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VIRTUAL MEETING

13 - 17 September 2021 - ~~Antibes, French Riviera~~

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PL1 ● Large volume liquid treatment with high-density microwave plasma

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Plasma-liquid interaction has attracted much attention for various applications such as water purification, decomposition of liquid waste, biotechnology, agriculture, and material synthesis. For such purpose, dielectric barrier discharges, spark discharges, etc. have been used as the plasma source, because these atmospheric pressure plasma sources are compatible with liquid environment. These discharges also have merit of low power consumption with energy saving. However, some applications such as hydroponic culture, liquid waste management etc. requires large amount of liquid plasma treatment and efficient plasma treatment system is essential.

For efficient liquid treatment, pressure reduction is one of the solutions because the discharge ignition in much easier at reduced pressure condition, not only in the case of DC discharge but also in the case of RF discharge including microwave. Based on this, we made various approach to liquid treatment under reduced-pressure condition using microwave power. In the presentation, effectiveness of the reduced-pressure process will be shown. Furthermore, to realize sustainment of stable plasma close to the liquid surface, an alternative way of liquid treatment set-up is proposed, where reduced pressure is automatically formed by liquid flow with the aid of Venturi effect. This concept also has a merit of compatibility with the liquid treatment because the liquid can be treated with in-line process.

With using this concept, new microwave plasma treatment source will be presented. As an example of the water waste treatment, organic decomposition by the in-line liquid treatment system will be shown. Furthermore, the microwave liquid treatment system is applied to materials processing. Recently, silver nanoparticles have given much attention as silver “nano-ink” in printing electronics. For such application, silver nanoparticles are produced from silver nitrate or other related solutions by the in-line liquid treatment system. By optimizing liquid compound, conversion efficiency to silver nanoparticle was more than 5%, which is promising to suppress production cost of silver nano particles.

SURF / Plasma-surface interactions

PL2 ● Renewable energy driven non-thermal chemistry: Plasma chemistry as the special case

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The worldwide energy crisis and environmental issues have greatly driven the current research on exploring and efficiently utilizing the environmentally-friendly and sustainable energy sources. Most sustainable sources such as solar and wind energy are in principle scalable and able to meet the global energy demand. Nevertheless, they are intermittent and require new concepts of conversion and storage of electricity. Chemical feedstock, i.e. storing energy in form of the binding energy of molecules, is an economically feasible option for long term (seasonal) storage. However, the main challenge is how to address the problem of developing an effective and economical process for converting electrical energy into molecules of high energy for chemical feedstock.

In a circular CO2 neutral society, where the use of dense energy carriers based on carbon will still be needed, the re-use of (air captured) carbon dioxide is required. These dense energy carriers can be utilized to mitigate intermittency of renewable energy sources by providing seasonal storage, as feedstock for the chemical industry to replace fossil based feedstock and as green synthetic fuels for long haul and air transport. Also in this context, nitrogen fixation is unquestionably one of the most important chemical conversion process since it converts atmospheric nitrogen (low energy molecule) into molecules of high energy (e.g. NH3, NO). The use of electrons, from renewable electricity, or photons, directly from the sun, provide scientific and technological opportunities to develop novel pathways for chemical conversion.

In this talk, after an introduction to the challenges facing the world in the next decades, I will discuss the opportunities of using plasmas, powered by renewable electricity, for scalable gas conversion of key molecules such as CO2 and N2. In particular I will address the use of microwave plasma to dissociate CO2 into CO and O2, and the possible, often claimed, role of nonequilibrium vibrational kinetics. The separation of the products CO2/O2/CO will discussed briefly. Inspired by this approach, I will present a unique hybrid type reactor consisting of a plasma reactor and solid state water electrolysers with oxygen ion or proton conducting membranes. One aided benefit of this proposed approach is that both technologies, i.e. water electrolyser and plasma activation, utilize base molecules (N2 and H2O) and can be directly powered by renewable electricity. Such a scheme may be a stepping stone to zero carbon footprint processes. Moreover, the advantages of proposed approach will be also compared to conventional plasma catalysis or pure plasma processes.

ENER1/ Renewable energies

● Investigation of the aptness of pulsed laser deposition for the sequential fabrication of Cu(In,Ga)Se_2-based thin-film solar cells

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Thin-film photovoltaic (PV) technologies, and Cu(In,Ga)Se_2 (CIGS) thin-film solar cells in particular, have been the subject of increasingly rigorous study of late. There are several motivating factors for the development of thin-film photovoltaics, such as the reduction in raw material usage, the decrease in solar cell weight, and the possibility of deposition on flexible substrates. Furthermore, CIGS-based thin-film solar cells hold several advantages compared to rival solar cell technologies. Specifically, they have the highest conversion efficiencies among chalcogenide thin-film PV technologies [1] (23.35% for cells and 17.5% for modules), high radiation resistance [2], and outstanding stability [3]. The typical CIGS-based solar cell consists of a soda-lime glass (SLG) substrate, a Mo back contact, CIGS as the p-type absorber layer, CdS as the n-type buffer layer, and i-ZnO/ZnO:Al as the decoupling and transporting window layers, respectively. However, in the state-of-the-art CIGS-based solar cells, each of these layers is deposited with a different method; co-evaporation for the CIGS layer, chemical bath deposition for the CdS layer, and reactive sputtering for the i-ZnO/ZnO:Al bilayer. This work reports on the utilization of pulsed laser deposition (PLD) as a single technique for the preparation of the aforementioned layers of a complete CIGS-based solar cell stack. Employing a single deposition technique greatly reduces manufacturing complexity. Furthermore, it potentially decreases processing time and associated fabrication costs through streamlined production lines. The presented results discuss the challenges faced in the completion of this task. The properties of the PLD-grown thin films with respect to structure, composition and morphology are parametrically investigated. Hence, the influence of PLD process parameters on film growth is evaluated. TCAD simulations are utilized for the optimization of the function of the cell. Electrical and optical measurements are used to assess the photovoltaic behavior of the complete structure and, critically, the CdS/CIGS junction heterointerface. The solutions implemented, involving modifications to the typical PLD process, are discussed. Finally, the resulting improvement in conversion efficiency is demonstrated.

References

[1] SolarFrontier, Solar Frontier Achieves World Record Thin-Film Solar Cell Efficiency of 23.35%, 2019. http://www.solar-frontier.com/eng/news/2019/0117_press.html (accessed 31 January 2021)
[2] J. Guillemoles, The puzzle of Cu (In, Ga) Se2 (CIGS) solar cells stability, Thin Solid Films 403 (2002) 405–409[3] U. Rau, A. Jasenek, R. Herberholz, H.-W. Schock, J.-F. Guillemoles, D. Lincot, L. Kronik, The inherent stability of Cu (In, Ga) Se2-based solar cells, 2nd WCPEC, (1998), pp. 428–433.

ENER1/ Renewable energies

● Influence of the silver content in (Ag,Cu)I thin films on their optical and electrical properties

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Transparent semiconductors are well-known as electrical contacts and light transmitters for their use in optical devices like display panels, solar cells, etc. In this experimental work, thin AgCuI films have been synthesized by iodination of AgCu thin layers with iodine vapor to study films properties and their photovoltaic performances. AgCuI alloy semiconductor system can be either p-type or n-type, depending on Ag concentration.X-ray diffraction (XRD), Hall effect and UV-visible spectrometry techniques were used to investigate structural, electrical and optical properties of AgCuI thin films deposited on silicon and glass substrates. For further investigations on optical characteristics of the ternary alloy (direct-gap semiconductors), photoluminescence measurements have been performed at room temperature for different silver concentrations. Variation of grain size has been analysed under different experimental conditions examined by scanning electron microscopy (SEM). We obtained transparent p-type thin films at low silver content and n-type materials at high silver content. Both kind of semiconductors crystallize in the FCC structure of copper iodide. The results on structural characterizations suggest new ways to control the synthesis process in order to improve the solar cells and to optimize AgCuI photovoltaic devices.

ENER1/ Renewable energies

● Tailored electrodes for solid acid fuel cells via sputtering: improved platinum utilization via optimized layer microstructure

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A solid acid fuel cell (SAFC) is an encouraging type of fuel cell because it combines a high conversion efficiency with an intermediate operating temperature. Therefore, they are very interesting for a wide range of applications in view of the ongoing energy transition towards the increased use of renewable sources. One of the challenges towards a commercial application of SAFCs is increasing the performance while reducing the cost by lowering Pt loading. A deep understanding of the reaction paths is highly desirable for enhancing the catalyst utilization based on a rational electrode design. Here, we produce tailored Pt electrodes with tuned thin film porosities by adapting the working gas pressure in a DC magnetron sputtering process. In that way, very dense to highly porous, nanostructured layers could be produced. In a fuel cell, the porous layers combine increased electrochemical activity with a significantly reduced use of platinum at a constant layer thickness. An observed degradation of the highly porous Pt films was studied by analysing the electrodes pre and post fuel cell operation state by ex situ SEM and STEM. The results shed light onto the importance of the catalytic reaction paths in the operation of a SAFC. The combination of mass determined and thickness-controlled film depositions, characterization methods like SEM and XRD and operando performance measurements like impedance spectroscopy enables us to gain insights into reaction paths and degradation causes and to draw conclusions on catalytic active sites. The presented work establishes guidelines on how to design solid acid fuel cells for high performance at low Pt loading.

ENER1/ Renewable energies

● Carbon-based coatings deposited by HiPIMS for metallic bipolar plates with enhanced durability performance

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Metallic bipolar plates (BPPs) are a promising candidate to replace conventional graphite BPPs due to higher power density and lower costs in proton exchange membrane fuel cells (PEMFCs). However, great challenges still exist for the application of metallic BPPs since they are working in acidic, humid, warm and polarized environment that reduce the lifetime of BPPs. The application of coatings is essential to enhance interfacial conductivity and corrosion resistance. In this study, three different metal-doped amorphous carbon coatings (a-C:Cr, a-C:W and a-C:Ti) have been deposited by HiPIMS on stainless steel BPPs and their performance have been investigated. Raman analysis has been carried out to analyze the influence of metal content on carbon structure. The sp^3-sp^2 ratio has also been assessed with EELS spectroscopy. High-temperature nanoindentation has been used to obtain the hot hardness of the coatings at working temperatures. Interfacial contact resistance (ICR) has been measured. Potentiodynamic and potentiostatic tests have been conducted to evaluate the corrosion resistance of the coated samples. Hydrogen permeation have been measured by using a gas driven permeation (GDP) system working at temperatures up to 500 K. Metal-doped carbon coatings deposited by HiPIMS provide enhanced finishing, mechanical properties and corrosion resistance. The results obtained show great potential of application in PEMFC.

