical measurements were performed in various geometry (diameter, length, cpi), feed gases (air, N2, O2, H2O) and power supplies (AC, DC, pulsed) of both polarities. Electrical diagnostics included oscilloscopic measurements and power consumption evaluation. The optical diagnostics included optical emission spectroscopy and measurements of discharge propagation velocity. Chemical activity was monitored by FTIR spectroscopy. The discharge in a single capillary tube was investigated to understand a fundamental mechanism of its formation and propagation [2]. The propagation velocity increased with the decreasing tube diameter. It was found 4.3x10^7 and 9.9x10^7 cm/s for 1 and 0.2 mm diameter, respectively. Onset and breakdown voltages increased with the decreasing tube diameter, while stable discharge generation was improved by extending its length. Propagation velocity was higher for smaller tube diameters and higher O2 content. Tests with a bundle of capillary tubes were performed to assess the overall stability and spatial homogeneity of the discharge. The discharges were generated by a DC high voltage, eventually assisted by auxiliary AC driven discharges in a pellet bed [1] or in a multi-hollow DBD [3]. The homogeneity and the stability largely depended on the discharge polarity, ballasting resistor, and feed gas humidity. At last, the discharges generated directly in ceramic honeycombs of various geometry (length, cpi) were tested. They were also briefly subjected to the investigations of its plasma chemical activity (generation of O3 and NOx removal). Tentative results were quite promising and are expected to be further improved in systems with honeycombs supported by various catalysts.

Thanks/Acknowledgement
APVV-20-0566, VEGA 1/0822/21

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PLACC1-O4-027 ● Synthesis and effect of $BiVO_4$ thin films heterojunctions deposited by reactive magnetron co-sputtering on photogenerated charges for visible light photocatalysis.

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Photocatalytic materials are strongly studied in order to enhance the use of solar energy for pollutant degradation or H2 production by water splitting. Bismuth vanadate, BiVO4, is an interesting photocatalyst thanks to its band gap near 2.4 eV, which makes it able to harvest visible light, and its suitable band positions for the targeted applications. However, pure BiVO4 displays a strong recombination rate of photogenerated electron-hole pairs. In this present paper, we explore the possibility to decrease the charges recombination by making heterojunctions.

Thin films were deposited by radiofrequency reactive magnetron co-sputtering of bismuth and vanadium in a mixture of argon and oxygen. By tailoring the power applied to the targets, we were able to adjust metal ratios (determined by Rutherford Backscattering Spectroscopy (RBS)) and control the phase segregations. The as-deposited films being amorphous, annealing treatments were studied to observe the influence on structural change. After a treatment at 450°C in air during 2 hours, X-ray diffraction analysis shows that heterojunctions are formed according to the V/Bi ratio. For V/Bi = 1, pure mBiVO4 in monoclinic phase is formed, whereas for V/Bi > 1, we observe heterojunction formation between V2O5 and BiVO4. For V/Bi < 1, we record the formation of heterojunction between mBiVO4 and tBiVO4 (tetragonal phase) but also with Bi2O3 at lower ratio. The X-ray Photoelectron Spectroscopy (XPS) was also performed to determine the chemical environment and confirmed heterojunctions formation following the shift of binding energy positions. The film morphologies were also checked by scanning electron and atomic force microscopy to investigate their surface roughness and porosity. The optical properties were studied by ellipsometry and UV-visible spectroscopy. The films exhibit direct band gaps between 2,4 and 2,6 eV: films made with V2O5 tend to have a lower band gap than mBiVO4 and films with bismuth excess. The photocatalytic activity was first check by photodegradation of pollutant under irradiation. All the films were able to degrade methyl-orange solution but heterojunctions stand to have enhanced performances as they degrade the dye quicker than pure BiVO4. Thereafter, photoelectrochemical measurements were carried out by examining the photocurrent in order to quantify the amount of charge carriers available for water splitting. Interesting properties have been highlighted as heterojunctions are able to improve carrier transport properties and photogenerated charges lifetime.

HELIAG1-O1-037 ● Bactericidal surface treatments for dental implants based on silver and copper MEVVA ion co-implantation

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In the field of dental implantology, the widespread use of dental implants has been one of the most important changes and advances in dental practice in recent years. However, in spite of the predictability of dental implant treatments, which show success rates of around 90% after 10 years of insertion, there are still important problems to overcome, with a group of pathologies that cause the loss of peri-implant bone and, finally, the loss of the implant. In particular, infection caused by bacterial colonization (peri-implantitis) is one of the main causes of implant failure. Among the different approaches proposed to solve this problem, the surface treatment of implants by incorporating bactericidal metal ions (Cu, Ag, Zn) has been studied. Silver is by far the most effective biocidal metal element, acting on a broad spectrum of bacteria (both gram-negative and gram-positive), showing a low tendency to develop bacterial resistance, and inhibiting polymicrobial colonization. Its bactericidal efficacy has been demonstrated against pathogens commonly found in peri-implantitis: S. mutans, S. aureus, S. oralis, P. gingivalis and A. actinomycetemcomitans. Moreover, since ancient times, copper ion has been recognized as a potent bactericidal agent agaisnt a wide range of bacteria, fungi and viruses.

On the basis of the foregoing, in this work, bactericidal surface treatments on titanium grade 4 have been developed by means of silver and copper ion co-implantation using a Metal Vapor Vacuum Arc (MEVVA) ion source. Morphology, structure and silver/copper concentration depth profile were characterized by SEM and XPS as a function of ion implantation voltage and dose. Mechanical properties were analyzed by means of nanoindentation. Electrochemical corrosion tests were conducted in Hank's solution at 37ºC. Cytotoxicity was studied using mammal fibroblasts BALB/3T3. The antibacterial activity against S. aureus and E. coli, and the resistance to the formation of a biofilm composed of the bacteria F. nucleatum, P. gingivalis and A. actimomycetemcomitans was analyzed.

Thanks/Acknowledgement
This work has been financed by the Ministry of the Science and Innovation of Spain under the project BIOIMPLANT project (RTC2019-006803-1)

HELIAG1-O2-093 ● Combination of plasma-polymer thin films and topography to limit bacterial adhesion

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Biofilm is a global problem that affects many different fields and is generally tackled by killing the bacteria. However, another way to fight biofilm is to inhibit the initial adhesion of bacteria. This is commonly seen in nature where many species have developed strategies to inhibit bacterial adhesion. For instance, lotus leaves show self-cleaning properties thanks to a superhydrophobic surface composed of wax crystals which give nanostructuration as well as favourable surface chemistry[1].
Biomimicking these complex surfaces to develop substrates that limit bacterial adhesion and biofilm formation is the aim of this study. To do so, hydrophobic organic thin films are deposited on various silicon-based samples, which can be planar, micro and/or nanostructured.
To carry out a systematic study of the effect of structures on the adhesion of bacteria, microstructures with pillars and lines of different sizes were created by NanoImprint Lithography (NIL) of an organosilicate resin[2]. Additionally, different plasma etching were performed on some samples to induce roughness at the nanometric scale.
Trivinyltrimethylcyclotrisiloxane (V3D3) was used to create thin films, on planar and modified surfaces, using Dielectric Barrier Discharge Cold Atmospheric Plasma (DBD-CAP)[3]. This technique lead to cross-linked thin films with precursor cycle-opening and oxidation, with a Water Contact Angle around 85°. Adjusting the deposition parameters allowed tuning of the surface chemistry. In this study, we also compared DBD-CAP to Initiated Chemical Vapor Deposition (iCVD) which, as it is based on radical polymerisation, did not denature the chemical functions of the V3D3[4].
These substrates were tested against *E. coli* and *S. epidermidis* adhesion. After incubation, LIVE/DEAD staining and fluorescence microscopy was carried out to visualise bacterial adhesion and viability. Poly(V3D3) showed fewer adhered *E. coli* bacteria in comparison to SiO2 substrates, and microstructures seemed to have a bactericidal effect when compared to planer surfaces. However, testing with *S. epidermidis* led to different observations, demonstrating the difficulty of finding a universal antibiofouling surface.

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HELIAG1-O3-122 ● Investigation of the antibacterial properties of silver-doped amorphous carbon coatings produced by low pressure magnetron assisted acetylene discharges

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Hospital-acquired infections are responsible for a significant part of morbidity and mor- tality. Among the possible modes of transmission, this study focuses on environmental surfaces by developing innovative antibacterial coatings that can be applied on interior fittings in hospitals. This work aims to optimize a coating made of an amorphous carbon matrix doped with silver (a-C:H:Ag) produced by a hybrid PVD/PECVD process and to evaluate its antibacterial activity. We present a coating characterization (chemical composition and morphology) as well as its stability in an ageing process and after multiple exposures to bacteria. The antibacterial activity of the coatings is demon- strated against Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) bacteria through several bioassays. Moreover, the data suggest a crucial role of silver diffusion towards the surface and nanoparticle formation to explain the very promising anti-bacterial activities reported in this work.

Thanks/Acknowledgement
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Job, V.; Laloy, J.; Maloteau, V.; Haye, E.; Lucas, S.; Penninckx, S. Investigation of the Antibacterial Properties of Silver-Doped Amorphous Carbon Coatings Produced by Low Pressure Magnetron Assisted Acetylene Discharges. Int. J. Mol. Sci. 2022, 23, 563. https://doi.org/10.3390/ ijms23010563

HELIAG1-O4-153 ● The role of short- and long-lived reactive species on the anti-cancer action of plasma-treated liquids: *in vitro* and *in vivo* applications

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Two methods of plasma cancer treatment have been mainly used: direct and indirect treatments. Direct treatment consists of two phases: the plasma treatment, during which cells, covered by a liquid, are exposed to plasma (Phase I), and the incubation time, during which RONS, generated in or transferred into the treated liquid, interact by diffusion with the cells (Phase II). Indirect treatments consist only of Phase II. During direct treatments, short- and long-lived RONS contribute to cancer cells death. In indirect treatments, only long-lived species, such as H_2O_2, NO_2^- and NO_3^-, are to be considered. The aim of this study was to investigate these two modes of plasma treatment and unveil the role of different RONS on the selective nature and anti-cancer action of plasma-treated PBS (pPBS). We assessed *in vitro* the anti-tumour capacity of direct and indirect plasma treatments, using two models of cancer cells and three normal cell lines [1]. We observed a selective anti-cancer action of the indirect plasma treatment and an anti-selective action of the direct plasma treatment. We demonstrated that the hypersensitivity of normal cells to direct plasma treatment cannot be explained only by the action of long-lived RONS, but it also requires the participation of short/intermediate-lived RONS [1]. Considering the selective nature of the indirect plasma treatment, we decided to use pPBS as an anti-cancer drug both *in vitro* and *in vivo* in combination with electrochemotherapy (ECT). We firstly determined the pertinent storage conditions of pPBS, for which the concentration of the long-lived RONS and, thus, the anti-cancer action of pPBS is conserved for a long period of time. Followingly, we investigated the potential capabilities of the combined application of pPBS and microsecond-pulsed electric fields (µsPEFs) to outperform *in vitro* cell electropermeabilisation, the basis of ECT [2]. We showed that the combined treatment opens the possibility to reduce the amplitude of the µsPEFs, allowing an ECT treatment with reduced side-effects. Finally, the *in vivo* application of pPBS on mice was also studied. We observed that the combination of pPBS and µsPEFs delays the tumour growth and increases the probability of survival compared to µsPEFs or ECT treatments alone.

Thanks/Acknowledgement
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ITEC2-O1-030 ● DLC coatings with tailorable functionalities as a function of sp^3/sp^2 hybridization

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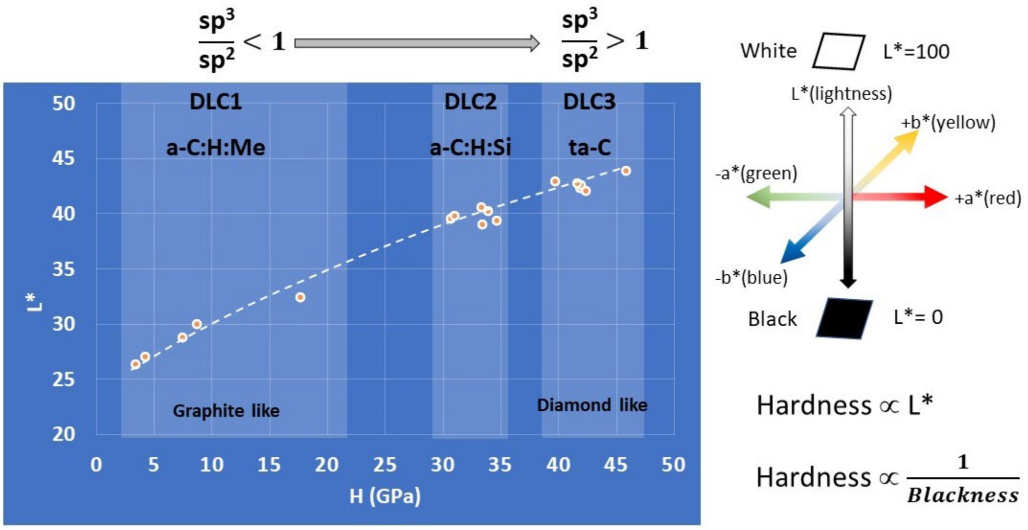
DLC (diamond like carbon) coatings offer a variety of exceptional mechanical (hardness, elastic modulus, friction coefficient), physical (optical, electrical), chemical (chemical inertness), and biomedical (biocompatibility) properties. The greatest advantage of this family of coatings is that their properties can preferentially be tailored by tuning the ratio of sp^3/sp^2 hybridization in the coatings. For example, with 100% sp^3 content, monolithic tetrahedrally-bonded coatings (ta-C) provide the highest hardness, while a-C coatings with $sp^3/sp^2 < 1$ provide softer a-C coatings with low friction coefficient, useful for many applications. PLATIT's advanced coating units, integrating sputtering, arc and PECVD techniques, provides the unique scope to grow a plethora of DLC coatings with varying functionalities, categorized as DLC1(metal doped a-C:H), DLC2(Si doped a-C:H), and DLC3(hydrogen free ta-C with $sp^3 > 50\%$, i.e., $sp^3/sp^2 > 1$). DLC1, with $sp^2 > 50\%$ (i.e., $sp^3/sp^2 < 1$), is grown by sputtering from Ti or Cr-targets in acetylene atmosphere, offering the scratch proof aesthetic black coatings, useful for decorative and biomedical applications. DLC2 is grown by PECVD technique, offering the hard coatings (Hardness = 30-35 GPa, Lc2 = 30 N) for cutting tools applications. DLC2 being grown by PECVD technique, it offers the coating possibilities on difficult parts with complex geometries and miniaturized dimension (e.g., microtools). This is because, PECVD technique, unlike sputtering technique, does not depend on the line of sight of the sputtered species. DLC3 coatings are done by sputtering from C-target at low temperature, providing remarkably high hardness (H) > 40 GPa and Lc2 > 30 N, while coefficient of friction (COF) < 0.2. With such high hardness and low friction coefficient DLC3 offers the best coating solution for machining nonferrous materials. The physical properties of DLC coatings are found to be directly corelated to their color, which is defined in terms of L*a*b* values. Figure 1 shows the variation in hardness of different DLC coatings as a function of L*, where high L* value for DLC3 indicates its higher transparency, attributed to its higher degree of sp3 hybridization compared to that of DLC1 and DLC2.

Hardness of DLC coatings as a function L value.*



ITEC2-O2-168 ● Optical emission spectroscopy of carbon plasma discharged by constant pulse current high power impulse magnetron sputtering

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Diamond-like carbon (DLC) coatings are widely used due to their multifunctional properties such as very low friction coefficient, great hardness, high elastic modulus or biocompatibility. Recently, a high interest in DLC coating deposited using high power impulse magnetron sputtering (HIPIMS) is observed. High carbon ion density in HIPIMS discharge plasma leads to tetragonal bonds of carbon atoms which results in higher hardness and better wear resistance of the coatings. However, a common issue in C sputtering is the occurrence of arcs, which leads to coating defects and drop in coating quality. This effect is even more prominent in high current discharges. A way to mitigate arc occurrence is to use high frequency pulses with short pulse time. Another way to reduce arc count is control of discharge current within the pulse, in order to avoid “runaway” region, where spontaneously jump of the discharge current is observed[1]. Active current control allows use of longer pulses thus higher deposition rate due to increased duty cycle.

This work focuses on determining the effect of the duty cycle, pulse time, frequency and peak current on the carbon ionization. Using a graphite target, OES spectrums of HIPIMS discharge in argon atmosphere for various power supply parameters was observed. Initially, peak current density was increased from 0,5 to 2A/cm2. Following, pulse time and frequency were varied between 5 – 200 µs and 300 – 10’000 Hz respectively. Finally, HIPIMS OES spectra were compared to pulsed DC discharge spectrum. Additionally, the quartz crystal microbalance investigations show increasing deposition rate with increasing pulse time.

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ITEC2-O3-078 ● Optimized cylindrical Inertial Electrostatic Confinement plasma source for thin film applications

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For many decades, plasma sources with electrostatic inertial confinement (IEC) have been investigated for space propulsion [1, 2] and fusion reactors [3]. Depending on the geometry of the source, an emitting plasma plume can be generated [4]. This plasma plume can be used for surface treatment, such as thin film deposition and surface etching [5]. Another possible application is the ionization of the sputtered metal flux during magnetron sputtering in ionized physical vapor deposition processes. For this purpose, an application-oriented cylindrical IEC plasma source was developed and characterized. With particle-in-cell simulations the general operating principle of the IEC plasma source in cylindrical form was identified and the plasma properties in the center of the source as well as in the plume determined. Furthermore, the operating pressure of the source can be adjusted by varying the geometrical properties such as cathode diameter and cathode voltage. With these parameters, simultaneous operation with conventional magnetron sputtering is possible resulting in improved coating properties. A proof of concept with sputtered chromium is shown.

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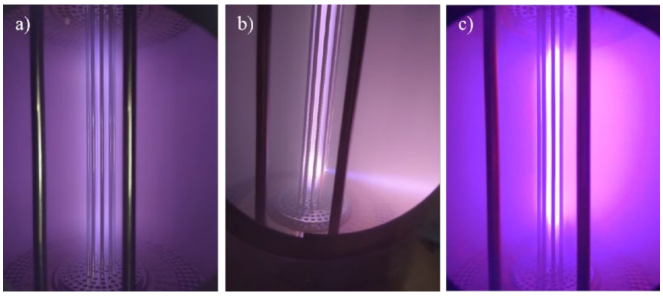
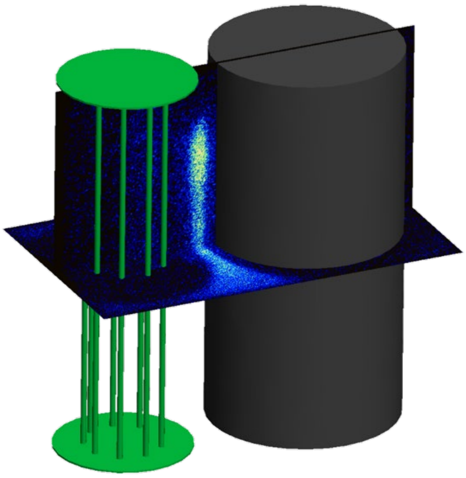


Operating modes of the cylindrical IEC Source



Simulation of the IEC-source for coating

ITEC2-O4-125 ● Deposition of SiOx based functional thin films for adhesion promotion and corrosion resistance using atmospheric pressure plasma jet

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To reduce Volatile Organic Compounds (VOC) emission coming from solvent cleaning and chemical primer application prior bonding, atmospheric plasma processes have been more and more considered in the industry and identified as environmental friendly processes able to remove organic contaminations and at the same time increase the surface energy of the treated surface. Moreover, atmospheric plasma processes (figure 1) can also be considered to deposit functional coatings such as barrier coatings, adhesion promoter and anticorrosion layers [1,2]. To improve the coating performance and consider them for industrial application it is necessary to understand the influence of deposition parameters on the coating composition and at the same time the thickness of the films deposited.

The influence of deposition parameters on the anticorrosion properties of plasma polymerized SiOx thin films on Aluminium surfaces is reported in this study. Influence of the thin film thickness characterized by ellipsometry and film composition characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) will be discussed. Using ellipsometry characterization and with a silicon dioxide model approximation, the film thickness on Si wafer was estimated at 400 nm and coated aluminium samples were able to withstand up to 720 hours in salt spray chamber environment. Moreover, an overview of actual challenges and a presentation of different application of plasma deposited coatings for anticorrosion and adhesion promotion as alternative environmental friendly process for the industry will also be presented.

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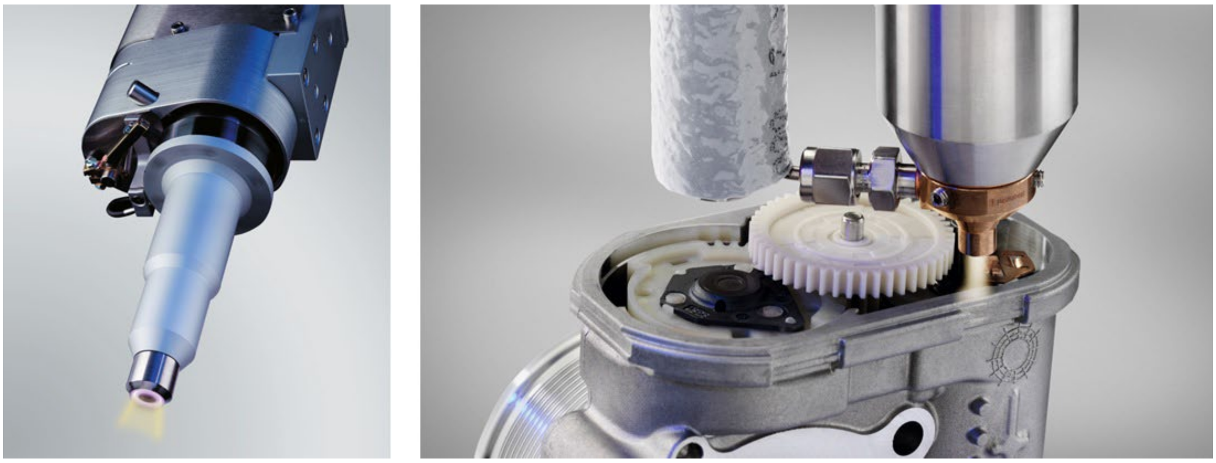


Atmospheric pressure plasma processes

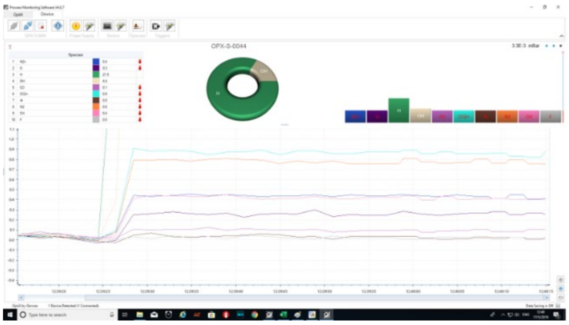
ITEC2-O5-171 ● Remote optical gas sensing to improve plasma and thin film quality & repeatability

N. Kaabeche[1], D. Monaghan[1], J.O.S.E.P. Brindley[1], B. Daniel[1], V. Bellido-Gonzalez[1]
Gencoa Limited - LIVERPOOL (Royaume-Uni)

Thin film vacuum coating is extremely sensitive to moisture and contamination in the process chamber. Film quality, repeatability and properties (i.e., composition, thickness, roughness, conductivity) along with productivity can be severely affected by leaks and contamination.
Direct sensing in the plasma is not always possible and quadrupole RGAs are not suited for sensing at process pressure. They also are difficult to implement for industrial process monitoring and difficult to maintain.
An alternative gas sensing technique that operates at a wide range of pressures up to 0.5mbar has been built around remote plasma emission monitoring – called the OPTIX device (show inGencoa-Optix-0456-1200px.jpg).
This technique involves the generation of a small sized remote plasma using an inverted magnetron within the gas sensor. Consequently, species that are present within the vacuum become excited in the sensor's plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species.
the OPTIX has already used in the monitoring and control of industrial coating PVD processes for various applications (photovoltaics, semiconductor, decorative coatings, electronics, bio medical coating etc)
This presentation will demonstrate that this versatile sensing method is robust and sensitive in magnetron sputtering environments and additionally for use in ALD. It also benefits from user friendly, clear live data visualisatiuon as sowhn in picture Optix screen shot.png.
The talk will highlight the use of the OPTIX for close loop control of the deposition process.

Thanks/Acknowledgement
Joespeh Brindley
Benoit Daniel

Gencoa optix



Gencoa optix partial pressure

PL5 ● Low temperature plasmas for conductive carbons and multimaterials

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Low-temperature plasmas are used in a wide variety of applications ranging from the production of astro-analogs, interface systems and renewable energy systems, to applications in biomedicine, electronics, micromaterial processing and photovoltaics. The use concerns mostly the functionalization, activation, cleaning and etching of surfaces and the deposition of thin films. In addition, an important aspect of basic plasma research concerns the synthesis of nanoparticles in the bulk of the plasma and the growth of 2D and 3D structures on different surfaces.

Despite the successful use of low-temperature plasmas in industrial applications, the tailored synthesis of materials remains an exciting challenge that requires a deeper understanding of the underlying plasma chemical and plasma physical processes in all stages of the process. An Important factor in this context are the impurities, or for example, the conditions of the walls of the plasma reactor and their great influence on the results of the material synthesis.

Characterization and monitoring of the plasmas by means of e.g. optical emission spectroscopy, plasma (ion) mass spectroscopy or microwave interferometry is therefore an indispensable prerequisite for the controlled production, *leading to tailored conductive carbon materials (2d and 3D), or multimaterials as for example MoS2/graphene structures for cells and Al ion batteries.*

Authors acknowledge the project PEGASUS (Plasma Enabled and Graphene Allowed Synthesis of Unique nano- Structures), funded by the European Union's Horizon research and innovation programme under grant agreement No 766894 and the EU Graphene Flagship FLAG-ERA III JTC 2021 project VEGA (PR-11938), Slovenian Research Agency for the program ARRS No. P1-0417 , Z2-4467; HZB for the allocation of synchrotron radiation beamtime at the HE-SGM beamline of BESSY II, and also for support obtained via ARD MATEX Region Centre.

PROC3-O1-061 ● Investigation of ionized metal flux fraction at industrial conditions

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Ionized metal flux fractions (IMFF) were analysed by a biasable quartz crystal microbalance [1,2] and the saturated ion flux was measured by flat Langmuir probe. The experiments were performed at industrial conditions employing deposition system developed by company SHM (Sumperk, Czech Repulic) which was equipped with a titanium cylindrical rotating target with a racetrack area of approx. 100 cm2. A very efficient target cooling system allowed to deliver the DC power of up to 35 kW to the central sputtering cathode, which resulted in an ionized metal flux fraction of 23 percent measured at the substrate level. This value is extremely high and is close to the values achieved typically by high power impulse magnetron sputtering (HiPIMS) technology. The measurement of this high value contradicts the generally accepted statement that the IMFF in a DC magnetron sputtering is typically only a few percent at the substrate level [1,2,3]. It is explained by the possibility of using extremely high-power density due to the technical advantages of this equipment. In this contribution, we also show the results of a systematic study where the dependence of the IMFF on the pressure and power supplied to the target was investigated. IMFF increases linearly with power and decreases slightly with pressure. We also show the possibility to increase the IMFF by up to 10 percent using a hybrid deposition system combining lateral glow discharge with magnetron sputtering, which allows to independently control the ion and the neutral fluxes on the substrate [4].

Thanks/Acknowledgement
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PROC3-O2-071 ● Study of the ion energy distribution in the ALE process of GaN

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Atomic Layer Etching (ALE) on GaN consists in modifying the upper monolayer to enhance its removal using Ar ions. Fluorine-based gases such as SF_6 can modify the GaN and form GaF_x molecules [1]. The ALE precise control in the removal step depends on the ion energy. We correlated experimental conditions of ALE for GaN to its Ion Energy Distribution Function (IEDF) measured by a Retarding Field Energy Analyzer (RFEA) to optimize the removal. The reference energy is the sputtering threshold of the GaN (YGaN), around 40 eV [2]. Two configurations of the ALE process using inductively coupled plasma (ICP) are described. We positioned the RFEA in the reactor at two heights from the plasma source: one at 12 cm (high position) and the other at 20 cm (low position). The IEDFs comparison is in the Figure below. The maximum ion energy peak of the RFEA bimodal distribution should not be significantly higher than the YGaN. Otherwise, the etching selectivity between the modified layer and the pristine material is poor. The removal doesn't cease after all the modified layer is etched, and the self-limiting is not observed.

Consequently, the average ion energy should be around 40 eV with the low disparity of the two peaks [3]. The low position shows a great portion of energetic ions reaching 80 eV that can influence the selectivity. In the higher position configuration, the self-limiting regime is reached during the removal. Also, the synergy is 78 %, compared to 35 % in the low position. Several measurements demonstrate the optimized ion energy can reduce contaminations during the etching and avoid remaining residues of the modified layer.

Thanks/Acknowledgement
The authors would like to thank the European Union (IPCEI), the French region of Centre-Val de Loire, CERTeM 2020, the University of Orléans, and GREMI for their support and funding in Nano2022 project.

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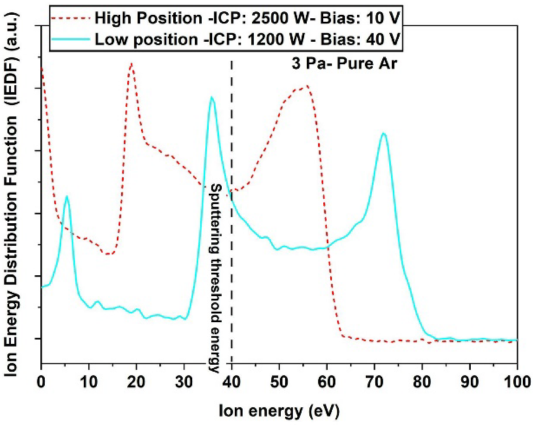

IEDFs for diferent position in an ICP reactor

PROC4-O1-033 ● Plasma chemical reactions governed by the specific energy input

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A low temperature plasma provides highly non-equilibrium conditions, meaning that the light particles, the electrons, pick up energy from the electric field in collisions with the heavy particles, the gaseous atoms and molecules. While the latter might remain close to room temperature, the electrons gain high kinetic energies that must be sufficient for ionizing reactions to sustain the plasma. For molecular gases, an average energy per heavy gas particle is thus available in the plasma, known as specific energy input (SEI), yielding plasma chemical reactions by inelastic collisions (excitation, dissociation, and ionization). Since the mean free path lengths for such activation reactions follow a distribution law, the probability for the activation mechanism can be described by a simple Arrhenius-like equation, where temperature is replaced by SEI. The potential of this approach is demonstrated on the basis of plasma polymerization of siloxane and hydrocarbon thin films (and others).

Hexamethyldisiloxane (HMDSO) has been well studied in the past revealing insights into the plasma chemical reaction pathway, which can thus be used as a model monomer following Arrhenius-like behavior [1]. Since actual plasma polymer film growth also involves the sticking probability of the film-forming species that are converted in the plasma, this parameter becomes accessible by comparing, for example, plasma polymerization with different hydrocarbon molecules. It is demonstrated that C_2H_4 and C_2H_6 approach the same chemical reaction pathway as observed for C_2H_2 for sufficiently high SEI.

Finally, an outlook is given about the applicability of the presented approach for plasma CO_2 conversion. Additional energy can be transferred by inelastic collisions among the many vibrationally excited CO_2^* species which can further enhance conversion for energies below the dissociation enthalpy [2]. Thus, enhanced energy efficiencies have been observed, which will be discussed regarding efficiency as a function of conversion based on Arrhenius-like behavior. The optimum that can be achieved by electron impact activation in low temperature plasmas is thus indicated that can be compared to additional ways of energy transfer, probably depending on certain constraints.

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PROC4-O2-095 ● Analysis of low-pressure misty plasma processes by optical emission spectroscopy

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Nanocomposite materials are considered one of the most effective ways to achieve multifunctionality in thin films. Many different strategies aiming for the growth of high-quality nanocomposite thin films were developed in the last few years. One of them consists in combining sol-gel-synthesized nanoparticles and plasma deposition [1]. In these 'misty' plasma experiments, liquid colloidal solutions are injected as droplets during matrix deposition, as a direct supply of nanoparticles.

We recently developed such a hybrid reactor, operating in the mTorr range, for the growth of high-purity inorganic nanocomposites [2]. Although film growth is now fairly well understood [3], the impact of liquid injection itself on the plasma species still calls for attention. In this work, we present the time-resolved spectroscopic analysis of the plasma's behavior after liquid injection.

1-ms pulses of various pure liquids (water, methanol, propylene carbonate) were injected at different temperatures in 3-mTorr plasmas generated from pure Ar or O_2/Ar mixtures. In oxygen-containing plasmas, actinometry is used to probe the evolution of O atom population. In pure Ar plasmas, the evolution of metastable species density was obtained as a function of time using a simple gain/loss model and adequate spectral lines ratios.

The immediate effect of liquid injection was a sharp increase in pressure due to evaporation, leading to a decrease in electron temperature and therefore on Ar signal. During this first, swift disturbance, the number of oxygen atoms was found to increase, before decreasing on a slightly longer timescale (~ a few seconds). We ascribe the excess O atom population to modified loss dynamics at the reactor walls, and correlate its timescale to typical evaporation rates [3]. Indeed, results show that the transitory effects due to liquid injection are strongly dependent on the droplets' initial temperature and overall evaporative properties. High-volatility liquids produced short but distinct changes, whereas propylene carbonate had a more modest, slower effect.

Thanks/Acknowledgement
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PROC4-O3-105 ● How carbon nanoparticles affect the behaviour of the plasma electrolytic oxidation process

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It is now well established that oxide layers grown by plasma electrolytic oxidation (PEO) of valve metals (e;g. Al, Mg, Ti, Zr) exhibit a high porosity resulting from the numerous micro-discharges that ignite on the metal-oxide surface. Nanoparticles previously dispersed in the PEO electrolyte can be inserted in that porosity, thus providing the coating with new or enhanced properties depending on the nature and properties of the particles [1]. While the influence of nanoparticles on the coating properties has been rather well reported, the effect of NPs on the behaviour of the PEO process was much less investigated. This work aims at investigating the PEO of aluminium performed under current control mode within a suspension of carbonaceous nanoparticles, especially carbon nanotubes (CNT) and carbon black (CB). The work focuses on the transition from arc regime to the so-called "soft" regime [2].

Results show that the presence of carbon particles promotes an earlier transition from arc to "soft" regime, which has never been reported before. This is particularly noticeable when looking at the variations of the voltage amplitude that exhibits a more or less sharp decrease at the transition (figure 1). Meanwhile, the presence of CNT or CB particles results in a change in the morphology of the oxide coating, together with a change in the global growth rate [3].

Conversely, a too high concentration of particles in the electrolyte is shown to be detrimental to the coating morphology that exhibits therefore large craters and defects, thus proving that an optimum in carbon particle concentration exists.

Finally, the correlation between the ex-situ characterization of the coatings and the in-situ electrical response during the PEO treatments allows further understanding of the mechanisms of the "soft" regime appearance as well as the mechanisms of carbonaceous nanoparticles incorporation into the PEO oxide coating.

Thanks/Acknowledgement
This work is supported by the French National Research Agency under contract ANR21-CE08-0029.

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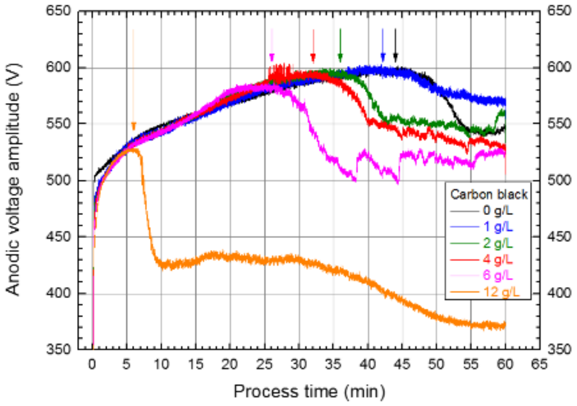

Figure 1. Variations of the anodic voltage amplitude over a one-hour PEO process for various carbon black nanoparticle concentrations in the electrolyte. Arrows indicate the beginning of the transition from arc to soft regime.

PROC4-O4-087 ● Nanocrystalline diamond coatings of titanium and titanium alloys for biomedical applications using distributed antenna array microwave system

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Biomaterials are intended to interface with biological systems to evaluate, treat, augment, or replace any tissue or organ of the body. Among the metals used in biomaterials research, titanium possesses the best combination of mechanical and biocompatible properties. However, the performance of titanium biomaterials can still be improved because some titanium implants integrate incorrectly into the surrounding bone tissue, loosen over time or cause severe inflammatory responses. To address this problem, titanium surfaces can be modified or coated to enhance cellular behaviour on the biomaterial. The use of Nano-Crystalline Diamond (NCD) films would be a new way to overcome these problems since they combine surface smoothness, high hardness, low friction coefficient and biocompatibility suitable for biomedical applications.

Among the microwave processes operating in $H_2/CH_4/CO_2$ gas mixture and allowing the synthesis of diamond films on large surfaces and at low substrate temperature, the distributed antenna array (DAA) microwave system, composed of 4x4 source planar matrix, permits to achieve NCD coatings down to 100°C on 4-inch wafers. It has shown its efficiency for NCD growth on conventional (silicon) and unconventional 2D and 3D substrates (stainless steel, polymeric material, piezoelectric multilayered structures, glasses…) [1,2]. Such microwave system design provides high density plasma and presents the advantage to be scaled up to very large dimensions without limitation [3].

In this work, we carry out a thorough characterization of a DAA reactor under conditions suitable for NCD growth, especially on 3D complex-shaped substrates, through experimental diagnostics and plasma modelling. Optical emission spectroscopy, infrared absorption spectroscopy and Langmuir probe measurements are conducted in order to estimate the gas and electron temperatures and the density of some key-species such as CH_3, H and electrons. A 2D self-consistent plasma model [4] is used to further describe the synthesis discharge, especially in terms of spatial homogeneity of temperatures and densities as a function of the gas pressure and microwave power. The microstructure of NCD films grown on titanium and titanium alloys and the biocompatibility of such NCD-coated systems are assessed and point out promising results in terms of surface topography, cytotoxicity, cell adhesion and osteointegration.

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PROC4-O5-055 ● Reduction of oxide using an electron cyclotron wave resonance Ar/H_2 plasma - towards lunar raw materials use for H_2O production

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As a necessity for humankind for interplanetary travel and to sustain life on other planets, it is imperative to establish sustained habitation and industrialisation of the Moon. Therefore, the Moon is soon to become important first link of the chain for the future explorations of solar system with human crew. As such, there is a need in developing processes to use in-situ primary resources because the transportation of goods from Earth is not economically viable. Consequently, In Situ Space Resources Utilisation (ISRU) becomes crucial. One of the most important aspects is the production of O2 for use as breathable oxygen, in life support system and for rocket fuel. Lunar soil, or so-called regolith, is mainly composed of metal inorganic oxides such as SiO2, MgO, CaO, FeO, .. which makes it a readily available source of oxygen.

Among the different existing processes to extract oxygen (pyrolytic, electrolytic,...) from oxide material, H2 plasma reduction of lunar soil producing water is very attractive. H2 plasma processes provide atomic H, which is very efficient for metal oxides 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 these sources provide a high dissociation rate of diatomic gases.

This work focuses on the plasma-oxide interaction with the aim of understanding the mechanisms at stake as well as to optimise the reduction process. The plasma is monitored through Optical Emission Spectroscopy whereas the reduction of oxide samples is investigated using XPS, FTIR and XRD. Various oxide samples such as Iron Oxide thin films and lunar regolith simulants pellets are used. Several experimental parameters are explored (pressure, power, gas mixture) and correlation between plasma observation and reduction efficiency are done

Experimental results point out the high importance of plasma gas mixture composition as well as the strong influence of the pressure on the reduction kinetic. The presented experimental findings will contribute to the development of the processes mandatory to establish a permanent human presence on the Moon.

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GROM1-O1-160 ● Molecular dynamics approach for the calculation of surface loss probabilities during the growth of C:H films from an argon-methane plasma

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Low-temperature hydrocarbon plasmas are media where a large variety of different species coexist, encouraging their use in many different applications requiring the deposition of thin films or the synthesis of nanoparticles and nanocomposites [1]. The complex chemistry occurring in these plasmas makes their understanding and controlling rather difficult, as it involves reactions in both the plasma volume and on the surrounding surfaces. The present work deals with molecular dynamics simulations of the interaction of the main neutral species previously obtained using a 1D fluid model [2] (H_2, CH_4, C_2H_4, C_2H_2, CH_3, and C_2H) of an argon-methane plasma with the grounded electrode of a capacitively-coupled rf discharge. Simulations were performed by sending all the species (49200 molecules) towards the surface, at a rate of one molecule every 2000 time steps (i.e. every 500 fs), taking into account the molar fraction of each species. The study was carried out at temperatures from 300 K to 1000 K over a total simulation time of 26 ns. The results showed that the C_2H radical is the main precursor of the film growth even if its bonding coefficient progressively decreases as the film grows due to an increased probability of formation of volatile species after its interaction with the surface. The CH_3 radical very little contributes to the film growth as most of these molecules interact with the surface to give new volatile species. The stable molecules such as CH_4 and C_2H_4 are mainly reflected from the surface as they are, except at 1000 K where they can be fragmented after their interaction with the surface. A summary of the surface loss probabilities (due to sticking and recombination) [3] of each species on the electrode covered by a C:H film is presented in the figure 1 below.

Thanks/Acknowledgement
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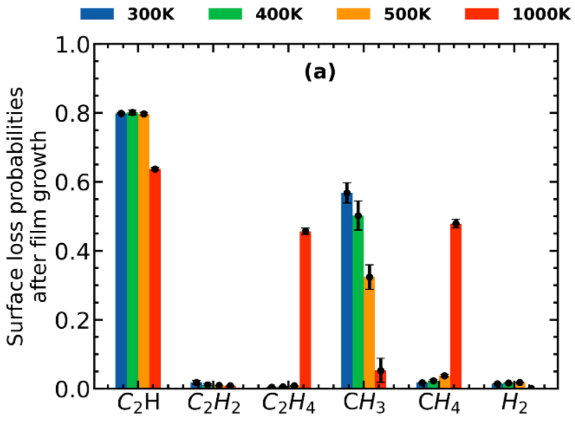

Surface loss probabilities of the initial species

GROM1-O2-116 ● Multi-level investigation of the formation of silicide interface during Cu/Si energetic deposition process; a combined ab-initio, molecular dynamic, in-situ stress measurement and kinetic Monte Carlo simulation study

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Nowadays, research in the field of nanoscale thin film growth is exceptionally active as new emerging fields related to plasmonics or energy-harvesting applications rely on a 3D integration of nanoscale layers into complex architectures for the next generation of electronic devices. It is well established that there exists a complex dependence of the film microstructure and the resulting properties on the deposition conditions (kinetic energy of the deposited particles, substrate temperature) and on the chemical interaction with the substrate (surface reactivity, adatom mobility, intermixing)[1,2].

Here we want address fundamental questions on the complex interplay between alloying formation, growth morphology and stress generation occurring during the initial stage of the growth of copper (Cu) ultrathin films. To this end, a multi-level investigation, combining multiscale atomistic simulations and real-time experimental characterizations, has been implemented..

We have first determined the reactivity of Cu adatom on the silicon (100) surface by calculating the adsorption energy landscape by density functional theory (DFT). Stable atomic configurations, activation barriers of the surface driven mechanisms, as well as intermixing mechanism give the first clues to the formation of a silicide interface.

In a second level, molecular dynamics calculations have been performed to simulate the growth of Cu onto amorphous silicon (a-Si) substrate for different deposition angles and energies of incoming particles. Results suggest that an interfacial silicide layer initially forms stages at low angle (up to 25°) and low energy (up to 25 eV). It consists a Si-rich layer "floating" underneath the surface. This finding will be compared to real-time wafer curvature measurements during growth of Cu on a-Si which clearly show a change in stress evolution below 2 nm compared to growth on SiO2.Complementary TEM observations are in progress to study the structure of this interlayer.

In order to rationalize these observations, the dynamic formation of this intermixing layer has been investigated using kinetic Monte Carlo simulations. The influence of the incident angle of the particle flux and the substrate temperature regarding surface roughness evolution will be also discussed.

Thanks/Acknowledgement
This work has been done in the framework of the INTEGRAL 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. This work was also supported by the French government program "Investissements d'Avenir" (EUR INTREE, reference ANR-18-EURE-0010). This work was supported by the French government program « Investissements d'Avenir » (LABEX INTERACTIFS, reference ANR-11-LABX-0017-01).

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GROM2-O1-112 ● Nanostructured plasma polymers fromcCitronellal: the role of substrate’s chemistry

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The use of bio-based precursors for plasma polymerization allows to bring a recognized coating technology closer to the demands for sustainable procedures. One type of promising bio-based functional polymers derives from plant secondary metabolites[1]. Among those, a component of several essential oils, citronellal is a monoterpene containing an aldehyde functional group. Those chemical properties make citronellal a prospective precursor for functional polymers. 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. Furthermore, the effect of the chemistry of the substrate’s surface on the morphology of the plasma polymers was assessed. At the same deposition condition and position in the reactor, the formation and growth of plasma polymers was affected by the substrate chemistry that was either methyl- or hydroxyl-terminated. The analysis of the growth of the nanostructures formed in methylated surfaces revealed a distinguishable growth in the normal direction to the surface, leading to nanostructures that grow with increasing deposition time. A different behavior was observed in hydroxyl-rich surfaces, in which by increasing the deposition time the nanostructures disappeared and a homogeneous thin film was formed (Figure 1). Those results highlight that tailoring surface chemistry is an effective strategy to control the formation and growth of nanostructures through plasma polymerization. The formation of nanostructures during plasma polymerization have been previously analyzed as a function of some characteristics of the plasma phase[2], but the consideration of the surface chemistry diversifies the variables that have to be considered in such complex analysis. This work is part of the efforts from our research group to complement that knowledge.

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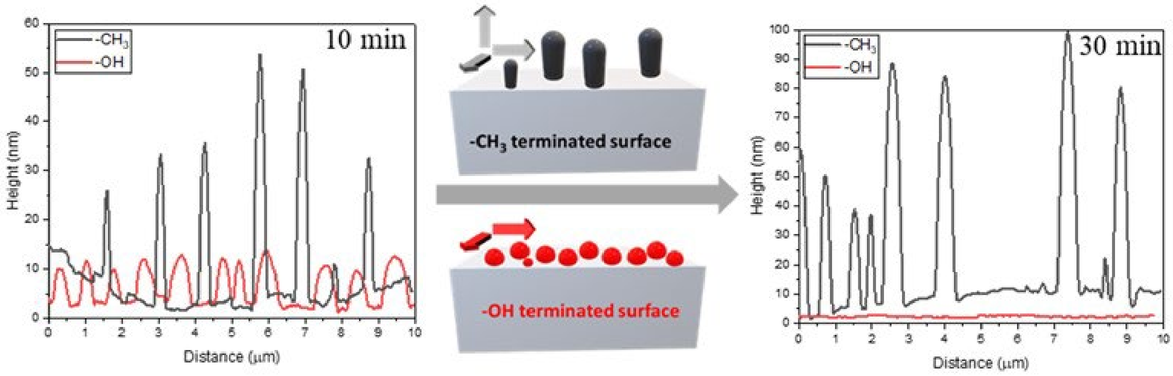
Figure 1: AFM roughness profiles



GROM2-O2-046 ● Polymerization mechanisms in complex geometries using HMDSO low-pressure plasmas

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Hexamethyldisiloxane (HMDSO) low-pressure plasmas are known due to their versatility to deposit plasma polymer films with different properties and applications [1]. Although they have been studied since decades, the reaction mechanisms of plasma polymer formation remain unclear, even more when 3D materials with complex geometries such as undercuts and cavities are used as substrates. In the present study, the polymerization mechanisms of HMDSO without and with O_2 admixture have been studied in low-pressure plasmas. The experiments have been carried out in a RF plasma reactor with a parallel-plate set-up with the substrates placed on the bottom electrode. To simplify the study, the main operating conditions have been fixed: flow rate of the monomer (2 sccm HMDSO), HMDSO to O_2 ratio (1:10), pressure (7 Pa), and applied power (30 W). Inspired by the traditional cavity technique, [2] two configurations named as *undercut* and *cavity* (see Figure *(a)* and *(b)*, respectively) have been selected as substrates to study the influence of ion bombardment, diffusion of film-forming species, and surface reactivity. The study of these geometries can shed light on the coating of 3D materials (e.g., scaffolds or textiles), [3] of high interest for biological applications. Although ion penetration is usually not considered in similar studies [2,4], the obtained results and additional etching experiments indicate that ion effects still need to be considered underneath small openings. Furthermore, a varying spatial chemical composition of the polymer along the *undercut* indicates, on the one hand, the different sticking probability of the film-forming species for HMDSO plasmas, and, on the other hand, the relevance of oxidizing chemical reactions taking place at the surface inside the configurations when O_2 is added to the plasma.

Thanks/Acknowledgement
M.B. thanks the OP RDE that finances the project Quality Internal Grants of BUT (KInG BUT), Reg. No. CZ.02.2.69 / 0.0 / 0.0 / 19_073 / 0016948.

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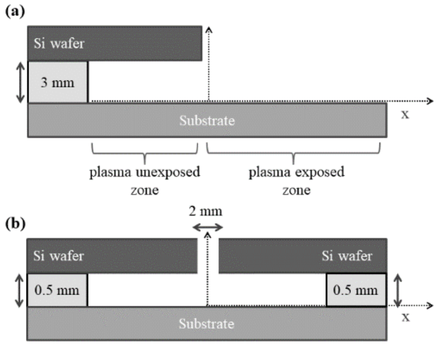

Experimental configurations

GROM2-O3-147 ● Boron-carbon thin films deposited via plasma-enhanced atomic layer deposition (PE-ALD)

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Boron carbide (B_xC) finds diverse applications due to its superior hardness, high neutron absorption, and semiconducting nature. The band gap for boron-rich B_xC films is known to increase with an increasing B:C ratio. Magnetron sputtering[1], and high temperature (≥ 1000 °C) chemical vapor deposition (CVD) are the conventional processes to obtain boron carbide thin films. CVD involves boron hydrides[1] or halides[2] as precursors along with dihydrogen or simple hydrocarbons. Such precursors come with challenges such as high toxicity and/or corrosive by-products. Furthermore, conformality and thickness control of these films is still a challenge. To overcome it, atomic layer deposition (ALD) appears as a technique of choice, however, B_xC has never been synthesized by this technique so far.
From triethylborane (TEB) and hydrogen gas (H_2) as precursors, amorphous B_xC thin films with atomic-level thickness control on Si 100 substrate using plasma-enhanced atomic layer deposition (PE-ALD) are successfully obtained. The use of hydrogen plasma to remove ethyl groups of TEB to deposit B_xC films at low substrate temperatures (≤ 200 °C) is demonstrated. It should be noted that in this process the expected by-products are non-toxic and non-corrosive.
Here, the influence of the deposition parameters on the film growth rate, composition and structure will be discussed. The ALD reaction temperature is investigated between 150 °C and 250 °C alongside spectroscopic ellipsometry. Additionally, the pulse/purge of precursors is optimized to ensure a saturated self-limited surface reaction, and the role of H_2 concentration and plasma power in the composition and growth of the deposit is explored.
In-situ optical emission spectrometry (OES) is also performed to detect and compare the intensity of hydrogen lines, and to look at species responsible for etching and deposition during the ALD cycle. The impact of plasma-activated hydrogen species (as a function of plasma power and H_2 concentration) on the morphology and B:C ratio of the deposits is preliminarily assessed via secondary electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Moreover, surface-sensitive quantification and bonding information are obtained via time-of-flight secondary-ion mass spectrometry (ToF-SIMS) and ex-situ x-ray photoelectron spectroscopy (XPS).

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GROM2-O4-035 ● Study of III-V thin films growth directly on silicon by remote-plasma CVD: Towards a reduction in solar cell industrialisation costs

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Solar cells based on III-V materials have reached the highest efficiency of any solar technology available today [1]. Nevertheless, their cost is a hundred times higher than that of c-Si solar cells [2]. Most of this cost difference comes from i) the substrate required to grow a single crystal layer and ii) the growth process. In a recent project we have shown how the use of a virtual substrate can tackle the first part of the challenge [3]. In this work, we address the second one. To this end, we have developed a new strategy for the epitaxial growth of III-V materials by using Remote-Plasma Chemical Vapor Deposition technique (RPCVD). Indeed, plasma use allows us to work at lower temperatures thus reducing thermal stresses and thus defects. Moreover, this process enables low pressure operation, which reduces drastically the precursor consumption when compared to classical Metal Organic CVD (MOCVD).
Recently, we have shown that it is possible to grow gallium nitride (GaN) films by RPCVD at rather low temperature (500°C). By tuning the deposition conditions, thanks to a large number of parameters such as precursor flow rates, plasma power, chamber pressure, substrate and trimethylgallium bubbler temperatures, we were able to grow GaN layers directly on silicon substrates. An Optical Emission Spectroscopy (OES) study was carried out in order to qualify the ICP plasma source of the reactor. The obtained thin films show columnar grain structure and uniform Ga and N depth profiles with Ga/N ratio close to 1:1. The crystalline quality is promising with a preferred growth orientation along the c-axis of the wurtzite structure. An arsine line has been added to the RPCVD reactor in order to move on to the study of GaAs growth, the results of which would be presented at the Plathinium conference.
Our preliminary results raise the prospects of a more affordable method for the growth of III-V materials, with the potential to obtain large-scale epitaxial films, thus addressing the important issue of costs for III-V device industry.

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GROM2-O5-053 ● Sputtering and annealing of Mg_2SiO_4 films as proxy of pristine component of the Solar System

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Several meteorites of carbonaceous chondrite groups host Amoeboid olivine aggregates (AOAs), a pristine object formed by condensation in the early Solar System. A series of high temperature annealing of amorphous Mg_2SiO_4 films under argon atmosphere were used to explore further possible mechanisms responsible for the formation of AOA in chondrites [1-3]. This presentation is a highlight of how material science can contribute to cosmochemical studies.

Deposition of amorphous Mg_2SiO_4 films was done using magnetron sputtering by an Alliance Concept EVA450 for thickness ranging from 1 µm to 1.5 µm. Films were subsequently annealed for different durations between 800 and 1325°C under Ar atmosphere.

Scanning electron microscopy (SEM) images show an evolution for the surface topology of the Mg_2SiO_4 polycrystalline film from a dendritic morphology (Fig. 1a) at low temperature to an equiaxed morphology for temperature above 1200 °C (Fig. 1b). Crystallographic study using Transmitted electron microscopy (TEM) showed a variation in crystallite sizes when annealed at 900°C, with longitudinal shape from few up to several hundred of nm. Films annealed at 1200°C presents more well-defined crystallites of homogeneous sizes with equiaxial morphology. Annealed films at higher temperatures - i.e. 1300°C – are also composed of equiaxial crystallites with an increase in size, up to 1 µm (not shown). Annealing temperature is thus a key element in the crystallite formation to obtain homogeneous shapes with equiaxed growth, with a threshold between 900 °C and 1200 °C.

Magnetron sputtering of Mg_2SiO_4 films were used to simulate chondrites meteorites formation. Annealings at different temperatures to study mechanisms involved in the crystallization. Homogeneous equiaxial crystallites of hundreds of nm were obtained at 1200 °C, as confirmed using SEM and TEM. Synthesized crystals overall present similar morphologies and size dispersion compared to natural AOA.

Thanks/Acknowledgement

The work was carried out in the O-Return project and supported by UCAJEDI Investments in the Future both funded by French Agence Nationale de la Recherche with respective numbers ANR-21-CE49-0005-02 and ANR-15-IDEX-01.

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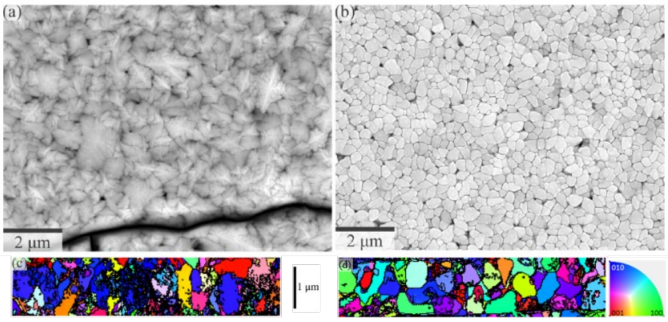

SEM and cross-section at (a,c) 900 (b,d) 1200°C

PL5 ● How reactive species from cold plasma are transported into liquid water bulk/aerosol

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Atmospheric air plasma produces a cocktail of reactive oxygen and nitrogen species (RONS) with multiple functions relevant to applications in biomedicine, agriculture, air and water cleaning, matertial treatment, etc. In plasmas interacting with liquids, the transport of RONS into the liquid through plasma–liquid interface can be significantly enhanced by converting bulk water to aerosol microdroplets [1]. The expected solubility of various RONS with different Henry's law coefficients is very different. We verify the applicability of Henry's law coefficients under strongly nonequilibrium conditions characteristic of plasma–liquid interaction, with water in the form of bulk vs. nebulized or electrosprayed microdroplets. This fundamental understanding can lead to optimized designs of plasma–water interaction systems for multiple applications in biomedicine, environment, and agriculture.

Figure 1 shows the schematic diagram of elementary processes of ionization, excitation and dissociation in air plasma, the formation of radicals and other RONS, as well as their mutual reactions in the gas phase. Then it shows their transport into the liquid water based on their solvation, indicating the Henry's law coefficients. Finally, in the liquid, the plasma-formed, as well as the new ionic RONS, diffuse and undergo further reactions. The RONS transport processes in water are compared in the bulk and in two types of microdroplets: charged ones produced by electrospray (ES), and nebulized non-charged microdroplets. The amount of H_2O_2(aq) and NO_3^-(aq) (mainly from gaseous HNO_3) dissolved in the nebulized microdroplets was ~1 order of magnitude higher compared to that in the ES microdroplets because it was enhanced by their larger plasma–water interface area. On the other hand, the production of NO_2^-(aq) (mainly from HNO_2 [2]) is higher in the charged ES microdroplets, which indicates the importance of the charge effects and ion mobility.

Thanks/Acknowledgement
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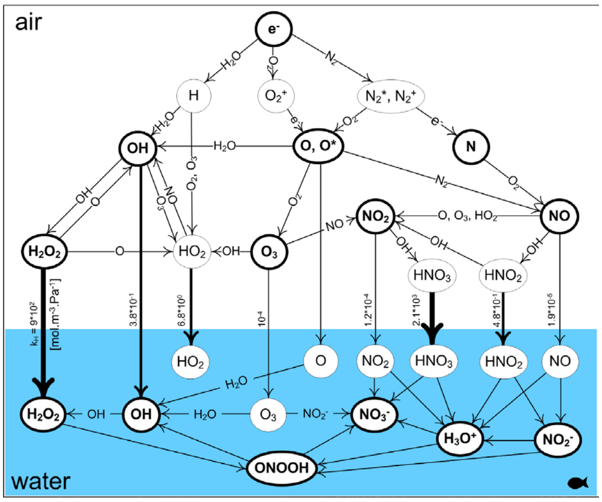

Plasma-liquid chemical and transport processes

LIQU1-O1-077 ● Gas phase properties and plasma-liquid interactions during DC and pulsed sputtering onto glycerol

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Pt nanoparticules (NPs) are commonly used as catalysts in electrochemical systems like proton exchange membrane fuel cells (PEMFC) for oxygen reduction reactions (ORR). NPs can be produced through physical, chemical, or physicochemical methods. Chemical methods offer control over NPs shape and size but often involve by-product-generating additives and lower NPs purity. In contrast, physical methods like magnetron sputtering on solid substrates produce pure metallic NPs without additives. The generation of NPs through magnetron sputter deposition of metal targets in liquids has been studied and developed in order to have colloidal solutions of small metal nanoparticles (NPs) without any additional reducing or stabilizing reagents. Despite that this synthetic approach is known for almost two decades, the detailed mechanism of NP formation is still unclear.

Our recent research has made the magnetron sputtering process compatible with conventional liquid ink preparation for fuel cell manufacturing by synthesizing Pt NPs over a liquid substrate (glycerol) under low pressure [1]. Molecular dynamics simulations reveal that NP diffusion in the liquid phase depends on the kinetic energy of Pt atoms upon arrival on the liquid surface and the plasma/liquid interaction properties. In this study, we investigated these interactions, the phase gas properties and the Pt NPs properties in three sputter plasma regimes : direct current magnetron sputtering (DCMS), pulsed DC magnetron sputtering (p-DCMS) and high-power impulse magnetron sputtering (HiPIMS). Different diagnotics techniques were used giving us access to the energy distribution of the sputtered species, total energy influx incoming onto the liquid, the gas phase composition and the plasma properties. These results are correlated to the NPs physical properties obtained by X-Ray Diffraction/Diffusion and High Resolution Transmission Electron, enabling us a better understanding of the Pt NPs growth phenomena on and in the liquid phase especially in pulsed regime.

Thanks/Acknowledgement
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LIQU1-O2-016 ● Atmospheric pressure plasma jet in contact with a liquid for the formation of silver and gold nanoparticles and their applications

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Plasma-liquid interactions have received an increasing attention by researchers in areas such as plasma science, fluid dynamics, multiphase chemistry and aerosol science [1]. Plasmas in liquid or in contact with a liquid have been the center of recent studies because of their various applications from metal nanoparticles synthesis to industrial materials processing [2][3]. In our study, an atmospheric pressure plasma jet was used to synthesize silver and gold nanoparticles by reducing $AgNO_3$ and $HAuCl_4$, respectively, without the use of toxic chemicals. This method proved to be scalable, environmentally friendly and versatile. Mono-dispersed spherical nanoparticles were obtained after 5 min of plasma exposure at atmospheric pressure. Nanoparticles in the nanometer range have unique properties that are considerably different than that of their bulk material; arising from quantum size effect. Nowadays, a wide range of biological applications including drug delivery, catalytic, anticancer, antifungal and parasitological applications use gold and silver nanoparticles. The formation of these metal nanoparticles was firstly confirmed by UV-vis spectra. The surface plasmon resonance (SPR) band resulted in a strong optical absorption in the 400-450 nm range for silver NPs and in the 520-550 nm range for gold NPs. Their morphology was observed by transmission electron microscopy (TEM). The effects of different parameters such as the plasma discharge duration, the precursor and the capping agent concentrations on the size and shape of the obtained nanoparticles were studied. We also characterized the DBD plasma using optical emission spectroscopy (OES) studies. The antibacterial effect of the synthesized Ag nanoparticles was also investigated, as well as the effect of different gases and the addition of a radio frequency plasma source on the formation of gold nanoparticles were all studied.

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LIQU1-O3-011 ● Growth mechanism of nanosheets by discharges in liquids

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The synthesis of nanosheets by discharges in liquid nitrogen is observed for given metals when they are used as electrodes.[1,2] Many metals have been tested. Bismuth, lead or zinc are prompt to form nanosheets (Fig. 1). Other metals do form sheets as well, like silver or indium, but with smaller aspect ratios (width/thickness). Cu and Al grow only as spherical nanoparticles.

Recently, we have demonstrated that these objects could also be grown in water and not only in liquid nitrogen. A pretreatment, based on chemical etching by Nital solution, increases spectacularly the efficiency of nanosheets production, from almost zero to nearly 100%.

Because of the presence of kinks on the lateral faces (clearly visible in Fig. 1-right), the shape of these single crystals is likely ruled by the so-called ledge mechanism. In solids, this approach states that the growth of a precipitate is dictated by the coherency of the interfaces between the precipitate and the matrix where the growth takes place. The development of the precipitate is more important for incoherent interfaces than for coherent ones.

The need for a pretreatment, the possibility of forming the same nanosheets in different liquids, and the observation of the electrode surface states before and after erosion enable us to propose a growth mechanism based on surface growth of nanostructures. These nanostructures are made of entangled nanosheets that are transferred mechanically into the liquid phase and separated during this step.

The understanding of this mechanism opens the way to a better control of nanosheet production by discharges in liquids.

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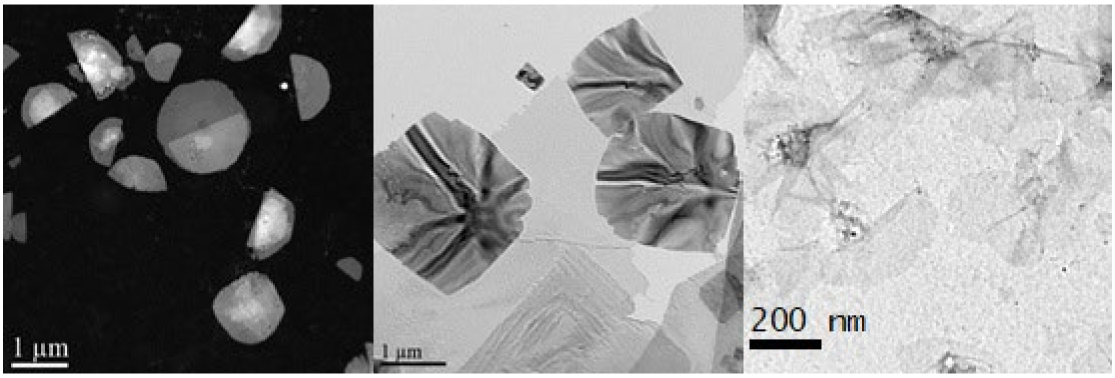
Fig. 1: Left: γ-PbO_2 nanosheets. Middle: $Bi_2O_2CO_3$ nanosheets. Right: ZnO nanosheets. These types of objects can be formed in liquid nitrogen as in water.



GROM3-K1-025 ● Growth mechanism of metallic foams synthetized by plasma electrolysis deposition: a numerical study

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The mechanism governing the growth of metallic foams synthetized by plasma electrolysis deposition remains poorly understood so far. These metallic foams are widely used in several domains for their ultralow density and their capability of absorption shock or acoustic waves. However, to be compatible with laser in inertial fusion experiments, these foams must have a very small pore size, i.e. less than one micrometer, a purity beyond 95 at.%; an apparent density that must be below 1 g/cm3 and a regular porous structure. Such characteristics cannot be achieved by conventional techniques. For this reason, CEA has developed a unique process known as plasma electrolysis deposition [1].

Thus-produced foams adopt shapes that are similar to the so-called “bush-like” discharges that propagate by branching in liquids as illustrated in Figure 1. In a previous work [2], the reduction of the metallic precursor was showed to happen in the gas phase created around the electrode where multiple streamers are spotted. Discharge propagation and branching might be responsible for the shape of the metallic deposit and then, could play a key role in mastering the design of foam microscopic structure.

In this context, a numerical study of discharge initiation and branching has been achieved in order to unravel the reduction mechanism that takes place inside the cathodic gas sheath. The possibility of breakdown in the studied conditions is associated with the creation of a shortcut mechanism through the hydrogen sheath in contact with the electrolyte. The study shows a sub-nanosecond transition to the arc regime, given the short electrode gap (around 100µm), but no branching at all during this step. Then, it can be concluded that branching and foam structure are not correlated at this stage.

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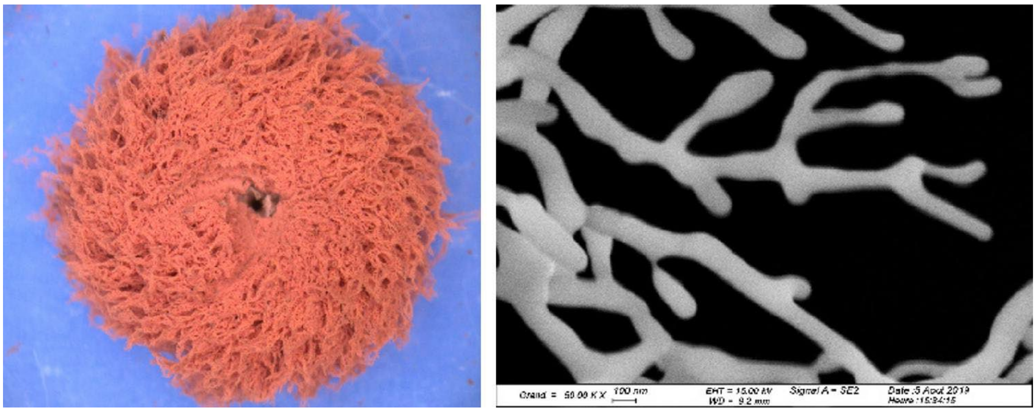

Figure 1. Left: Copper foam synthetized by plasma electrolysis deposition.
Right: Scanning electron microscopy image of the same object at higher magnification.

GROM3-O1-041 ● *In situ* study of the amorphous-to-crystalline phase transformation of thermochromic $SmNiO_{3-\delta}$ thin films

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Rare-earth nickelates ($RNiO_3$) are an intriguing system to study the structural changes correlated to the physical properties variations. They belong to the perovskite family and exhibit a fascinating and unusual property: the metal-insulator transition (MIT). It allows a change in the material behavior, particularly in the optical one, by varying the size of the rare-earth (*R*) and/or the temperature. Therefore, they are promising candidates for solar thermal applications, where a thermochromic absorber layer is crucial for passive thermal regulation. However, nickelates are complex to synthesize, and a simple way to elaborate them would make possible their use on an industrial scale. In this work, we provide an understanding of the mechanisms involved in our soft-synthesis process: deposition by magnetron sputtering and crystallization by air-annealing. Hence, a thermo-kinetic approach to the crystallization progression is proposed after following the evolution over time through in situ High-temperature X-ray diffraction (HTXRD) at different temperatures. Additionally, a Transmission electron microscopy (TEM) investigation was performed for the amorphous and annealed samples, revealing the crystallization evolution and the appearance of the grains in the layer. Moreover, the Ni^{3+} stabilization, which is a necessary condition to have a thermochromic effect, and the electronic structure with the annealing time were also analyzed by Electron energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS). Lastly, the optical transmittance change confirmed the thermochromic effect by Fourier-transform infrared (FTIR) measurements.

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GROM3-O2-031 ● Growth manipulation strategies of ultrathin metallic layers aided by in situ and real-time diagnostics

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Noble-metal ultrathin films, with nominal thickness smaller than ~15 nm, are ubiquitous in a wide range of plasmonic devices and other optoelectronic applications. Silver (Ag) layers are interesting candidates for use as transparent conductive electrodes (TCE) in flexible devices. However, the growth of Ag on weakly interacting substrates proceeds in a 3D fashion. Strategies to produce fully continuous, ultrathin and ultrasmooth Ag layers without compromising their electrical conductivity have lately been deployed. Among them, the use of gaseous additives, such as N_2 or O_2, or template layers appears to be an efficient route to promote wetting and the formation of a continuous layer at a lower nominal Ag thickness [1, 2]. However, understanding the entire evolutionary growth regime requires the implementation of *in situ* and real-time diagnostics.