SURF1/ Plasma – surface interactions

● Relation between CH_4 yield and CO emission intensity gradient in plasma-assisted CO_2 methanation

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NASA plans to employ the Sabatier reaction to produce the fuel on Mars for the manned exploration program to Mars [1]. The Martian atmosphere has an average temperature of -63°C and an average pressure of 750 Pa. Conventional CO2 methanation methods using catalysts that require high temperature and high pressure conditions are not suitable for the Martian environment. Catalyst degrades quickly under the high-temperature environment, making long-term operation difficult. We have studied a plasma catalytic method that excites CO_2 by non-equilibrium plasma to promote the Sabatier reaction at low temperature and low pressure [2]. The experimental apparatus was a capacitively coupled high-frequency plasma system. Hydrogen and carbon dioxide were flowed at 6.0 sccm and 1.0 sccm, respectively, and the pressure was set to 750 Pa. 60 MHz RF power supply was used with a duty ratio of 50% and a pulse frequency of 100 Hz to 30 kHz. Figure 1 shows the relationship between the gradient of CO Angstrom emission intensity near the electrode and the methane yield. The larger the gradient is, the higher the methane yield is. This emission intensity is probably proportional to CO excited state density, and hence this gradient indicates the excited CO flux to the catalytic electrode. CO Angstrom has an excitation threshold energy of 10.8 eV for the upper level CO(B), which correlates with the dissociation of CO (dissociation voltage of 11.1 eV). The clear correlation in fig. 1 indicates that CO species excited by the plasma near the electrode diffuse towards the catalyst surface and contribute to the methane production.

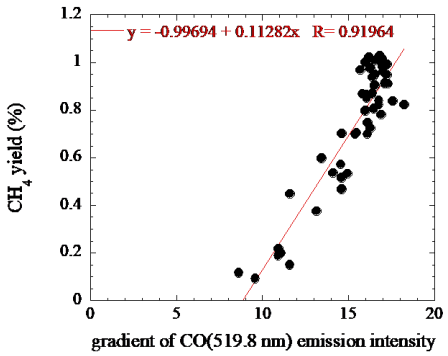
Thanks/Acknowledgement

This work is partially supported by Japan Society of the Promotion of Science (JSPS) Core-to-Core Program JPJSCCA2019002.

References

[1] Gerald Sanders, "Current NASA Plans for Mars In Situ Resource Utilization", NASA Technical Reports(2018). [2] S. Toko, et al. Sci. Adv. Mater., 10 (2018) 1087.

Relation between CH4 yield and the gradient



SURF1/ Plasma – surface interactions

● Molecular dynamics simulations of CH_4 plasma deposition on stainless steel surfaces: $C_2H_3^+$ bombardment on hydrocarbon films

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Reactive molecular dynamics is used to deposit a hydrocarbon film from an Ar/CH_4 plasma on the substrate. Ion species are considered as fast neutrals whose kinetic energy corresponds to the electrode potential. The initial plasma composition is determined from a 1D plasma model from which deposition is carried out. The resulting film is then bombarded by neutrals and ions. A particular attention is paid on the role of $C_2H_3^+$.

Complex Non-equilibrium Hydro-Carbon Plasmas are weakly ionized gases containing electrons, neutral and charged molecular species, large clusters and, possibly, solid particles. In this study, molecular dynamics simulations were used to first carry out a hydrocarbon thin film deposition by simultaneously sending neutral species to the surface at a temperature of 300K. The most important molecules (table 1) are determined using a 1D fluid model of an Ar/10% CH_4 capacitively coupled parallel plate plasma (see figure 1). The grown hydrocarbon film is then bombarded with $C_2H_3^+$ ions at energies of 50eV and 100eV. The evolution of the mass of the hydrocarbon film and the species formed in the gaseous phase following the ion impacts, are followed.

Table 1

Major neutral species	Molar fractions (Ar is 1)
H_2	$3.20\ 10^{-2}$
CH_4	1.40 10-2
C_2H_4	$5.40\ 10^{-3}$
C_2H	$3.20\ 10^{-3}$
C_2H_2	$2.70\ 10^{-3}$
CH_3	$2.30\ 10^{-3}$

MDs are carried on by sending a total number of 10,000 molecules that takes into account the molar fraction during deposition, towards a $Fe_{67}Cr_{17}Ni_{14}Mo_2$ substrate (4.018 x 4.018 x 5 nm^3), mimicking the stainless steel electrodes. C-C and C-H interactions are described with the REBO [1] potential whereas Me-C and Me-H interactions are modelled using Lennard-Jones potentials.

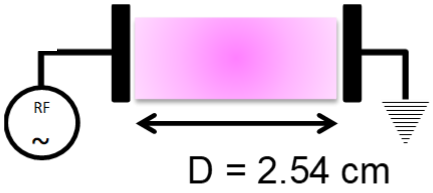
Thanks/Acknowledgement

This work was partly supported by the French National Research Agency (ANR) through the MONA project (ANR-18-CE30-0016)

References

[1] M. Zarshenas et al, J. Phys Chem. C 122 (2018) 15252-15263

Schematics of the 1D axisymmetric RF Plasma



P=70Pa, Vb =100V, T= 300, 400, 500 and 1000K

SURF1/ Plasma – surface interactions

● Plasma – surface interaction on InP studied by photoemission spectroscopies (XPS, HAXPES) inside a GD-OES crater

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The profiling rapidity of GD-OES offers interesting perspectives for the analysis of coated structures or stacks, enabling to easily reach buried interfaces. The GD-OES crater dimension of 2-8 mm diameter is compatible with many chemical, optical or electronic probes that can be directly implemented inside the crater. In particular, the quantification from photodiode voltage to atomic concentration is not arbitrary when a material system involves many elements and requires a calibration step. We propose here to combine surface analyses (XPS and HAXPES) to calibrate GD-OES profiles and bring an accurate overview of the chemistry. An important point concerns the reliability of the information inside this crater requiring to get insight on the plasma-surface interaction. Indeed, we have evidenced the systematic presence of an overlayer, damaged by the plasma and resulting from the shutdown procedure, whose physicochemical properties differ from the one of the original layer [1]. The determination of the nature of this layer and its thickness is essential for the development of adjusted procedures to remove it. In a previous paper, we have evaluated the chemical and optical perturbations in the case of InP (100) semi-conductor [2]. Combining XPS, EBSD and ellipsometry, we have demonstrated that the morphology and the atomic network are modified over approximatively 50 nm (partial loss of crystallinity, surperficial In enrichment, optical indexes modifications) but the exact impacted depth has still to be determined. Post-mortem analysis of GD-OES craters with HAXPES, using a higher energy X-ray source than XPS, is used to increase the sampling depth from 10 nm up to 30-50 nm for bulk-sensitive measurements, and detect the elemental concentration and chemical state within the whole damaged layer and probably below. Especially, additional core levels become accessible with HAXPES, and thus an extended escape depth range. The In/P ratio can be determined using different photoelectron peak combination, the conventional In 3d/P 2p (as a comparative point with XPS measurements), but also the In 2p/P 1s ratio. For this study, a GD-OES (Profiler 2, Horiba) and an XPS (Nexsa, Thermo Scientific) are combined with a novel laboratory-based HAXPES spectrometer using a Ga Ka (9.25 keV) X-ray source (Scienta Omicron GmbH) [3] which has recently been calibrated and elemental sensitivity factors calculated to enable quantification [4].

References

[1] D. Mercier et al. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.04
[2] S. Béchu et al, (2019), https://doi.org/10.1116/1.5121897
[3] A. Regoutz et al. (2018), https://doi.org/10.1063/1.5039829
[4] B.F Spencer et al. (2020), Sci.,;https://doi.org/10.1016/j.apsusc.2020.148635

SURF1/ Plasma – surface interactions

● Aspect-ratio-dependent etch effects in Titanium deep reactive ion etching

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Titanium-based microelectromechanical systems (MEMS) are attractive candidates for biomedical applications. For such devices, deep reactive ion etching (DRIE) is a key fabrication method that enables very high-aspect-ratio features to be performed into bulk titanium substrates. Most of the research work reported in the literature relies on a Cl_2/Ar chemistry to deep etch titanium [1]–[3].

However, the DRIE technology on bulk titanium is not as mature as that on silicon and undesired effects such as the aspect ratio dependent etching (ARDE) have not been widely studied. The ARDE phenomenon, also known as “RIE lag”, consists in a strong correlation between the etching rate and the aspect ratio of the features (AR): the first decreases when the second increases [4].

To experimentally investigate process parameters leading to ARDE, a $Cl_2/SF_6/O_2$ inductively coupled plasma (ICP) was used to etch deep trenches into bulk titanium substrates. The effects of ARDE are rather substantial in $Cl_2/SF_6/O_2$ plasmas because the etching rate is very sensitive to the variation in the local atomic fluorine concentration as well as to the variation in the amount of passivating species. The pressure dependence of RIE lag has been studied and the influence of gas flow rates is investigated with respect to the etch rates.

References

[1] R. d’Agostino, F. Fracassi, and C. Pacifico, ‘Dry etching of Ti in chlorine containing feeds’, Journal of Applied Physics, vol. 72, no. 9, pp. 4351–4357, Nov. 1992, doi: 10.1063/1.352199.
[2] F. Fracassi and R. d’Agostino, ‘Chemistry of titanium dry etching in fluorinated and chlorinated gases’, Pure and Applied Chemistry, vol. 64, no. 5, pp. 703–707, Jan. 1992, doi: 10.1351/pac199264050703.
[3] E. R. Parker, B. J. Thibeault, M. F. Aimi, M. P. Rao, and N. C. MacDonald, ‘Inductively Coupled Plasma Etching of Bulk Titanium for MEMS Applications’, J. Electrochem. Soc., vol. 152, no. 10, pp. C675–C683, Jan. 2005, doi: 10.1149/1.2006647.
[4] R. A. Gottscho, ‘Microscopic uniformity in plasma etching’, J. Vac. Sci. Technol. B, vol. 10, no. 5, p. 2133, Sep. 1992, doi: 10.1116/1.586180.

DEPO1 / Plasma - deposited coatings

● The potential of hydration in functional plasma coatings

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The use of plasma coatings is highly attractive to enhance biomaterials such as sensors, scaffolds, antibacterial surfaces and others. Control over the formation of plasma coatings on the nanoscale enables ultrathin films providing new surface properties. Investigations regarding mainly the interaction with bacteria and proteins will be presented. 2 nm-thick hydrophobic cover layers on PDMS substrates of different crosslinking degree are used to clarify the role of viscoelastic properties on bacterial growth indicating the lack of mechanosensing abilities [1]. Likewise, hydrophobic cover layers with varying film density are explored to control water intrusion [2]. Thus, a defined volume of water can be allowed to penetrate a porous base layer. Protein adsorption of BSA is found to be affected by this hydration effect due to orientation of water molecules in the subsurface inducing reordering at the surface [3]. Moreover, controlled drug release from a Ag reservoir is enabled for long-term antibacterial properties, while undesired release from conductive Ag-coated textile electrodes as used for ECG sensing can be avoided by passivation. As another approach, rapid and highly efficient antimicrobial effects are obtained by formation of reactive oxygen species at nanostructured metal oxide surfaces. Recent progress in the understanding of plasma deposition processes enables increased control and usability of functional plasma coatings at the nanoscale enabled by fast and economic low-pressure plasma engineering [4]. Dry and environmentally friendly processes can thus be implemented meeting the requirements for industrial applications.

References

[1] F. Pan, S. Altenried, M. Liu, D. Hegemann, E. Bülbül, J. Moeller, W. W. Schmahl, K. Maniura-Weber and Q. Ren, Mater. Horiz. 7, 2020, 93-103
[2] E. Bülbül, D. Hegemann, T. Geue, M. Heuberger, Coll. Surf. B: Biointerfaces 190, 2020, 110908
[3] E. Bülbül, D. Hegemann, K. Ataka, S. Lehner, J. Heberle, M. Heuberger, Surf. Interfaces, 2021; https://doi.org/10.1016/j.surfin.2020.100922
[4] D. Hegemann, E. Bülbül, B. Hanselmann, U. Schütz, M. Amberg, S. Gaiser, Plasma Process. Polym. 18, 2021, e2000176

● Silver influence on the antibacterial activity of multi-functional Zr based thin film metallic glasses

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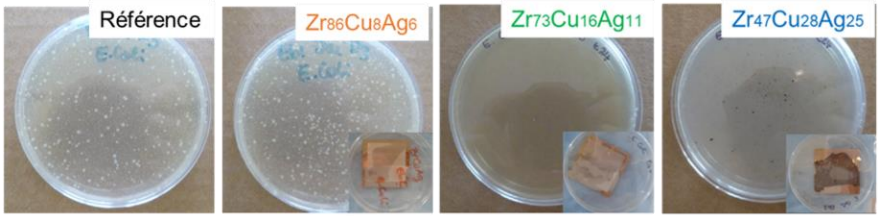
Thin film metallic glasses (TFMG) have recently emerged as alternative film materials for many applications, such as micro-electro-mechanical systems and biomedical [1]. Zr-based TFMGs can for example combine high durability and promising antibacterial activity for their used as coating for medical instruments. In this purpose, we recently characterized a silver-rich Zr-Cu-Ag (22 Ag at.%) TFMG [2]. Its high antibacterial activity was clearly established but some development are need to improve its corrosion resistance.

In this study, we investigated the impact of silver/copper content on properties and antibacterial activity of Zr-Based TFMGs. PVD magnetron sputtering, with a dual-target, was used for the deposition of Zr-Cu-Ag thin films with a wide range of Ag-content [6-32 at.%]. Their structural, microstructural, mechanical properties and antibacterial activity were then characterized.

XRD analysis showed that ternary Zr-Cu-Ag thin films were all amorphous. However, TEM analysis revealed the presence of nanoparticles embedded in amorphous matrix for silver-rich films (Ag at.% ≥ 25 %). These thin films also appear uniformly thick and smooth on SEM micrograph. Mechanical properties, determined by nanoindentation, evidenced the effect of silver percentage on Young's modulus and hardness of films. The silver content favors the corrosion protectiveness of TFMGs in moderately aggressive medium. However, the presence of nanoparticles induces pitting corrosion for Ag-rich thin films in chloride medium.The antibacterial activity of these TFMGs against Escherichia coli and Staphylococcus aureus was evaluated. A beneficial influence of silver addition on the antibacterial activity of TFMGs was clearly established and a critical silver content of 11 at.% leading to a biocide effect of coating and good corrosion resistance is determined as a promising film for the target application (Figure 1) [3]

References

[1] J.P. Chu et al. Thin film metallic glasses: Unique properties and potential applications. Thin Solid Films 520.16 (2012): 5097-5122 [2] A. Etiemble et al. Innovative Zr-Cu-Ag thin film metallic glass deposed by magnetron PVD sputtering for antibacterial applications. Journal of Alloys and Compounds 707 (2017): 155-161 [3] G. I. Nkou Bouala et al. Silver influence on the antibacterial activity of multi-functional Zr-Cu based thin film metallic glasses. Surface and Coatings Technology 343 (2018): 108-114.



Composition	Colony Counting Units ($CFU.m^{-2}$)	
	E. coli	S. aureus
Glass reference	$2.6.10^6$	$2.0 .10^6$
$Zr_{52}Cu_{48}$	$2.8.10^6$	$2.4 .10^6$
$Zr_{86}Cu_8Ag_6$	$2.6.10^6$	$3.1 .10^6$
$Zr_{73}Cu_{16}Ag_{11}$	0	0
$Zr_{47}Cu_{28}Ag_{25}$	0	0

DEPO1 / Plasma - deposited coatings

● Structure and mechanical properties of superelastic Ti-Nb-based sputtered thin films 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 stress-induced 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 nanoindentation 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. Using XRD θ/2θ scans, the films have been found to be highly textured: the main peaks are 002 α and 110 β. XRD, TEM and resistivity show that with increasing Nb and Zr content, the phase evolves from hexagonal α phase to orthorhombic α'' martensite and then to cubic β phase. The curvature measurements have shown that at low Nb content, the film first develops a compressive stress that evolves during continuing growth into tensile stress. At high Nb content, the stress remains compressive throughout deposition.

Thanks/Acknowledgement

This work is supported by the ANR Project 18-CE08-0017 Super-Rev.

DEPO1/ Plasma - deposited coatings

● Oxidation of sputter-deposited V_2N as an innovative precursor to achieve thermochromic VO_2 thin films

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VO_2 is a broadly studied thermochromic material, which undergoes a metal-insulator transition approx. at 68°C, accompanied by a crystallographic transition from a low-temperature monoclinic phase to a high-temperature tetragonal rutile structure. Optical and electrical properties change drastically with the phase transition and offer a path to various applications, such as smart windows, thermal solar collectors, ultrafast electronic devices... Nevertheless, the elaboration of pure VO_2 films on large surfaces remains a challenge due to the difficult task of avoiding other phases belonging to the vanadium-oxygen binary system [1].

In previous studies, we have demonstrated that the oxidation of VN thin films is a new method to form high-quality thermochromic VO_2 [2,3]. The present work aims to achieve thermochromic VO_2 from the controlled oxidation of another new precursor: sputter-deposited V_2N films. Thermochromic VO_2 films have been obtained by air oxidation of V_2N samples performed at two temperatures (450 and 550°C). X-ray diffraction and Raman spectrometry of the V_2N oxidized films evidence that VO_2 and V_2O_5 are the only phases obtained throughout the oxidation process. VO_2 is the first oxide formed coexisting with V_2N for a long time at 450°C or swiftly vanishing at 550°C. EELS results show that the oxidation of V_2N to VO_2 occurs in two stages. First, the V_2N turns into VN before the oxidation to VO_2. Further oxidation leads to the formation of V_2O_5, diminishing the thermochromic performance of the films. As the thickness of the initial V_2N layer increases from about 100 nm to 445 nm, the optical modulation properties of the obtained VO_2 films change from a negative value of the emissivity switch to a positive value. These results may pave the way for future research on the oxidation of V_2N as a new precursor to form high-quality thermochromic VO_2.

References

[1] Yang *et al.*, Annu. Rev. Mater. Res. **41** (2011) 337–367
[2] García-Wong *et al.*, Sol. Energy Mater. Sol. Cells. **210** (2020) 110474
[3] García-Wong *et al.*, J. Materiomics. (2020). In Press

PROC / Process control

PL 3 ● Influence of the electron description on the modelling of scenarios with interest for plasma-based applications

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The adequate description of the electron kinetics is paramount to capture the behaviour of low-temperature plasmas, becoming a critical aspect of modelling in scenarios with interest for applications. In this talk, we present two examples where modelling results can be severely affected by the formulation adopted to describe the plasma electrons.

The first example focuses on the temporal evolution of the electron kinetics in dry-air plasmas (80%N2:20%O2), excited by electric-field pulses with rise-times 10-9 and 10-6s, applied to a stationary neutral gaseous background at pressures 105 and 133Pa [2]. The study solves the electron Boltzmann equation (EBE) using the LisbOn KInetics Boltzmann solver (LoKI-B) [1] and adopts either (i) a time-dependent formulation that considers an intrinsic time evolution for the electron energy distribution function (EEDF); or (ii) a quasi-stationary approach, where the time-independent form of the EBE is solved for different values of the reduced electric-field during the pulse. The simulations show that (i) gives solutions similar to (ii) for rise-times longer than the characteristic evolution time of the EEDF, i.e. 20ns at 105Pa and 20ms at 133Pa, meaning that a quasi-stationary description is possible in microsecond pulses at atmospheric pressure, failing for nanosecond pulses at both pressures considered here.

The second example addresses capacitively coupled radio-frequency discharges in N2–H2 at low pressure (0.3–0.9mbar), low power (5–20W), and H2 concentrations up to 5% [3]. Simulations use a hybrid code that couples a two-dimensional time-dependent charged-particle fluid module to a zero-dimensional kinetic module, that solves the EBE and includes a detailed surface chemistry for NHx. The code includes a dedicated module for fast electrons generated by secondary emission. The inclusion of these fast electrons results in an exponential growth of the electron density at higher powers, which is not captured by the fluid code for slow electrons and allows fitting the measurements by tuning the secondary emission coefficient

(SEC). The results highlight the relevance of plasma-surface interactions, given the role of SEC in the electrical parameters and the critical influence of the surface production of ammonia in the plasma chemistry.

Thanks/Acknowledgement

This work received the financial support of the FCT (projects UIDB/50010/2020, UIDP/50010/2020, UIDB/04650/2019 and UTAPEXPL/NTec/0107/2017), and of the ERC (Starting Grant PRIMCHEM, Grant agreement no. 636829).

References

[1] Thanks/Acknowledgement
[2] This work received the financial support of the FCT (projects UIDB/50010/2020, UIDP/50010/2020, UIDB/04650/2019 and UTAPEXPL/NTec/0107/2017), and of the ERC (Starting Grant PRIMCHEM, Grant agreement no. 636829).

INDU1 / Industriel hot topics

● Prototyping a multi-cathode HiPIMS coating set-up for complex substrates

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The niobium coatings for Superconducting Radio-Frequency (SRF) cavities have long imposed some of the most stringent requirements in terms of purity, density and uniformity within the thin film community. In the frame of CERN's Future Circular Collider study, the Wide Open Waveguide Crab Cavity (WOWCC) has been designed [1], and still exacerbates these difficulties due to its three dimensional complexity. This is illustrated below by the generic schematic of the principal components of the WOWCC coating set-up inside the copper cavity. The six niobium cathodes (blue) are mounted around stainless steel tubes (cyan). Within, air-cooled neodymium magnets (green) move along pipes (beige), which inject the air into the bottom of the tubes. Through extensive studies [2,3], coating processes have yet been rising to the challenge, most recently through the adaptation of High Power Impulse Magnetron Sputtering (HiPIMS). In particular, the finely tuned addition of inverted, positive voltage pulses after the main discharge pulses improves the deposition onto substrates with complex shapes. This technique proved a viable alternative to substrate biasing, when dealing with large, grounded samples. Furthermore, the utilization of multiple, optimally positioned cathode tubes along the length of the cavity allows to limit shadowing effects. Since these measures have produced promising results on a small-scale set-up, we have been moving towards the implementation of a scale-one prototype. We will present its current state and a selection of important considerations that have shaped its design process. From the characterization of coatings to the movement and orientation of the magnets, we combine numerical, experimental and engineering efforts towards a practicable implementation of the system.

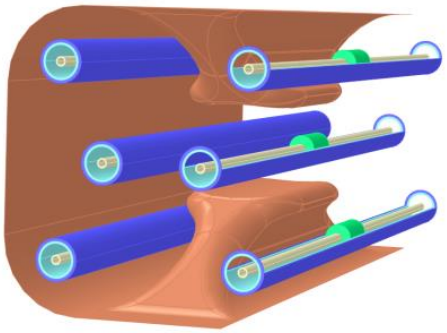
Thanks/Acknowledgement

The author acknowledges the support and funding from the CERN FCC study project, and contributions within the WOWCC working group. Further thanks are due for the many fruitful discussions and hardware support in the TE-VSC-SCC section.