In the present work, the impact of N_2 or Ge addition on the morphological and structural evolution of ultrathin Ag layers is investigated by coupling complementary *in situ* and real-time diagnostics. Lab-scale studies include wafer curvature, surface differential reflectance spectroscopy and electrical resistivity to determine morphological transition thicknesses such as percolation threshold and onset of continuous film formation [3]. These results are further comprehended using real-time X-ray synchrotron studies (SIXS beamline at SOLEIL) in which the grazing incidence diffraction and small-angle scattering signals are simultaneously recorded, together with stress evolution. This enables us to explore the influence of Ge and N_2 on island shape, texture and stress development, as well as relaxation mechanisms during growth interruptions.

In the case of Ag/N_2 system, we additionally compared the growth morphology of Ag layers obtained by evaporation (e-beam) and sputter-deposition (dcMS and Hipims) processes. These deposition methods enabled us to span a wide range of growth conditions with respect to energies of film-forming and plasma species, as well as N_2 dissociation rates, with the aim to obtain a mechanistic interpretation of the role of nitrogen.

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 “Investissements d’Avenir” EUR INTREE (reference ANR-18-EURE-0010) and LABEX INTERACTIFS (reference ANR-11-LABX-0017-01).

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GROM3-O3-117 ● Study on the effects of N_2 addition during Ag thin film sputtering deposition, using *in situ* and real-time measurements

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Magnetron sputtering deposition is the technique of choice for flat glass advanced functionalization, used at an industrial scale for the production of low-emissivity (“Low-E”) glazing products based on thin silver layers. The thermal insulation properties of these glazing products are based on the reflection of thermal radiation in the far-IR region, which is directly related to the electrical conductivity of their Ag thin films embedded inside complex dielectric stacks. A better understanding of the growth mechanism of Ag thin films during sputter deposition, as well as its dependence to process parameters, is necessary to control their microstructure and improve on their conductivity. In this context, *in situ* and real-time measurements are valuable tools to characterize the growth of this metal, so sensitive to atmospheric exposure.

The use of Ar/N_2 gas mixtures during magnetron sputtering deposition of Ag thin films was explored in this work. Real-time electrical resistance and surface differential reflectivity spectroscopy (SDRS) were combined to assess the effect of N_2 on the initial stages of film growth up to percolation, as well as on the resistivity of the continuous film. We will show how N_2 addition induces a decrease in the film percolation thickness value, and a change in the aspect ratio of Ag nanoparticles during initial growth stages. *In situ* X-Ray Photoelectron Spectroscopy (XPS) analysis rules out the formation of nitrogen compounds in the film, and *ex situ* transmission electron microscopy (TEM) showed a moderate impact on the surface Ag island density before percolation.

The present study shows that N_2 addition can be a practical tool to modify the microstructure of sputtered Ag films and their growth mechanism, even though this approach is not without effect on the final film resistivity.

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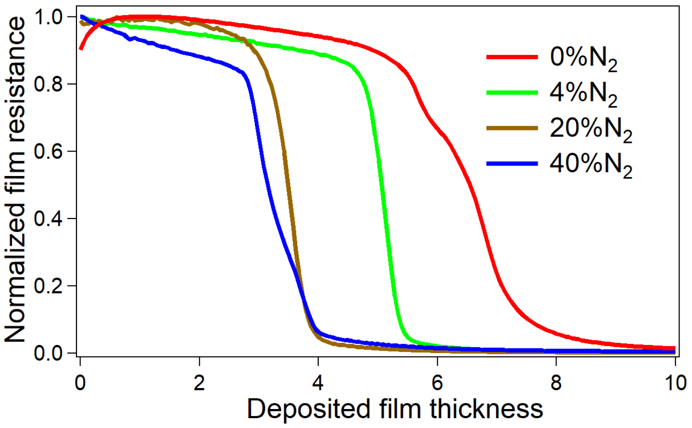

Real-time film resistance measurements

GROM3-O4-062 ● Initial phase formation during nitriding of austenitic stainless steel

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Expanded austenite formed by nitrogen insertion 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.%. While it can be formed using a multitude of methods, the actual nitrogen diffusion and the thermodynamic properties of this phase are still contentious.
Here, the initial phase formation is investigated in detail: Low ion current experiments prolonging the initial phase formation in combination with in-situ x-ray diffraction (XRD) experiments during nitriding allow a detailed, time-resolved view. Additionally, the formed layers are investigated by depth-resolved in-situ XRD measurements during successive removal of the surface layer by ion beam sputtering. This combination of a conventional, laboratory XRD setup including a high vacuum XRD chamber with a broad-beam low energy ion implantation/sputtering experiment yields a powerful tool for fundamental investigations of functional surfaces. Here, it is shown that two phases, a low-expansion phase and a high-expansion phase, are formed sequentially over time with the growth rate of the latter phase being much higher. As a result, the thickness of this initial, transient phase is restricted to less than 30 – 50 nm for thicker layers, leading to an abrupt interface between the substrate and the expanded austenite as observed in SEM cross sections. It is surmised that the driving force is a threshold in the nitrogen concentration which has to be reached.

TRIB1-01-060 ● Synthesis and characterization of the ceramic refractory metal high entropy carbide thin films from the Cr-Hf-Mo-Ta-W system

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High entropy alloys (HEAs) are multicomponent materials containing at least five main elements with contents between 5 and 35 at.%. HEAs are known to exhibit high strength and hardness at low and high temperatures, outstanding structural stability, good wear resistance and exceptional corrosion and oxidation resistance, making them possible replacements for traditional alloys. This concept was further extended to ceramics, such as oxides, nitrides, borides and carbides.

The aim of this study was to investigate the Cr-Hf-Mo-Ta-W system and prepare multicomponent carbides with a NaCl-type fcc structure. The materials were deposited in the form of thin films by reactive DC magnetron sputtering at ambient temperature and at 700°C. A mixture of argon and different acetylene flows (0-9 sccm) was used for the depositions. The structure and mechanical properties were heavily influenced by the chosen acetylene flow. In films deposited without acetylene flow, a bcc metallic phase was observed. Samples deposited under acetylene flow showed an amorphous structure or an fcc multielement carbide phase. Therefore, the ability of the system to form either metallic or ceramic single phases was confirmed. Amorphous coatings exhibited a dense microstructure while crystalline films were columnar. The mechanical properties of the deposited films were good, exhibiting a hardness of up to 25±1 GPa and an effective Young's modulus of up to 346±7 GPa. The results of the study confirm the expected good mechanical properties of the Cr-Hf-Mo-Ta-W system and the feasibility of their preparation via magnetron sputtering.

Thanks/Acknowledgement
This research was supported by project LM2018097, funded by the Ministry of Education, Youth and Sports of the Czech Republic and project GA23-05947S financed by the Grant Agency of the Czech Republic.

TRIB1-O2-206 ● High-power-density sputtering of industrial-scale targets: case study of (Al,Cr)N

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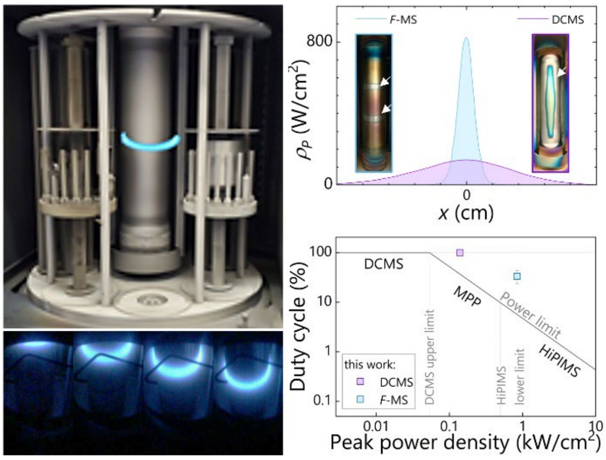
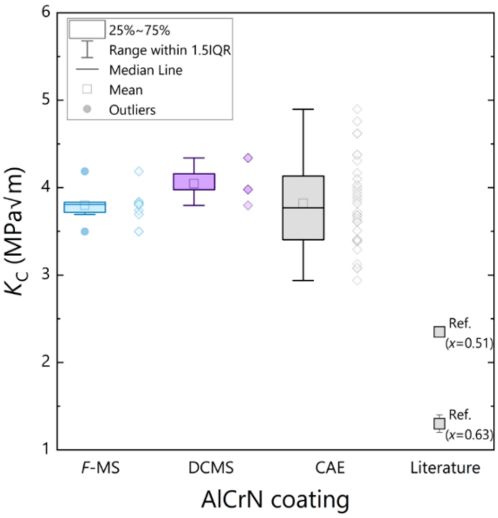
Large-scale sputter-deposition of hard protective coatings has not been prevalent as the large dimensions of the industrial targets posed an enormous technological challenge: only relatively low power (and plasma) densities could be achieved, resulting ultimately in poor performance of such coatings. Here, we introduce a novel sputtering technology allowing to reach high power densities for industrial tube targets. This is realised on the principle of a longitudinal movement of a reduced size magnetron inside the target. In doing so, peak power densities of 840 W/cm^2 have been achieved for the overall power of 25 kW and the target dimensions of Ø110 × 510 mm. To demonstrate the effectiveness of the solution, we chose cubic (Al,Cr)N, which is known for its exceptional protective properties, particularly high wear and oxidation resistance, produced a series of coatings by sputtering an $Al_{60}Cr_{40}$ target, and compared them to the coatings deposited by means of conventional magnetron sputtering (DCMS) and cathodic arc evaporation (CAE). Most of the sputtered coatings have a stoichiometric composition, smooth surface and a moderate amount of growth defects. Significant improvements through recipe optimisation could be achieved resulting in high hardness, fracture toughness, and low wear rates being equal to and even exceeding those of DCMS and benchmark CAE coatings. Our results open up great potential of the novel sputtering technique for the coating industry.



High-power-density sputtering of industrial target



Fracture toughness

TRIB1-O3-020 ● Oxidation resistance and mechanical properties of AlTiZrHfTa(-N) high entropy films deposited by reactive magnetron sputtering

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$(AlTiZrHfTa)_{1-x}N_x$ refractory high entropy films RHEFs were synthesized by Direct Current Magnetron Sputtering (DCMS) in different nitrogen ratios ($R_{N2} = N_2/(Ar+N_2)$) on flat glass, silicon and sapphire substrates. The nitrogen-free thin film is amorphous while the nitrides are single-phased solid solutions with Face-Centered Cubic (FCC) structure. The hardness of the films increased from 6.4 GPa for the nitrogen-free film to 25.3 GPa for the film with R_{N2} = 20 %. This increase is attributed to the formation of an FCC single-phased structure with a preferential orientation of (111). When R_{N2} increased further, the hardness of the thin films decreased to 19.2 GPa, resulting from the preferential orientation evolution from (111) to (200). According to the values of H/E and H3/H2 reports, the film deposited at R_{N2}=20% can be seen as the most promising for anti-wear applications. However, the film deposited at R_{N2}=10% showed the best compromise in terms of mechanical properties, related to a lower residual stress value, which could lead to avoid delamination during usage. The $(AlTiZrHfTa)_{1-x}N_x$ RHEFs deposited at $R_{N2} \geq$ 5% films showed a good thermal stability when annealed at 800 °C for 3 h under vacuum. Improved oxidation resistance is observed for the nitrides compared to the metallic RHEFs due to the formation of strong ionico-covalent Metal-Nitrogen bonds. $(AlTiZrHfTa)_{1-x}N_x$ RHEF exhibited an unsatisfying oxidation resistance, which was illustrated by an elevated Kp ($1.77\ 10^{-6}\ g^2\ cm^{-4}\ h^{-1}$ for nitrogen-free film and $1.22\ 10^{-7}\ g^2\ cm^{-4}\ h^{-1}$ for nitride films at 800°C) and low Ea values (45 KJ/mol, 94 KJ/mol) for nitrogen-free and nitride films respectively. This pesting oxidation resistance of $(AlTiZrHfTa)_{1-x}N_x$ RHEF could be connected to the lack of formation of protective oxide scales, due to the expansion volumetric mismatch between High-Entropy Alloys (HEAs) structure – formed oxide and the accelerated internal oxidation.

Thanks/Acknowledgement
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TRIB2-K1-162 ● A small-scale approach to characterize Ti-Based thin films tribological behavior in *operando* conditions

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Nature of interfaces in contact with living species is important for biosensors… This interface can be modified by PVD films. Recently, intense research were devoted to Ti-Ag coatings [1,2]. Even though some papers are focused on optimizing films' chemical composition, no data are available on their wear resistance.

To better understand the tribological behaviour of this metallic system, a laboratory-made ball-on-disc mini tribometer, specifically-designed to be introduced into SEM [3], was built. It allows a small-scale *in situ* characterization of the damaging surface (Fig. 1). An environmental SEM was used, in which the contact environment is controlled (vacuum, water..). The objective is to link the tribological behaviour of films both with their characteristics and atmosphere.

A hard TiN rubbing on a steel ball is first used as model contact to test the mini-tribometer [4]. In a second time, titanium-based films were deposited by magnetron sputtering, silver content was being controlled by the relative Ag/Ti areas ratio of targets. Considering a previous study on both flexibility and electrical conductivity of films [1], 4 compositions were identified (Ag-free, low-, moderate and high-Ag contents).

Even if mechanical properties are not really influenced by the silver content of films, their microstructure is drastically changed with presence of Ag-rich submicrometric particles for high silver enrichments. The presence of this further phase strongly modifies the rubbing dynamics. A model of degradation is proposed involving the dynamic of debris, the silver particles and the atmosphere of the contact area (Fig. 2).

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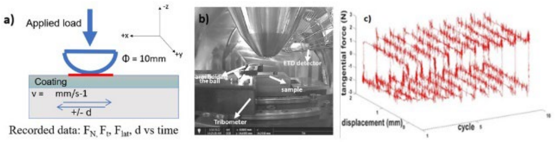
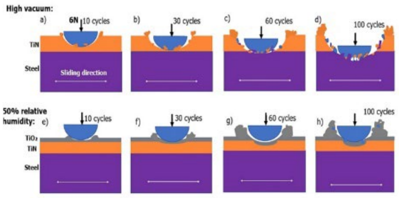


Mini tribometer: dynamic, in-SEM view, tan force



Wear mechanism under vacuum or humid environment

TRIB2-O1-141 ● Neon enhanced plasma ionization in Cr films deposition by HiPIMS-DOMS

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In magnetron sputtering-based deposition processes, particles that arrive at oblique angles relative to the growing film's surface promote the atomic shadowing effect which, ultimately, results in porous and underdense columnar microstructures. Energetic particles bombardment helps to prevent this effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and/or triggering re-deposition processes. However, bombarding the film's surface with highly energetic particles comes with a heavy cost: the formation of a high density of defects, which disrupts the crystalline structure of the films, and the creation of compressive stresses.

In a previous work, the authors have shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material[1]. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment. The most straightforward route to achieve high ionization of the sputtered species in HiPIMS is to increase the peak power. However, this also increases the average energy of the sputtered species and brings about energetic bombardment. Partially replacing Ar by Ne in the process gas promotes an increased mean electron energy which increases plasma ionization, as the ionization energy of Ne (21.56 Ne) is significantly higher than that of Ar (15.75 eV). In this work, partial substitution of Ar by Ne in the DOMS process gas was investigated as a mean to increase the ionization degree of the sputtered species without increasing their average energy.

In this work, Cr thin films were deposited by DOMS in pure Ar and mixed Ar + Ne plasmas up to 60% Ne. Adding Ne to the plasma resulted in 25% increase in the ions saturation current density (ISCD) as measured by an electrostatic flat probe placed at the substrate location. All the deposited films have a dense and compact columnar microstructure with an almost complete [110] out of the plane preferential orientation. The lattice parameter of the Cr films increased with increasing Ne content in the plasma while their surface roughness decreased from 6 to 3 nm. The hardness and young's modulus of the Cr films were evaluated by nanoindentation.

Thanks/Acknowledgement
The authors acknowledge the Portuguese Foundation for Science and Technology for funding of this work through project IoShad PTDC/CTM-REF/1464/2021.

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TRIB2-O2-043 ● Tribological characterization of TiO_2 thin films prepared by magnetron sputtering: the link between color change and TiO_2 wear

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Although titanium is not a noble material, it is of great interest to the luxury industry for its lightness, hypoallergenic properties, and especially for the many colors it can present when coated with a thin layer of TiO_2. Nevertheless, its use in luxury goods is currently limited because of the low durability of the colors. The color degradation of anodized titanium is well-studied in the field of architecture [1,2] and is in this case mainly related to a change in the thickness of TiO_2 in the presence of acid rain. Diamanti et al [3] have shown that prolonged rubbing in an artificial sweat solution causes partial discoloration of the anodized titanium surface. However, the origin of the color degradation, in this case, has not been identified. The interferential origin of the color makes it particularly sensitive to a variation in thickness but also to a variation in chemical composition which then modifies the refractive index of the layer.
This study aims to understand the origin of the color modification of titanium samples coated with a thin layer of TiO_2 by magnetron sputtering during dry rubbing and rubbing in the presence of artificial sweat. Tribological tests were conducted and showed a change in color under the effect of friction (see for example Figure 1 in the presence of artificial sweat). Structural, chemical, and optical characterizations of the surface were carried out to understand the mechanisms responsible for the color change. Changes in the morphology, microstructure, and chemical composition of the coating induced by the deposition parameters were also studied and correlated with the oxide film damage mechanisms and color variation that occur in each system.

Thanks/Acknowledgement
This work was supported by the LABEX MANUTECH-SISE (ANR-10-LABX-0075) of Université de Lyon, within the program "Investissements d'Avenir" (ANR-11-IDEX-0007) operated by the French National Research Agency (ANR).

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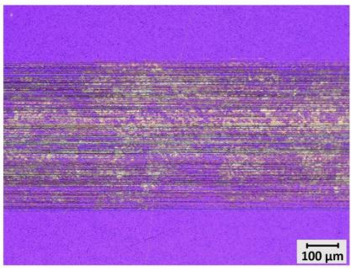

Optical image of a wear trace

TRIB2-O4-113 ● Role of Ti-Al-based thin films modified wettability on heat transfer exchange during droplet impact onto a heated surface

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Around 70% of the world's primary energy usage is employed for heat production. A step toward the energy transition process would be improved thermal management of industrial processes. An urgent industrial challenge is the design of extractors and heat exchangers that are small and reasonably priced. Spray cooling on a hot surface is one of the most effective heat extraction techniques. When the droplet touches the hot wall, the liquid heats up and boils, removing a high energy amount in this process. Nevertheless, the full potential of this cooling method hasn't yet been realized, due to the lack of dedicated exchange surfaces. The investigation of heat transfer related to the impact of a water drop on heated surfaces with specific properties (roughness, wettability) is paramount to accomplishing this purpose. To determine the surface temperature and calculate the heat extracted by the droplets, we utilized time-resolved infrared thermography (TR-IRT). For this goal, a layer highly emissive in the IR is deposited in a sapphire substrate, transparent in the (2-5) µm range. The coating layer must meet particular requirements, opaque with a micrometer thickness to neglect the layer's thermal resistance and be thermally stable withstanding the droplet impacts. The TR-IRT technique enables measuring the temperature reduction produced by the droplet impact through the sapphire without being disturbed by the drop presence[1].

We showed that TiAlN and TiAl thin films are suitable options for this application. Magnetron sputtering was employed to deposit each of the examined films. X-ray diffraction, optical profilometry, and scanning electron microscopy were used to characterize the films' morphology and structure. Additionally, Fourier transform infrared spectroscopy and contact angle measurements allowed us to investigate the emissivity and wettability of the films. The wettability effect of the Ti-Al-based films on the heat transfer during droplet impact at various temperatures from 80 to 300°C was explored by TR-IRT. Thanks to these measurements, the heat flow and energy extracted by the drop projection were determined. Due to the greater surface-drop contact area, superhydrophilic TiAlN samples perform better than hydrophobic TiAl films. Biphilic surfaces with spatially variable wetting properties could enhance the heat transfer of the boiling system [2]. We are currently exploring the effect of different sizes of hydrophobic patches in a hydrophilic matrix to assess the impacts on the cooling efficiency.

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PL6 ● Surface engineering for sustainable future: multifunctional coatings for optics, energy, aerospace and manufacturing applications

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Surface engineering approaches, especially those involving low pressure plasma processing, allow one to develop new and highly efficient solutions for advanced application in the areas of optics, energy, aerospace, manufacturing, biomedical and others. Besides their primary function, the film and coating systems face increased technological, environmental and economic challenges, especially since the performance of modern equipment and components is pushed to and beyond their limits. Frequently, the primary functional and multifunctional characteristics of the coating systems are limited by materials deterioration accelerated in hostile environments involving excessive wear, erosion, corrosion, and other mechanisms related to the surface damage, resulting in increased operation costs, decreased efficiency, and premature failure.

In depth understanding of materials primary functional characteristics, their design and fabrication, as well as of the deterioration processes helps to develop appropriate strategies to increase durability, while taking into account the complete life cycle of the device or component.

This presentation will illustrate the performance of coatings developed for different sectors of application by specific case studies representing various coating microstructures, architectures and new and novel fabrication methods. This includes: (a) High Power Impulse Magnetron Sputtering (HiPIMS) for optical coatings in architectural glazing for smart eco-energetic windows; b) Ion Beam Assisted Chemical Vapor Deposition (IBA-CVD) of hybrid organic-inorganic optical coatings for advanced ophthalmic lenses, (c) Pulsed hollow cathode PECVD coatings for high erosion resistance inside narrow tubes and cavities, and (d) Importance of the optical properties of thermal barrier coatings in new-generation aircraft engines.

DEPO5-O1-167 ● VO_2 thin films for thermal devices, the beginnings of a radiative thermal transistor

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This study is devoted to the development of SMT (Semiconductor to Metal transition) thin films materials for an experimental approach aimed at controlling radiative heat flow. The vanadium dioxide ($VO_{2)}$ is well-known for its first order Semiconductor to Metal transition (SMT) and the drastic physical variations in its optical, electrical, and thermal properties at a temperature close to room temperature (341K). The remarkable evolution of its infrared (IR) emissivity around the SMT allows the rectification phenomena of radiative heat currents in the far field regime [1].As an effort to optimize and enhance the rectification factor, pulsed laser deposition (PLD) has been used to develop high quality vanadium dioxide thin films on both-side c-sapphire substrates, on a quite large surface for PLD ($2\times2cm^2$) with a thickness dispersion lower than 8%. In order to improve the variation in the VO_2 infrared (IR) emissivity around the SMT, and to control the properties of the two-sides VO_2 thin films, the fabrication process includes a rapid thermal process (RTP) in a background atmosphere of oxygen.This combined methodology of PLD and RTP leads to a contrast in the electrical resistivity of more than five orders of magnitude between the insulator and metallic states, placing these films among the best results in the literature. A new technique based on a thermal wave resonator cavity (TWRC) is developed to measure the variation in the infrared emissivity of the films during its heating and cooling by monitoring the changes in the phase and amplitude of the pyroelectric signal [2]. The TWRC is a photothermal technique that considers the oscillatory component of the temperature by heating the VO_2 thin film with a modulated laser. The notable evolution of the emissivity allows to demonstrate the reliability of the two-sided VO_2 thin films for the conception of the thermal rectifier and other revolutionary sensitive temperature devices

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DEPO5-O2-135 ● Pulsed magnetron sputtering of strongly thermochromic VO_2-based coatings with a low transition temperature

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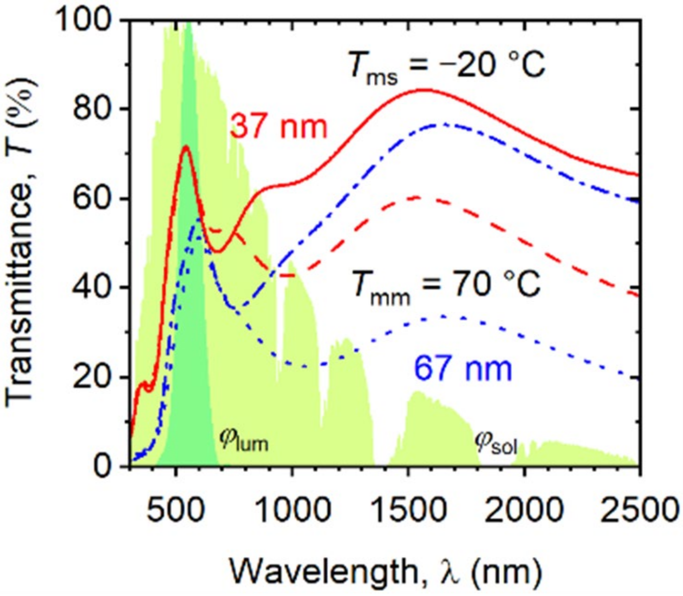
The reversible semiconductor-to-metal transition of vanadium dioxide (VO_2) makes VO_2 -based coatings a promising candidate for thermochromic smart windows, reducing the energy consumption of buildings. We report on a scalable sputter deposition technique for fast preparation of strongly thermochromic YSZ/$V_{0.986}W_{0.014}O_2$ /YSZ coatings, where YSZ denotes Y-stabilized ZrO_2, on conventional soda-lime glass at a relatively low substrate surface temperature (350 °C) and without any substrate bias voltage. The thermochromic $V_{0.986}W_{0.014}O_2$ layers and the antireflection YSZ layers were deposited using a controlled high-power impulse magnetron sputtering of a single V-W and Zr-Y target, respectively. A coating design utilizing a second-order interference in the YSZ layers was applied to increase both the integral luminous transmittance (T_{lum}) and the modulation of the solar energy transmittance (ΔT_{sol}). We present the phase composition (X-ray diffraction) and microstructure (high-resolution transmission electron microscopy) of the coatings and their optical properties (spectrophotometry and spectroscopic ellipsometry). The YSZ/$V_{0.986}W_{0.014}O_2$ /YSZ coatings exhibit a transition temperature of 33-35 °C with T_{lum} = 64.5 % and ΔT_{sol} = 7.8 % for a $V_{0.986}W_{0.014}O_2$ thickness of 37 nm, and T_{lum} = 46.1 % and ΔT_{sol} = 13.2 % for a $V_{0.986}W_{0.014}O_2$ thickness of 67 nm. The results constitute an important step to a cost-effective and high-rate preparation of large-area thermochromic VO_2 -based coatings for future smart-window applications.



Spectral transmittance of the coatings

DEPO6-K1-080 ● Photochromic properties of rare-earth oxyhydride thin films for smart windows applications

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Photochromic materials change their absorption properties under light illumination and can be employed in smart windows – devices that enable passively controlling energy and light transfer between buildings and outdoors. While there are numerous materials known to show a photochromic effect (i.e. some transition metal oxides), they typically feature a rather narrow absorption band in the photodarkened state, affecting their appearance, unless doping or multi-layered structures are used.

Thin films of several rare-earth metal oxyhydrides (like YHO, GdHO, NdHO, DyHO and ErHO) have been shown to exhibit colour-neutral photochromic properties at ambient conditions[1]. The transmittance of these materials decreases uniformly in the visible and near infrared region when exposed to light of energy exceeding the band gap of the material. Bleaching of the material starts once illumination is stopped.

Photochromic thin films are commonly prepared following a two-step procedure: first, a rare-earth metal dihydride ($REMH_2$) is deposited using either reactive magnetron sputtering or e--beam evaporation; then the $REMH_2$ is oxidized, e.g. by exposure to air and forms an oxyhydride (REMHO) [2,3]. For photochromic films, properties like band gap, photodarkening and bleaching rate depend on their chemical composition and thickness [3,4]. The former one can be altered adjusting deposition parameters. While the material is of great interest for a plethora of applications, the physics behind the photochromic effect is not yet well understood.

In this work, we present our advances in studying photochromic properties of REMHO from both fundamental and applied perspectives. Photochromic thin films were produced using magnetron sputtering and characterized with respect to their optical properties and chemical composition using ion-beam based analytical techniques. Further, the thermal stability of the samples was assessed exposing them to elevated temperatures in ultra-high vacuum and simultaneously monitoring optical transmittance. We found that H starts leaving the material at the temperatures above 90°C depending on its initial content in the sample. The effect of different gaseous environments (UHV, H_2, O_2, air) and temperatures as well as annealing time on photochromic characteristics was also studied. The temperature effect might be related to the defect structure of the material, therefore photochromic films were irradiated with keV or MeV ions and their photochromic performance was examined for different fluences of ion beams.

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DEPO6-O2-010 ● Growth mechanisms and properties of magnetron sputtered TiO_2 thin films on complex 3D foam substrates

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The synthesis of functional material (e.g. TiO2) on foams is a becoming an important research area, particularly in photocatalysis [1,2]. However, coatings on foams are most of the time synthesised using the sol-gel and soft template methods, or even the hydrothermal and calcination routes. PVD methods are rarely used to coat such substrates and when it is, the growth mechanisms are never mentioned. However, PVD deposition can bring significant interest on those complex 3D foam substrates, such as accurate control and tuning of film morphology, composition, and/or synthesis of metastable phases.
The scope of this work is to study the growth and properties of TiO2 films deposited on Ni and C foams by the means of DC magnetron sputtering and HiPIMS, and to get insights on how the film grows on such complex 3D substrates, especially regarding the crystal structure of the coating inside the foam and how it relates to photocatalytic performance. The physico-chemical properties of the deposited films are investigated using XPS, SEM and XRD, while the photocatalytic performance of the TiO2@Ni foam and TiO2@C foam assemblies is assessed by photoelectrochemical measurements. Thanks to high resolution XPS spectra, the chemical environment as well as the stoichiometry is studied. SEM cross-sections of the TiO2@C foam assemblies allow to observe the change in coating morphology with increasing depth inside the foam. XRD confirms the synthesis of crystalline TiO2, whose structure is either anatase, rutile or a mix of both depending on the deposition technique. The photoelectrochemical measurements, combined with the XRD results, highlight the superior photocurrent generation provided by the samples having the anatase structure.

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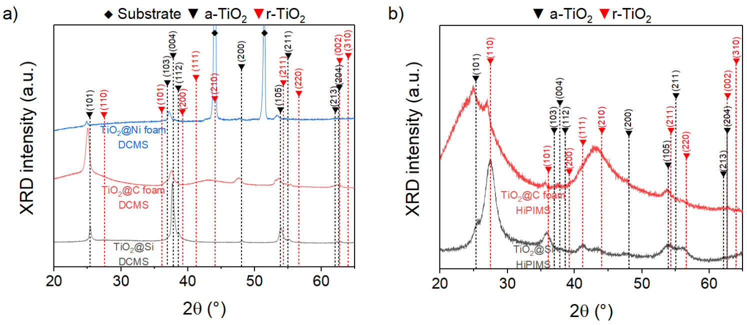
XRD of TiO2 deposited on Si, Ni foam and C foam



DEPO6-O3-022 ● Plasma diagnostics of a pulsed hollow cathode discharge and deposition of copper nickel oxide thin films.

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A hollow cathode discharge with a CuNi (Cu50Ni50) cathode is operated inside a vacuum chamber with Ar gas flowing through its nozzle. O_2 gas is admitted to the vaccum chamber. Typical Ar+O_2 gas pressures are in the range of 2-50 Pa. The energy distribution of plasma ions is investigated with the help of energy-resolved mass spectrometry. Singly charged Ar^+ and molecular O_2^+ ions are the most abundant ionic species. Deposition rate and heat flux to a substrate increase as function of discharge current. At high pressures, the deposition rate is further increased by the directional gas flow, which becomes more focused onto the substrate. Deposited and annealed thin films are analysed by X-ray diffraction and Raman spectroscopy. As-deposited films are composed of a mixed $Cu_xNi_{1-x}O$ cubic phase with a preferred (111) orientation. Upon annealing at 600 ^oC, the mixed $Cu_xNi_{1-x}O$ phase separates into two sub-phases composed of NiO and CuO. Deposited thin films are further investigated for photoelectrochemical (PEC) activity. Annealed films show PEC activity as a photocathode which deteriorates with time, however.

DEPO6-O4-036 ● Reactive D.C. magnetron sputter deposition of crystalline silver niobate thin films

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Due to its high energy storage density at room temperature, silver niobate ($AgNbO_3$) is one of the most promising lead-free dielectric perovskites for energy storage applications. In this work, $AgNbO_3$ thin films were deposited on Si (100) substrates at different substrate temperatures by direct current reactive magnetron co-sputtering from Nb and Ag targets in Ar-O_2 atmosphere. X-ray diffraction indicated the formation of crystalline silver oxide (Ag_2O) and metallic silver at substrate temperatures up to 500 °C, whereas at 550 °C the $AgNbO_3$ phase was formed. With further increasing substrate temperature, $AgNbO_3$ becomes the predominant phase, while fractions of metallic silver are still clearly observable. Raman spectroscopy confirmed the existence of the $AgNbO_3$ phase, while characteristic Raman bands for silver oxide could not be verified. In films deposited at room temperature, $AgNbO_3$ was formed after annealing in ambient air at temperatures of 525 °C. Microstructural inhomogeneities in the form of metallic silver are detectable in all films using scanning electron microscopy. Single phase $AgNbO_3$ films were formed at a substrate temperature of 650 °C, when a bias voltage was applied to the substrates during deposition. The elemental distribution is homogenised by the ion-assisted film growth, compared to depositions without bias voltage, and metallic silver could not be detected, enabling electric measurements. In conclusion, this study reports for the first time on the synthesis of lead-free crystalline perovskite thin films based on $AgNbO_3$ by reactive direct current magnetron sputter deposition, opening paths for future process scalability.

SURF2-O1-042 ● Plasma-surface interactions in oxygen-containing plasmas

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Heterogeneous surface kinetics plays a role in most plasma processes, where surfaces interact either with active discharges or their afterglow. It can affect both plasma and surface properties. In particular, in oxygen-containing discharges, the adsorption and recombination of atomic oxygen on reactor surfaces determine the gas composition, the availability of O for important volume reactions (e.g.: $CO_2 + O \rightarrow CO + O_2$; $CO + O + M \rightarrow CO_2 + M$) and eventually the flux of reactive oxygen species (ROS) towards target surfaces.

In Booth et al. (2019) [1], the wall loss frequencies of O-atoms have been measured in the positive column of an oxygen glow discharge in a Pyrex tube (borosilicate glass) of 10 mm inner radius, for several pressures and currents. However, the surface mechanisms determining recombination are not fully known yet. In particular, the increasing recombination with decreasing pressure below 1 Torr (see figure 1) is not understood. In this work we employ Deterministic and Kinetic Monte Carlo methods [2-4] to simulate the surface kinetics of O-atoms in the experimental conditions of Booth et al. (2019) and highlight the relevant mechanisms.

The newly developed model describes the experimental dependence of the atomic oxygen recombination probability on pressure, current, gas temperature and wall temperature and allows to identify the most important recombination mechanisms for each condition. Moreover, this work demonstrates that the plasma has important effects on the surface at low pressures. This is due to fast particles that produce dangling bonds on the surface. Figure 1 shows the effect of dangling bond production on the atomic oxygen surface recombination frequency below 1 Torr, agreeing with experimental measurements.

Thanks/Acknowledgement
This work was partially supported by the Portuguese FCT-Fundação para a Ciência e a Tecnologia, under projects UIDB/50010/2020, UIDP/50010/2020 and PTDC/FIS- PLA/1616/2021 (PARADiSE).