References

[1] K. Papke et al, Phys. Rev. Accel. Beams 22, 072001, 2019
[2] F. Avino et al, Plasma Sources Sci. Technol. 28, 01LT03, 2019
[3] F. Avino et al, Thin Solid Films 706, 138058, 2020

WOWCC coating set-up geometry



INDU1 / Industriel hot topics

- Atmospheric plasma technology: Innovative solutions for biomedical, agricultural, aerospace, defense, and energy applications

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Plasma, discharged under vacuum conditions, underpins the development of the silicon wafer industry, which makes the devices that you're using to read this abstract. Atmospheric plasma technology - discharging plasma in the air - has been under development for several decades and has many benefits over vacuum technologies: in surface engineering applications there is no limit on component size and processing can be undertaken much faster as there is no requirement for a vacuum chamber. Atmospheric plasma generation has many other applications beyond surface engineering, which includes increasing the range planes can fly on a certain amount of fuel, increasing the energy efficiency of solar energy plants, creating functional nanomaterials, chemical analysis for forensics, active stealth technology, and decontamination of microorganisms: fungi, bacteria and viruses. The inactivation of viruses is, clearly, of extreme importance to us all with the COVID-19 pandemic, which is still affecting us all today. This presentation will give an overview of these exciting technologies and show you videos of some technology in operation.

Thanks/Acknowledgement

Aspects of this presentation come from workpackages supported by the UK EPSRC under grant EP/K503241/1 (Centre for Doctoral Training in Ultra Precision Engineering) and EP/L016389/1 (Centre for Doctoral Training in Sustainable Materials and Manufacturing). The author would also like to thank ADTEC Plasma Technology, ADTEC Healthcare, the Manufacturing Technology Centre, and BAESystems.

References

P. John, 2010, 'The Flapless Air Vehicle Integrated Industrial Research Programme In Aeronautical Engineering', Proceedings of the Institution of Mechanical Engineers Part G, Journal of Aerospace Engineering, Volume 224, Issue 4, 25 J. Lee et al., 2018, 'Attenuation Effects of Plasma on Ka-Band Wave Propagation in Various Gas and Pressure Environments', Journal of Electromagnetic Engineering and Science, Volume 18, Issue 1, 63 - 69 P. Shore et al., 2012, 'Ultra-Precision: Enabling Our Future', Philosophical Transactions of the Royal Society A, Volume 370, Issue 1, 3993 – 4014 A. Bennett et al., 2020, 'Cleaning Concentrating Solar Power Mirrors WithOut Water', AIP Conference Proceedings, Volume 2303, Issue 1, 210001 H. Metelmann et al., 2018, 'Comprehensive Clinical Plasma Medicine: Cold Physical Plasma for Medical Application', Springer Press, Chapter: MicroPlaSter and SteriPlas, 503 - 509

INDU 2 / Industrial hot topics

- Modification of 3D printed objects properties with interlayer plasma treatments using a built-in DBD micro torch

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The Fused Deposition Modeling (FDM) technology is a now well-known process designed to build three-dimensional polymer objects from computer-aided-design (CAD) models in a layer-by-layer way. First dedicated for prototyping, this technology is now widely spread on the additive manufacturing (AM) and production market. With the decreasing costs of the equipment and materials needed as well as the growing simplicity of use and reliability of the technique, 3D printers can now be found for the same cost and as user-friendly as regular desktop inkjet printers.

However, FDM 3D printed objects still suffer from poor mechanical properties that arise from the anisotropy induced by their layered structure. Combining different polymers in a same object build with this technique is also a big challenge as chemical mismatches and different thermal expansion coefficients add to the equation, leading to a very weak bonding at the interface between the different materials.

This is a well-known issue in polymer chemistry that can be overcome by modifying the physicochemical properties of the later deposited polymer layer. In this work, we propose to study the interest of a plasma post-discharge in order to tune interface characteristics and improve the compatibility between materials. Indeed, phenomenon induced by plasma excitation including coating, cleaning, ablation and crosslinking may result in an increased surface free energy, promoting a better interfacial bonding.

Treating the interlayers of 3D printed objects would normally present the major drawback of stopping the printing process after each layer completion to carry out the deposition. To overcome this disadvantage, we present in this work a newly designed device, where a dielectric barrier discharge (DBD) micro plasma torch has been integrated on a commercial 3D printer. The micro torch is mounted on the printing head and thus, is able to be controlled to apply a plasma treatment at desired areas, within the printing process of the object, namely after each layer completion prior to directly start over with the next layer printing. The device has been designed cost-effectively so that to be considered as an essential appliance to overcome the hindrance of anisotropic mechanical properties of FDM 3D printed objects, where those have to be considered as functional parts.

Thanks/Acknowledgement

The Luxembourg National Research Fund (FNR.lu) is acknowledged for its financial support.

TRIB / Plasma - deposited protective and tribological coatings

● Tribological properties of self-lubricant DLC coatings on additive manufactured AlSi10Mg alloy of different surface roughness

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Additive Manufacturing (AM) is a production process able to realize complex geometry with high speed and high efficiency. As in the case of standard-fabrication products, there is a lot of interest in the improvement of AM physical/chemical surface properties by means of functional coatings. One of the most promising materials to enhance the tribo-mechanical properties of surfaces is DLC [3,4]. In DLC, the tuning among sp2-sp3 bonds and the amount of hydrogen enables to produce coatings with good mechanical properties and low friction, making this material very appealing for many mechanical devices. However, AM materials still shows some drawbacks with respect to standard materials, in particular the ultimate surface finishing, the hardness and the defectiveness. It becomes mandatory the investigation of the feasibility of DLC growth on AM materials and the related tribo-mechanical characterization. In the present work non-hydrogenated DLC was deposited on AM AlSi10Mg alloy by means of plasma-enhanced magnetron sputtering. The roughness of the AM substrates was mechanically modified to obtain 4 different values, and the surfaces were covered by 0.3μmCr-CrN+1.5μmDLC layers. The related coefficient of friction was measured by ball-on-disc tests using a 4 mm 100Cr6 steel ball at a load of 1N and a linear velocity of 100mm/s. The DLC coatings are perfectly adherent to the AM substrates, no matter the roughness. The tribological tests show that the typical CoF of DLC vs steel. Contrary to what expected, the roughest sample shows the lower and most stable CoF. This low friction is very long-lasting, showing a very high wear resistance and suggesting the formation of a tribofilm. These results clearly show that DLC can be used to improve the tribo-mechanical properties of AM materials as well as it does for standard materials, and promote the investigation of other coatings deposited on AM substrates.

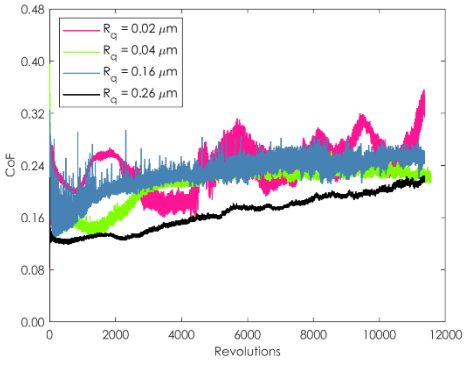
Thanks/Acknowledgement

This work was funded by POR-FESR 2018 Emilia Romagna region - RIMMEL Project.

References

[1] M. Jiménez, et al. 10.1155/2019/9656938.
[2] M. Molitch-Hou https://doi.org/10.1016/B978-0-12-812155-9.00001-3
[3] P. Kodali, et al. Tribol. Int. 30 (8) (1997) 591-598.
[4] M. Moriguchi, et al. Sei Technical Review 82 (2016) 52-58

Figure 1



TRIB / Plasma - deposited protective and tribological coatings

● Highly transparent and scratch resistant thin film multilayer developed by DC reactive sputtering

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With the increasing integration of human-machine interfaces in the Automotive industry, motivated by the search for a more pleasing and efficient experience for the end-user, there has been a surge in the development of nanometric coatings on polymeric substrates for touch display applications, that can combine several functionalities such as scratch, abrasion resistance, anti-reflection behaviour, and hydrophobicity, which can be developed by a wide range of technologies. Focusing on two main functionalities, the coating's resistance (to radiation, chemical or mechanical) and optical performance, a wide range of materials can be explored such as TiO2, ZrO2 and Al2O3 for increased resistance and a combination of the abovementioned films with SiO2, HfO2, and MgF2 for optimization of the coating's optical performance. The present work focuses on the development of a thin film multilayer, with a high optical performance and mechanical resistance, developed through Reactive DC and Pulsed DC Magnetron Sputtering Technology with differing deposition properties (Work Pressure, Ar/O2 Ratio and Target's applied Voltage, Pulse Frequency, and Duty Time), with the intent of improving the multilayer's quality. Using materials such as TiO2, ZrO2, plus the non-typically used ZnO, a complex multilayer was modelled by numerical simulations, exhibiting high optical performance on the entire visible spectrum. Also, the mentioned coatings were developed on polymeric substrates, allowing the combination of the previously mentioned properties with a certain degree of flexibility and weightlessness. The multilayer's microstructure and morphology studies were accomplished by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and profilometry, while the optical properties were analysed by an UV–Visible–NIR spectrophotometer. The mechanical characteristics were studied through several methods such as pencil indentation.

Thanks/Acknowledgement

This work was developed in the scope of i4REV project (n.42783), which was co-financed by Portugal 2020, under the Operational Program for Competitiveness and Internationalization (COMPETE 2020) through the European Regional Development Fund (ERDF).

References

1. "Anti-reflection coatings with enhanced abrasion and scratch resistance properties", Carnegie, M., et. al, 2015
2. "Transparent anti-fogging and anti-scratch SiO2/SiO2–TiO2 thin film on polycarbonate substrate", Shahnooshi, M., et. al, 2019
3. "Antireflective Coatings for Glass and Transparent Polymers", Buskins, P., et. al, 2018

PROC / Process control

- Transport of ions and neutrals in high power impulse magnetron sputtering discharges studied by particle-based simulations

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High-power impulse magnetron sputtering (HiPIMS) technique is being increasingly used for deposition of films due to its ability to deliver more energy into the growing film via target material ions. A fraction of the ions return onto the target and the deposition rate is generally lower than in DC sputtering [1]. Discharge conditions can be optimized to obtain the desired balance between the ionization fraction in the flux onto the substrate and the deposition rate. Volume-averaged plasma models, such as [2], have been used to calculate this balance based on experimental data. But volume-averaged models cannot resolve the non-equilibrium velocity distribution functions of plasma species (especially target material atoms and ions) nor the spatial gradients of the species densities. On the other hand, the use of self-consistent (particle-in-cell) simulations is still restricted to short pulse lengths and low plasma densities, e.g. [3]. A fully three-dimensional magnetron simulation using the Direct Simulation Monte Carlo method was developed to bridge the gap between existing volume-averaged and particle-in-cell models [4]. The focus is to simulate the time evolution of plasma species densities (excluding electrons) and their fluxes onto the substrate. The spatial distribution of electron density and electric field (time-dependent) is estimated based on the recent experimental studies and the simulation is also constrained by a given target current. The calculated densities are in a good agreement with density maps obtained by optical methods. The simulation allows quantitative evaluation of the gas rarefaction effect. The ionization fraction of sputtered atoms incident on the substrate is found to strongly depend on the plasma potential drop across the ionization region in front of the target. If the ionization degree is known from experiments, an effective value of this potential drop that reproduces the experimental results can be determined from the simulations. Moreover, the effect of collisional processes in the plasma or the effect of varying electric field, e.g., due to spokes, can be simulated.

Thanks/Acknowledgement

This work was supported by the Czech Science Foundation under Project No. 19-14011S.

References

[1] Vlček J and Burcalová K, *Plasma Sources Sci. Technol.* **19** (2010) 065010
[2] Huo C, Lundin D, Gudmundsson J T, Raadu M A, Bradley J W and Brenning N, *J. Phys. D: Appl. Phys.* **50** (2017) 354003
[3] Revel A, Minea T and Costin C, *Plasma Sources Sci. Technol.* **27** (2018) 105009
[4] Kozák T and Lazar J, *Plasma Sources Sci. Technol.* **27** (2018) 115012

PROC / Process control

● Optimisation of hexagonal boron nitride deposition by micro hollow cathode discharge

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Hexagonal boron nitride (h-BN) is a strategic material for electronic and optoelectronic applications. Synthesis of h-BN on large area remains a challenge because of the difficulty to produce enough atomic nitrogen to obtain a stoichiometric ratio B/N of 1 in the deposited film. In our group, we have developed a deposition process based on a Micro Hollow Cathode Discharge (MHCD), which consists of a dielectric layer between two electrodes, with a 400 µm diameter hole drilled through the structure. This source, which works at relatively low injected powers (~ 1 W) compared to traditional sources, was expected to yield an efficient dissociation of nitrogen thanks to its high power density inducing high electronic density (10^{13} cm^{-3} in DC regime and up to 10^{16} cm^{-3} when pulsed). With this MHCD structure working in Ar/N_2 mixture, and using boron tribromide as the boron precursor, we have shown the feasibility of h-BN deposition on large area (2 inches), at low temperature (800°C) [H. Kabbara]. Routes for the optimization of this deposition process have been explored. Characterization of the MHCD plasma source, by VUV high resolution Fourier Transform absorption spectroscopy at the DESIRS beamline of the SOLEIL synchrotron (Saint-Aubain, France), powered with a continuous voltage, has shown that it can produce a density of N atoms up to 10^{15} cm^{-3} (with a corresponding dissociation degree of 1.5%) which can be further optimized using a nanosecond pulsed excitation [S. Kasri]. The effect of other parameters, such as the gas pressure, percentages of Ar and N_2 in the gas mixture and the hole diameter, on the production of N atoms and the quality of the deposited films has been studied. Particularly, it was shown that increasing the hole diameter of the MHCD did not deteriorate the B/N ratio in the deposited films, despite a decrease of the N atoms density produced suggesting another limiting phenomenon. The influence of the substrates has also been studied, with depositions on native SiO_2, Si and sapphire (0001) substrates.

Thanks/Acknowledgement

This work was supported by the French Research National Agency (ANR) through the DESYNIB (ANR-16CE08-0004 JCJC), and PlasBoNG (ANR-20-CE09-0003 PRC) projects.

References

[H. Kabbara] H. Kabbara *et al.*, Appl. Phys. Lett. **116**, (2020) 171902
[S. Kasri] S. Kasri *et al.*, Plasma Sources Sci. Technol. (2019) **28** 035003

SOUR / Plasma sources and electrical discharges

● Streamer discharges on a dielectric surface: mechanism and high-resolution electric field development

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Streamer discharges are frequently utilized sources of non-equilibrium plasmas, both in fundamental research as well as applications. While their development in the free space at high pressures is rather well understood, both experimentally and theoretically, the understanding of streamers on dielectric surfaces still lacks comparable depth. The fully-3D complexity, substantial surface-related effects (charging, electron emission), and multi-scale nature both in time and space, are the reasons for many unanswered questions. In this contribution, we offer experimentally based answers to two such questions: What amplitudes can the electric field strength reach during the streamer-surface interaction? What is the possible initiation mechanism of hot plasma filaments on the dielectric surface? We apply the time-correlated single-photon counting-based optical emission spectroscopy to surface barrier discharges in atmospheric air. Using a well-established method for electric field determination from an intensity ratio of spectral bands of molecular nitrogen we determine the electric field strength in developing streamer heads with a resolution of approximately 30 microns and temporal sampling of 50 picoseconds. We show that the electric field amplitude reaches values of 400 kV/cm as the positive streamer propagates directly on the surface and about half of this value for the negative streamer in coplanar surface barrier discharge [1]. Furthermore, we reveal an ultra-fast development of a remotely initiated streamer cascade in the case of surface barrier discharge operated at high overvoltage. We show that this previously unknown mechanism can lead to the generation of an intense cathode spot, which is a crucial condition for plasma transition to a highly-ionized state [2].

Thanks/Acknowledgement

This work was supported by the project LM2018097 funded by the Ministry of Education, Youth, and Sports of the Czech Republic.

References

[1] Jansky J, Bessieres D, Brandenburg R, Paillol J and Hoder T 2021 Electric field in streamer discharge on dielectric surface, in preparation
[2] Kusyn L, Synek P, Becker M M and Hoder T 2021 Remote streamer initiation on dielectric surface, Plasma Sources Sci. Technol. https://doi.org/10.1088/1361-6595/abe4e2 accepted as letter

SOUR / Plasma sources and electrical discharges

- Microwave plasma source in overmoded cavities: space-time plasma steering source

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The aim of this communication is first to present the concept of the innovative plasma source we introduced recently, namely the “space-time plasma steering source”. It has been introduced to address the challenge of controlling plasmas in large cavities (multimode) that has been identified in the literature [1,2]. Contrary to conventional microwave plasma technologies, the idea is not to ignite a plasma occupying the entire volume of a plasma vessel, but rather to ignite a localized plasma whose location in the vessel can be dynamically controlled. This dynamic control is made possible by changing the temporal waveform of the transmitted signal to a overmoded cavities. It is then the behavior of the waves inside the cavity that control the plasma location, hence the name of space-time plasma steering source (see Figure 1). Based on this principle, we successfully managed to control in a pulsed regime the plasma location on several ignitors in a overmoded cavities using time reversal [3] and later using a more elaborated technique [4]. In the present communication, we will focus on the unusual characteristics of this microwave plasma source: plasma dimensions and location are uncorrelated from the cavity design, low rise time (in the order of the nanosecond) and very low duty cycle (in the order of 0.05%). This work is a continuation of our paper [5], in which we proposed a first spatio-temporal description of these original plasmas.

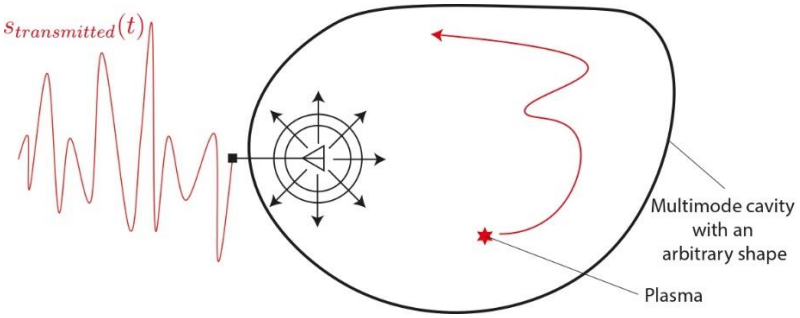
Thanks/Acknowledgement

Acknowledgements: DGA/AID (funding); CEA-Gramat (material support).

References

[1] S. Samukawa et al, “*The 2012 Roadmap*”, J. Phys. D: Appl. Phys. 45.25, juin 2012, p. 2530012. **[2]** G. S.J. Sturm, et al, “*Microwaves and microreactors: Design challenges and remedies*”, Chemical Engineering Journal, Volume 243, 2014, p. 147-158. **[3]** V. Mazières, et al, “*Plasma generation using time reversal of microwaves*”, Applied Physics Letters, 115.15 (oct. 2019), p. 154101. **[4]** V. Mazières et al., “*Transient Electric Field Shaping With the Linear Combination of Configuration Field Method for Enhanced Spatial Control of Microwave Plasmas*”, IEEE Access, 8 (2020), p. 177084-177091. **[5]** V. Mazières et al, “*Spatio-temporal dynamics of a nanosecond pulsed microwave plasma ignited by time reversal*”, Plasma Sources Sci. Technol., 29 125017, 2020.

Principle of the "wave plasma brush”



SOUR / Plasma sources and electrical discharges

● Spoke-less sputtering at high working gas pressures in HiPIMS discharges

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High-power impulse magnetron sputtering (HiPIMS) discharges are known for providing a flux of energetic ions to the growing film. While ions in the 10-30 eV range can help to improve some general properties of the growing material, some ions reach energies up to 100 eV – and although it is beneficial for deposition of hard coatings, it may create problems in applications where the structure of the substrate and the film must not be damaged. To have more control over the energy distributions of ions, the acceleration mechanism needs to be understood better. Magnetron discharges are known to exhibit instability regions of enhanced ionization and excitation, called spokes, which are thought to play an important role in ion acceleration. In the present work, we observe the disappearance of spokes and change of ion energy distribution functions (IEDFs) with increasing Ar working gas pressure from 0.5 to 5 Pa on a magnetron discharge with an aluminium target. The spokes are captured using high-speed imaging with narrowband filters while the IEDF is simultaneously measured by energy-resolved mass spectrometry. It was found that spokes disappear at pressures between 2 and 3 Pa, and the high-energy tail of the Al^+ IEDF shifts to lower energies with an increase of working gas pressure. It is shown that the changes in high energy tail are due to the combined effect of thermalization and the disappearance of spokes as the sources of ion acceleration. This observation emphasizes that the working gas pressure is an important knob for tuning the maximum ion energy in a HiPIMS discharge.

SOUR / Plasma sources and electrical discharges

● Plasma spokes in RF and DC magnetron sputtering discharges

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Studies of magnetron discharges in the last decade have shown that plasma in HiPIMS and DCMS discharges is concentrated in dense regions called spokes or ionization zones [1,2]. These plasma structures rotate in the angular direction and form periodic or quasi-periodic patterns. Here, we show that periodic spoke patterns also form in RF magnetron sputtering discharges and are present over a wide range of discharge conditions [3]. The presence of spokes in all magnetron regimes, i.e., continuous, pulsed and oscillatory, leads to conclusion that plasma self-organization is a fundamental characteristic of magnetron discharges. To gain better insight into plasma self-organization in different magnetron regimes, we investigated spokes in RFMS and DCMS at similar discharge conditions using an ICCD camera and electrical probes. In both regimes, spokes were observed for a wide range of discharge powers (50-150 W) and pressures (0.25-2 Pa). The number of spokes in the RFMS was always larger than in the DCMS when operating the discharge at the same pressure and discharge power (Figure 1). The number of spokes increased with increasing gas pressure for both magnetron regimes. The influence of discharge power on the number of spokes was less pronounced. These observations suggest that the plasma self-organization in RFMS and DCMS is mainly related to the electron energy dissipation due to collisions with the background gas. Following this reasoning, we examined the inelastic collisions between electrons and argon atoms. We calculated the dissipation of electron energy in the drift direction and compared the calculations to the length and number of spokes for particular discharge conditions. Overall, the calculations agree well with the observed lengths and number of spokes for both regimes.