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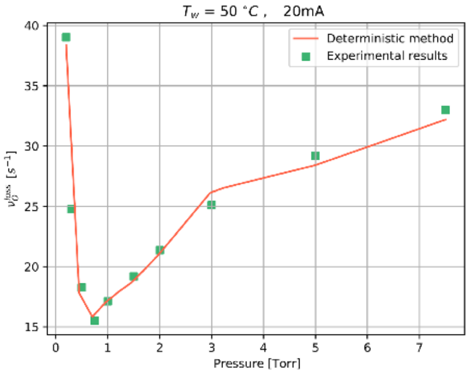

SURF2-O2-109 ● Plasma electrolytic oxidation of aluminium with incorporation of carbon black nanoparticles

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Plasma electrolytic oxidation (PEO) is a surface treatment that can create thick, hard and well adherent oxide layers on the surface of metals such as aluminium, titanium or magnesium [1]. Due to the multiple discharge breakdowns on the surface, the oxide layers exhibit a high porosity that can be used to give the coating improved properties. Indeed, the porosity can be filled with nanoparticles dispersed in the electrolyte, which allows reducing the porosity and confer the coating the targeted properties depending on the particle nature [2]. Among the various types of incorporated particles, carbon particles showed good results for various applications like corrosion and wear resistance [3] or in reducing friction coefficient [4]. Graphite, graphene, diamond and carbon nanotubes are the carbon allotropes that have been mainly studied in PEO. Although there are very few works dealing with the incorporation of carbon black, such nanoparticles can be of great interest because of their spherical shape that can facilitate their incorporation into the coatings.

This talk aims to discuss the incorporation of carbon black Vulcan XC72 nanoparticles into alumina layer grown on pure aluminium. Plasma electrolytic oxidation was performed using a pulsed bipolar current generator into a low concentration alkaline electrolyte. The thickness of the layers, their morphology and the incorporation of carbon black have been characterized using complementary techniques such as scanning electron microscopy, X-ray diffraction and Raman spectroscopy.

Results show that increasing the concentration of carbon black particles in the electrolyte seems to improve the growth rate, leading to a more homogeneous coating on the sample surface. Carbon black particles are mainly located into the top layer of the coating where they line the pore walls. Chemical analysis and Raman spectroscopy also confirm that carbon is present in the top layer of the coating. The presence of particles into the inner layer is still to be confirmed but these first results show that incorporation of carbon black nanoparticles is possible and that it could possibly replace more expensive carbon allotropes such as graphene or carbon nanotubes in order to improve the performance of PEO coatings.

Thanks/Acknowledgement
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SURF3-K1-068 ● Electrochemical characterization of surface damage in n-type GaN induced by inductively coupled plasma reactive ion etching (ICP-RIE) and atomic layer etching (ALE)

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GaN manufacturing processes are not fully optimized and can generate detrimental defects in power and photonic devices. Among the main bottlenecks, the plasma-etching process drives to nanoscale defects, which alter GaN electronic properties and interfaces [1]. In order to improve the etching process, defects created during plasma process must be characterized and quantified. However, the standard electrical methods such as capacitance/voltage measurement on MOS capacitances or current-voltage measurement on Schottky diodes [2], fabricated on n-GaN etched wafers, are time and wafer consuming because of required technological steps.

At CEA LETI, an electrochemical "short loop" technique using Mott-Schottky plots and based on an electrochemical impedance spectroscopy technique [3] is conducted in order to characterize the damaging effect induced by the plasma etching on n-GaN [4]. This electrochemical characterization enables to study three kind of etching processes based on ICP-RIE and ALE. The calculations of the barrier height from electrochemical data indicate how plasma is modifying electronically the GaN surface compared to as-grown samples. It gives access to which energy the Fermi level is pinned depending on the plasma treatment. This calculated barrier height seems to be efficient criteria to characterize surface modification and improve plasma processes involved in GaN HEMT fabrication.

Probing Conventional LETI plasma process with the electrochemical Mott-Schottky method demonstrates a good reproducibility and confirms the reliability of the developed method. Various electrochemical tests conducted on the 3 plasmas recipes demonstrated that: 1) the RIE is damaging, 2) the optimized RIE (Steady A) is less damaging than the other RIE (Steady B) and 3) the RIE associated with ALE process shows the least damaging plasma recipe, as expected. XPS, AFM are coupled to electrochemical study to give conclusion for each recipe.

Thanks/Acknowledgement
This work was supported by the French national program "Programme d'Investissements d'Avenir PSPC n°9 – G-Mobility"

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SURF3-O2-050 ● Deep etching of bulk titanium in fluorinated plasmas for biomedical devices

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Titanium is a commonly used material in medicine for various applications, such as prostheses and surgical tools, due to its biocompatibility. Additionally, it is also a suitable material for the housing of smart medical devices, known as Active Implantable Medical Devices (AIMD), such as pacemakers and defibrillators. As the demand for smaller and more functional devices increases, the need to functionalize titanium through microtechnology techniques is becoming more relevant. Thus, the focus is on researching methods to effectively and efficiently etch bulk titanium, particularly through the use of fluorine-based plasma chemistries, as demonstrated by the work of D'Agostino and colleagues [1,2].
According to the context provided, we have demonstrated that using a SF_6, O_2, and Ar plasma mixture is efficient to etch anisotropic features such as trenches (see Figure 1). While this type of fluorine-based method has not been extensively studied on titanium, if the right conditions are met, such as increased temperature to promote oxidation on the sidewalls and the removal of low-volatility TiF_4, it is possible to minimize lateral etching and achieve profiles with straight sidewalls. An investigation of the passivation mechanism, where temperature plays a critical role, will be presented. It will be shown that an increased substrate temperature, due to the self-heating of the substrate, enhances the desorption of the etch products and promotes titanium oxidation. This will be correlated to etch profiles.
This research project at GREMI also aims to have optimal control over the etching process and to minimize contamination in the plasma reactor. Various characterization techniques, such as scanning electron microscopy, X-ray photoelectron spectroscopy, and optical microscopy, are used to study the etched titanium surface and the contamination in the reactor. Based on these analyses, the composition of the layer deposited at the reactor walls during etch processes will be discussed.

Thanks/Acknowledgement
The Centre-Val de Loire Region has provided funding for this work through the CERTeM 5.0 initiative and the PSPC-Regions Project Tech2AIM (Turnkey TECHnologies to enable next generation Active Implantable Medical devices).

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Cross-section view of 20 µm wide titanium trenches etched by $SF_6/O_2/Ar$ plasma (2 µm/min). The Ni mask has been cleared before observation by optical microscopy.

Cross-section view of etched Titanium trenches.

SURF3-O3-145 ● Properties of nitrided layers produced in an active-screen plasma nitriding process

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Plasma-assisted nitriding is usually used to improve mechanical properties of metal parts. The common process is based on the diode discharge where the specimen to be treated are placed in a low-pressure reactor. They are connected to the cathode since the walls of reactor serve as the anode. In this DCPN (Direct Current Plasma Nitriding) configuration, nitrogen-based plasmas form directly around the load. There is thus a coupling between treatment temperature and sample biasing, which can lead to hollow cathode phenomena or to significant sputtering mechanisms. In this case, the parts can be damaged. To eliminate these risks, the Active Screen Plasma Nitriding concept (ASPN) has been recently developed. In this process, the samples are placed inside a cylindrical metal mesh to which a high cathodic potential is applied. The plasma is thus created on this screen that is a source of both nitriding species and heat [1].

Currently, this system is not as promising as expected: the growth kinetics of nitrided layers are lower than those obtained by diode process. In this presentation, we will show that one of the limiting factors for ASPN is the reactor contamination when it is opened to introduce the samples. This issue is enhanced by the high temperature of the reactor walls due to the closeness of the screen. Our objective being to improve this process, it is necessary to develop a joint study by means of plasma diagnostics (optical emission and electrical measurements) and materials characterization (X-ray diffraction, glow discharge optical emission spectroscopy, X-ray photoelectron spectroscopy, metallography, electronic microscopies). In pure nitrogen plasma, the oxygen pollution is evidenced by the presence of NO γ-bands (210-290 nm) emission and missing of nitrogen fourth positive system [2]. NO detection is correlated with the formation of a superficial oxide on the specimen that partially blocks the nitrogen diffusion. We will show that this oxide does not have the same properties depending on the plasma used: pure nitrogen or N_2/H_2 mixture. Our study shows that hydrogen does not suppress oxygen contamination but limits its negative effects on the treatment properties.

Thanks/Acknowledgement
Authors thank IRT-M2P to financial support RESEM project PIPERADE allowed the design and study of ASPN set-up.

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SURF3-O4-104 ● Dual-phase nanocomposite coatings based on crystalline ZrN and glassy ZrCu

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Recently, magnetron sputter deposition has been demonstrated to be a suitable deposition technique for the preparation metallic glasses as thin films (TFMGs). Thanks to non-equilibrium conditions of the low-temperature plasma and very high cooling rates on atomic scale at the substrate, TFMGs can be prepared with much wider composition variety and solubility than bulk metallic glasses (BMGs). Moreover, TFMGs have showed properties and characteristics that are superior to BMGs, and metallic and ceramic coatings, e.g., a better balance of ductility and strength. The amorphous structure of TFMGs along with their unique properties also provides a possibility to combine TFMGs with nanocrystalline materials in a heterogenous dual-phase structure. This might allow to overcome the shortcomings of both types of materials and further improve the properties or even discover novel properties based on the synergetic effect of the two phases.

The study focuses on the preparation of dual-phase thin-film materials in the ternary Zr–Cu–N system by reactive magnetron co-sputtering and systematic investigation of their structure and properties. The coatings were deposited in argon-nitrogen gas mixtures using three unbalanced magnetrons equipped with two Zr targets and one Cu target. The magnetron with the Zr targets were operated in dc regimes while that with the Cu target in a high-power impulse regime. All the coatings were deposited onto rotating substrates with rf biasing without external heating. The elemental composition of the coatings was controlled in a very wide composition range.

We have demonstrated that reactive magnetron co-sputtering allows to prepare a new type of the Zr–Cu–N coatings with a nanocomposite structure consisting of two phases, crystalline ZrN and glassy ZrCu. So far, only the nanocomposite Zr–Cu–N coatings based on ZrN and Cu phases have been reported in the literature [1]. We show that by varying the process parameters, such as the target power densities, repetition frequency and nitrogen fraction in the gas mixture, we are able to control the elemental composition of the coatings so that the stoichiometry of the two phases remains as much the same as possible and only the volume fraction of the phases is varied. The structure of the as-deposited coatings exhibits a gradual transition from amorphous-like to very fine-grained to nanocrystalline. This transition is reflected in changes in the microstructure and surface morphology and affects the mechanical properties, deformation behavior and corrosion resistance.

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PLATHINIUM

PLASMA THIN FILM INTERNATIONAL UNION MEETING

POSTER PRESENTATIONS

- Session #1 - Tuesday 12 September
- Session #2 - Wednesday 13 September

DEPO-P1-018 ● Effect of interfacial SiN_x ultra-thin film on optical and electrical properties of PVD Antireflective coating

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Thin dielectric films are nowadays widely used in the photovoltaic field (PV). But thermal silicon dioxide (SiO2) has become undesirable for industrialization due to high temperatures deposition and relatively long processing times. While silicon nitride turns out to be a good candidate for photovoltaic applications, combining excellent surface passivation quality with excellent anti-reflective properties. These films are very suitable for backside passivation of bifacial solar cells, as evidenced by efficiencies above 20% due to optimization of certain characteristics compared to SiO2.

The a-SiNx is known for its high band gap (Eg≈ 4.5 eV) as well as a high refractive index n of the order of 2 and a high density of the order of 3.2 to 3.5 g/cm3 which give it interesting properties in this field.

In this work, a-SiNx films are elaborated by a reactive deposition process using non-toxic gases (N2, Ar2) involving radio-frequency plasma on Si (100) and (111) substrates. However, the interface between antireflective films and the Si substrate play a key role on the yield of PV cells. Thus, we focused our attention on an original surface passivation method, consisting on a nitriding process using N2 plasma glow discharge source (GDS) under ultra-high vacuum.

Several experimental parameters as nitridation temperature and time, initial substrate state have been studied to create a very thin SiNx film (less than 10 nm). In situ Angle Resolved-X-ray Photoelectron Spectroscopy (XPS) measurements combined with surface models and Density functional theory (DFT), allow controlling the stage of the elaboration and allow the determination of the composition and the thickness of the nitride layer formed.

The aim of the elaboration of SiNx thin film is to minimize the dangling bonds and therefore to reduce the interface state density. Metal-Insulator-Semiconductor (MIS) electrical characterizations have been applied in order to extract information from the interface.

Thanks/Acknowledgement

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DEPO-P1-026 ● Effect of Tantalum Addition on Properties of Cu–Zr–Based Thin Film Metallic Glasses (TFMGs)

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LASMIS (FR)

Cu–Zr–Ta ternary thin film metallic glasses (TFMGs) were deposited through the direct current (DC) magnetron sputtering of pure metallic targets in a dynamic mode. The effect of tantalum addition on the microstructure, mechanical properties, and thermal behavior of TFMGs were investigated. Nanoindentation measurements showed that an increase in tantalum content from 0 to 47 at % favored hardness and Young's modulus, which rose from 5.8 to 11.23 GPa and from 90 to 136 Gpa, respectively. XRD analysis and differential scanning calorimetry (DSC) measurements highlighted an improvement of thermal stability with the tantalum addition from 377 to 582 °C when the tantalum content increased from 0 to 31 at %.

DEPO-P1-039 ● Development and characterization of chromium-based PVD coatings for the protection of stainless steel bipolar plates for PEM fuel cells

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PEM fuel cells are economically viable, relatively compact, have a high power density, are quick to start up, operate at low temperatures, have good durability, are very low emission of greenhouse gases, and have high overall efficiency. These functional characteristics make PEM fuel cells the leading candidate to replace internal combustion engines in transportation applications today. However, there are some aspects related to their performance, durability and cost, which limit their effective implementation in the field of electromobility. These technical limitations are mainly associated with the durability of metallic bipolar plates, a key component of PEM fuel cells, which homogeneously distribute the reactant gases on the surface of the catalysed electrodes, serve as collectors of the generated electric current, and separate the individual cells that form a stack, preventing gas leakage and supporting the assembly.

Stainless steels and aluminium alloys are suitable materials for the fabrication of bipolar plates. However, their corrosion resistance is not high enough to withstand the acidic and humid environment under which a PEM fuel cell operates. This fact increases the interface contact resistance, contaminates the proton exchange polymeric membrane, thus reducing the energy efficiency of the cell. A solution to this problem involves the application of electrically conductive coatings with good resistance to corrosion.

Coatings obtained by means of vacuum-based deposition technologies, such as PVD (Physical Vapor Deposition), offer sufficient electrical and thermal conductivity, corrosion resistance, gas impermeability and good adhesion to metals. PVD coatings have been extensively applied and tested on stainless steel bipolar plates. These coatings are based on noble metals (gold, silver or platinum), transition metal nitrides and carbides, and amorphous carbon-based coatings. Precious metal coatings show excellent electrical and corrosion protection properties, but are not appropriate in terms of costs.

In this work, chromium carbide coatings obtained by means of cathodic vacuum arc have been deposited on austenitic stainless steel bipolar plates in an industrial PVD reactor. The chemical composition, morphology, thickness and microstructure of the coatings have been analysed by Field Emission Scanning Electron Microscope (FESEM) equipped with an Energy Dispersive X-Ray Spectroscopy probe (EDS), X-Ray Diffraction (XRD) and High Resolution Transmission Electron Microscopy (HR-TEM). The measured Interface Contact Resistance (ICR) has been 1.7 mW cm^2 at 1.4 GPa with a current density (Icorr) of 7 mA cm^{-2} at 0.9 VSHE.

Thanks/Acknowledgement
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DEPO-P1-067 ● Tailoring surface properties of Zr-V thin films by competitive self-separation of crystalline and amorphous phases during sputtering

Q. Liebgott[1, 2], A. Borroto[3], S. Bruyère[1], A. Ahmed[2], D. Müller[2], Z. Fernandez-Gutierrez[1], R. El Beainou[1], S. Migot[1], F. Mücklich[2], D. Horwat[1]
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Competitive self-separation of crystalline and amorphous phases has been reported by our group for Zr-based binary alloys during thin film deposition 1–3. This leads to peculiar morphologies, and allows to control surface topography and, thus, surface-related properties. This study focuses on Zr-V thin films that were synthesized by magnetron co-sputtering of pure Zr and V targets. With this process, in a narrow range of composition, it is possible to observe a competitive growth between the amorphous and crystalline phases during film growth; the amorphous phase grows as columns while the crystalline phase grows as cones (Fig. 1 (a)). The surface of the cones is dome-shaped, and the surface of the amorphous columns is flat (Fig. 1 (b)). As a consequence, increasing film thickness increases the surface coverage by the crystalline phase, changing the surface roughness and functional properties of the films. This study focuses on increasing the antibacterial properties of surfaces, by coating the aforementioned Zr-V films with a 65nm-thick Cu layer. It is shown that this process increases the antibacterial properties of the films as compared to a flat surface.
Fig. 1: (a) Cross-section and (b) surface SEM micrographs of a Zr-V thin film showing amorphous columns and crystalline cones and the surface of the film.

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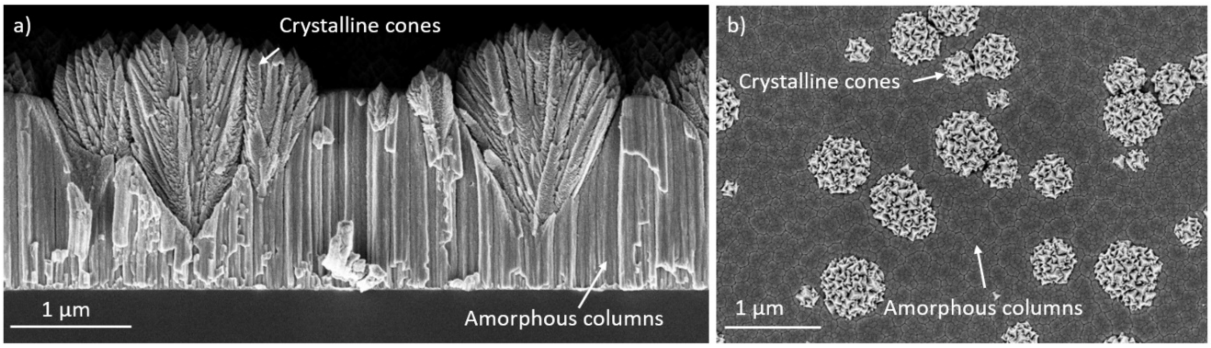

SEM (a) cross-section and (b) surface micrographs.

DEPO-P1-182 ● Synthesis of multifunctional flexible Zn-Al based oxide thin film with antibacterial and moisture barrier properties using Atomic Layer Deposition system

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Antibacterial moisture barrier thin films have attracted considerable interest in various industries, including food packaging, medical devices, and electronics, due to their potential benefits. These films offer a dual advantage by effectively inhibiting bacterial growth while providing excellent moisture barrier properties. In this study, we present the development of an antibacterial moisture barrier thin film using a zinc-aluminium-based oxide composite. Our aim was to create a thin film that could effectively inhibit bacterial growth while providing excellent moisture barrier properties. The thin film was deposited on a substrate using atomic layer deposition and its structure, morphology, and antibacterial properties were extensively characterized. Our results show that the thin film has a dense structure with uniform coverage on the substrate and exhibits exceptional moisture barrier performance. Antibacterial tests showed its efficacy against both gram-positive and gram-negative bacteria. Based on these results, we conclude that the zinc and aluminum oxide thin film has significant potential for a wide range of applications, particularly in sectors where moisture barrier and antibacterial properties are required simultaneously, such as food packaging and medical devices.

Thanks/Acknowledgement
This work was supported by a grant from the Korea Research Institute of Chemical Technology (KRICT) (Project No. KK2352-20) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MIST) (No. 2020R1A5A1019649).

DEPO-P1-193 ● Impact of plasma assistance on SiO_2 and HfO_2 thin films physicochemical and photometric aging properties

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The Megajoule laser facility fires deuterium-tritium targets to study fusion. High-power lasers working at λ=1053 nm require high performance coatings on optical components to maximize the laser energy. SiO_2 and HfO_2 deposited by evaporation are the most adequate materials to achieve a balanced compromise between photometric properties, mechanical stress, metric-scale coatings and laser resistance [1,2]. Moreover, the impact of transport, storage and metrology conditions shall be considered to best accommodate laser specifications [3].

Optical components are sensitive to an aging effect leading to photometric spectral shifts toward longer wavelengths [4]. We quantified this shift over a 1-year storage in ambient environment for single layers deposited by e-beam and Plasma Ion Assisted Deposition (PIAD). An exponential decay behavior of the spectral shift was found for SiO_2 and HfO_2 layers fabricated by e-beam, which did not stabilize after about 6 months. A slower spectral shift evolution was found for SiO_2 deposited by PIAD which did not stabilize. However, HfO_2 layers fabricated by PIAD seem to not be impacted.

Long-term aging phenomenon is often considered to be the result of chemical reactions in the pores (oxygen sensitive layers) [5] and stress relaxation [6]. X-ray photoelectron spectroscopy confirmed that stoichiometric SiO_2 and HfO_2 were deposited. Transmission Electron Microscopy observations showed that the SiO_2 layers are amorphous for both deposition processes. HfO_2 layers are polycrystalline in monoclinic system with less than 15 nm diameter crystallites and amorphous initial growth for layers fabricated with PIAD. The HfO_2 layers present columnar morphology ($\phi_{columns}$~30nm). Presence of pores was not evidenced with microscopy. However, ellipso-porosimetry data seemed to indicate that water absorption takes place when relative hygrometry is below 20%; suggesting the presence of microporosity (ϕ_{pores}<2 nm). Ellipsometry analysis also indicated that the layers fabricated by PIAD have higher refractive indexes, and therefore higher density. Since PIAD deposited layers have slower spectral aging kinetic, the density of the layers seems to be one of the main properties influencing the long-term stability of these coatings.

Thanks/Acknowledgement
I acknowledge the LLE and the IRCER members for all efforts made in production, characterization, analysis and discussions for this study.

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DEPO-P1-197 ● Sputtering techniques for smart textiles

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Over the past decade, metallized fibers have gained significant attention in the field of smart textiles. PVD (Physical Vapor Deposition) technologies, such as magnetron sputtering, have enabled the metallization of fibres at the nanoscale, allowing the combination of electrical conductivity with textile properties. This has paved the way for innovative applications in various domains as shown in three sections.

The first section of this study focuses on the metallization of fibres by magnetron sputtering and examines the increase in electrical conductivity with increasing layer thickness. These coatings enable new applications for fibers, such as the transmission of electrical data signals, antistatic, low-friction textiles, medical devices like embroidered body electrodes for electrocardiogram measurements and the development of textile capacitive touch sensors.

The second section explores the deposition of an ultrathin titanium film as a passivating adlayer using sputtering. Pure silver surfaces tend to tarnish in the presence of hydrogen sulphide and release silver ions when exposed to oxygen in aqueous solutions. To stabilize the silver layer and to limit the silver ion relaease to an appropriate level, a passivation layer is applied. Thus, the thickness of the Ti adlayer is examined. This passivation process ensures the avoidance of cytotoxic conditions for moistened electrodes used in applications like long-term electrocardiography (ECG) measurements.

In the third section, the use of fibers, ropes, and belts as load-bearing and supporting elements in construction, mountain climbing, and safety belt applications is investigated. These textile components are subjected to wear and thermal history. Thermal history cannot be visually inspected by users, leading to unexpected failures. To address this issue, the study explores the application of phase-change-material germanium antimony tellurium (GST) semiconductors as thin films on fibers. These films exhibit a color change that indicate the exposure to a specified temperature causing damage to the fiber.

In conclusion, this research shows the significant advancements achieved through PVD technologies for fibers in the field of smart textiles. These findings open up new ways for the development of functional textiles with enhanced electrical conductivity, passivation capabilities, and temperature-sensitive properties.

DEPO-P1-207 ● Using evaporation to create hydrophobic coating

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Introduction

Empa, a Swiss Federal Laboratory for Materials Science and Technology, uses a Bronkhorst evaporation system named CEM (Controlled Evaporation & Mixing) in their quest to develop hydrophobic coatings for water-repellent fabric. Empa uses plasma polymerisation to deposit thin layers on top of fabrics and fibers.

Application requirements

The vaccum polymerization process at Empa activates the HMDSO (C6H18OSi2). The primary objective is to polymerize and deposit the vapor onto the surface of the fiber. To achieve a stable flow of the polymer precursor vapor, precise control is required for both the liquid HMDSO flow and the carrier gas flow. The HMDSO vapor is introduced into the plasma chamber at defined flow rates, where higher rates facilitate rapid deposition and processing.

Process solution

In this process, liquid HMDSO is supplied from a pressurised vessels at ambient temperature, and the flow rate is measured and controlled by a mass LFC combined to a mixing valve. This valve mix also the liquid HMDSO with the carrier gas Argon, coming from a MFC. The mixed fluid is instlantly evaporate due to a heat exchanger, enabling the liquid phase to change to the vapour phase.

Conclusion

Empa achieves a higher gas yield of 50 ml/min compared to the previous bubbler system, which only allowed 4-5 ml/min of gas flow and the flow of HMDSO liquid has been increased. The results demonstrate a very stable, precise and efficiently regulated vapour flow. This setup enables polysiloxane coatings at low temperatures, making it suitable for coating textile fibers that cannot withstand high temperatures.

Empa's efforts to conduct plasma polymerization at low pressure aim to increase production yield by facilitating heterogeneous deposition on the fiber's surface and reducing the amount of chemicals involved.

Thanks/Acknowledgement

Acknowledgement to EMPA, Bronkhorst SW and Bronkhorst High-Tech.

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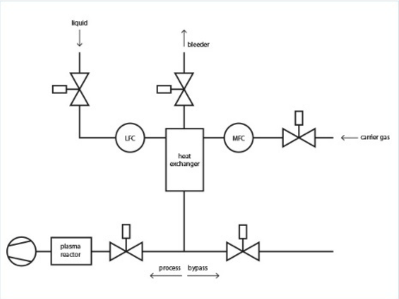
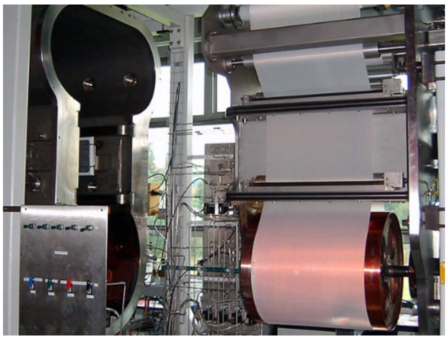


Flow scheme showing CEM evaporation system



Plasma coating

GROM-P1-063 ● Depth resolved XRD measurements using in-situ XRD during Ion beam sputtering

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In-situ X-ray diffraction (XRD) during ion implantation or thin film deposition is a powerful method to follow the time evolution of diffusion and phase transition processes in thin films, even though the depth resolution still is dominated by the information depth of the X-rays, hence, no depth-resolved information is available. Contrasting is the case of sputter etching with energetic ions of nobles at moderate temperatures: here, no diffusion or phase transformation processes are active and depth-resolved information can be extracted from the time-series of diffractograms obtained during progressive removal of the surface layer. The combination of both approaches yields a powerful tool for fundamental investigations of functional surfaces.
Thus, thin surface layers which are removed by sputtering can be identified with a depth resolution of 25 nm or better. Here, this method is detailed, describing which depth resolved properties of thin films can be accessed using such in-situ XRD measurements during ion beam sputtering in the model system austenitic stainless steel + nitrogen: i) the influence of concentration gradients on the XRD peak shape and peak width; ii) correlations between the local nitrogen concentration and the local lattice expansion; iii) the evolution of the scattering intensity with depth.

GROM-P1-123 ● "MISSTIC": a multi-tool experimental setup for magnetron sputtering deposition combined with *in situ* and real-time characterization

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Magnetron sputtering deposition is widely used in the glass industry because of its versatility ranging from metals to insulators, its deposition rate, and its compatibility with large substrates. Current research efforts in thin film growth and characterization are often hindered by interactions and impurities stemming from contact of the film surface with the atmosphere during the time between the film elaboration and ex situ characterization steps.

To overcome these challenges, the MISSTIC (Multilayers and Interfaces Sputtered-deposition on STructured substrates and In-situ Characterization) setup was developed at SVI. This equipment is composed of a deposition vessel with real-time characterization tools and an in situ analysis chamber, connected via a load-lock mechanism. Sample transfer under high vacuum avoids contact with the atmosphere and/or the need for capping (protective) layers on top of the deposited metallic films, therefore strongly reducing phenomena such as surface oxidation or contamination. This way, in situ X-Ray Photoemission Spectroscopy (XPS) in the MISSTIC analysis chamber can be used to characterize the deposited film surface chemistry, without any depth profiling through capping layer needed. In addition to this, sample annealing under vacuum up to 1000°C can be used for studying layer crystallization or elemental diffusion in thin film stacks during post-deposition treatment. Furthermore, surface characterization using in situ Low Energy Electron Diffraction (LEED) is used for the study of crystallized surfaces.

Two optical and one electrical real-time characterization techniques can be applied during film deposition and allow for the detection of different stages of film growth. These include real-time techniques such as Surface Differential Reflectivity Spectroscopy (SDRS), optical measurement of the film mechanical stress (PReMC set-up: Pattern Reflection for Mapping of Curvature [1,2]), and film electrical resistance. In the case of film growth for metals such as Ag, real-time measurements allow for the detection of the nucleation, growth, coalescence, percolation, and continuous film formation threshold thicknesses. Combinations of these techniques are used for studying the effects of different parameters of the sputtering deposition process (gas pressure, underlayer, overlayer, power, discharge, plasmagenic gas composition…). SDRS and electrical resistance measurements can be conducted simultaneously.

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GROM-P1-126 ● Augmented reality representation for the investigation of simulated inclined chromium thin films

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The Oblique Angle Deposition (OAD) is a PVD (Physical Vapor Deposition) process in which the variation of the deposition angle modulates the properties of the film. Through the shadowing effect, the OAD introduces a change in the structure of the film, leading to a porous columnar microstructure. Several means to predict the structure and the resulting properties of the film exist, through either experimental models or numerical simulations. Simulation based on the whole process, which consist of sputtering [1], transportation [2] of the atoms and growth of the substrate [3], are used to evaluate some of the film properties. However, these simulations use a point-based system. This point-based system directly comes from the atomistic aspect of the interactions; hence, each point represents a single atom in the film. That system is well suited for the process simulation, however, many novel tools for precise investigation of the properties requires specially built structure like CAD-models (Computer Aided Design) or meshes, in particular for FE (finite elements) mechanical simulations.

Apart from the generation and the investigation of meshed structure, this study also tackles an issue about the geometrical representation of the simulated thin film. PVD researchers commonly use 2D images of the film, mostly taken from SEM imaging, so that naturally also became the norm for the representation of simulated thin films. However, 3D simulated films are not limited by this 2D representation. Nevertheless, AR (Augmented Reality) tools has yet to be developed.

The aim of this work is to present a novel immersive and interactive poster experience. Several 3D structures linked to different process conditions will be presented as virtual incrustations. The audience, equipped with the dedicated device, will be then able to explore it in augmented reality.

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GROM-P1-149 ● Chromium carbide coatings by DC sputtering of a sintered target.

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Chromium carbide coatings are commonly synthesized by PACVD with a chromium target and acetylene gas. However, hydrogen can be trapped in the coating, decreasing the final mechanical properties. To overcome this shortage, the use of chromium carbide targets in DC magnetron sputtering can be a solution.

In this project, a Chromium carbide target is sintered by powder metallurgy using the Spark Plasma Sintering (SPS) process. Pure chromium and pure carbon powders are mixed in the desired proportion before sintering. The obtain target is then characterized in terms of chemical and phases compositions. Unreacted carbon and chromium are found, surrounded by the three typical chromium carbides, i.e. Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$.

The target is then used in the DC sputtering deposition system to synthesized the chromium carbides films. The films are then characterized by SEM, XPS, XRD, nanoindentation and four-probes measurement to investigate their morphological, chemical, structural, mechanical and electrical properties.

GROM-P1-199 ● Ion beam sputter deposition of epitaxial Ga_2O_3 thin films on *c*-plane Al_2O_3

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Ion beam sputter deposition is an energetic deposition technique, which provides unique opportunities to control the sputtering and the growth processes, and to study the correlations between process parameters and thin film properties. The process provides intrinsic heating and kinetic assistance to the growing film by energetic particles arriving at the substrate surface, which can be used to tune various thin film properties such as density, microstructure, and forming phase. In particular, the energy distributions of film-forming particles are controlled by changes of the sputtering geometry and the energy of primary ions. This is crucial since the goal is to find the optimal energetic assistance while minimizing the damage to crystalline quality caused by too energetic particles.

In the present study, the deposition of epitaxial Ga_2O_3 thin films on Al_2O_3(0001) by reactive ion beam sputtering is demonstrated and the impact of energetic bombardment by film-forming particles on the growing film surface is investigated. The influence of various process parameters on the epitaxial quality of the films is analyzed. The varied process parameters are substrate temperature, ion energy, ion beam current, sputtering geometry, and background oxygen pressure. The resulting films are characterized regarding growth rate, roughness, crystalline structure, and microstructure.

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HELIAG-P1-044 ● Polysaccharide coatings for urinary catheters

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Urinary catheters are medical devices used by patients to drain the bladder before surgery, and by patients having problems with urinary incontinence, urinary retention, problems with the prostate or other health problems causing patients` inability to urinate on their own. Urinary catheters are long flexible tubes made from medical-grade polymers. However, such medical devices also provide a suitable habitat for the growth of microbial biofilms which are a major cause of hospital infections. The problem can be solved by using bio-based coatings (i.e. polysaccharides) having antibacterial and antioxidant (anti-inflammatory) properties, inhibition of biofilm growth, and low surface friction. Chitosan is a naturally abundant polysaccharide for which it was already shown to have a potential application in medical applications because of its good antibacterial, anti-inflammatory, and antioxidant properties. However, the immobilization of chitosan to a bare polymer surface is not sufficient [1]. Therefore, plasma treatment was applied as a method for obtaining improved adhesion of chitosan coating to the polymer surface [2]. A two-step plasma-treatment procedure was used, followed by the deposition of chitosan from the acidic aqueous solution. In the first plasma treatment step, the urinary catheter was treated with hydrogen plasma which was a source of intensive vacuum ultraviolet radiation that caused the creation of dangling bonds. In the second plasma treatment step, the catheters were treated with oxygen plasma. Such a two-step treatment caused the formation of a highly hydrophilic surface that enabled uniform wetting and improved adhesion of the chitosan coating [2]. Chitosan adhered only to plasma-treated catheters, whereas for non-treated catheters, chitosan did not adhere. The effect of plasma treatment on immobilization was explained by noncovalent interactions such as electrostatic interactions between protonated chitosan amino groups and carboxylic functional groups formed by plasma treatment as well as by the formation of hydrogen bonds.

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HELIAG-P1-099 ● Plasma polymer coatings of non-planar materials for bioapplications

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Synthetic polymer materials used in bioapplications are usually coated by functional plasma polymers (PPs) to enhance their biocompatibility and bioactivity. In our previous research, amine or carboxyl-anhydride PPs coated culture dishes and polycaprolactone nanofibers proved to be suitable surfaces for the growth of different cell types (mouse myoblasts, fibroblasts, keratinocytes, vascular smooth muscle cells, and endothelial cells), but, at the same time, cell proliferation was strongly dependent on chemical composition and stability of PPs [1, 2, 3, 4]. Nevertheless, it is often omitted that non-planar geometries of the substrates, such as culture dishes or well plates for *in vitro* cell culturing or porous scaffolds and nanofibrous mats for tissue engineering, can affect the deposition process and, thus, properties of a resulting PP.