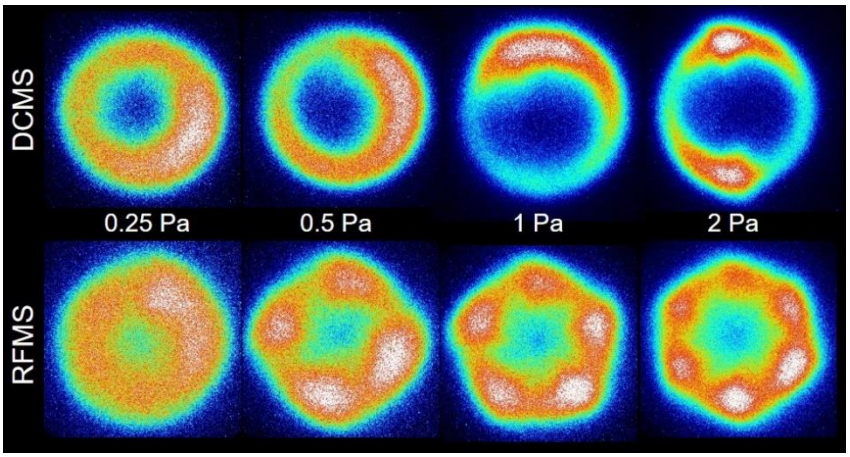
Thanks/Acknowledgement

This research was financially supported by the Slovenian Research Agency (project J2-2509).

References

[1] A. Anders et al. *J. Appl. Phys.*, **111** (2012) 053304
[2] M. Panjan et al. *Plasma Sources Sci. Technol.*, **24** (2015) 065010
[3] M. Panjan *J. Appl. Phys.* **125** (2019) 203303

Spokes in DCMS and RFMS discharges



SOUR / Plasma sources and electrical discharges

● Capillary and slit RF plasma jets interacting with surfaces and liquids

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Atmospheric pressure discharges offer unique possibilities for non-vacuum surface modification applications, creating local structures and utilizing liquid precursors, including biomolecules or drugs [1-3], which are all significant advantages in the age of nanotechnologies and biotechnologies. Therefore, the research of cold atmospheric pressure (CAP) discharges, related plasma chemical processes, and plasma-surface interactions became one of the leading plasma physics topics. Two typical configurations of CAP discharges are planar dielectric barrier discharges and plasma jets. Different electrode designs and various excitation frequencies from kHz to tens of MHz are investigated in different research groups. An incomprehensive list includes the kINPen having central radio-frequency (RF) electrode and Ar as working gas [1], the COST reference microplasma jet in He with parallel RF and grounded electrodes [4], and the RF plasma pencil (also called barrier torch discharge, BTD) developed by M. Klíma [5]. The plasma pencil RF electrode (13.56 MHz) is a ring placed around a dielectric capillary with a flowing argon. The grounded electrode has either a shape of the second ring or is missing (unipolar discharge). In this work, we investigated the unipolar capillary jet excited with variously structured RF electrodes when interacting with dielectric, metal, or liquid surfaces and when aerosol admixed outside of the capillary into the plasma plume. The plasma filament dynamic was visualized with a fast camera, and the electromagnetic field was measured with dipole-type antennas. Comparative studies were also performed with a more complex RF plasma slit jet that produces wide plasma plum (up to 300 mm) consisting of highly dynamic filaments.

Thanks/Acknowledgement

This research was carried out under the project 20-14105S supported by the Czech Science Foundation.

References

[1] J. Schäfer, et al., Thin Solid Films 630 (2017) 71.
[2] N. D. Bosher et al., J. Nanosci. Nanotechnol. 16 (2016) 10097.
[3] C. Lo Porto et al., Plasma Process Polym. 15 (2018) e1700232.
[4] P. A. C. Beijer et al., J. Phys. D: Appl. Phys. 49 (2016) 104001.
[5] M. Klíma et al., Patent CZ 286310 (2000), US 6,525,481 (2003), EP 1077021 (2005).

TRIB 2 / Plasma - deposited protective and tribological coatings

● Small-scale tribological behaviour of Ti-Based PVD thin films in operando conditions

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The nature of interface in contact with living species is the prime interest in the field of biomaterials, prostheses, biosensors, implants… This interface is easily modified through PVD processes in terms of chemistry, structure, microstructure… In the past decade, intense research activity was devoted to Ti-Ag coatings for biosensors, titanium being strongly biocompatible, while silver brought its good electrical response and ductility[1]. Even though some papers are focused on optimizing the films' chemical composition and phases, no data are available, to the best of our knowledge, on the wear resistance of these films. Such a requirement is crucial for biosensors, if we consider rubbing against the body, skin, clothes…

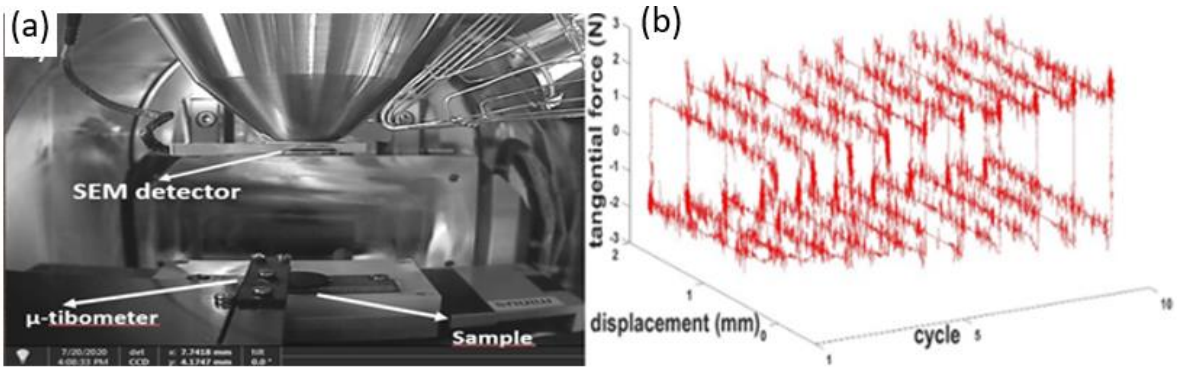
To better understand the tribological behaviour of this metallic ductile thin system, an original approach is required. It consists of using a laboratory-made reciprocating ball-on-disc mini tribometer which was specifically-designed to be introduced into an SEM chamber (Figure 1)[2] or under a Raman spectrometer, allowing a small-scale in situ characterisation of the damaging surface. An environmental SEM was used, which is able to expose the contact area to different environments (vacuum, water, nitrogen..). The study's objective is to link the tribological behaviour of films with their characteristics on the one hand, to the atmosphere on the other hand.

Titanium-based films were deposited by magnetron sputtering, silver content 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). Films characteristics were determined by RBS spectroscopy, TEM, XRD and high-temperature XRD.

References

[1]Etiemble, A. et al. Fracture resistance of Ti-Ag thin films deposited on polymeric substrates for biosignal acquisition applications, Surf. Coat. Technol., 358, (2019) 646.
[2]Krid, A., (2018), & Jin, L., (2019), Masters' internship reports, LaMCoS & MATEIS, Tribometry and In-situ Instrumentation in E-SEM and Raman spectrometry.

a) micro-tribometer in e-SEM, b) tangential force



TRIB 2 / Plasma - deposited protective and tribological coatings

● TiAlN coating by bipolar sputtering: mechanical properties and thermal oxidation

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New machining methods, including high-speed machining and/or dry machining, requires hard coating with excellent performance. Indeed, a typical temperature higher than 800°C are easily reached, and coated tools must retain its excellent mechanical properties (hardness >20GPa). In this view, TiAlN based coatings are among the best candidates. While most of the studies dealing with TiAlN deposition are focused on cathodic arc deposition, we present here a methodology purely based on bipolar sputtering. Bipolar discharge allows the formation of defects-free coating, with considerable amount of ions, allowing the hardening of the coating while applying a bias to the substrate The influence of the coating composition, the substrate bias and the discharge parameters (duty cycle, frequency) on the coating performance (hardness, young modulus) and thermal stability have been studied using extensive material characterization (XPS, XRD, nanoindentation, SEM). Thanks to the optimization of the discharge parameter, TixAlyN coatings with H > 20 GPa and E >250GPa are obtained, with excellent thermal stability. The coating are then tested during machining, via the deposition onto endmills.

TRIB 2 / Plasma - deposited protective and tribological coatings

● Comparison of the oxide growth mechanism at 950°C for a TiAlCrN, a TiAlSiN and a TiAlCrSiN coating deposited by HIPIMS

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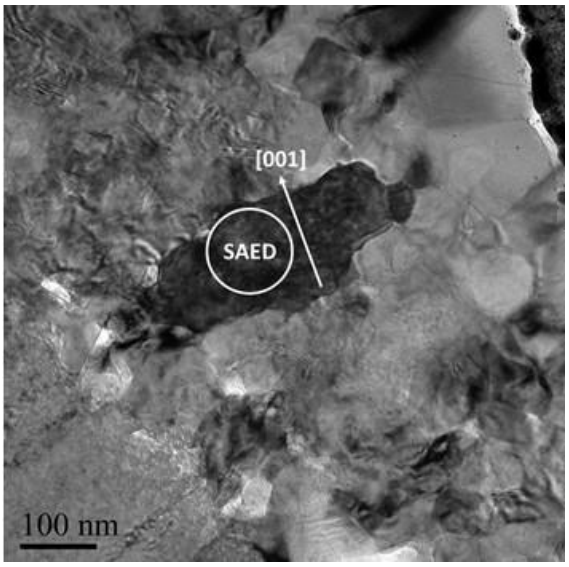
Titanium nitride coatings have been applied as hard coatings because of their high hardness wear resistance and chemical stability. Oxidation of TiAlN is not observed up to 750°C but the addition of other oxidation protective elements as Chromium, Silicon has provided solutions to a further improvement of its high temperature resistance. By combining high resolution Transmission Electron Microscopy (TEM) observations with ultra-shallow depth profiling analysis by dynamic Secondary Ion Mass Spectroscopy (SIMS SC-Ultra), it is possible to go very deep into the metallurgical characterization of the protective layers based on the stacking of different nanometric oxide layers. This approach will be here reported for the investigation of different TiAlN coatings oxidized at 950°C. For a better understanding of the different mechanisms controlling the oxidation kinetics, a special isotopic oxidation experiments under alternative atmospheres containing $_{16}O$ gas and $_{18}O$ gas were carried out. Different oxidation times were performed between 15 to 90 min and on these coated samples, a complete structural and chemical study was done for each thin oxide layers. Also, depending of the alloying element Cr, Si or Cr-Si, several diffusion paths for oxygen following different new oxidation growth areas can be reported, connected with the layered structure of the scale. The evolution of the oxygen isotope profile after the different total oxidation times have been also reported. If the inward diffusion of oxygen is the main process which control the oxidation kinetics at the nitride-oxide interface, it is also possible to show that both cation and anion diffusion processes are active. Depending of the allowing elements in the TiAlN coatings, the anionic diffusion mechanisms are different and they can explain the stacking of the different oxide layers and consequently, the reason of different oxidation kinetics

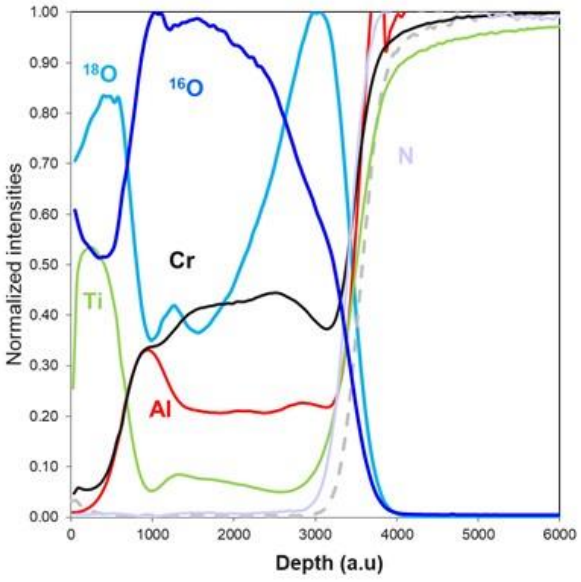
Thanks/Acknowledgement

This work was supported by the FNR under the BRIDGE project NANOPIMS.