Therefore, we studied deposition penetration depth and sticking probability of film-forming species using the example of amine [5] and carboxyl low-pressure plasma polymerization at different radio-frequency discharge conditions. Cyclopropylamine was used as a precursor for amine PP deposition, and carboxyl PPs were prepared from a mixture of ethylene and carbon dioxide. The deposition rate in well-like structures (Petri dishes, well plates) decreased according to increasing aspect ratios of wells. The chemical composition of PPs differed from the PP coating on a planar Si substrate. Based on the combined analysis of the deposition into microtrenches and slit cavities (Figure 1), models representing sticking probabilities were formulated. Whereas the majority of the film-forming species in carboxyl PPs has a very high sticking coefficient, the species in amine PPs can be divided into two populations. Three-quarters of species in amine PPs have a sticking probability of 0.2; a still significant remaining part has a sticking probability of two orders lower.

Thanks/Acknowledgement
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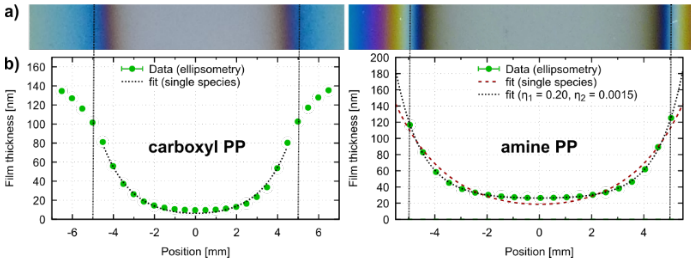

Photo a) and thickness b) of PP-coated slit cavity

HELIAG-P1-101 ● Towards a development of integrated micro-electro-apta-sensors into a diabetes organoid-on-a-chip device.

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Type 2 diabetes is a serious metabolic disease. A better understanding of the mechanisms involved represents a major public health issue. In both diabetic and obese individuals, adipose tissue cells exhibit insulin resistance and chronic low-grade inflammation(1), the mechanisms of which are not yet clearly established. In order to better understand those mechanisms and associated secretions, scientists are developing organoid-on-a-chip systems that mimic the biological functions of organs of interest in perfectly controlled fashion. These tools are very promising for both basic research in biology but also for drug screening. However, there is a need to develop integrated miniaturized sensors to monitor chemical or biological markers secreted by organs. The aim of our work is to develop a multiplexed miniaturized system for continuous, real-time and non-invasive monitoring of the secretion of blood markers of the inflammation in an organoid-on-a-chip device. In order to produce this system made of electrochemical microsensors based on aptamers, we assayed the possibility to co-deposit a conductive polymer and the selected aptamers on gold electrode thanks to Dielectric Barrier Discharge Cold Atmospheric Plasma (DBD-CAP) (2). Two aptamers are studied, one that targets human thrombin and another that targets human interferon-γ. Both aptamers are modified at the 3' end with methylene blue, which acts as redox probe. The first results of the study will be presented, including the deposition of different conductive polymers by DBD-CAP characterized by Cyclic Voltammetry, Impedance measurement and QCM-D coupled with electrochemistry measurement.

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HELIAG-P1-177 ● Influence of varying plasma parameters on the response of MG-63 osteoblast-like cells onto poly(allylamine) thin films

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Temporary and permanent orthopedic implants are becoming more and more relevant because of humans' continually extending lifespans. The aging population in developed nations may soon be linked to a rise in cases of diseases like osteoporosis. As a result, there will be a greater demand for bioactive implants that have a greater ability to integrate into osteoporotic bone. Among the techniques used to develop bioactive implants is by coating materials with an amino-rich polymers such as plasma polymerized allylamine (PPAAm) [1-2]. In this study, we investigated the effect of varying different plasma parameters, such as power, duty cycle, polymerization time, and reactor geometry, on the polymerization of allylamine and the response of MG-63 osteoblast-like cells on the poly(allylamine) thin films.

The thin films were prepared by plasma polymerization of allylamine on 1 x 1 cm titanium-coated flat and micro-grooved silicon wafer substrates. Two different home-built radio frequency plasma reactors were utilized, a horizontal and a vertical configuration [2-4]. The plasma polymerization of allylamine was performed at a controlled pressure of 0.2-0.4 mbar with power varying from 20 W to 60 W, polymerization time of 1 min to 300 min, and duty cycle varying from 2% to 100%. The thin films were then characterized by water contact angle measurements and X-ray photoelectron spectroscopy. Cell spreading and cellular abrogation assay using MG-63 osteoblastic-like cells were investigated using LSM780 and LSM800 confocal microscopes. The physico-chemical characterizations confirmed the presence of poly(allylamine) on the substrates with varying percentages of amino groups. The calculated average power and specific energy delivered to the allylamine precursor were correlated to the percentages of amine groups on the polymer coatings. The MG-63 osteoblast-like cells exhibited enhanced cellular spreading behavior on amino-rich surfaces as compared to the titanium coated silicon wafer control sample and cellular abrogation potential were observed on some of the polymer coatings.

Thanks/Acknowledgement
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HELIAG-P1-203 ● Investigation of toxicity of Plasma Activated Water on *Lemna Minor*

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Cold plasmas with their highly reactive chemistry of Reactive Oxygen and Nitrogen Species (RONS) are of a key importance in biomedical applications [1, 2]. The production and composition of RONS (O, O_3, OH, NO, H_2O_2, O_2^- etc.) depend on plasma parameters and the success of creating adequate plasma chemical cocktail for certain treatment rely on the control of these parameters. In case of treatments of water RONS created in gas phase interact with liquid interface and are deposited in the water creating Plasma Activated Water (PAW). It is shown that PAW has a positive effect on germination percentage, its application as a watering agent results in a better yield of plants etc. [3]. But it is still unknown how the PAW released into land water bodies can influence a wildlife. Here we will present results of PAW effect on the Lemna minor, a model plant used for toxicity tests in environmental sciences. We have used an Atmospheric Pressure Plasma Jet (APPJ) configuration with sharped-end powered electrode that generates a streamer discharge above the water sample (tap water). The plasma source was powered by a continuous kHz signal and as working gas we used Argon. After the treatment we have performed detailed physico-chemical analysis of PAW including RONS detection, pH, temperature and electrical conductivity. PAW was then used in 5 different dilutions (100%, 90%, 60%, 30% and 10%) in order to investigate its influence on Lemna minor samples. The samples were kept in controlled conditions (temperature, humidity) for three weeks after which we have measured lengths of the roots, surface of the leaves and percentage of chlorophyl. It was shown that small percentage of PAW can have positive effect, while for higher percentages it is completely toxic. For all samples the length of the roots reduced. On the other hand, PAW diluted to 10% and 30% resulted in the increase of the leaf surface and in percentage of chlorophyl when compared to control samples.

Thanks/Acknowledgement

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ITEC-P1-107 ● Industrial Technology for ta-C Coatings Deposition

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Platit Pi411 PLUS represents an extremely flexible coating unit. It can be operated in several different configurations what enables deposition of various types of PVD and PECVD coatings. Among these coatings the DLC and especially ta-C coatings occupy a very important place. In this perspective Pi411 PLUS offers not only one but even two distinct technologies to achieve high quality ta-C with significant sp3 content and unique mechanical and also other properties. These two technologies are Platit Scil and Platit F-Type. Although both of them are based on magnetron sputtering, each represents a very specific solution. Therefore also the ta-C coatings achieved by Scil and by F-Type do not overlap fully with their properties. According to the needs of the target application one or the latter technology can provide the best results.

Common base for Platit Scil and Platit F-Type is the central rotating cylindrical cathode with very efficient target cooling. Whereas in the case of Scil the magnetic field design corresponds to more or less conventional cylindrical arrangement, the F-Type is equipped with a specific moveable magnetic core. The core is periodically moving in the longitudinal direction along the cathode axis. It results in the possibility to reach very high power densities, especially for industrial DC magnetron sputtering. For the delivered power of 25kW the maximal value of power density goes up to 800W/cm2.

ta-C coatings are synthetized by both mentioned technologies in a fine-tuned coating process with especial attention to the substrate heat management. Main characteristics of these coatings comprise microhardness above 45 GPa, surface roughness Sa below 25 nm per 1 µm of coating thickness and friction coefficient lower than 0.1.

ITEC-P1-110 ● Innovative conformal deposition solution into TSV integration for oxide, nitride, and metal layers by pulsed liquid precursor injection

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The Plasma Enhanced Chemical Vapour Deposition (PECVD) and the Atomic Layer Deposition (ALD) show complementary advantage and bottleneck. Both methods cannot successfully overcome the conformality issue combined with high deposition rate, to solve the fabrication of Through Silicon Via (TSV) with limited cost, in high volume 3D integration advance packaging manufacturing.
The innovative Fast Atomic Sequential Technology (FAST®) [1], is a unique combination of optimized CVD reactor with pulsing capability, and dual frequency plasma generation. FAST has been developed and proposed to answer the thick and conformal layer request of TSV integration scheme [2]. FAST® tool can be used in different mode: continuous mode (PECVD-like), pulse-purge mode (ALD-like) or pulse only mode (FAST), fig.1.These three kinds of deposition processes are obtained by managing separately, the pulsing position of precursor, of reactant, and of HF (13,56MHz) with or without LF (380kHz). Thanks to a large library of “liquid precursor” molecules already implemented in industry, insulator or conductive layers can be elaborated (for example: TDEAT for TiN, or TEOS for SiO2). The compromises of FAST® make it ideal for a wide field of application where thick and conformal layers are required.
A detailed investigation of FAST® deposition combined with alternated etch steps (usually used to clean the process chamber), will be presented. This method delays and minimizes voids usually present during oxide or nitride deposition and allows to fill gaps between pillars.

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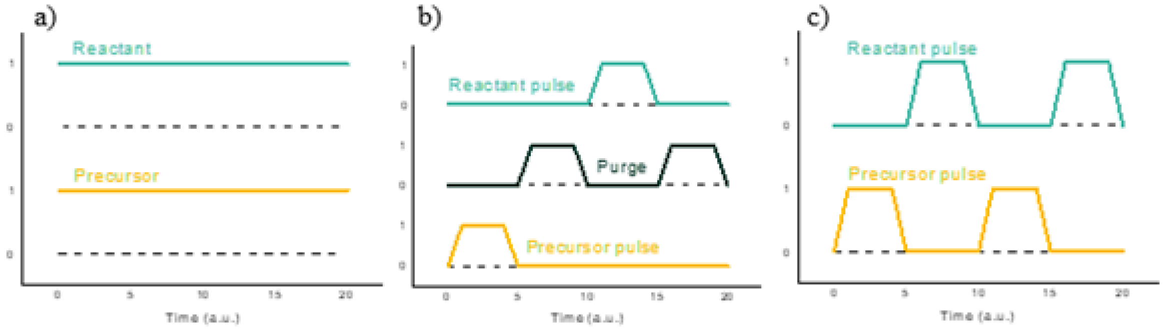

Figure 1. a) CVD mode b) ALD mode and c) FAST mode

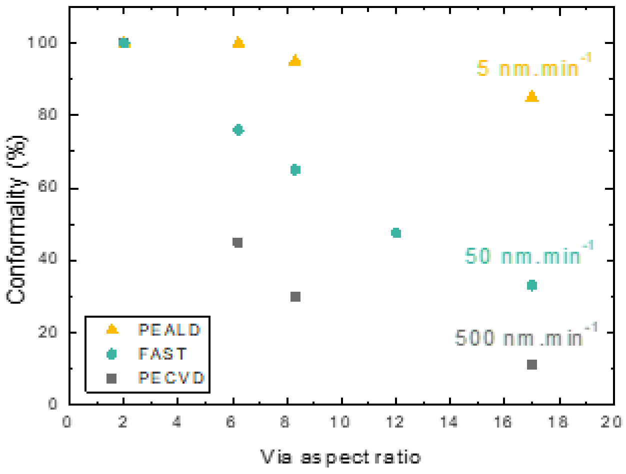

Figure 2. SiO2 layer conformality evolution

NANO-P1-017 ● Localized laser texturing of passivating nano-layer deposited by PVD for industrial olfactory sensors applications

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Perfluorinated coatings are attractive candidate materials for passivation due to their hydrophobic and lipophobic properties [1] with contact angle against deionized water around 110°. Adding localized texturing to the passivation process allows to create preferential adsorption areas of volatile organic compounds. In this project, we develop selective surfaces for the immobilization of molecular probes responsible of different affinity to various smells [2]. The objective stands in removing the total passivation layer thickness (about 10 nm) without damaging the sensors surface. Olfactory sensors are based on two technologies [3]: Surface Plasmon Resonance imaging (SPRi) [2] and integrated photonic on silicon (MZI Mach-Zehnder Interferometers) [4].
Our presentation will focus on the description and the analysis of the different processes developed in this study. First, the passivation layer is deposited by PVD in an industrial vacuum chamber. Deposition process was developed to obtain high hydrophobicity on various substrates like gold coated prism or silicon chip, used for the different generation of olfactory sensors. Then, this passivation coating was selectively removed following a variety of pattern with a femtosecond laser process. The image below describes the successive steps of the process on gold coated prism (SPR technology) on the left and on silicon chip (MZI technology) on the right. The main challenge was to remove the total passivation layer thickness without damaging the sensor surfaces at the nanometric scale. Precise laser modification with suitable parameters was performed to specifically eliminate the passivation, keeping functional sensors operational analysis with and without water vapour will be presented to observe the passivation layer effect and its removal without damaging the sensor.

Thanks/Acknowledgement
This work has been carried out within the framework of SILINOSE project thank to the financial support of BPI France and AURA Region.

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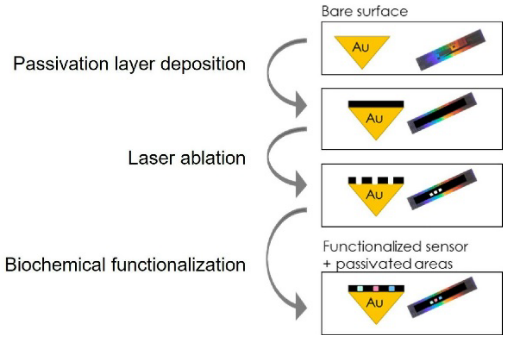

Description of the successive steps of the process

NANO-P1-096 ● Zirconium-based nanocatalysts by sputtering onto glycerol and solid carbon

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Zirconia-based compounds has gained significant attention as a potential catalyst material for the oxygen reduction reaction (ORR) due to its high electrochemical stability in acidic media and oxidative atmospheres [1]. The formation of oxynitride and under-stoichiometric compounds by nitrogen doping and oxygen vacancy formation seems to enhance the ORR catalytic activity [2]. In this study, ZrO_x and ZrO_xN_y materials were synthesized using two techniques: i) the direct deposition onto carbon support (plane and porous) by reactive magnetron sputtering (rMS) assisted to an inductively couple plasma (ICP) and ii) the growth of nanoparticles inside glycerol by the reactive magnetron sputtering onto liquid (rMS-SoL) technique (adapted for Pt catalyst [3]). Various gas compositions ($Ar + O_2 + N_2$) were used and small amount of H2 admixture was employed in order to enhance the formation of excited and ionized nitrogen species. The properties of the catalytic materials were investigated by Rutherford backscattering spectroscopy, electron energy loss spectroscopy and nuclear reaction analysis (composition), scattering electron microscopy, X-ray diffraction and high-resolution transmission electron microscopy (morphology and nanostructure). Finally, the ORR catalytic activity was investigated for different nanostructures, morphologies and compositions. These findings provide insight into the potential of ZrO_xN_y as a cost-effective and efficient catalyst for fuel cell, and could pave the way for further research in this field.

Keywords: Magnetron sputtering, sputtering onto liquid, oxinitride, catalyst, oxygen reduction reaction

Thanks/Acknowledgement
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NANO-P1-132 ● Direct liquid reactor-injector of nanoparticles: a safer-by-design aerosol injection for nanocomposite thin-film deposition adapted to various plasma-assisted processes

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The properties of nanocomposite multifunctional thin films are controlled by the characteristics of the matrix, of the nanoparticles, including their concentration, size, shape, and distribution and, consequently, of the interfaces between the nanoparticles and the matrix. Aerosol-assisted plasma processes used to prepare these coatings usually involve the direct spray of colloidal solutions into the plasma phase. However, this technique does not necessarily meet the specifications of the plasma process (i.e. the flow rates and the pressure), the requirements of nanocomposite thin films (i.e. small nanoparticles, homogeneously-dispersed and non-aggregated), and implies environmental and safety risks. Most of these limitations can be overcome by using a Direct Liquid Reactor-Injector (DLRI) of nanoparticles. This method allows in-situ synthesis of nanoparticles by mixing liquid and gas phases prior to their injection in the downstream plasma process. As this pulsed injection does not require handling of the nanoparticles, it is thus safer for manufacturers and users, as well as environmentally friendly. In addition, DLRI is fully compatible with various dry processes, including those based on plasmas. In this study, it is il-lustrated in an asymmetric low-pressure RF plasma and in a plane-to-plane atmospheric pres-sure Dielectric Barrier Discharge. The effects of the plasmas on the deposited nanocomposite thin films are assessed. The results show that in both cases, the deposited material consists of small ZnO nanoparticles (< 10 nm) in a diamond-like carbon matrix and that this method overcomes the drawbacks of the injection of preprepared nanoparticle solutions. Nevertheless, the nano-composite thin film composition varies with the plasma process. It is attributed to different mechanisms of transport of the aerosols in the plasma volume. Overall, this study proposes the DLRI as a generic technology for the preparation of nanocomposite thin films by plasma deposition and highlights some of the scientific mechanisms.

Thanks/Acknowledgement
This work was financially supported by the Université Toulouse III - Paul-Sabatier, the CNRS, and the Direction des Relations Internationales of the Université de Montréal through their contributions to the Québec-France International Research Network on Nanomatériaux Multifonctionnels Contrôlés (IRN-NMC).

NANO-P1-194 ● Structural and chemical characterizations of nanostructured cermet aluminium oxy-nitride / copper films

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Wide band-gap (BG) materials (TiO2, ZnO[1,2], recently nitrides[3]) as matrices associated with a metal under the shape of nanoparticles present very interesting potentials for diverse applications as concentrated solar power systems, photocatalysts… AlN, chemically stable, biologically inert[4] with a direct BG (5-6.2 eV) associated with copper well known for its anti-bacterial/fungal properties[5], could also be an interesting candidate as a photo-active antibacterial material.

Al-N-O-Cu thin films are prepared by Direct Current Reactive Magnetron Sputtering. The effect of the discharge power is studied to assess its influence on the structure, morphology and chemical composition of the film. The aim of the approach is to control different shades of material and qualify precisely the elaborated films in order to further correlate their nature with antibacterial/photocatalytic activity or optical properties.

The combination of High Resolution-TEM, 4D-EDS-STEM, STEM-HAADF and X-Ray Photoelectron Spectroscopy allowed getting fine and complementary analysis of the chemistry and structure of the films. The poster will present this investigation and will focus on the chemical environment and structural state of copper rich phases through these techniques. Results show that the films are composed of three phases, either AlN-rich or Cu-rich. STEM-EDS analysis of cross-section views and XPS chemical depth profiling proved essential to assign the presence of oxygen from ex-situ contamination or during film elaboration. It also revealed the presence of a primitive layer that future elaboration protocols will have to eliminate.

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NANO-P1-202 ● Synthesis of ultra-thin film MAA:PEGDMA hydrogels with customized properties by atmospheric pressure plasma

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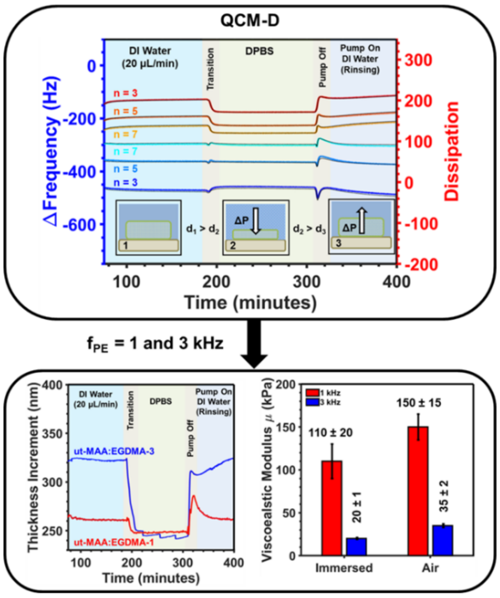
The synthesis of ultra-thin film (utf) hydrogels to develop novel biomedical applications (such as sensors or artificial skins) is raising the interest of the scientific community. Up to the date, the main challenge is related to the achievement of utf-hydrogels with accurate control on the thickness and structure. Certainly, synthesizing utf-hydrogels with thicknesses below 1 µm while maintaining a proper control on the resultant hydrogels properties, but without restricting their scalability and applicability, becomes highly complex when approached through conventional techniques. Herein, we explore the use of atmospheric-pressure (AP) plasma deposition method as a viable alternative to design utf-hydrogels with excellent thickness accuracy, versatility and foremost, customized properties. We report for the first time a procedure able to control independently the nature and generation of cross-links, based only on the plasma exposure frequency (f_{PE}) rather than relying on varying initial chemical formulation. Therefore, utf-hydrogels (MAA:EGDMA) were successfully synthesized and directly deposited with customized viscoelastic properties (ranging from 150 to 20 kPa) and swelling ratios (> 130 %). Both topographical and structural analyses by means of FTIR, XPS and AFM measurements allowed elucidating the effects of the f_{PE} on the cross-link generation mechanism. Moreover, results confirm that changing the f_{PE} does not affect the thickness accuracy reported for the AP plasma techniques. The structural results obtained have been completed with quartz-crystal microbalance with dissipation (QCM-D) coupled with spectroscopic ellipsometry (SE) studies. Hence, coupled SE/QCM-D technique has been put in the spotlight as an efficient alternative for characterizing the resulting properties of utf-soft materials, providing interesting information of the phenomena related with the interface. Due to its relevance in biological applications, the presence of a hydrated layer is discussed and characterised.



PROC-P1-098 ● Optical diagnostics of a N_2/Ar microplasma for the deposition of hexagonal Boron Nitride

B. Menacer, A. Remigy, C. Lazzaroni, K. Gazeli, G. Lombardi, S. Prasanna, X. Aubert
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Boron Nitride with a hexagonal (*h*-BN) crystalline form is a relevant material that has interesting properties for various applications involving Van der Waals (VdW) heterostructures. As an example, Magnetic Tunneling Junction (MTJ) or Tunneling Field-Effect Transistors (TFET) can be developed using VdW heterostructures of graphene and h-BN [1]. The main goal of this work is the deposition of *h*-BN using a Micro Hollow Cathode Discharge (MHCD) operating in a N_2/Ar mixture coupled with a polarized substrate (found few cm away from the MHCD). This configuration is known as a Micro Cathode Sustained Discharge (MCSD). To optimize the deposition process, a detailed study of main plasma properties, such as emissive species, gas temperature (T_{Gas}) and N-atom density, is required. To understand the dynamics of reactive emissive species, we used Optical Emission Spectroscopy (OES). OES was also used to determine the rotational temperature of N2(C) (Figure 1) and OH(A), which is assumed to be close to T_{Gas}. Furthermore, we determined N-atom absolute density in the deposition chamber by means of Two-photon Absorption Laser Induced Fluorescence (TALIF) [2] and Vacuum Ultra Violet Fourier Transform Spectrometry (VUV-FTS; SOLEIL synchrotron). Regarding TALIF, a 2D mapping of the N-atom density was performed at different discharge conditions. Concerning VUV-FTS, the absolute N-atom density was obtained directly by absorption of VUV radiation between the $3s^4P_J$ (J = 1/2, 3/2 and 5/2) and the fundamental $2p^3\,{}^4S_{3/2}$ N-atom levels (four different positions outside of the MHCD were probed). When a major part of the electric current was delivered to the substrate, our experiments revealed a homogenisation of the N-atom density in the deposition chamber. The OES measurements indicated that the gas temperature does not change very much with the electric current, pressure and %N2 in the gas mixture

Thanks/Acknowledgement
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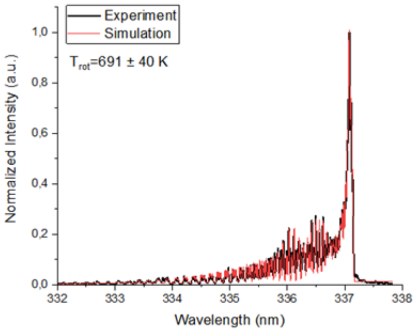

Figure 1. Experimental N_2(SPS)(C, v′=0 – B, v′′=0) rotational spectrum fitted with a simulated one generated with a MATLAB code. The error of the method does not exceed 40 K.

PROC-P1-129 ● Tuning plasma-droplet interactions in dielectric barrier discharge at atmospheric pressure for thin-film deposition

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Atmospheric-pressure plasmas operated in reactive gas mixtures are widely used for (multi)functional thin-film deposition. Among them, Dielectric Barrier Discharges (DBD), one of the most well-developed non-equilibrium plasma source at atmospheric pressure, are frequently used to deposit thins films on large area surfaces. The studies conducted on thin-film deposition by plasma polymerization at atmospheric pressure show that the morphology of the deposited material depends on the nature and flow of the precursor, which is usually introduced into the plasma chamber either directly as a gas (for example, silane) or as a vapor from the liquid phase through an atomizing system (for example, HMDSO).

This work investigates the effects of discharge parameters on the deposition of organosilicon thin films by pulsed direct liquid injections of hexamethyldisiloxane (HMDSO) into a plane-to-plane dielectric barrier discharge generated in nitrogen at atmospheric pressure. At low frequency of the applied voltage, plasma-deposited thin films exhibit viscous and droplet-like morphologies. Such feature is linked to the charging of HMDSO droplets in the discharge and their transport towards the substrate by the low-frequency electric field. Comparatively, the thin films obtained at high frequencies present rough morphologies with dust formation. In such conditions, the deposition efficiency decreases due to confinement of charged HMDSO droplets in the inter-electrode space. In addition, enhanced plasma-droplet interactions linked to neutral gas heating induce precursor evaporation. This yields to solid particles formation due to the onset of gas-phase association of precursor fragments.

Overall, the results presented herein show that tuning plasma-droplet interactions, droplet transport, and droplet evaporation play a crucial role on the thin-film deposition kinetics and plasma polymerization dynamics in aerosol-assisted processes.

Thanks/Acknowledgement
This work was financially supported by the Direction des Relations Internationales of the Université de Montréal and Université Paul-Sabatier de Toulouse through their contributions to the Québec-France International Research Network on Nanomatériaux Multifonctionnels Contrôlés (IRN-NMC).

PROC-P1-131 ● Time-resolved optical emission spectroscopy analysis of a low-pressure RF plasma with pulsed Injection of argon, pentane, and ZnO nanoparticles

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Nowadays, the concept of multifunctional materials combining various properties in a single system has become a prerogative in the development of innovative surfaces. However, for several applications, one of the main challenges is obtaining coatings formed of isolated (non-aggregated) nanoparticles dispersed in a controlled manner in a matrix. In this context, we started working on the development of a new flexible, green, safe and industrializable method for the synthesis of multifunctional nanocomposite thin layers. This method is based on a reactor-injector of nanoparticles that can synthesize nanoparticles from liquid organometallic precursors just before injecting them into a plasma deposition reactor. Recent studies have shown that this approach limits the agglomeration associated with the vaporization of droplets and avoids possible toxicity problems related to the manipulation of nanoparticles before deposition.

In the present study, time-resolved optical emission spectroscopy is used to examine the behavior of a capacitive RF plasma under pulsed gas and precursor injection conditions. Time-resolved optical emission spectroscopy is a valuable tool for understanding the behavior of plasmas under dynamic conditions. Experiments are done in the specific case of pulsed injection of Ar gas, Ar gas with pentane precursor, and Ar gas with pentane precursor and ZnO nanoparticles. Such conditions are relevant for the deposition of thin films made of ZnO nanoparticles contained in a diamond-lie carbon matrix. Ar emission line emission intensities (2p-to-1s transitions) recorded as a function of time are compared to the predictions of a collisional-radiative model to obtain the temporal variations of the electron density, electron temperature (assuming Maxwellian EEDF), and number density of metastable Ar atoms. Significant variations of these fundamental plasma properties are observed and will be used as building blocks for further process development.

PROC-P1-137 ● Developing a method with optical emission spectroscopy to control thin layer in R-HiPIMS deposition process

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Time-resolved plasma diagnostics are implemented to investigate a reactive HiPIMS (R-HiPIMS [1]) TiO2 deposition process running at a repetition rate of 1 kHz. A specific method, developed in our team, based on the coupling of optical emission spectroscopy (OES) with electrical measurements [2], is used to control the thickness of the coating. The study focuses on the influence of the erosion profile of the target as well as the influence of the heating of the substrate holder through deposition and hysteresis measurements.
From these measurements, it is shown that the ratio of the normalized titanium line light intensity and the discharge current (<signal TA_SOE(Ti)/Iint >) is a suitable and reliable parameter that reflects the deposition rate quite well as shown figure 1, whatever is the erosion state of the Ti target. Moreover, this parameter was also successfully used to control the process in the transition regime between metallic sputtering and compound sputtering. A global method is thus proposed to monitor and control the R-HiPIMS deposition process, which can be of great interest at an industrial scale.

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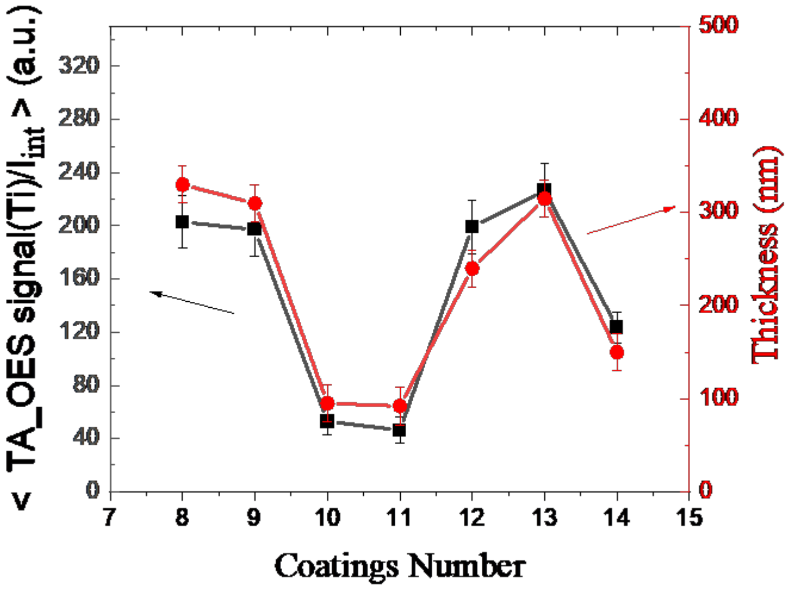

Figure 1 : Comparison between the thickness of deposits #8 to #14 and the corresponding <signal TA_SOE(Ti)/Iint > of neutral titanium (line at 365.35 nm). Each deposits correspond to an unique set of plasma parameters (substrate holder heating or not, with or without O2 in gas mixture, erosion state of the target). The pressure is 0.7 Pa, T=1ms, Td=20 µs and <P>T=45 W. The deposition time is 4h and the silicon substrates are placed 11 cm in front of the target.

PROC-P1-142 ● Study of N_2/H_2 plasmas produced by an active screen source: contamination due to NO production and role of hydrogen in the gas mixture

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The active screen plasma source concept was developed at the beginning of the 21st century to improve the conventional diode nitriding process [1]. In this transferred plasma configuration, a metal mesh serving as cathode surrounds the samples to be treated, the reactor walls acting as anode. The plasma is thus formed on the grid which is a source of active species and heat.

Currently, this system is not as efficient as expected, and many questions remain concerning the nature and kinetics of the species created in the plasma phase. These knowledges are however fundamental to understand the mechanisms of nitriding with, in-fine, the optimization of this type of process. We have designed an ASPN (Active Screen Plasma Nitriding) equipment with a stainless steel (AISI 304 L) cylindrical mesh screen connected to DC-pulsed power supply.

The so-created plasmas were investigated by using optical emission spectroscopy (OES), voltage and current probes. In pure N2, we have observed a strong emission of the NO g-bands (210-290 nm). Its presence is linked to the reactor contamination by oxygen and water vapor when it is opened to introduce the samples to be treated. Time tracking of the light emission in the UV spectral band showed the gradual appearance of the 4th positive of N2, when the NO intensity becomes sufficiently low [2]. Although NO species in the plasma phase have negative effects on nitriding performances, their production in this type of equipment can also be a real opportunity for atomic nitrogen fixation, an opportunity for hydrogen storage for example[3].

In this presentation, we will also try to describe the role of hydrogen. For nitriding, it is well known that N2-H2 mixtures containing around 20% hydrogen are generally used to get better results. What kind of species are formed in the plasma phase in these conditions? What is the effect on NO production? Does hydrogen play a role in the reactor decontamination process? We will address these issues in light of the results obtained with plasma analyses.

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PROC-P1-174 ● Impact of electronegativity and monoenergetic electrons on the properties of electrostatic sheaths in magnetized discharge plasmas

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The dusty plasma is a complex mixture of electrons, ions, neutral particles, and charged dust grains that are commonly observed in both space and laboratory environments. Over the past few years, numerous studies have been conducted to explore different aspects of collective processes and to observe the crystalline structure formation processes of dust in dusty plasmas. These studies have primarily focused on electrostatic sheaths, linear and nonlinear dust waves, instabilities, and the formation of dust crystalline structure.

The present study is concerned with the properties of electrostatic sheaths in magnetized discharge plasma in the presence of dust grains of various sizes and monoenergetic electrons in an electronegative environment. Electrons and negative ions are considered to be in thermodynamic equilibrium, whereas positive ions, fast monoenergetic electrons, and dust grains of different sizes are described by fluid equations. The size distribution of dust grains is modeled using a Gaussian law, while interactions between dust grains are ignored. The limited orbital motion (OML) model is used to describe the charge of dust grains. The numerical results obtained indicate that the presence of fast monoenergetic electrons has an impact on the velocity of positive ions, which increases. However, electronegativity has the opposite effect, decreasing the velocity of positive ions. Other parameters were also investigated, and the results were analyzed in detail.

PROC-P1-185 ● Pulsed aerosol assisted plasma deposition: influence of the injection parameters

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Aerosol-assisted processes enable to deposit various thin films [1,2,3]. It frequently involves the nebulization of liquids, from pure solvent to solutions of nanoparticles. By analogy with dusty plasma, the continuous injection of liquid droplets in the plasma volume introduces additional electron losses as, for example, electron attachment on the liquid particles that can further modify the plasma deposition process.

Alternative means of continuous aerosol injection into the plasma deal with Pulsed, Direct Liquid Injection (PDLI) [4,5]. Although the pulsed injection temporarily affects the density of neutrals, a stationary state can be restored between pulses, and the plasma can return to equilibrium. This optimizes the ionization rate and, consequently, the thin film deposition.

This work deals with aerosol-assisted plasma deposition in a low-pressure RF plasma. Considering the times for droplet charging, evaporation, transport and confinement, depending on the injection parameters (injection times and frequency), it is possible to tune the plasma deposition mechanisms. It is shown that the operating window enables to deposit thin films with an extended range of material balance.

Thanks/Acknowledgement
Ce projet est développé dans le cadre de 4 projets, à savoir, l'ANR LuMINA (partenariat entre IMN, Laplace et LCC), le projet SHealing (Laplace, LCC et CNES), le défi CNRS NanOnline (IMRCP, Cordouan Technologies et Météo-France), et le projet PRIMA-Québec / CRSNG RI-plasma (UdeM, Laplace, LCC, Safran, Cordouan Technologies).