Cross section TEM of an oxi dized AlTCrN coating

SIMS profiles of the oxide layer after 30 min





TRIB 2 / Plasma - deposited protective and tribological coatings

● General remarks on TiN and Ti(C,N) thin-films used for orthodontic applications

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The entire principle of orthodontics is based on the movement of the teeth; in order to initiate this, force have to be applied using proper application point, direction and magnitude. Shortly, after the application of the force, a tipping movement of the tooth starts, as a result of this, an angle between the bracket slot and wire is generated. When this arrangement reaches a specific contact point, adhesion between the metallic surfaces will occur resulting in friction resistance to sliding.The main scope of this study is to reduce the friction between brackets and wires in order to enable fast tooth movement. Thus, within the frame of this work, titanium-nitride and titanium-carbon-nitride coatings have been deposited onto the surface of standard stainless-steel samples using the magnetron-reactive sputtering technique. The obtained samples have been characterized in terms of mechanical and tribological properties. Nanoindentation and scratch tests were made in order to measure the hardness and adherence of TIN and TICN coatings. The static and kinetic friction coefficients of as deposited samples were measured for similar oral cavity conditions, using artificial saliva, with a ball-on-disk tribometer. Taking into consideration the application of these thin-films, a characterization of color was done, in a colorimeter with results according to the CIELAB color space scale. The results of nanoindentation test present the hardness of TiN and TiCN coatings, starting from 3.033GPa to 7.97 GPa. The adhesion to the substrate of coatings, tested under micro scratching for all samples revealed only second and third critical-points, without the presence of a first critical-point, with the TiC0.23N0.77 thin-film variant being the most adherent to the substrate, having the third critical point at 8.06N while other variants went as far as 5.01N. The results of the present study shows that TIN and TICN coatings provided a significant reduction in friction coefficient in comparison with the non-deposited ones. Among the coatings examined the TICN presented the lowest static friction under wet condition, with a mean value of the friction coefficient (μ) of 0.265, while TiN had a mean value of 0.295. Represented by the CIELAB colorimeter these thin-films exhibit bright gold-like yellow (for TiN) and brown color (for TiCN), the TiN being a lighter and more pleasant color it's more suitable from the esthetic standpoint, but TiCN has better mechanical properties. The TICN is highly promising in promoting effective and easier tooth movement and shortening treatment time for orthodontic applications.

● Sputtered ZnO:Al/NiCr thin layer stack: influence of the operating conditions on the oxidation states

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Nanometric thin layers are often used within stack in order to modify the properties of an interface (for example, adhesion improvement) or to protect the adjacent layers during the deposition process or the post-treatments like thermal annealing. In case of functionalized glazing in glass industry, low E stacks deposited by magnetron sputtering typically include a thin layer of metal at the Ag interfaces to protect silver and to maintain its high conductivity. In previous works, the oxidation state of nano layer of titanium in contact with ZnO ones has been studied by HAXPES [1,2] : an oxidized thickness of ~1nm of the Ti layer is revealed when the metal is deposited on the ZnO seed layer and the oxidation thickness reach ~2nm when ZnO is deposited onto Ti layer. The present work concerns another metals used as “blocker” layer: 1nm-thick nickel chromium alloy in contact with zinc oxide [3]. We studied the impact of the protocol of deposition of zinc oxide onto the NiCr morphology and oxidation (reactive DC mode from Zn:Al target, rf mode from AZO ceramic). To do this, we used an equipment allowing a deposition chamber connected to the analysis one with XPS. The evolution of the NiCr redox was studied after the deposition of different zinc oxide layers (equivalent of 1,2,3nm thick). Particular attention has been paid to the determination of the oxidation state of nickel and chromium with the help of “reference layers” and literature [4]. The link with the species present in the plasma during the deposition process will be discussed.

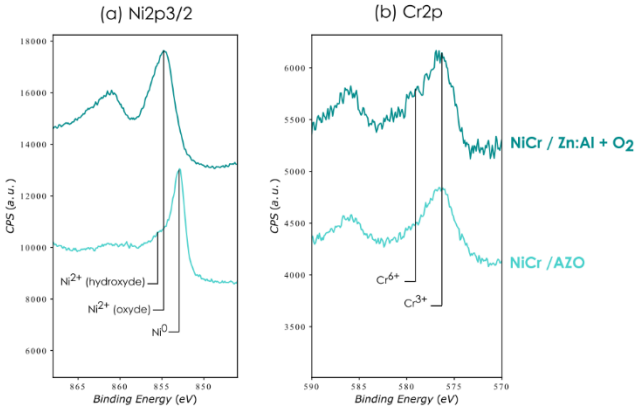
Thanks/Acknowledgement

L largeau, K Burov, A Portavoce and D Mangelinck for J.V. PhD co-supervision J.V. benefited from PhD grant funded by SGR Paris and ANRT

References

[1] R Knut et al. Reactive ZnO/Ti/ZnO interfaces studied by hard x-ray photoelectron spectroscopy, Journal of Appl. Phys. 115 (2014), 0437141-7 [2] Zinc oxide growth and its interfaces with metals observed by photoemission, E Chernysheva PhD, Sorbonne Université, 2017 [3] Interactions dans les empilements de couches NiCr/ZnO déposées par pulvérisation : impact couplé des paramètres de dépôt et de recuit, J Voronkoff, PhD, Sorbonne Université, 2020. [4] http://www.xpsfitting.com/

XPS spectra of Ni 2p and Cr 2p after deposition



DEPO 2 / Plasma - deposited coatings

● Monitoring tantalum nitride thin films structure by reactive HiPIMS magnetron sputtering: from microstructures to properties

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In this study, cubic metastable phase and hexagonal stable phases are obtained by RF magnetron sputtering and Reactive High Power Impulse Magnetron Sputtering (HiPIMS). Both are successfully deposed as single phase and continuous films. Although it is widely known that the hexagonal phase of TaN is quite hard to isolated using RF magnetron sputtering. Our previous results demonstrated that this crystalline phase growth was promoted using conditions increasing adatoms mobility on the substrate surface. Based on high power density pulse applied to the target during few tens of microseconds, HiPIMS technology allows reaching a high ionization degree of the plasma species. TaN hexagonal phase layer is more complicated to deposed using HiPIMS due to a lot of additional process parameters directly impacting the energy of the plasma and its composition. We therefore investigate influence of target power density, N2 partial pressure, total gas (Ar + N2) pressure and target-to-substrate distance on film crystalline structure. Hexagonal and cubic TaN films are also characterized : evolution of the microstructure and properties (mechanical, electrical and optical). A comparison the mechanisms of stabilization of each crystalline structure depending on the process is attempted.

Thanks/Acknowledgement

This work was founded partly by French National Research Agency through the project ALTERCHROM and partly by the "Ministère des armées – Agence de l'innovation de défense". the authors thank Stéphane Jouannigot (LCTS, Pessac, France) for the nanohardeness measurements.

References

[1] Monitoring tantalum nitride thin film structure by reactive RF magnetron sputtering: influence of processing parameters, M. Cheviot, M. Gouné, A. Poulon-Quintin, Surface Coating and Technology, 284 (2015) 192–197.
[2] Keynote: Nanostructuration of thin films an alternative solution for hard chromium coating replacement, A. Poulon-Quintin, B. Giroire, G. Aubert, L. Teule-Gay, D. Michau, M. Cavarroc, C. Aymonier, 12th International Conference and Exhibition on Materials Science and Chemistry 2019, May 20-22, 2019, Zurich, Switzerland

DEPO 2 / Plasma - deposited coatings

- Ion assistance selection during film deposition using HiPIMS with Positive Pulsing

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This paper describes a method which allows elemental selection of the ions assisting a thin film deposition process. To achieve this, a first magnetron device is supplied with an Asymmetric bipolar HiPIMS signal comprising a negative pulse followed by a positive pulse with independent control of amplitude and duration time, while the second magnetron is operated in conventional DC or Dc-Pulsed signal. The ions generated during the negative phase of the HiPIMS discharge are accelerated towards the substrate during the positive phase with an energy proportional to the positive pulse amplitude. The substrate can be biased with conventional DC Bias power supply, grounded or floated.

By varying the negative pulse duration time, this solution allows the selection of: - gas ions such as Ar, Kr, Xe, N2 or O2 to promote etching at the substrate to be coated, - metal ions, either light metal ions such as Al or V, or heavy metal ions such as Hf, Ta, Mo, W, Zr or Cr to promote coating densification at the substrate. As an example, this solution is used to deposit hard TiN coatings (hardness up to 25GPa) on insulating substrates at RT upon irradiation with heavy-metal W ions. A low atomic concentration of W in the TiN matrix (<10%) is sufficient to provide the required recoil energy to achieve coating densification. Experimental results showing hardness, stress, composition and dep. Rate measurements are presented in the paper.

DEPO 2 / Plasma - deposited coatings

PL4 ● Plasma nanofabrication challenges for future semiconductor and quantum device manufacturing

D. Graves
PPPL, Princeton/NJ (US)

SURF 2 / Plasma - surface interactions

● SiO_xF_y layer deposition for cryogenic nanoscale etching

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Cryogenic deep etching of Silicon is a well-known process. It consists in using SF_6 / O_2 plasma in order to etch Si anisotropically. A pure SF_6 plasma etches isotropically Si by creating SiF_4 etch by-products. The addition of O_2 enables the creation of a silicon oxyfluoride passivation layer, which is only stable at low temperature and sensitive to ion bombardment. Hence, this layer only builds up on the trench sidewalls, preventing lateral etching [1].
This passivation layer has been the subject of several studies. It inspired the development of the STiGer process, which consists in alternating a passivation step of SiF_4 / O_2 plasma and a SF_6 plasma for Si deep etching [2]. However, new characterizations have brought a new insight. In the results presented in this paper, the SiO_xF_y layer is deposited by using SiF_4 / O_2 plasma at different temperatures and for different gas ratios. Then, the layer composition, the deposited amount, the layer desorption and finally the robustness to etching are investigated.
A cryogenic ICP reactor was used to deposit the SiO_xF_y layer on Si coupons. The thickness evolution during the deposition was monitored using an in-situ Spectroscopic Ellipsometer (SE) in kinetic mode. A Quadrupole Mass Spectrometry (QMS) coupled to this reactor has also been used to detect the desorbed species when the sample is brought back to room temperature.
For the layer composition, another ICP reactor coupled to an X-Ray Photoelectron Spectroscopy (XPS) was used. A moving sample rod, that can be cooled, is used to transfer the sample from the ICP reactor to the XPS chamber to perform quasi in-situ measurements.
These different characterizations offered a better understanding on the formation of the SiO_xF_y layer and its dependence towards the temperature. In particular, it was shown that the process can switch from deposition to etching regime just by changing the temperature, keeping the same process parameters.
This study has also inspired the development of new cryogenic processes that can be applied at the nanoscale.