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PROC-P1-189 ● In-situ temperature measurement of components in PECVD machines with a 3-fold rotation

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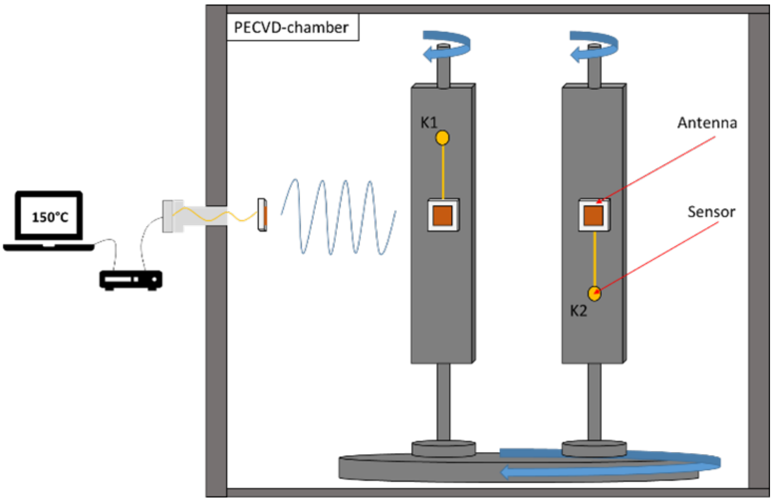
The measurement of temperature, particularly surface temperature, during the PECVD (Plasma-Enhanced Chemical Vapor Deposition) process poses a complex scientific challenge. Various technologies, such as thermocouples and pyrometers, are employed for this purpose, but encounter specific difficulties. Pyrometers, for instance, must contend with changes in surface emissivity throughout the coating process, and require protection from coating material. Classical thermocouples, on the other hand, involve intricate wiring, especially in the case of a 3-fold rotation.

To address these challenges, an In-Situ measurement system utilizing Surface Acoustic Wave (SAW) technology and resonators is employed to measure both surface and internal component temperatures in PECVD coating machines without limitations imposed by 3-fold rotation. The system offers several advantages, including the absence of wiring through the rotation feed-through, a passive nature that eliminates the need for active components such as batteries inside the chamber, and exceptional versatility. It comprises a reader positioned outside the chamber, a feed-through, antennas mounted on the chamber wall/ground/cover, and additional antennas connected to the sensor (figure).

By comparing the temperature readings obtained from the machine's temperature sensor (thermocouple) with those derived using SAW technology during various heating processes, the deviations are demonstrated. These results provide a deeper understanding of the significance of machine configuration, fixture, and part geometries, as well as process control, thereby enhancing insights into temperature height distribution.

Consequently, the identified deviations contribute to an optimized heating process, resulting in reduced energy consumption and enhanced process efficiency. These optimizations were derived and implemented based on a series component. This serves as the foundation for prospective temperature simulations aimed at cost-efficiently optimizing heating processes for other components, with minimal experimental iterations. Moreover, these findings facilitate the optimization of machine components, such as heaters, to improve temperature uniformity over the height.



Schematic drawing of the measuring system setup

PROC-P1-195 ● Equivalent electrical circuit modeling of a He dielectric barrier discharge plasma jet

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A model of an electrical circuit characterizing dielectric barrier discharge (DBD) jet is proposed. Characterization is done by analyzing waveforms, phase shifts and *V-I* characteristics when plasma is interacting with three different targets: Cu, PET and H_2O, respectively. The schematics of the DBD jet is presented in Figure 1.a). The lower electrode is powered with high-voltage sinusoidal signal at 30 kHz frequency, while the other electrode and target holder are grounded. Scheme of the equivalent electric circuit is presented in Figure 1.b). Left-hand side scheme corresponds to the plasma OFF regime. The circuit is the same for all three targets, R_t is zero, and the grounded elements R_{ge} and C_{ge} do not change. As expected, small changes are observed only in the elements corresponding to the target electrical characteristics, R_{te} and C_{te}. As for the plasma ON regime, it is found that the shape of the $i_{te}(t)$ signal shows a streamer (bullet) appearing in the last quarter of the positive part of the input voltage amplitude. The shape of the streamer current corresponds to the third harmonic, oscillating at 90 kHz, with some delay compared to the voltage. Hence, the plasma ignition is reflected in the form of a large resistor R_t, in orders of MΩ, and by voltage controlled current source in the additional branch of equivalent electric circuit representing streamer current (right-hand side of the Figure 1.b)).

Thanks/Acknowledgement
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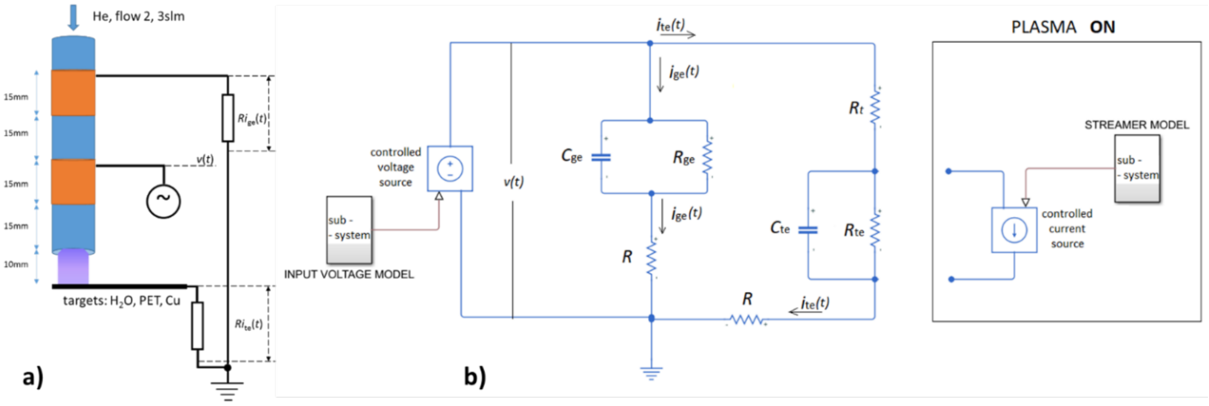

Figure 1. a) Schematics of the experimental setup. Voltages on R=100 kΩ resistors are used for monitoring the grounded electrode current $i_{ge}(t)$ and the target current $i_{te}(t)$;
b) Schematics of the equivalent electrical circuit. Left-hand side of scheme corresponds to the plasma OFF regime, right-hand side corresponds to the plasma ON regime.

SOUR-P1-143 ● Dynamics of the material ejection in a dipolar arc in DC regime and its connection to the arc noise

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The electrification of transport modes and more generally of the society is based on the use of Direct Current (DC) electrical systems whose power is constantly increasing. The risk of arcing in such a system is not negligible and requires the development of specific high-precision protection systems. DC arcing is therefore a current topic of study that is attracting a lot of interest.
In order to carry out studies on this topic, we have developed an experimental test-bench which makes it possible to produce DC arcs at voltages of up to 1500 V in a simple and reproducible way. The arc is triggered by contact separation and studied with several synchronized diagnostics. In particular, an ultra-fast camera capable of recording up to 2 million frames per second is used to interpret the current and voltage measurements.
In this contribution, we demonstrate that a significant part of the so-called "arc noise" in the kHz range can be attributed to the ejection of materials (cf. Fig. 1). Depending on the experimental conditions (arc power, air pressure), various types of particle emissions are observed and discussed: ejection of micron-sized solid dust or liquid metal droplets, ejection of nanoparticles, vaporization, massive ejection by bursting bubbles. The dynamics of micron-sized particles is investigated by Particle Tracking Velocimetry and Artificial Intelligence methods and it is shown that at least a fraction of the particles are charged.

Thanks/Acknowledgement
This work was supported by the French national research agency (ANR) under project ANR-19-CE30-0033-01 and by the PLUS project co-founded by FEDER-FSE Lorraine et Massif des Vosges 2014-2020. It is also supported by the Region Grand-Est and APREX Solutions company.

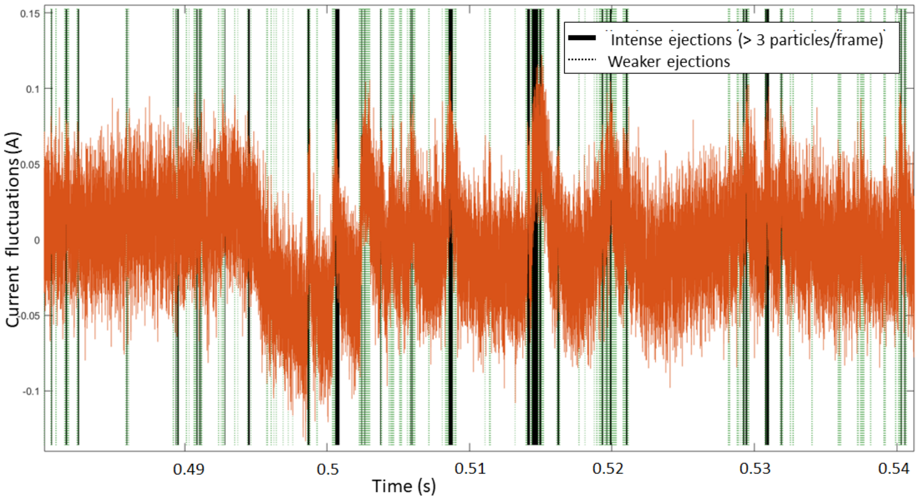

Figure 1: Arc current fluctuations versus time

SOUR-P1-152 ● O_2 shielding modulates the spatiotemporal density of Ar($1s_5$) in argon atmospheric-pressure micro-plasma jets

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Atmospheric pressure plasma jets provide an unobtrusive plasma source for different industrial applications. Argon DBD micro-plasma jets produce ionization waves that propagate through the gas jet [1] while ionizing and exciting species such as argon metastables [2]. Because these streamers propagate in a varying gas mixture, as the argon jet mixes with the shielding air, they create a challenge for modeling and experimental studies.

In this work, we explored the effect of the shielding with pure O_2 gas by using a co-axial argon jet, i.e., an argon jet flow (1slm) with an annular shielding co-flow (3slm). The plasma is produced by a square high-frequency high-voltage pulse (1µs, 4kV, 20kHz), producing a first discharge during the rising edge of the pulse and a second one during its falling edge. We varied the shielding gas mixture with different N_2-O_2 fractions. For each condition, the local temporal absolute density profile of Ar($1s_5$), see Figure 1, was estimated by applying an Abel inverse on the temporal absorbance profiles. Finally, these results were compared with optical emission spectroscopy data.

A 100% N_2 co-flow leads to the lowest maximum Ar($1s_5$) density and the lowest reproducibility for both discharges. With 2%O_2 shielding, the peak density increases for the first discharge, while the reproducibility increases for both. Increasing the O_2 fraction increases the excitation velocity for the first discharge but decreases it for the second one. The temporal profiles show a two-step Ar($1s_5$) density increase for the first discharge and different propagation behavior between the first and the second discharges.

Finally, by varying the shielding O_2 fraction, we can further discuss hypotheses on the flow dynamics, the electronegative shielding, the photoionization, and the quenching rates, providing valuable input and validation data for models.

Thanks/Acknowledgement
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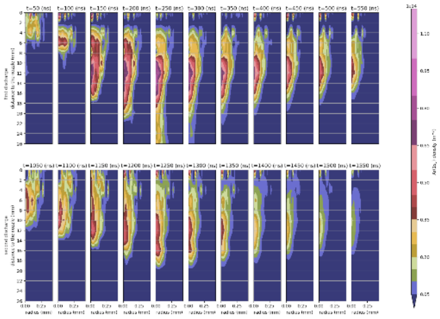

Ar(1s5) density for a 50%O2-50%N2 co-flow.

SOUR-P1-158 ● New micro-plasma reactors for the synthesis of heterostructures of 2D films of hexagonal Boron Nitride and Graphene

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Graphene is a material of choice for a wide range of promising technological applications in nano- and optoelectronics. Being only one atom thick, it is extremely sensitive to its environment, which strongly modifies its properties. To prevent the hindrances of the substrate, graphene could be encapsulated in a material that preserves its properties. The search for new substrates revealed that hexagonal Boron Nitride (h-BN) buffer layers can preserve the properties of graphene [1], thus potentially leading to new disruptive technologies. However, there is still no cost-effective method for the deposition of high-quality films of graphene encapsulated in h-BN on large surface areas. To try to answer this issue, our work focuses on the development of a new deposition process using a new micro-plasma configuration based on the classical Micro-Hollow Cathode Discharge (MHCD), which has shown promising perspectives [2-4].

The physico-chemical properties of the micro-plasma have been studied, in order to optimize the production of the key species required for the deposition and growth of h-BN (atomic nitrogen) and graphene (carbon radicals) films. A detailed electro-optical characterization of the different micro-plasma devices used has been performed, for several operating conditions, from pure argon to argon-nitrogen mixtures, from few tens to several hundreds of mbars of pressure, from DC to high-frequency (tens of kHz) nano-second pulsed electrical schemes. The complementarity of electric measurements and fast ICCD imaging allowed to highlight the link between the cathodic expansion and the current deposited in the plasma. Advanced optical diagnostics such as time and spatial-resolved optical emission spectroscopy and tunable diode laser absorption spectroscopy have also been used to determine the gas temperature, the electron density and the absolute density of argon metastable (Ar(1s5) and Ar(1s3)) and radiative (Ar(1s4)) states inside the micro-plasmas and throughout the plasma expansion towards the deposition substrate.

Thanks/Acknowledgement
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DEPO-P2-021 ● Plasma magnetron sputtering using combinatorial approach to deposit complex alloys thin films

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In the current context of the SARS-COV-2 pandemic, there is an urgent need to find "multimaterial" solutions to prevent the formation of biofilms and to promote the bactericidal and virucidal properties [1] of surfaces (metallic or plastic) in regular contact with users. Current solutions make it possible to limit the formation of a biofilm (by anti-adhesive or contact killing strategies) or to form films, with proven anti-bacterial properties (release killing). Their anti-viral properties, when they exist, do not cover the novel corona virus (SARS-CoV-2). This work aims to synthesize thin films of complex alloys (poorly ordered metallic multimaterials, HEA: High entropy alloys [2]) by plasma magnetron sputtering deposition using a combinatorial approach in order to deposit films of a large range of composition in one run of experiments. Actually, in this kind of alloys, morphology, phase formation and crystalline structure, that determine the final properties, are strongly dependent on the chemical composition.
The selected alloy families are CuTiZn and CuZrZn since Cu, Zn and Ti and their associated oxides [3,4] are used as bactericidal agents. Zr and Ti are also present in order to add good mechanical properties to the coating such as abrasion resistance, required especially during cleaning cycles. The structure and crystallography of thin films analyzed by scanning electron microscopy and X-ray diffraction in order to determine the relevance of the use of amorphous materials, solid solutions or intermetallics for anti-bacterial and anti-viral applications (contact-killing or release-killing). All these analyses are coupled in parallel with molecular dynamics simulations. Moreover, abrasion resistance is also studied.

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DEPO-P2-032 ● Solar-blind photodetectors based on β-Ga_2O_3 fabricated by oxygen plasma assisted-pulsed laser deposition

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Solar-blind deep ultraviolet (DUV) is fully absorbed by ozone and the atmosphere, resulting in wide applications of DUV photodetectors in the military and industrial facilities without a sun light effect [1]. In the many kinds of semiconductors for photodetection, β-Ga_2O_3 is widely used to detect DUV due to a wide bandgap of 4.7 eV (~ 280 nm) for maximizing DUV absorption and selectivity [2,3]. However, there are still challenging issues to improve the β-Ga_2O_3 DUV photodetector despite excellent material properties.

In this work, the Ga_2O_3 films were deposited on quartz substrates using plasma-assisted pulsed laser deposition (PLD) system. A neodymium-doped yttrium aluminum garnet (Nd: YAG) laser with wavelength of 266 nm was operated with an energy of 95 mJ/cm^2 and a pulse rate of 10 Hz. The RF power of the oxygen plasma was varied from 0 to 100 W. After the deposition process, post-annealing treatment was performed at 600 °C under vacuum conditions for 30 min. The metal–semiconductor–metal-structured β-Ga_2O_3 photodetectors were fabricated with electrode length and width of 300 μm and 1000 μm, respectively. All optoelectronic properties of the material were enhanced as increase the RF power. From the space charge-limited current measurements, it is considered that the oxygen plasma power leads to VO and improves the crystallinity arising from additional oxygen reactions. The β-Ga_2O_3 photodetector with RF power of 100 W showed the best optoelectronic characteristics, such as photoresponsivity of 0.39 A/W, external quantum efficiency of 192.61%, and detectivity of 9.09×10^{13} cm Hz$^{1/2}$/W. In addition, photo-switching analysis revealed the fastest photoresponse speeds of 1.46 s and 0.21 s for on/off switching. These results might be originated from the decrease of V_O defect density in the β-Ga_2O_3 films by the ionized oxygen atoms.

Thanks/Acknowledgement
This work was supported in part by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2021R1A2C1093652 and 2022M3I8A2085434).

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DEPO-P2-090 ● Plasma decontamination of surfaces using a microwave torch – assessment of the additional role of a TiO_2 photocatalytic layer

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Nowadays, atmospheric pressure plasma torches find applications in a wide variety of fields such as production of thin layers by PECVD, surface cleaning or decontamination. The use of plasma has a significant advantage from an environmental point of view compared to processes using liquid phases which generate effluents to be reprocessed. The plasma source used for this study was an Axial Injection Torch (or TIA for “Torche à Injection Axiale”). It is a microwave torch operating at atmospheric pressure and ambiant air.

In a first step, the plasma conditions were optimized for the treatment of surfaces contaminated with Escherichia coli microorganisms. To discriminate the role of temperature from the other effects induced in a plasma like the production of reactive species and UV, low temperature conditions were investigated. A 4.2 Log reduction was obtained, corresponding to disinfection.

To improve this inactivation process, TiO_2 thin layers with photocatalytic properties were produced by PECVD using the same plasma source and TTIP as titanium precursor. The surface temperature was correlated to the structure and microstructure of the TiO_2 thin layers. As the surface temperature was increased, the proportion of the rutile phase was increased up to 30%. The best photocatalytic efficiency was obtained for the TiO_2 film produced for a microwave power of 500 W and 8 slpm of argon plasma gas flowrate (Figure 1). This layer (Figure 2) was deposited on the surface to be decontaminated in order to couple its action to plasma disinfection. A 5.3 Log reduction was achieved for a 1 min 30 duration of plasma exposition, exceeding once again the disinfection threshold of 4 Log. These results suggest the synergy effect between the plasma role and titania film photocatalytic activity for surface disinfection.

Thanks/Acknowledgement
The authors thank the Region Nouvelle-Aquitaine for financial support provided by the project PMO#Innovation.

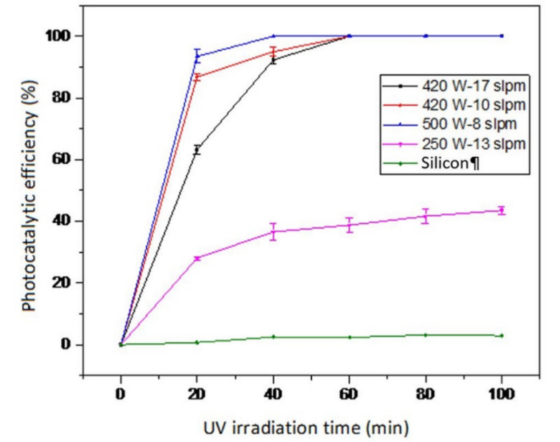

Figure 1: photocatalytic efficiency of thin titania films deposited on silicon substrates for different microwave powers and argon plasma flowrates

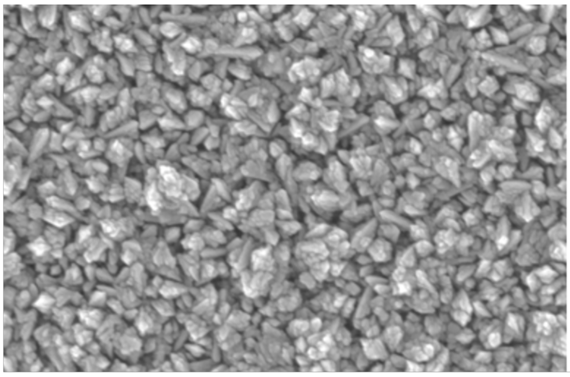

Figure 2: scanning electron microscopy top view image of the titania film deposited at a microwave power of 500 W and an argon plasma gas flowrate of 8 slpm

DEPO-P2-094 ● Elaboration and characterization of WO_3/TiO_2 nanostructured photoanodes for solar water splitting

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LISE (UMR8235) - Sorbonne University - CNRS – Paris (FR)

This work is related to the problem of sustainable hydrogen production by photoelectrolysis of water. The objective is to develop and then characterise the photoelectrochemical properties of photoanodes based on nanostructured semiconductor oxides using sunlight. In a first step, TiO2 nanotube arrays obtained by electrochemical anodization of Ti substrate in water/ethylene glycol/NH4F mixtures. This process allows us to obtain quite regular nanotube networks with a diameter of around 70 nm and a depth of up to 1 µm [1]. The nanotubes are then covered by a WO3 layer deposited by rf reactive magnetron sputtering from a W target in an Ar-O2 plasma. The deposits are then annealed at 525°C to obtain the anatase phase of TiO2 while WO3 is in the orthorhombic one. The objective of combining these two oxides is to form a Z-scheme TiO2/WO3 heterojunction for enhanced charge carrier separation [2]. In this study, the effect of the oxygen content in the plasma gas on the properties of the WO3 nanolayers and on the poisoning of the target is studied. Photoelectrochemical characterization such as incident photon-to-current efficiency (IPCE) or intensity-modulated photocurrent spectroscopy (IMPS) [3] are carried out to understand and evaluate the mechanisms involved in the photoanode produced.

Thanks/Acknowledgement
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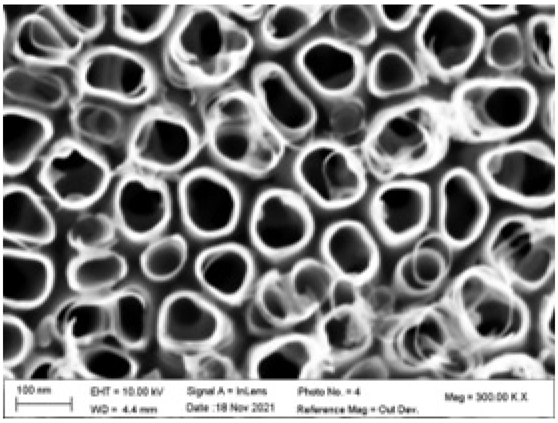
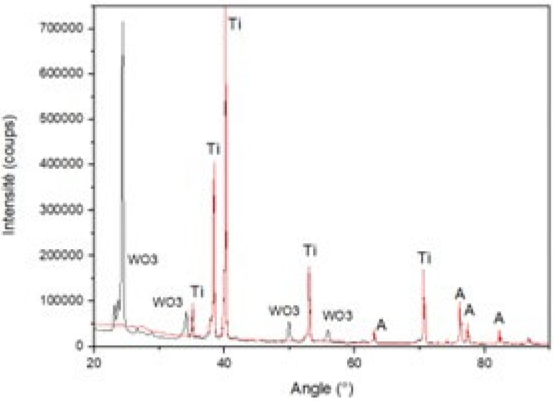


TiO_2 nanotubes grown on Ti by anodization



XRD analysis of a $Ti/TiO_2/WO_3$

DEPO-P2-130 ● Superelastic TiZrNb and TiZrNbSn coatings for biomedical applications

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Titanium alloys are propitious materials in biomedical implants for their mechanical properties and biocompatibility. Nitinol (Ni-Ti), especially, has been used because of its superelasticity (up to 12% recoverable strain) due to a reversible martensitic transition. Ni, however, has been proven allergenic and so in the past decade, research has focused on β-type titanium alloys with non-toxic and non-allergenic elements such as Nb, Sn, Ta or Zr with the aim of replacing Ni-Ti. In this study, novel coatings based on ternary and quaternary titanium alloys have been elaborated. Their properties have been studied for bulk materials; however, the structural and mechanical properties for their thin film counterpart remain to be elucidated, which is the aim of the present study.

Ti-Nb-Zr and Ti-Nb-Zr-Sn coatings have been elaborated at room temperature by magnetron sputtering at a working pressure of 0.26 Pa. By using different targets and by changing the power applied to them during deposition, different chemical compositions have been obtained, with Nb content ranging from 0 to 33 at.%. The focus has been on identifying the crystallographic structure and the mechanical properties of the films depending on their chemical composition. XRD, TEM and resistivity measurements were performed to study the phase formation with respect to the Nb content. The stress induced during film growth has been evaluated *in situ* using wafer curvature measurements and the mechanical properties were evaluated using nano-indentation and tensile tests. To assess the biocompatibility of the films, early cell behavior (cell adhesion, spreading and morphology) will be characterized and standardized cytotoxicity assay will be conducted.

XRD, TEM and resistivity measurements evidence that with increasing Nb and Zr content, the phase composition evolves from hexagonal α phase to orthorhombic α’’ martensite and then to cubic β phase. The curvature measurements show that at low Nb content, the film first develops a compressive stress that gradually evolves towards tensile direction with increasing film thickness. At high Nb content, the stress remains compressive throughout the entire deposition. The biocompatibility of the coatings with different microstructure, roughness and porosity has been assessed *in vitro*. All samples exhibit cytocompatibility with fibroblast cells and good adhesion of pre-osteoblast cells after 72 h has been observed.

DEPO-P2-183 ● Fabrication of high-quality moisture barrier film using SiN_x/SiOF/SiN_x via Pilot-Scale Roll-to-Roll PECVD System

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The aim of this study was to address the challenge of moisture and oxygen degradation in OLED displays and organic/inorganic hybrid perovskite-based electronic devices. To overcome this problem, a high-performance moisture barrier film was developed using silicon oxyfluoride (SiOF), which is known for its exceptional moisture adsorption properties. However, the low density of SiOF posed limitations as a barrier material. To compensate for this, a silicon nitride (SiNx) thin film with superior moisture barrier properties was applied. The deposition of SiOF at the interface between the SiNx thin films was carried out using a pilot-scale plasma-enhanced chemical vapour deposition (PECVD) system. The composition and moisture-trapping capabilities of the SiOF film were evaluated using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). An in-situ deposition of a SiNx/SiOF/SiNx multilayer film with a thickness of 200/50/200 nm was performed. The physical and optical properties as well as the moisture barrier performance of the film were evaluated using scanning electron microscopy (SEM), Aquatran-2 (Mocon Inc.), and UV spectroscopy.

Keyword
fluorine-doped silicon oxide, hygroscopic, plasma-enhanced chemical vapor deposition, roll-to-roll, three-layered moisture barrier

Thanks/Acknowledgement
This work was supported by a grant from the Korea Research Institute of Chemical Technology (KRICT) (Project No. KK2352-20) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MIST) (No. 2020R1A5A1019649).

DEPO-P2-198 ● Thin-film hydrogels deposited by atmospheric-pressure nano-second plasma-induced polymerization of MAA:EGDMA

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Hydrogels are hydrophilic polymeric networks that can absorb and retain high amount of water. Applied as thin films to substrates, hydrogels can provide biocompatibility, functionalities, swellability, and stimuli responsive properties to the uncoated surfaces [1]. Plasma-induced free-radical polymerization enable a fast, solventless approach for the preparation of polymeric thin-film hydrogels, without the use of a chemical initiatior [2]. In this study, hydrogels from free-radical copolymerization of methycrylic acid (MAA) and crosslinking monomer ethylene glycol dimethacrylate (EGDMA) are polymerized within minutes using a plasma curing-alike approach from liquid layer deposited over the uncoated substrates. FTIR spectroscopy enabled to confirm the free-radical polymerization and retention of the monomer functional groups (Figure 1b). By controlling the amount of EGDMA (from 1 to 10%), differences are noticed on the surface hydrophilicity of the thin-films (Figure 1c). Hydrogel properties were determined by quartz-crystal microbalance with dissipation (QCM-D) coupled with spectroscopic ellipsometry (SE) (Figure 1d). Series with 5 and 10% of EGDMA do not display any mass loss during the measurements, indicating their stability in water and PBS. Hydrogel swelling ratio increased and viscoelastic properties determined for these series show a 1.5 fold increase with a larger decrease of 180 fold, respectively (Figure 1d). The hydrogel thin film with composition of 10EGMDA:90 MAA although showing a decrease in hydrophilicity, revealed an excellent stability in liquid and higher swelling ratio.

Thanks/Acknowledgement
The Luxembourg National Research Fund (fnr.lu) is thanked for financial support through the COATIHN project (C19/MS/13641732).

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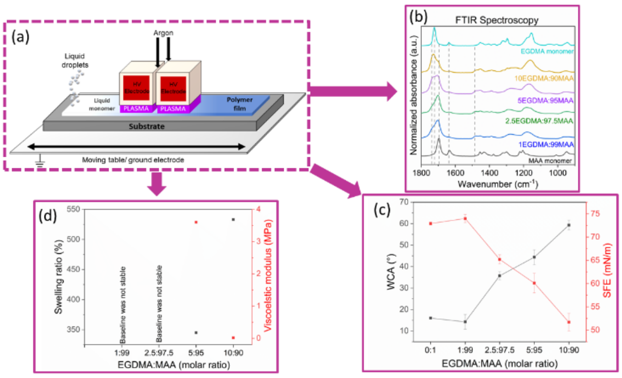

Figure 1: (a) Schematic of the atmospheric-pressure dielectric barrier discharge used in this study. (b) FTIR spectra of the thin films and MAA and EGDMA monomers (c) WCA and sur-face free energy (SFE) and (d) Swelling ratio and viscoelastic modulus determined by QCM-D of MAA:EGDMA thin films obtained from 1 to10 % of EGDMA cross-linker.

DEPO-P2-208 ● Synthesis and characterization of chromium doped VO_2 thin films for new applications

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Vanadium dioxide (VO2) is well known for its insulator-metal transition (IMT) and drastic physical variations in its thermal, electrical and optical properties near room temperature (68°C). The introduction of a small percentage of chromium during the synthesis of VO2 thin films may help to stabilize metastable phases at room temperature and lower the Fermi level of the semi-conductor material [1]. This could allow to explore new applications of such chromium doped VO2 thin films such as microelectromechanical or optomechanical devices or batteries

Chromium-doped VO2 films are grown using pulsed laser deposition (PLD), a technique well suited to the deposition of high-quality oxides. In the standard PLD process, a nanosecond KrF laser is used to vaporize the material from a target. Two deposition systems are used, with different ways to control doping. The first system employs a single target of chromium-doped vanadium, allowing doping with a pre-established stoichiometry [2]. The second system involves two targets, one composed of chromium and the other of vanadium, in order to control the doping concentration with an accuracy better than one percent [3].

In this study, 150 nm-thick VO2 thin films were synthetized on Si/SiO2 substrates. Chemical, electrical, morphological and structural characterizations were performed to achieve a better understanding of the importance of the deposition parameters (single or multi-target) and the effects of chromium doping.

Thanks/Acknowledgement

This work was fully supported by an international collaboration between the Institut National de la Recherche Scientifique (Québec) and the Institut de Recherche sur les Céramiques (Limoges) for a master's project in Energy and Materials Sciences.

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PLACC-P2-014 ● Synthesis of Nanoparticles by reactive magnetron sputtering on Ionic Liquid for photocatalytic applications, from metallic to Bi-based compound nanoparticles

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With the need for green and sustainable energy growing higher research has focused towards new photocatalytic materials and the performance enhancement of existing ones. Lately Bi-based materials have shown a great potential for such applications due to their low toxicity, low solubility and corrosion resistance. Indeed, recently produced thin films of Bi/Bi_2O_3 and Bi/BiO_xF_y exhibit a higher degree of photocatalytic activity in pollutant degradation and in photoconversion of CO_2 to CO compared to their powder counterparts. To further enhance their performances, we now study the effect of their nano-structuration.

Since few years, sputtering onto liquids with low vapor pressure (castor oil, ionic liquid…) demonstrate its interest to form nanoparticles (NPs) with high purity and sharp size distribution. However, up to now, this technique was only used to form metallic NPs in pure Argon plasma. In the present paper, we investigate this technique in reactive mode to form compound NPs. Indeed, we explored the sputtering of a Bismuth target onto [BMIM][NTf2] ionic liquid (IL) in various gas atmospheres: pure Ar, Ar/O_2 and Ar/O_2/CF_4.

In pure Argon plasma, we showed by HR-TEM, that spherical, well crystallized and dispersed Bi NPs of 3-7 nm are obtained. The diameter and the size distribution of these NPs do not significantly vary with the power, gas pressure, and sputtering time; but these sputtering parameters seem to influence the NPs concentration. The XRD and XPS analysis of NPs extracted from the liquid confirm their metallic nature. In reactive mode, in Ar/O_2 and Ar/O_2/CF_4, we succeeded in synthesizing spherical and crystallized Bi_2O_3 or $BiO_{0.5}F_2$ NPs with a size distribution ranging between 3 and 10 nm. Depending on the O_2 and CF_4 flow rates, these Bi-compound NPs could be in mixture with metallic ones. We demonstrate that radicals from the plasma do not modify compounds into ionic liquid. And we propose a mechanism to explain the NPs formation into reactive mode, where the content of compound NPs versus metallic ones is controlled by the equilibrium between the sputtered Bi flux from the target and the reactive gas flow rates, similarly to thin film deposition, but also by the time for cluster solvation into the IL volume and by the reactive species consumption by the IL itself. Finally, we tested the photocatalytic activity of oxyfluorides NP and saw the metyl-orange photodegradation acceleration in their presence.

PLACC-P2-047 ● Dissociation of ammonia by microwave discharges in medium pressure range: an experimental study

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Ammonia is a promising energy vector as it is much easier to store and transport than hydrogen. It benefits from large infrastructures already available worldwide and about 20 million metric tons of NH_3 are traded every year for a year production of 150 million tons. If many works focus on the production of ammonia by electrical discharges [1], only a few are devoted to the splitting of ammonia [2].
In this work, the dissociation of anhydride ammonia is studied in situ by Fourier-transformed infrared absorption, a convenient method to determine the dissociation yield. Measurements are complemented by optical emission spectroscopy to have access to plasma parameters in a pressure range spanning from 1 to 100 mbar. A microwave surfaguide wave launcher, excited at 2.45 GHz, is used to ignite an electrodeless plasma confined in a fused silica tube (85 cm long, 2.6 cm in diameter).
The influence of the ratio power/flowrate will be discussed in detail as it is a key parameter to evaluate the energy balance for an expected dissociation yield of 100%. It must be compared with thermal processes using catalysts like ruthenium which is the most efficient known to date.

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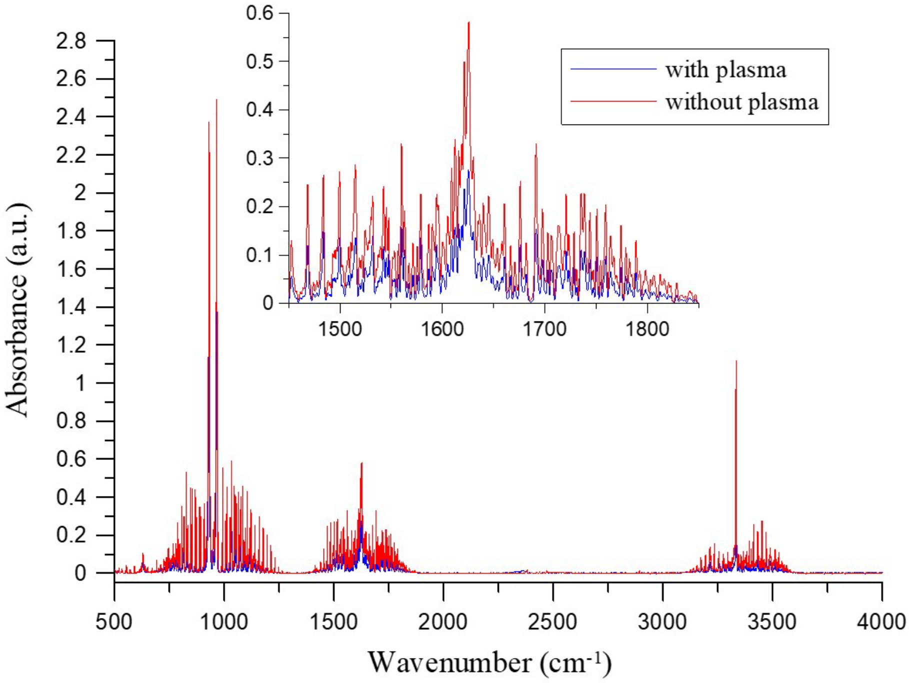

In situ FTIR spectrum of a pure ammonia gas phase

PLACC-P2-186 ● Discharge initiated synthesis of molecular life precursors in carbon monoxide based atmospheres

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This work focuses on the discharge-initiated processes in prebiotic atmospheres based on carbon monoxide. The aim of this work was to determine how the composition of different reaction mixtures consisting of carbon monoxide with gaseous additives influences type and amount of the plasma-generated products. The audio frequency glow discharge was generated at the atmospheric pressure in the flowing regime between two stainless steel electrodes at the ambient temperature. Pure CO and mixtures of CO with 0.5 % of hydrogen or nitrogen with the total flow of 200 Sccm were used in the current study. High resolution optical emission spectroscopy was used for the plasma observation. The atomic hydrogen, carbon and oxygen, CO and C2 molecules and CN radical were determined in the spectra. Based on their measured intensities, some temperatures were calculated. The compositions of gaseous products formed by the chemical reactions initiated by the discharge were investigated using in situ mass spectrometry (proton transfer reaction ionization with time-of-flight detector). The presence of tens hydrocarbons, nitriles, amines, aldehydes and alcohols was confirmed. The obtained results significantly enrich the existing knowledge about prebiotic atmospheres, chemical processes in interstellar clouds and atmospheres of diverse exoplanets because carbon monoxide is one of the most common molecules present in the Universe.

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PLACC-P2-205 ● Impact of water on atmospheric plasma ethanol conversion for hydrogen production using nano-pulsed plasma reactor

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At the present, most of the hydrogen (H_2) is produced by steam methane reforming (SMR) and water electrolysis. Atmospheric plasma assisted H_2 production from renewable liquid hydrocarbons such as alcohols seems a prospective alternative for H_2 production, because some experimental atmospheric plasmas are capable of producing H_2 with lower energy costs than water electrolysis or SMR. Interestingly, in several studies, water was mixed with alcohols during plasma conversion. However, the role of water in plasma conversion of alcohols is not yet sufficiently understood. It has been reported that the addition of water increased the selectivity of H_2, and decreased the selectivity of co-produced hydrocarbons (C_2H_2, CH_4, C_2H_4, C_2H_6), but there is scarce information on the influence of water on CO_2 formation and the mechanisms of alcohols decomposition in plasma.

In this study, it was investigated how addition of water to ethanol alters H_2 formation and energy consumption during ethanol conversion in a nano-pulsed plasma reactor using 6 pin-to-mesh electrodes configuration. The generator was set to 20 kV with a frequency of 10 kHz and a pulse width of 150 ns. The gap between mesh and pins was 4.5 mm and the height of the liquid above the mesh was 3.5 mm. An Ar flow of 100 sccm was used as a feed gas to ignite the plasma. A mass spectrometer and an oscilloscope were utilised to determine products composition and the energy consumption during plasma conversion of pure analytical grade ethanol and ethanol-water mixture at molar ratio of 1:1.

The active power with pure ethanol was 38.3 W, but dropped to 37.2 W with an ethanol water mixture conversion (50 mol % of water). Main products were H_2, CO, C_2H_2, CH_4, C_2H_4, C_2H_6, CO_2. Addition of water increased the H_2 selectivity from 53.6 to 58.9 % and decreased total formed hydrocarbon selectivity from 24.1 to 17.9 %. Despite H_2 selectivity increased, H_2 flow actually decreased from 85.3 to 78 sccm (total flow of products also decreased). A very interesting finding is that CO2 content stayed bellow 0.3 % also when water was added despite more oxygen was introduced into the system. Addition of water increased the energy consumption from 7 kWh/nm^3H_2 to 7.4 kWh/nm^3H_2.

NANO-P2-054 ● GLAD sputtering of nanostructured Ta thin films: Influence of deposition angle on electrical resistivity at cryogenic temperature

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In the present work, pure Ta thin films were deposited on glass and (100) silicon substrates by DC magnetron sputtering. Films were prepared by the glancing angle deposition method [1]. The deposition angle α was systematically changed from 0° to 85° following 6 different angles keeping constant all other working parameters. The Ta target current was set to 200 mA and the argon sputtering pressure inside the chamber was fixed at 0.3 Pa. For each angle, the deposition time was adjusted in order to get a film thickness close to 400 nm. Dense and compact films were produced with a normal incident angle α = 0° (Fig. 1a), whereas inclined and porous columnar architectures were clearly obtained for the highest deposition angles (Fig. 1b). Evolution of the films crystallographic structure was also investigated by X-ray diffraction, especially changes of the crystal size with α. Electronic transport properties of Ta GLAD films sputter-deposited on glass substrates were studied measuring DC electrical resistivity r as a function of the temperature T from 7 K to 300 K (Fig. 2). Residual Ratio Resistivity (RRR), Temperature Coefficient of Resistance (TCR) and r vs. T were strongly influenced by the deposition angle rising from 0° to 85°. These behaviors were directly connected to the increase of the voided microstructure induced by the shadowing effect during the deposition, especially for the most grazing angles (α > 60°). Furthermore and for each angle, the typical metallic-like behavior of resistivity vs. temperature was discussed assuming the Bloch–Grüneisen model [2].

Thanks/Acknowledgement
This work was supported by the EIPHI Graduate School (contract ANR-17-EURE-0002), the Region of Bourgogne Franche-Comté and the French RENATECH network.

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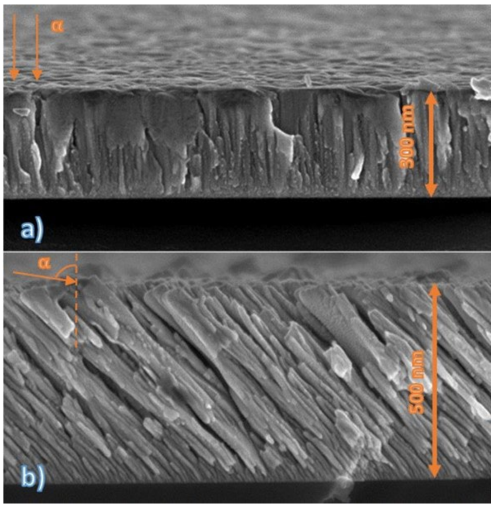
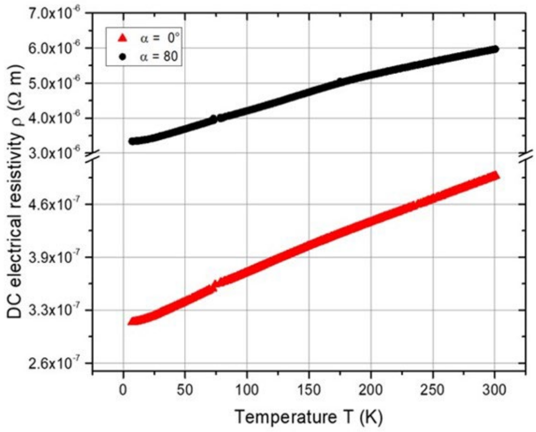


SEM cross-section observations of Ta GLAD films



DC electrical resistivity ρ vs. temperature T

NANO-P2-072 ● Galvanic corrosion-based antibacterial bimetallic nanoparticles produced by cylindrical gas aggregation source

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Antibacterial coatings represent a highly important class of materials in protecting patients and combating the spread of infectious diseases. Because of this, the development of novel strategies allowing reliable production of such materials as well as strategies for the enhancement of their efficiency against different types of bacteria is of paramount importance. Concerning the antibacterial efficiency of metal-based materials, the principal challenge is their ability to release sufficiently high amounts of biocide metal ions. From this point of view, an interesting option is based on galvanic corrosion. Although galvanic corrosion is usually described as a negative process in which one of the metals in bimetallic compounds is corroded, the effect of corrosion may be used to increase the number of ions of the metal needed for the assurance of a strong antibacterial effect. To demonstrate the positive effect of galvanic corrosion on the release rate of bactericidal copper ions, Cu and heterogeneous bi-metallic Ag/Cu nanoparticles (Ag/Cu ratio 1:1 as determined by EDX) were deposited onto polypropylene and poly(ethylene terephthalate) meshes by means of novel gas aggregation sources of nanoparticles that utilizes a cylindrical post-magnetron [1]. Based on the measurement of the kinetics of the copper ions released in water by atomic absorption spectroscope, it was observed that the presence of Ag caused an increase in the number of released Cu ions by approximately 50%. Concerning the fact that copper is more anodic, i.e., less stable, in the Ag-Cu pair, such enhancement can be ascribed to galvanic corrosion. This result on bimetallic nanoparticles, which, as far as we know, has not been reported before, thus paves the way for the rational development of advanced nanostructured bi-metallic antibacterial materials.

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NANO-P2-118 ● Laser beam nanostructuring of gadolinium-doped cerium oxide (GDC) oxide thin films deposited by plasma magnetron sputtering

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In ceramic solid oxide electrochemical cells (SOEC), a thin film of gadolinium-doped cerium oxide (GDC) is deposited (by plasma sputtering) between the electrolyte (yttrium-stabilized zirconia, YSZ) and the oxygen electrode (lanthanum-strontium-cobalt ferrite, LSCF) to reduce the formation of insulating phases at the electrode/electrolyte interface. In order to improve the adhesion between these layers as well as the ion exchange surfaces, we have considered a micro/nanoscale morphological structuring process using picosecond UV laser beams. Our study specifically focuses on the formation of laser-induced periodic surface structures (LIPSS) patterns on a 700 nm GDC film under both static and scanning irradiation conditions. A picosecond Nd: YAG laser (355 nm, 40 ps, 10Hz) with a relatively large laser beam spot (~500 µm) was used. In static mode, both parallel and perpendicular LSFL (low spatial frequency LIPSS) were formed simultaneously within the irradiated area in ambient air, which is unusual.

The LSFL// parallel formation is attributed to a thermochemical process produced in the center of the irradiated area corresponding to the highest local fluence, while perpendicular LSFL that are detected at the edges of the laser spot were generated by a soft ablation process. X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the chemical state of GDC (oxygen content and Ce3+/Ce4+ ratio) before and after laser irradiation. To further investigating the chemical modification that may occur during laser irradiation of GDC surface, laser nanostructuring under controlled atmosphere or vacuum has been carried out. Preliminary results will be discussed.

Fig1: SEM image of the irradiated CDG film, for F = 125 mJ/cm2 and N = 10 pulses. The insets show the non-irradiated (untreated) surface as well as two different LIPSS patterns (LSFL// and LSFL⊥) and the transition zone. W0 is the beam spot size; W⊥ and W// are the estimated diameters of LSFL⊥ and LSFL// regions, respectively. [1]

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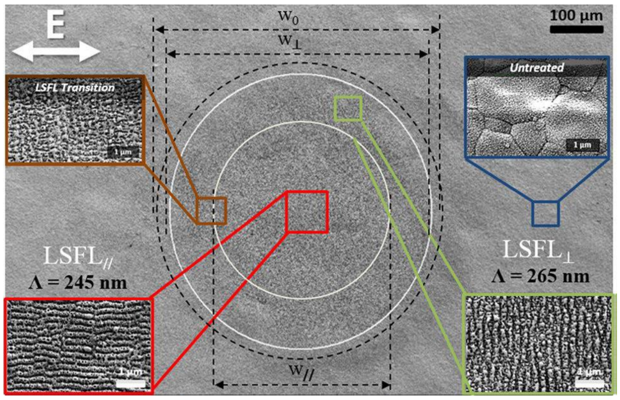

SEM image of the irradiated CDG film

NANO-P2-190 ● Plasma Assisted Nitriding of 2D transition metal carbide (MXene) thin films

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MXene are an interesting new class of materials, corresponding to 2D transition metal nitrides or carbides sheets, with outstanding properties like high electroconductivity and tunable hydrophilicity. They are usually prepared by chemical selective exfoliation of the “A” element layer from the corresponding MAX phase precursor. In this study, we focus on $Ti_3C_2T_z$ MXenes prepared from the Ti_3AlC_2 MAX phase. T_z corresponds to the surface terminations, usually -OH, -F, -Cl, and /or =O, which passivate the pending Ti bounds after exfoliation. The nature and content of these T-groups depend on the chemical protocol used for the exfoliation and on the surface history of the MXene.

This study aims at modifying the chemistry of the $Ti_3C_2T_z$ benchmark MXene by plasma assisted surface treatment in order to modify the properties (e.g. conductivity, energy storage capacities), by tuning either the T_z surface functionalization groups like $-NH_x$ species, or by nitrogen substitution of carbon in the core of the $Ti_3C_2T_z$ sheet.

Several ~60 nm thick $Ti_3C_2T_z$ thin films were deposited on SiO_2 quartz substrates by spin coating. The $Ti_3C_2T_z$ suspension was obtained by chemical exfoliation in LiF-HCl solution from Ti_3AlC_2 MAX phase powders. The samples were treated by plasma assisted nitriding at room temperature or 300°C, in N_2/H_2 reactive low pressure gas atmosphere, with a RF plasma power of 700 W. Some samples were previously treated by H_2 plasma exposure before the nitriding treatment. The layers were then characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS) for microstructure and composition determination.

No nitrogen was detected by EDS in SEM examinations of the treated thin films and the diffraction pattern obtained by TEM correspond to the Ti_3C_2 phase, without significant modification of the interplanar distance. However treated sheets reveal additional diffraction rings that may be attributed to rutile-TiO_2 and to graphene oxide, likely resulting from the degradation and/or oxidation of the initial MXene during nitriding and/or manipulation in air. EELS analysis clearly demonstrates the introduction of Nitrogen in the octahedral sites of the MXene sheets, from few at.% up to 11%, combined with some carbon elimination. Preparing the surface by H_2 treatment and performing the nitriding at 300°C seems to slightly improve the nitrogen incorporation efficiency although the local composition values obtained by EELS are dispersed within the same treated layer.

Thanks/Acknowledgement
This work was supported by the France 2030 program (LABEX INTERACTIFS, reference ANR-11-LABX-0017-01).

NANO-P2-204 ● Yttria-stabilized zirconia thin films prepared by radio frequency magnetron sputtering for oxygen sensors

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Oxygen sensors are widely used in many sectors such as automobile, and process control.SETNAG company leader in oxygen analysis would like to miniaturize their zirconia probe called "MicroPoas" [1] which works under electrochemical principles. SETNAG's analysers are very efficient for precise measurement of oxygen (ppm to %) level.However,they have drawbacks in terms of size and power consumption in addition of manufacture delay.A campaign is conducted at IM2NP to study the deposition of 8%mol of Yttria Stabilized Zirconia (8YSZ) to realize an integrated oxygen microsensor. In the literature,studies justify the zirconia/yttria percentage chosen being that with 8% mol of yttria, zirconia we can have an optimal ionic conduction [2].Deposition of thin films of 8YSZ by Radio Frequency magnetron sputtering has been studied using an 8YSZ target at 60 W and 20 cm3/min of total Argon flow rates.Different pressures (20,30,40,50,60).10-3mbar have been tested and the profilometry measurements shows that the deposition rate at 30.10-3 mbar is the highest one (9.8 nm/min).The work is then carried with the previous sample annealed at (500°C, 600°C, 700°C, 800°C and 900°C).The morphological structure was investigated by SEM image,and the composition and crystalline phases were investigated using (EDX) and (XRD).Figure 1 shows these analysis results. The SEM image shows a crystallized layer with grain size from 15 to 65 nm confirmed by XRD as well as the presence of pores, which will enable the diffusion of oxygen into the solid electrolyte. Electrical characterization has been made on YSZ deposited on an interdigitated Pt/SiO2/Si transducer and shows a response to 5 min oxygen exposition under bias voltage of 0,2 V at 700°C (figure 2).

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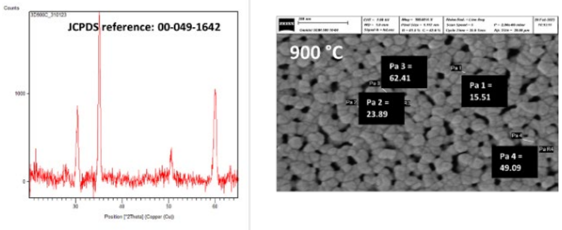
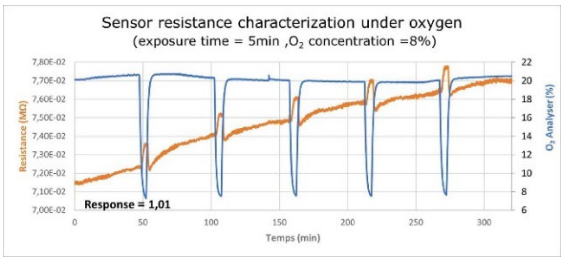


XRD, SEM image and EDS analysis of thin film YSZ d



Resistive measurements of YSZ, thickness =200 nm d

LIQU-P2-178 ● Influence of σ and ε on the streamer dynamics at water surface

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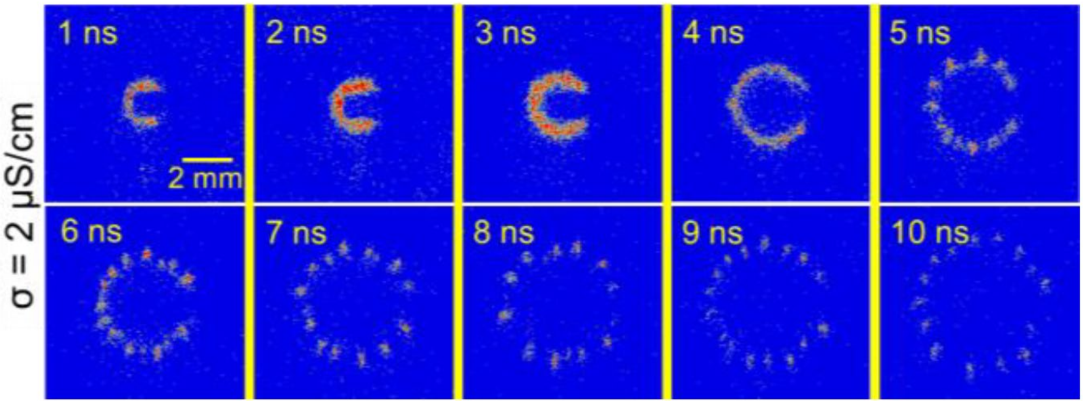
Streamer propagation in gaseous medium, including air, is rather well understood, but it quickly becomes a complex phenomenon as soon as it approaches a solid or a liquid surface. Indeed, the properties of the surface, such as its electrical conductivity (σ) and dielectric permittivity (ε), strongly influence the streamer dynamics. Although it is a fundamental subject, understanding streamer-surface interaction remains a cornerstone in the context of applications. Initiated by electronic avalanches, streamers take place if the number of produced electrons is higher than 10^8, i.e. Meek's criterion. In these conditions, the E-field produced from electrons-ions separation becomes relatively high and controls the following steps of streamer propagation, mainly by initiating secondary avalanches close to streamer's head. It is stated that as the streamer approaches the surface, the production rate of photoelectrons decreases significantly leading to a cease of its vertical propagation. Meanwhile, charges accumulate at the surface and produce a radial E-field. If this latter is strong enough, radial avalanches ignite and lead to the formation of radial streamers at or near the surface. In the case of liquid surfaces, streamer propagation is strongly influenced by the liquid properties, mainly σ and ε. The former can be controlled by adjusting the concentration of ions in solution, while the latter can be controlled by choosing liquids with different permittivity. Herein, the influence of σ, from 5 to 1000 µS/cm, and ε, from 25 to 80, on the streamer propagation at water surface is presented. The discharges are produced by single shot nanosecond high voltage, and they are characterized electrically as well as by time-resolved imaging with a 1-ns-temporal resolution (Fig. 1). σ influences the movement of ions present in solution, and they reorganize in response to the E-field. Such reorganization can significantly influence the E-field near or at the solution's surface and, therefore, the streamer's propagation dynamics. ε influences the E-field distribution and charge accumulation at the liquid surface, thus, the streamer's propagation dynamics.



LIQU-P2-192 ● Plasma assisted modification of colloidal Zn nanoparticles

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A new methodology is tested for the modification of colloidal Zn nanoparticles. The method relies on the use of reactive oxygen and nitrogen species (RONS) enriched liquids. The reactive species are deposited into the liquid through the interaction of an atmospheric pressure surface-wave microwave discharge with the liquid [1]. During plasma-liquid interaction high reduction potential metal, Zn or Mg, powder is added to the liquid in order to compensate for the plasma induced acidification and thus ensure a long life-time for the RONS [1]. The Zn NPs are deposited into the filtrated RONS enriched liquids by laser ablation of Zn foil in liquid (LAL). The 1064 nm Nd:YAG laser is focused using a 250 mm lens on the target positioned from the lens at 125 mm distance in 20 ml solution. The energy delivered to the target surface is 320 mJ, the duration of the ablation is 60 s with 6 ns pulses at 20 Hz repetition rate. Fig. 1 shows the UV-VIS absorption spectra of the different Zn NP colloids, which in the case of the RONS enriched water solutions indicate the presence of high concentration of RONS (200-240 nm) together with the Zn NPs (240-400 nm). Comparing to the NPs created in deionized water, in the RONS enriched liquids both the structure and oxidative state of NPs are found to be modified during their LAL production. The band gap energies calculated from the UV-VIS absorption spectra show a significant change in the case of the presence of Mg ions, namely it is decreased to 3.08 eV comparing to the 3.33 eV of the DIW based Zn NP colloids. Fig 1. also shows the photoluminescence of the colloids, indicating the significant increase of the emission when using RONS and Mg ion enriched solutions for the colloid preparation.

Thanks/Acknowledgement
This work was supported by Hungarian NKFIH Science Founds K-132158.

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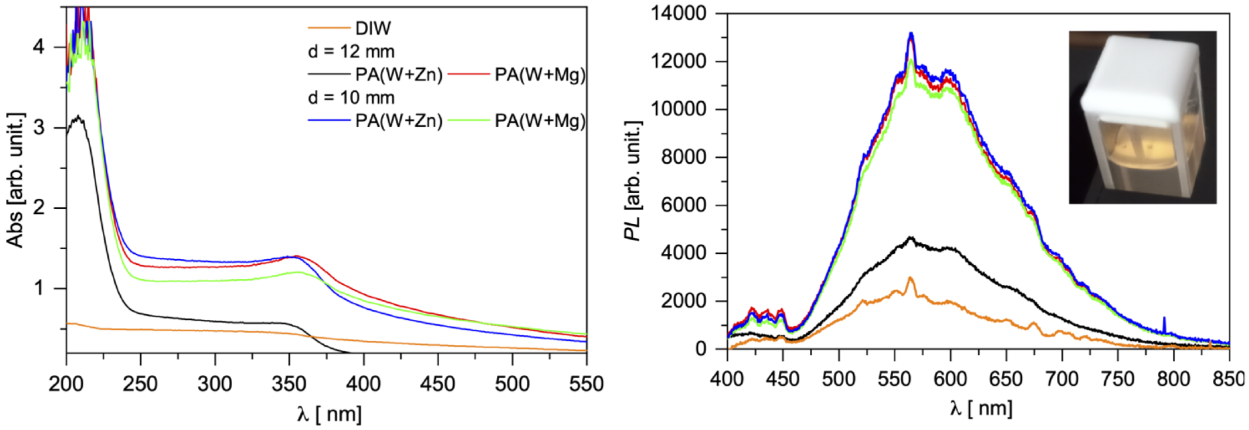

Fig.1 The UV-VIS absorption spectra and the photoluminescence of the colloids when excited with 351 nm light.

LIQU-P2-200 ● Can process parameters significantly influence the size of Silver nanoparticles synthesized by sputtering onto liquids?

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Owing to their antibacterial properties, Silver (Ag) nanoparticles have found increasing use in various fields such as the biomedical industry, food packaging or waste water treatment. Each application requires specific nanoparticle properties and purity. Magnetron sputtering onto low vapor pressure liquids (SoL) offers an interesting and versatile route to synthesize pure nanoparticles, utilizing only a metallic target and a host liquid. The complex processes at play in the formation of the nanoparticles, *i.e.* interactions between the gas and liquid phases, as well as between the metal species and the liquid, are not yet fully understood [1].

In this context, sputtering of Ag onto two biocompatible liquids – castor oil and polyethylene glycol – was conducted. A comprehensive monitoring of the SoL process was carried out to identify the effect of the plasma type, the flux and the energy of sputtered species on the nanoparticles' size. Direct current and pulsed direct current plasmas were used, with pressures ranging from 0.2 to 2 Pa, to tune the flux and kinetic energies of sputtered species. *In situ* and *ex situ* flux measurements performed with a quartz crystal microbalance and by thickness measurements on solid thin films, respectively, revealed strong differences depending on plasma type and pressure. The influence of these parameters on the rise in liquid surface temperature was also recorded *in situ*.

The difference in color between solutions synthesized in both liquids showed a strong influence of the liquid nature on the prepared solutions and no modification of the liquid phase after plasma exposure was detected by attenuated total reflectance infrared spectroscopy. The size distributions of the synthesized nanoparticles, obtained from scanning transmission electron microscopy images, differed over the size range from 1 nm to 5 nm diameter, depending on the liquid nature and, especially in the case of polyethylene glycol, on the sputtering conditions. The combination of the kinetic energy of the sputtered species arriving at the liquid surface, estimated by SIMTRA [2], and of their flux, influenced the size distribution of nanoparticles synthesized onto polyethylene glycol. In the case of castor oil, the results suggested a larger contribution of the flux on the size distribution.

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GROM-P2-007 ● The influence of structural design on the properties of TiN coatings

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Surface treatment technologies by vapour deposition (plasma assisted) of coatings have gained an extremely special and important place in various application fields and industrial sectors. It is known that by applying a coating on the surface of a product, a set of desired surface properties can be obtained that complement the other properties of the base material. Moreover, there is also the possibility for a coating, having a certain composition, to modify its properties by changing the structural design.
Within the frame of this work, normal, inclined and zigzag-like structures of TiN coatings were prepared in a Ar+N_2 plasma, using a magnetron sputtering deposition system in a GLancing Angle Deposition configuration (GLAD). The obtained samples were characterized in terms of composition, topography, morphology and structural aspects; the optical, thermal, electrical and tribological properties were also evaluated. The obtained results clearly highlight the major influence of the structural design on the physical properties of the TiN coatings. The films became darker, less conductive and lost the ability to conduct and/or diffuse heat thermal energy (decreased thermal diffusivity) as the inclination of the TiN growth columns increased and rougher surfaces, highly-porous and less-dense microstructures were produced. A general worsening of the mechanical and tribological properties was recorded along with the deviation from normal columnar structure of the obtained coatings.

GROM-P2-070 ● Modelling of thin film deposition into nanofibrous mats

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Nanofibrous mats, e.g. prepared by electrospinning, are a material with great potential in biomedical applications. To tailor their properties they frequently have to be further functionalised or modified. Deposition of thin films into the mat by plasma polymerisation is an effective method for such modification. Recent results have experimentally demonstrated rather deep penetration of deposition into the structure in a low-pressure discharge [1]. The theoretical understanding is, however, still limited and quantitative relations between mat geometry, process parameters such as sticking coefficient, and deposition profiles are lacking. The aim of this work was to bridge the gap using numerical simulations. The stochastic mat geometry was modelled by virtually laying nanofibres in a large *xy*-periodic 3D simulation domain (50μm × 50μm × 100μm – a small section is in Figure 1), representing the fibres as chains of conical frusta. Their mean microscopic parameters were estimated by combining mat SEM image analysis with macroscopic measurements (area density and thickness). Custom software was developed for tracing particle paths (about 10^7/run) through the mat and depositing them according to effective sticking probabilities. Simulations were run in the low pressure limit, i.e. free path limited by the mat, not collisions in the gas phase. The obtained records of each particle path were statistically analysed; the depth parameters were obtained by fitting the profiles with exponentials for each value of sticking coefficient and also varying mat density/fibre radius. Scaling arguments lead to a universal relation $h\alpha\sqrt{\eta} = cR$ between fibre radius R, fill ratio h, sticking coefficient η and mean penetration depth h, and constant $c \approx 0.8$ according to the numerical results. This relation makes the stochastic mat geometry in some sense simpler than regular geometrical shapes like wells or trenches. Directional coverage of fibres, mat ‘reflection coefficient’ and other quantities were similarly analysed and theoretical vertical:horizontal 2:1 free path anisotropy in a mat with horizontal fibres was confirmed numerically.

Thanks/Acknowledgement
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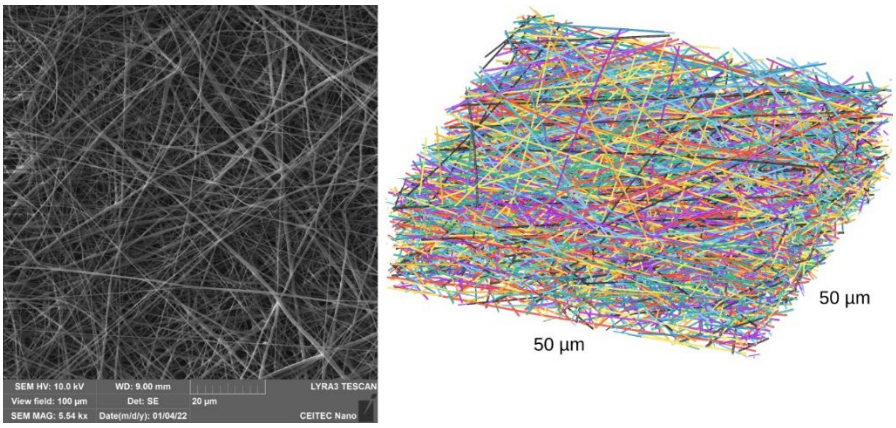

Nanofibrous mat SEM image and model visualisation

GROM-P2-127 ● Analyse of the angular distribution of the columns of chromium tilted thin films through a comprehensive simulation

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The comprehensive simulation of PVD deposition is currently made by the successive computation of three steps, the sputtering of the matter from the target, followed by the transportation from the target to the substrate and finally the growth of the film on the substrate. NASCAM [1] is a software specialised in the computation of the film growth, which can compute the morphology of the film from the results of the first two steps (e.g. SRIM [2] and SIMTRA [3]). Several plugins also help users in the analysis of the properties of the simulated coating. However, NASCAM does not explicitly computes the columns but represent the film as a unique point-plot. However, the "history" of the simulation steps is recorded, even if not explicitly provided to the user. Not considering the columnar microstructure is an approximation fitting classical PVD coating with dense columns. However, in the case of tilted deposition, the columnar microstructure is responsible for the modification of the properties of the coating. Hence, for more precision, it must be taken into account.

An algorithm that takes as an input the NASCAM simulation results (i.e. the "history") has been designed and prototyped for the sake of this study. It returns, as an output, the calculated columnar microstructure taking into account the separation between different columns. It is not a new simulation but the post-processing of NASCAM simulation result for segmenting a unique film into columns and computing their geometrical characteristics.

This study presents an analysis of the distribution of the columns size, morphology and angles for simulated tilted chromium coatings using different incident angles. All the simulations are conducted using successively SRIM [2], SIMTRA [3], NASCAM [1], and the developed plugin.

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GROM-P2-134 ● Biased reactive high power impulse sputtering of silica

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High power impulse sputtering (HIPIS) of a Si target in Ar/O2 mixtures has been studied. The use of biased HIPIS is shown to considerably influence the process characteristics compared to conventional sputtering. A bias in the form of pulses was applied to the substrate. The effect of the amplitude and timing of the bias pulse on the optical properties of the thin film was systematically investigated. Consequently, silica with different optical quality can be deposited under stable process conditions at high rates. Possible explanations for this behavior as well as a model qualitatively describing the process are presented.

SURF-P2-059 ● *In-situ* FTIR spectroscopic analysis of plasma activation and plasma polymer film deposition on polylactid acid

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The importance of sustainable biodegradable polymers as alternative to synthetic polymers in various applications such as food packaging is steadily increasing. E.g. polylactic acid (PLA) as a polyester formed out of 100% renewable raw materials is of high interest as a polymeric packaging material [1]. However, the related barrier properties of such biopolymers are worse in comparison to synthetic polymers such as PP or PET. Thus, plasma polymer thin barrier film deposition on biopolymers for packaging applications is an promising technology to overcome the low barrier properties [2].
In the here presented approach, we analyze the interfacial processes during plasma activation and ultra-thin film deposition by means of in-situ FTIR spectroscopy under grazing incidence under polarization modulation (PM FT-IRRAS) [3]. Thin PLA films are applied on inert gold surfaces by means of spin coating and characterized by means of optical spectroscopy, ellipsometry and AFM. Due to the low film thickness, surface enhancement of the electric field vector during the IRRAS measurement allows for the analysis of even monolayer changes at the plasma/PLA interface. Ex-situ studies by means of atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) complement the FTIR-spectroscopic analysis.
The barrier properties of the films are analyzed by means of electrochemical and spectroscopic measurements such as electrochemical impedance spectroscopy and FTIR spectroscopy under attenuated total reflection (FTIR-ATR). The results show how the barrier performance of the films can be correlated to the interface chemistry between the plasma polymer film and the substrate as well as to the chemical composition of the plasma film.

Thanks/Acknowledgement
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SURF-P2-136 ● How to functionalize PVD ZrCu-based thin film metallic glasses? Effect of an ultrashort laser surface treatment

P. Steyer[1], N. Lebrun[1], Z. Fernandez Gutierrez[2], H. Bruhier[3], M. Prudent[3], C. Der Loughian[1], S. Dassonneville[1], A. Borroto[2], F. Bourquard[3], M. Rousseau[4], J.F. Pierson[2], J.P. Colombier[3], F. Garrelie[3]
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Due to the lack of metallurgical defects, bulk metallic glasses (BMG) have displayed attractive physical and chemical properties. They have been intensively studied, but BMGs development was nevertheless limited to relatively small parts caused by required fast quench rates. Recently, thin film metallic glasses (TFMGs) have emerged as alternative materials for many advanced applications (MEMS, luxury or sport items...). It has been demonstrated that binary Zr-Cu TFMGs [13-85 at.%Cu], can be obtained using pure Cu and Zr targets [1]. Besides, their chemistry can be easily controlled, giving rise, for instance, to bactericide or bacteriostatic surfaces [2].

In the current study, we propose another alternative strategy to functionalize the surface, linked to the control of its topography at a sub-micrometer scale, by ultrashort laser treatments [3]. Laser-treatments were applied to binary Zr-Cu TFMGs, synthesized by magnetron sputtering. Films are amorphous and smooth. Modifying laser parameters, several designs were achieved, like LIPSS (Laser-Induced Periodic Surface Structures), grooves and nano-holes [4]. Behaviour of fs laser-treated surfaces, in terms of wettability, was measured at different scales: macroscopic as well as microscopic, using an environmental SEM under the humid *in situ* mode. Behaviour micro-organisms in contact with these surfaces is discussed in light of the laser texturing.

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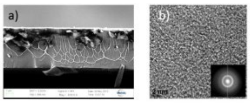
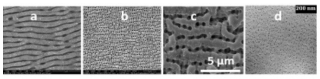


Texture Designs available by fs-laser

Microstructure of TFMG



SURF-P2-138 ● Functionalization of MIL-53(Al) by means of ECR plasma treatment: a feasibility study

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Metal-Organic Frameworks (MOFs) are an incoming class of materials, which have been extensively studied these last decades. Their high surface-to-volume ratio and low density resulting to be promising materials for many practical and industrial applications, such as gas storage [1].
Among the studies around MOFs, enhancing their sorption performance has been a significant challenge. A possible solution could be functionalizing MOFs' organic ligands to introduce specific feature depending on the chosen radicals (i.e. functional group).
Functionalization methods can be classified in two categories. The first one, called pre-functionalization, consists in chemically bond radicals to organic ligands right before MOFs synthesis [2]. As for the second one, called post-synthesis modification (PSM), this functionalization step occurs after MOFs synthesis [2]. The latter is a general, strategic approach due to a greater control of the functionalizing process to maintain the overall stability of the MOFs' initial lattice. While chemical wet methods have been widely carried-out, this study suggests a new route to functionalize by PSM approach: plasma treatments.
In this study, an electron cyclotron resonance (ECR) source has been used to investigate the feasibility to functionalize a MOF called MIL-53(Al) (MIL stands for Material of Institute Lavoisier) [3] by the mean of low-pressure cold N2-H2 plasma (~ 4 Pa).
On the first hand, ECR plasma was analyzed with optical emission spectroscopy in order to find a favorable condition where the NH per N2 intensity ratio is the highest. On the other hand, material characterization (FTIR, DRX, XPS) has been done to track the efficiency of NH-functionalization with different treatment conditions. Finally, DRX spectra exhibit a larger amount NP-form of the plasma-threated MIL-53(Al), indicating a micro-structural modification. Moreover, chemical analysis (i.e. FTIR reported in figure 1) bring out the presence of NHx, chemically bond with the organic ligand.

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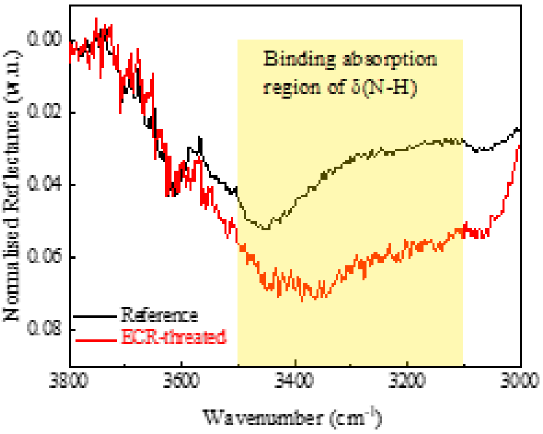

FTIR spectrum of an untreated and a treated MIL-53

SURF-P2-155 ● Increasing the hydrogen storage capacities of MIL-53 Al by amino-grafting functionalization using an impulse dielectric barrier discharge plasma

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Due to their structures and properties, metal-organic frameworks (MOFs) have attracted great interest in a wide range of applications, including gas storage and separation, catalysis, optics, batteries, among many other fields. One of the main advantages of these materials is the possibility to modulate or even improve their properties through functionalization. In the literature, several computational and experimental studies on MOFs' functionalization report the effectiveness of introducing specific substituent groups on the ligand structure. It has been shown that grafting functional groups, such as amino groups on the aromatic ligand, enhances the selectivity of MOFs towards certain gases, and improves the interaction between the adsorbent and adsorbate, particularly for CO_2 and H_2[1-2]

The functionalization of these materials is most often performed by wet chemical route that often presents constraints such as the reaction time, energy cost, vulnerability to chemical risks, etc. A possible novel route to achieve the functionalization of organic ligands in MOFs consists in using low temperature plasma treatments[3].

In this study, we investigate the efficiency of an NH_3 impulse dielectric barrier discharge (IDBD) to graft amino-groups on the organic ligand of MIL-53 Al. The presence of NH radicals in the plasma phase, determined by optical emission spectroscopy, together with structural modifications, proved by HTXRD, TGA-MS and XPS of the processed material, prove the effectiveness of the IDBD plasma treatment to graft amino groups on MOFs' organic ligands. Moreover, analyses of the textural properties and hydrogen adsorption capacities at room temperature and atmospheric pressure showed an improvement in the amount of hydrogen stored in the MIL-53 Al treated by IDBD. These results are promising to develop materials with higher hydrogen adsorption capacity at room temperature and atmospheric pressure.

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SURF-P2-157 ● Plasma surface modification of glass and stainless steel by an atmospheric-pressure air DBD treatment

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Glass and stainless steel are common materials widely used in our daily life and industrial applications, such as optics, automobile, etc. The surface properties of these materials can be modulated and enhanced by tuning the surface chemistry via functionalization. Among the possible ways to modify surface properties of materials, the use of low temperature plasma treatments[1-3] represents a promising functionalization process.

In this study, we investigate the effect of a Dielectric Barrier Discharge plasma treatment on borosilicated glass and stainless-steel surfaces at atmospheric pressure in ambient air, under two DBD regimes; pulsed and sinusoidal voltage regimes, respectively. A parametric study of the DBD conditions is investigated, particularly the effect of plasma treatment time, power, and aging time after DBD treatment, respectively. The obtained results highlight a hydrophilicity enhancement of glass and stainless steel by DBD treatment. WCA measurements show a rapid hydrophilization of the two materials, with an enhanced effect according to the treatment time (cf. fig.1) and the power of the DBD system, respectively. Moreover, the morphology of the materials before and after plasma treatment are performed by SEM. Subsequently, the surface chemistry of the two materials before and after plasma exposure will be analyzed by FTIR. At last, a comparison of the two DBD regimes and their impact on the materials will be discussed.

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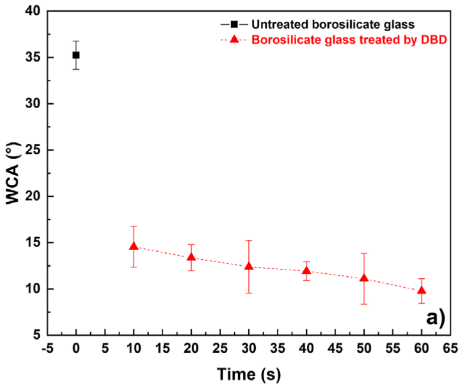
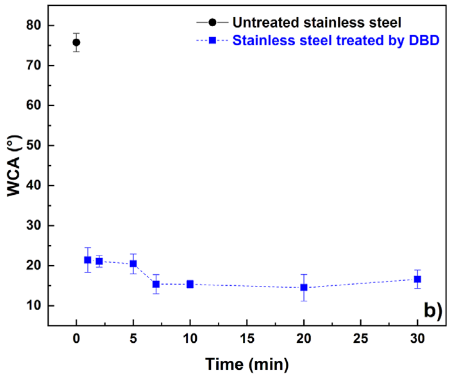


a.WCA of glass as a function of plasma treatment



a.WCA of st as a function of plasma treatment

SURF-P2-159 ● Study by optical emission spectroscopy (OES) of the characteristics of the plasma jet produced by an Axial Injection torch (TIA): influence of a substrate placed on the jet axis

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Nowadays, plasma torches operating at atmospheric pressure find applications in a wide variety of fields such as the production of thin layers, surface treatment or even sterilization [1-2]. Depending on the intended application, different substrates and different distances between the plasma torch outlet and the surface to be treated must be considered.

The device used for this study was composed of a microwave torch operating at atmospheric pressure, called Torche à Injection Axiale (TIA). The latter is mainly used at IRCER for surface inactivation and the production of thin oxide layers [3-4]. The plasma jet generated by the TIA is diluted in an air atmosphere at rest and the characteristics of the jet downstream of the nozzle outlet are conditioned by the air engulfment in the initially plasma jet.

The measurements carried out by optical emission spectroscopy showed that the addition of a substrate in the discharge axis (Fig 1), as well as its nature (Fig 2), has a marked influence on the excitation temperature and to a lesser extent on gas temperature. This influence was modulated by the choice of operating parameters such as the nozzle-substrate distance, the microwave power and the plasma gas flow.

Thanks/Acknowledgement
The authors thank the Region Nouvelle-Aquitaine for financial support provided by the project PMO#Innovation

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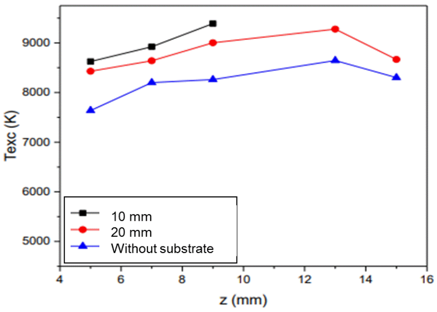

Figure 1: Excitation temperature evolution at 420 W and 17 slpm for different distanc substrate-nozzle (SiO_2 substrate)

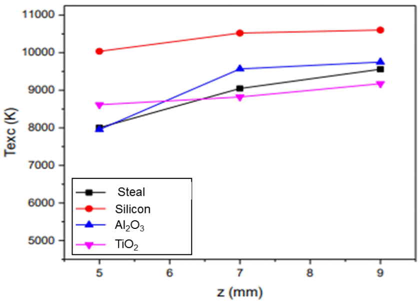

Figure 2: Excitation temperature evolution along the plasma jet for 4 types of substrate placed 10 mm from the nozzle (250W-13 slpm)

SURF-P2-181 ● Towards accurate sputtering simulations: developing machine learning-based interatomic potentials for silicon

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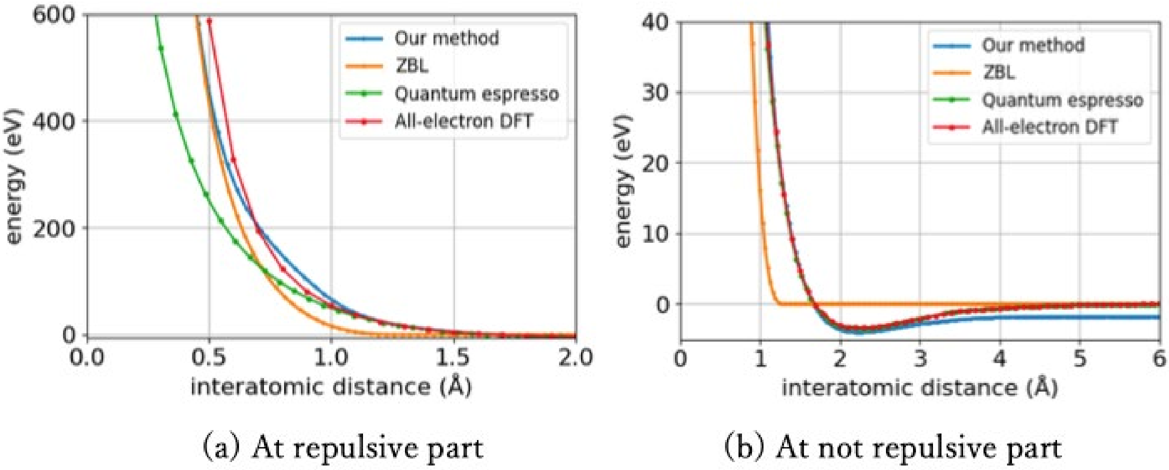
The goal of this study is to establish techniques to develop highly accurate interatomic potential functions to model plasma-surface interaction by molecular dynamics (MD) simulation, especially for sputtering phenomena. As the first example, we have developed machine learning (ML)-based interatomic potential functions among silicon (Si) atoms, so that we can simulate the self-sputtering of crystalline Si. Data to develop such an ML-based model is provided by the density functional theory (DFT) calculations. Recently, ML-based methods have been used to develop interatomic potential functions for various materials. Several studies have shown that ML-based interatomic potentials can achieve the accuracy of DFT calculations as well as the computational speed of classical potentials and MD simulations based on ML-based interatomic potential functions can predict material properties with high accuracy in thermal equilibrium. However, there remain some challenges in describing short-distance repulsive interactions, which typically do not exist in DFT calculation data for solid materials. To solve this problem, we incorporated the Ziegler-Biersack-Littmark (ZBL) potential function, which is known to be a good description for short-distance interaction. The newly developed potential functions were compared with other existing (non-ML-based) potential functions for the Si system and their accuracy was tested against experimentally measured materials and sputtering properties. Figure 1 shows a comparison among two-body interatomic potential functions of the ZBL function and the ML-based function as well as those obtained from all-electron DFT and Quantum Espresso. It is seen that, for short separation lengths, the all-electron DFT and Quantum Espresso differ, which may lead to a large discrepancy in sputtering yield simulation. The sputtering yields obtained from MD simulations based on the ML-based potential functions and the corresponding experimentally obtained yield data are found to be in good agreement.



(a) At repulsive part

(b) At not repulsive part

Plots of various interatomic potential functions b

SURF-P2-184 ● Surface wettability modification of polyimide films by pulsed magnetron sputtering

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Due to its outstanding heat resistance, excellent insulating characteristics, and chemical resistance, polyimide (PI) is used in a wide range of applications. However, because of its hydrophobic nature, it has poor adhesion to other materials [1]. Several authors report hydrophilic surface modification of polymers, but they experience hydrophobic recovery during the next few days or even hours after the treatment [2].

In this work, the wettability of 12.5 µm thick polyimide films (Upilex-S, Ube Industries) has been modified by pulsed magnetron sputtering under O2 atmosphere, combining surface roughening and thin film deposition. The film morphology was evaluated by scanning electron microscopy (SEM), and changes in the wettability were studied by measuring static water contact angle (WCA). Results about the influence of coating composition and storage conditions on the wetting properties of the PI foils will be presented.

As shown in Figure 1, PI films treated with Ti/Si targets exhibit extreme wetting behavior, even 257 days after treatment. Particular attention is paid to the ratio Ti to Si, since more Ti leads to less hydrophilicity of the PI films. This long-lasting superhydrophilicity is attributed to the modification of surface chemical composition combined with an appropriate physical topography. On the other hand, PI films treated with Al targets exhibit a WCA < 20° right after treatment, and then the surface undergoes a fast hydrophobic recovery with a WCA > 110° one week later. The superhydrophilic PI films are suitable for applications that require complete wetting of the surface by a fluid, e.g., in microfluidic devices, filters, and cooling components.

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WCA: Untreated (left), and treated PI film (right)

SURF-P2-187 ● Advancing NH_3 Sensing with Plasma Reduction of Graphene Oxide

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Reduced graphene oxide (rGO) has received extensive attention for gas sensing applications due to its tailorable electrical properties. Although various chemical and thermal methods are available for the reduction of GO, plasma-enabled reduction offers numerous advantages in terms of structural quality, reduction time and environmental impact. This work presents a plasma-enabled fast and facile approach for the surface reduction of GO films, aiming to enhance GO properties for the case of room-temperature ammonia detection. A thin layer of GO deposited on the copper electrodes by drop casting was subjected to a mild hydrogen plasma for surface reduction. The reduction process was investigated by varying the duration of plasma treatment for 10, 20, 40, 120 and 240s. Structural and chemical analysis of plasma-reduced GO confirmed that the GO surface was partially reduced within 10s, and reduction was further enhanced with longer treatment. As per ammonia detection, the 20s plasma rGO sensor exhibited the highest sensitivity, with a sensitivity of 23.9% at 100 ppm and 47.1% at 1049 ppm of NH_3, whereas the 240s plasma rGO sensor demonstrated the optimum recovery. This sensing behavior was attributed to the shift in the ammonia interaction mechanism from chemisorption-dominated to physisorption-dominated interactions. Such a straightforward, rapid and room-temperature reduction process, along with the good performance of plasma-reduced GO sensors, offers new potential for designing practical indoor gas sensors as presented for ammonia detection.

SURF-P2-188 ● Hydrogen plasma reduction of regolith simulant

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In the case of space missions to other celestial bodies, space resource utilisation refers to the exploitattion of indigenous materials to provide the essential mission needs like construction materials, water and oxygen for life support or fuel for the return journey [1]. On the moon, for instance, regolith is the first targeted material for this task as it is very accessible and abundant. Lunar regolith is the first layer of material that covers its body and consists of dust and fine rocks formed after bilion years of meteoroids impacts. The various minerals present in lunar regolith mostly contain silicon, iron, calcium, aluminium and magnesium oxides and many studies focus on oxygen extraction [2] while others investigate ways to valorise the other elements with additive manufacturing for example [3]. In this work, we report first results about the reduction of a lunar regolith simulant by microwave hydrogen plasma. The latter is generated in a quartz tube with the help of a WR340 Surfaguide from Sairem and a flow of an Argon-Hydrogen gas mixture (see figure). Samples of lunar regolith simulant are placed in the afterglow region and their oxygen reduction efficiency is investigated through the variation of different parameters such as the power output of magnetron as well as the gas flow and composition. The study is supported by optical emission spectroscopy analysis of the plasma and powder x-ray diffraction of the samples. Results will show, in some extent, an efficient, but selective reduction of certain minerals present in the raw sample.

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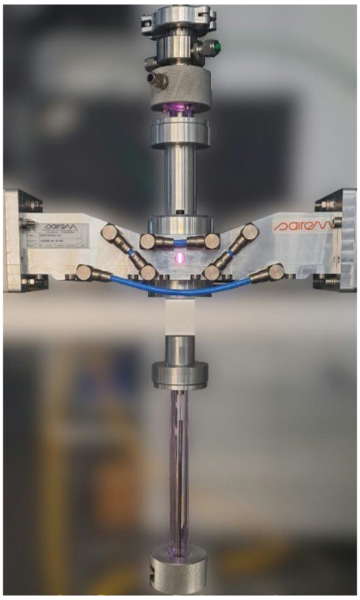

Ar/H2 plasma in a WR340 Surfaguide at 100 W

TRIB-P2-013 ● Mechanical properties and tribological performances of AlTiZrTaHf(-N) high entropy nitrides deposited by reactive magnetron sputtering

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There is a growing interest in the design of high entropy alloys [1, 2] due to their remarkable properties and applications in various critical sectors: aerospace, turbine or nuclear industries [3, 4]. AlTiTaZrHf(-N) high entropy metal-sublattice nitrides were deposited in various argon-nitrogen gas mixtures. A transition from amorphous to FCC single phase occurs by increasing the nitrogen flow rate ratio RN2=N2/Ar+N2. depending on RN2, compact or columnar morphology is obtained. XPS surface analysis reveal the formation of nitrides when the nitrogen is introduced. The maximum hardness and Young's modulus are obtained for the film deposited at RN2=10% and the values are of 27.67 GPa and 205.56 GPa respectively. The friction coefficient of AlTiTaZrHf is measured at 0.95. By increasing the nitrogen flow, the friction coefficient first decreases and then increases. At RN2= 10%, the friction coefficient of AlTiTaZrHf(-N) films reaches the lowest value of 0.7 (Figure 1). As RN2 increases from 20% to 30%, the friction coefficient increases. However, if RN2 continuously increases by more than 30% the friction coefficient decreases. This trend may be due to the increase in nitrogen content of the film leading to a structure refinement. This work conclusively demonstrates that high entropy nitrides can be efficiently generated with tunable properties.

Thanks/Acknowledgement
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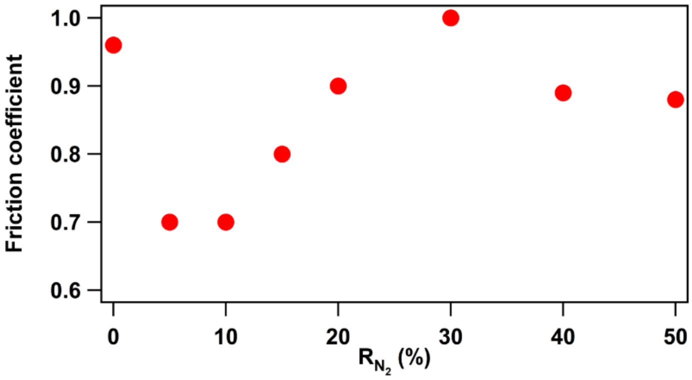

Figure 1. Fiction coefficient of AlTiTaZrHf(-N) fi

TRIB-P2-038 ● Development and characterization of ultra-hard DLC coatings for high quality machining of high strength aluminium alloys

J. Caro[1], G. Ramírez[1], J.M. Gonzalez Castro[2], J. Orrit-Prat[1], R. Bonet[1], N. Cuadrado[1], M. Visaleca[1], L. Carreras[3]
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The use of lightweight materials, such as ultra-high-strength aluminium alloys, has received a high demand in the automotive and aerospace industries where weight savings are critical. The tool materials used for high-speed cutting of these aluminium alloys are subjected to severe conditions that promote premature failure modes of cutting tools. The application of polycrystalline diamond (PCD) coatings provides cutting tools with increased mechanical and thermal fatigue resistance and improved tribological performance. Despite these good properties, their high cost remains a major limitation in this sector. Ultra-hard Diamond-Like Carbon (DLC) coatings offer a technologically and economically feasible alternative to PCD-coated tools for cutting and machining non-ferrous materials. In this work, hydrogen-free ultra-hard (68 GPa) and thin (400 nm) DLC coatings were deposited on commercial tungsten carbide inserts using the filtered cathodic arc deposition technique. The machining performance of coated and un-coated hard metal inserts in the turning of 7075 aluminium alloy has been explored. The surface quality of machined parts, the cutting tool wear resistance and the vibrations generated during turning of un-coated, PCD and ultra-hard DLC coatings on tungsten carbide inserts have been compared. The results obtained demonstrate that DLC coatings developed in this work offer optimal mechanical performance in terms of surface finish of machined aluminium parts. Although the low thickness of these coatings may limit tool durability compared to thicker PCD coatings, DLC coatings may prove to be a potentially interesting alternative to PCD coatings for machining high-strength aluminium alloys, where surface finish may be as or more important than tool durability.

Thanks/Acknowledgement
This work was funded by the Ministry of Science, Innovation and Universities of Spain under the project REDUCA (RTC-2017-6479-4)

TRIB-P2-056 ● Properties of tungsten-tantalum diboride coatings deposited by High power impulse magnetron sputtering (HiPIMS)

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We present the deposition and characterization of tungsten-tantalum diboride (W,Ta)B_2 coatings prepared by the high-power impulse magnetron sputtering technique. We evaluated the influence of pulse duration and substrate bias on the properties of (W,Ta)B_2 films. A high hardness of up to 35 GPa measured by nanoindentation was simultaneously obtained with good elastic properties. Changing the pulse duration greatly affected the B/(Ta+W) atomic ratio, which influenced the properties of the coatings. Figure 1 shows the inverse relation of boron content and mechanical properties of coatings, similar studies were done by Fuger et al.[1] by means of density functional theory. On the basis of X-ray diffraction, we determined that coatings consist mainly of WB_2 -P6/mmm phase. Increasing the bias voltage led to change of structure from nanocrystalline to amorphous/nanocrystalline. The deposited films are thermally stable up to 1000°C in vacuum and are able to withstand oxidation at 500°C.

Thanks/Acknowledgement
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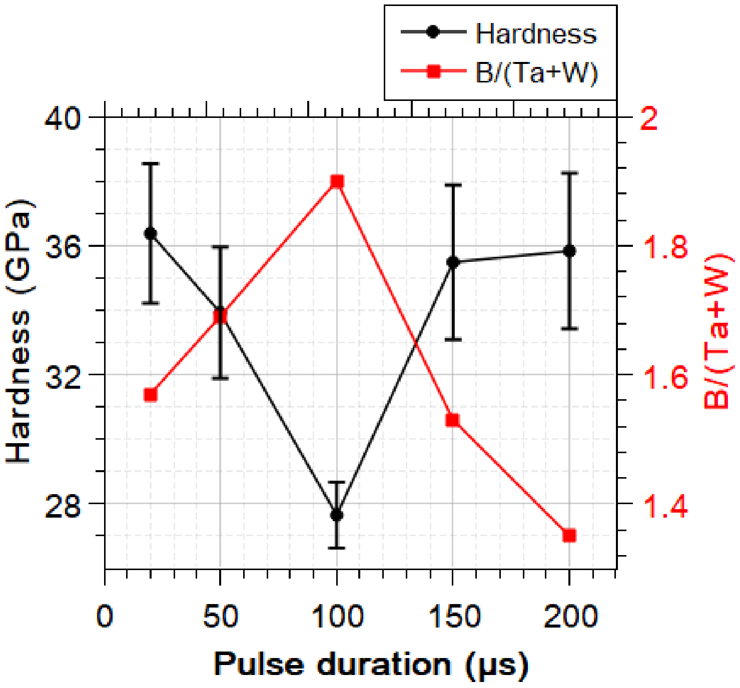

Hardness and B/(Ta+W) vs pulse duration

TRIB-P2-083 ● Effect of annealing temperature on morphological and microstructural properties of CrN-MoN multilayers deposited by reactive magnetron sputtering

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Nowadays, the magnetron process is widely used in academic research laboratories and in industries to synthesize functional thin films of high purity. In this work, the reactive magnetron sputtering technique has been used for depositing multilayer coatings consisting of alternating monolayers of CrN and MoN. Alternating the transition metal nitride monolayers generally increases the hardness [1] and allows to control the surface roughness of the coatings [2].

Different (CrN/MoN)x5 and (MoN/CrN)x5 multilayers (with thickness ≥ 1 µm) were deposited at 0.8 Pa and room temperature on Si (100) substrates. The morphology and crystal structure of the coatings were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD), before and after annealing at 500°C in an argon environment for 1 h. The coatings develop a columnar microstructure, with an alternating monolayers of 100 nm thickness. The monolayers have a cubic NaCl-type crystal structure with a preferential orientation [200] for CrN and [111] MoN. SEM observations show a topographic surface change and grain formation on the surface of the (MoN/CrN)x5 coating after annealing (see Figure 1.). XRD analysis in grazing incidence reveals that the grains formed on the surface of the (MoN/CrN)x5 coating are MoO_2 grains. A comparative study of the morphological and microstructural properties of these two multilayer materials will be presented.

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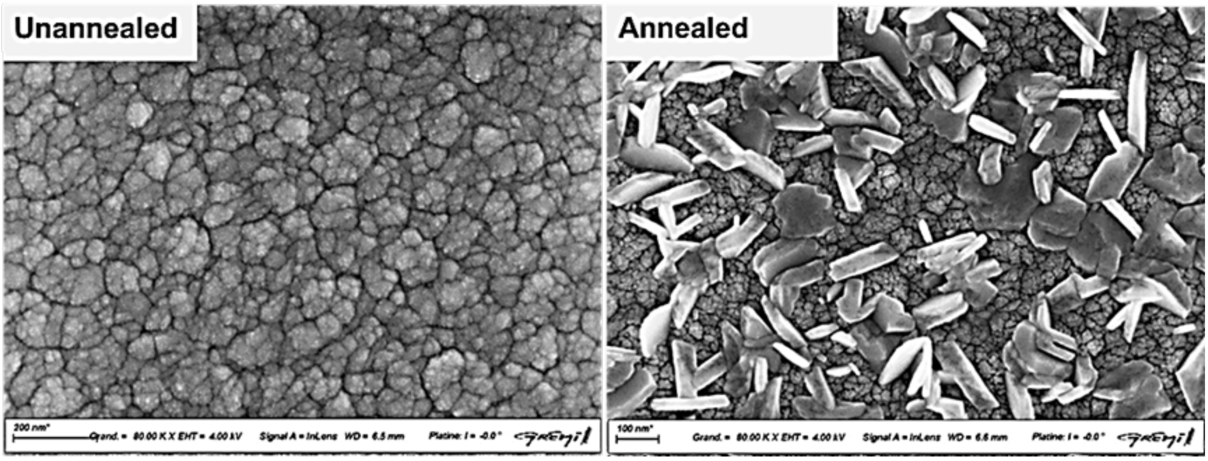

SEM images of the (MoN/CrN)x5 coating before and after

TRIB-P2-114 ● Zirconium-based thin film metallic glasses prepared by magnetron sputtering

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Due to their unique mechanical, hydrophobic, corrosion and other properties, metallic glasses have lately been the focus of research. These materials, with their composition being binary to quinary metal alloys, are typical by their amorphous structure, which is very uncommon for metals under normal conditions; therefore, the name amorphous metals is often used for these materials. Atoms in the structure of the metallic glasses are ordered in various types of clusters, and their variety hinders the bulk diffusion of atoms while not allowing for dislocation formation and movement. Instead, the deformation mechanism of metallic glasses is through the localisation of stress in shear bands. A large plastic zone at the head of a fracture in bulk metallic glasses makes them brittle, whereas thin film metallic glasses are ductile as the size of the plastic zone is similar to the thickness of the thin film allowing for stress relaxation via plastic flow. Another highlight of metallic glasses is their inherent hydrophobicity due to their low surface free energy. This all makes these materials industrially promising. However, their drawback is their relatively complicated manufacture by extremely rapid cooling, physical vapour deposition, solid-state reaction, ion irradiation, or mechanical alloying. The most often used of these is thermal/plasma/detonation spraying. The resulting coatings are inhomogeneous, porous, and thus not suitable for high-precision applications.
In this contribution, we will focus on the Zr1-X(Cu-Ni-Me)X system, where Me can be Al, Ti or Ta. This system is interesting for its ultrasmooth texture, corrosion stability due to passivation by ZrO2, strong hydrophobicity, low coefficient of friction, self-healing and antibacterial properties. The thin film metallic glasses will be prepared by DC and pulsed-DC magnetron sputtering to remain between the glass transition temperature of ~ 420°C while allowing us to tailor the energy distribution and flux of the ions bombarding the growing films. We will present the effect of the content of the constituent elements on the structure, morphology, mechanical properties, and hydrophobicity of the systems.

Thanks/Acknowledgement
The research was supported by project FW06010210 of the Technology Agency of the Czech Republic.

TRIB-P2-156 ● Increasing the thickness of sputtered Cr films by HiPIMS-DOMS

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Electroplated chromium coatings (EPC) are widely used in Industry for both functional and decorative applications. However, due to environmental and health concerns related to hexavalent chromium and, more recently, trivalent chromium, regulations severely restricting the use of EPCs have been issued both in Europe and the USA. Nevertheless, EPCs are still widely used in the coating industry. This is particularly evident in sanitary fittings, where 99% of sanitary fittings are chromium plated, although PVD technologies are already in the market. The main drawbacks of PVD coatings are the low maximum thickness (typically 3 to 5 micrometres) and the development of surface roughness with increasing film’s thickness, which degrades their aesthetic appeal.

The atomic shadowing effect is the main factors that limits the maximum achievable thickness of films deposited by magnetron sputtering. It drives the formation of open columnar anisotropic microstructures, with columns interspersed with voids or underdense regions, and increases the surface roughness as the film´s thickness increases. In a previous work, the authors have shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing effect is counteracted by the ionization of the sputtered material. Thus, at high ionization degree, dense and compact Cr films can be deposited without the need of high energy particles bombardment [1]. Successfully counteracting the atomic shadowing effect also opens the way for the deposition of much thicker films than achievable in classical sputtering.

In this work, thick and smooth Cr films were prepared by DOMS with increasing deposition times up to 6 hours. All the deposited films have a dense columnar microstructure with an almost complete [110] out of plane preferential orientation. Although the width of the columns increases significantly with increasing thickness, their surface roughness remained below 10 nm. The lattice parameter of the Cr films decreases with increasing thickness while their grain size increased from 18 to 28 nm. The hardness of the Cr films gradually decreased from close to 17 GPa to 10.5 GPa while their Young’s modulus increased from 275 to 425 GPa with increasing deposition time. Thus, dense, smooth and thick Cr films with a thickness above 10 micrometres were successfully deposited by HiPIMS-DOMS.

References

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TRIB-P2-176 ● Influence of temperature on the properties of W-Ti-B coatings deposited with the HiPIMS method

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This paper presents the properties of $(W,Ti)B_2$ films deposited by high-power pulsed magnetron sputtering. Studies have shown that it is possible to obtain the α-$(W,Ti)B_2$ crystal structure even at a substrate temperature of 300 ˚C. The (W,Ti)B2 coatings applied by HiPIMS have very interesting mechanical properties. At the same time, they are super hard (H>40 GP) and flexible [1]. XRD and nainoindentation studies have also shown that such coatings are stable at elevated temperatures. After continuous annealing (1 h at 800°C) and after 50 thermal cycles at a maximum temperature of 600°C, the coatings are still super hard fig.1. Tungsten-titanium diboride films have high thermal stability to 800°C in vacuum (invariance of the crystal phases), and it can withstand oxidation in 450°C.
Fig. 1. Load-displacement curves of $(W,Ti)B_2$ coatings: a) as deposited (solid line) and after an hour vacuum annealing at 800°C (dashed line), b) after 50 shocks (dotted line)

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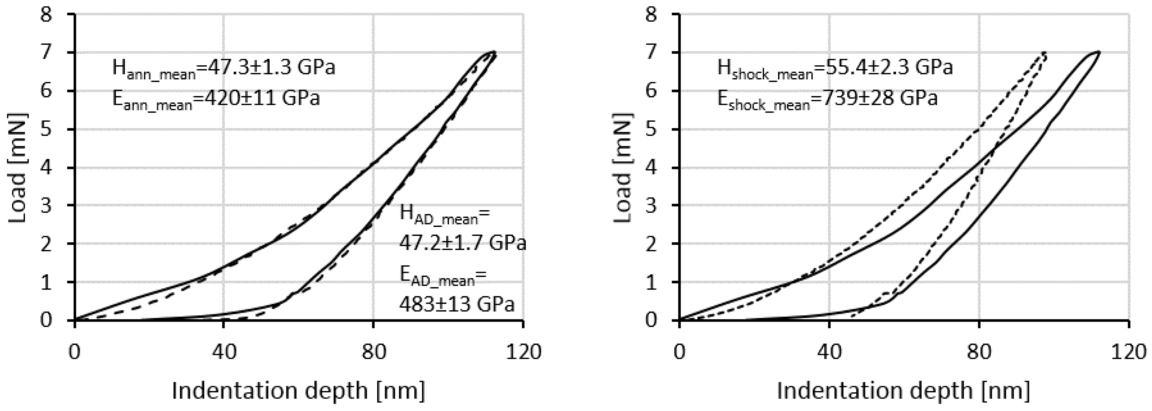

TRIB-P2-201 ● Plasma Electrolytic Oxidation of additively manufactured AlSi10Mg alloy

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Plasma Electrolytic Oxidation (PEO) is the most advanced of the anodizing methods. In comparison to traditional anodizing PEO provides coatings with higher wear- and corrosion- resistance and hardness. Moreover, PEO is carried out in an alkalic bath, instead of strong acids, which makes this method more environmentally friendly.

PEO is an excellent surface treatment for light metals, like magnesium or aluminium. More often light metals are produced by additive technologies (3d printing). The microstructure of additively manufactured alloys strongly differs from casting alloys. Characteristic melting pools are observed. AlSi10Mg alloy presents eutectic structure surrounded by Si-net. The microstructure is strongly connected to laser paths. Fine-grain microstructure results in higher strength than cast alloy.

In this study, traditional anodizing, hard anodizing (HA) and PEO were carried out on AlSi10Mg manufactured by Direct Metal Laser Sintering (DMLS). Moreover, PEO was also performed on cast AlSi10Mg alloy. Thin, conversion coatings were obtained (thickness under 10 μm). A microstructure of oxide coatings was observed. Scratch resistance was tested and allowed to describe the films' adhesion.

PEO coatings are vastly porous and include more SiO_2 oxides than traditional and HA coatings. SiO_2 oxides are more difficult to obtain as silicon has higher resistance than aluminium. Moreover, PEO guarantees more phase-mixed surface microstructure, including amorphous, ceramic phases, which cannot be formed in low-voltage processes. In comparison to traditional and HA oxide coatings, PEO coatings exhibit better adhesion and scratch resistance. Traditional anodizing and hard anodizing on additively manufactured AlSi10Mg provide the critical load LC1 at which coating begins to be broken of 8.5N and 10N respectively. A similar LC1 value can be obtained for PEO performed on cast alloy (7.8N), while in the case of additively manufactured AlSi10Mg this LC1 is increased four times to 42.1N.

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