Thanks/Acknowledgement

The authors thank S. Tahara for all the helpful discussions.

This work was supported by CERTeM 2020 platform, which provides most of the equipment; the CNRS-Réseau des Plasmas Froids is also acknowledged for giving access to the Optimist platform.

References

[1] X. Mellhaoui et al., J. Appl. Phys, vol. 98, no. 10, p. 104901, 2005
[2] T. Tillocher et al., J. Electrochem. Soc., vol. 155, no. 3, p. D187, 2008

SURF 2 / Plasma - surface interactions

● An investigation of adhesion mechanisms between a PMMA support and aluminum thin films deposited by cold plasma

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[3] Univ. Clermont Auvergne, CNRS, Institut Pascal - Clermont-Ferrand (FR)
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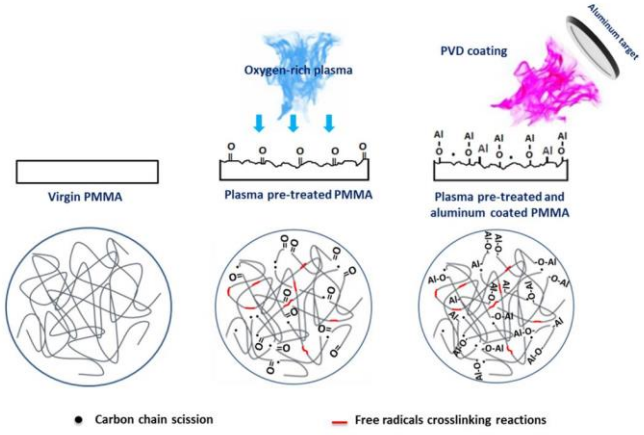
Polymethylmethacrylate (PMMA) is one of the most convenient polymers for optical and decorative applications. It offers excellent transparency, high molding precision, and low costs. Unfortunately, PMMA shows poor adhesion for plasma deposited coatings (PVD, PECVD). We are interested in understanding the adhesion phenomena of thin films on PMMA. Two types of PMMA: cast and extruded are studied during this project. Aluminum films are deposited by DC magnetron sputtering. The adhesion is characterized by tape test from crossway cuts, according to the DIN EN ISO 2409 standard. The location of adhesion failure between PMMA and aluminum films after the adhesion test was investigated by performing scanning electron microscopy (SEM) analysis on the PMMA samples and ATR-FTIR analysis of the tape used for the adhesion test. In order to improve the adhesion of aluminum films on PMMA supports, cold plasma treatment was performed using microwave or pulsed DC power. A surface treatment experiment plan in various oxidizing atmospheres allowed us to produce samples having different levels of aluminum coating adhesion strength. To understand more about adhesion mechanisms, XPS analyses are used to characterize chemical modifications during plasma activation. Decomposition of C1s peak measured by XPS on untreated PMMA revealed the contribution of three types of chemical bonding: (C-C), (C-O), and (O=C-O). The evolution of these bonds during polymer treatment under plasma process is investigated to explain the adhesion improvement. The organic radicals and dangling bonds of PMMA are characterized by EPR (Electron Paramagnetic Resonance) to investigate the phenomena of PMMA surface degradation during exposure to cold plasmas. In situ optical emission spectroscopy (OES) of the plasma is used to assess the amount of radicals created during surface treatment and evaluate how these species can be at the origin of the surface degradation of the polymer which leads to a lack of adhesion to aluminum thin films.

Interactions between PMMA and cold plasma



SURF 2 / Plasma - surface interactions

● Plasma etching of PP, PET and RPET foils used for advanced packaging material

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Cargo containers to transport vaccine at low temperatures require heat-reflecting advanced packaging materials. Therefore, metallized (Al or Ag) foils are thermoformed into honeycomb structures as a main part of the container walls. Polyethylene therapthalate (PET) material is widely used due to its excellent mechanical and electrical properties in packaging, agriculture, automotive, building and construction, medicine, electrical, and electronics. For environmental reasons, PET is recycled for consumer goods such as textiles, beverage bottles and also to produce foils. [1] To enable sufficient adhesion of metal layers on recycled RPET foils for deep-drawing, the recycled polymer is processed and treated with plasma techniques.[2] Low-pressure plasma etching is common on polymer foils as a cleaning step, activation or pretreatment for coatings such as metallization but also SiOx barrier coatings. In the focus of reusing polymer material, we studied RPET, PET and PP foils. The foils were etched with Ar/O_2 in a capacitive coupled, low-pressure plasma reactor. The foils are directly placed on the electrode and at floating potential two centimeters above the electrode to simulate an industrial process. Weighing before and after the plasma etching process is used to observe the etching rate taking degassing in vacuum and water uptake at atmosphere into consideration. The etching rate is studied depending on plasma conditions and substrate surface area. For substrates as large as the electrode area an enhanced etching on the substrate side facing the electrode could be observed. The behavior of etching rate over time was determined by repeated plasma etching of the same sample showing a slight decrease in etching rate over time. By varying the Ar/O_2 concentration the highest etch rate was found for pure O_2 plasmas. Optical Emission Spectroscopy (OES) was used as a plasma diagnostic tool to gain insight into the plasma etching processes. Finally, the etch rate was calibrated by OES for the three foil types examined. Surface characteristics are also performed to examine the polymer oxidation degree and adhesion to the metal layer.

References

[1] M. Kampmann Eriksen, K. Pivnenko, G. Faraca, A. Boldrin, and T. Fruergaard Astrup, Dynamic Material Flow Analysis of PET, PE, and PP Flows in Europe: Evaluation of the Potential for Circular Economy, *Environmental Science & Technology,* 2020, 54 (24), 16166.
[2] M. M. Hossain, D. Hegemann, A.S. Herrmann, P. Chabrecek, Contact angle determination on plasma-treated poly(ethylene terephthalate) fabrics and foils, *Journal of Applied Polymer Science*, 2016, 102, 1452.

SURF 2 / Plasma - surface interactions

● Spacer dry etching for 2D & 3D CMOS devices: towards atomic precision

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Because of transistors size scaling down, device processing requirements become more and more stringent. Today, for technology node beyond 10 nm, the etching of silicon nitride (Si_3N_4) spacers is considered as one of the most challenging etch process for 3D CMOS devices realization such as FinFET or Stacked Nanowires. New material like silicon oxycarbide (SiOC) is also proposed to replace Si_3N_4. It allows to reduce the dielectric constant and therefore to increase devices' performance.

Currently hydrofluorocarbon etch chemistries like $CH_3F/CH_4/He/O_2$ are no longer suitable for 2D and 3D CMOS integration where long over-etch is necessary. A tradeoff need to be found to fully remove Si_3N_4 or SiOC residue on the active area sidewalls while limiting underlayer recess. It requires a perfect anisotropy and selectivity to maintain spacer critical dimension without damaging [1] or consume the exposed material like silicon, silicon germanium and silicon oxide under penalty of loose transistor performances [2 & 3].

In the first part, we show the beneficial role of $SiCl_4$ addition to a hydrofluorocarbon-based plasma combined with a cyclic approach to etch Si_3N_4 spacer selectively to silicon. X-ray photoelectron spectroscopy is used to improve our understanding of the etch and deposition mechanisms while transmission electron microscopy images obtained on patterned samples (Figure 1) demonstrate the interest of the approach. In the second part, based on surface composition and etch rate analysis, we discuss the mechanisms to etch SiOC material in various hydrofluorocarbon-based plasma (Figure 2).

References

1. N. Kuboi, T. Tatsumi, T. Kinoshita, T. Shigetoshi, M. Fukasawa, J. Komachi, and H. Ansai, JVST A 33 (6), 061308 (2015).
2. B. E. E. Kastenmeier, P. J. Matsuo, and G. S. Oehrlein, JVST A 17 (6), 3179 (1999).
3. K. Eriguchi, Y. Nakakubo, A. Matsuda, Y. Katao, K. Ono, IEEE Electr. Device L. 30 (7), 712 (2009).

Fig1: TEM/EDX of Si3N4 etching for 3D architecture

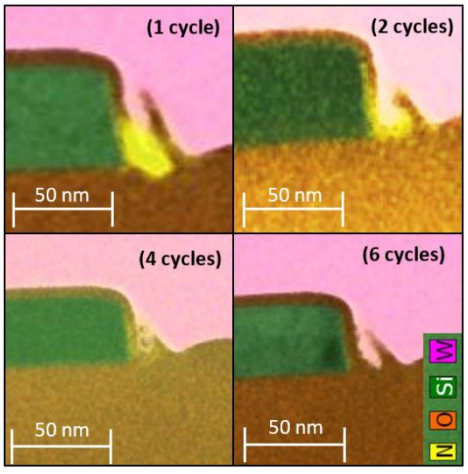
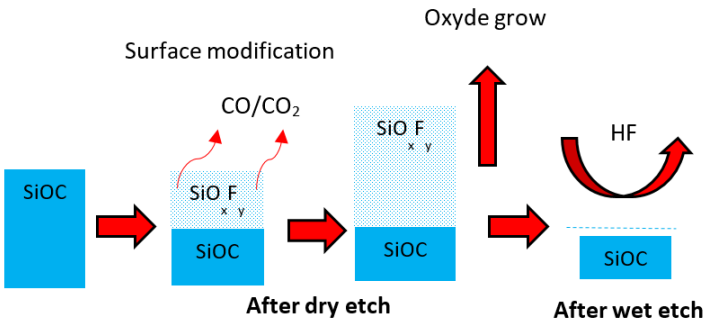


Fig2: Step of SiOC etch with hydrofluorocarbon



SURF 2 / Plasma - surface interactions

● Amino-grafting on terephthalic acid by Dielectric-Barrier Discharge (DBD) plasma treatment for MOFs functionalization

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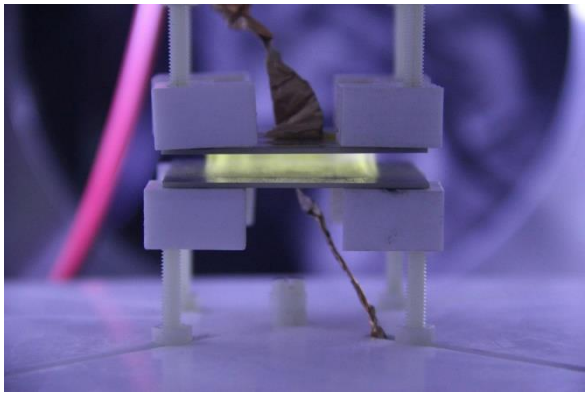
Considered as one of the most promising novel materials, Metal-Organic Frameworks (MOFs) are porous hybrid compounds formed by self-assembly of metal clusters (secondary building units) with organic ligands to form crystalline networks. These compounds have shown great interest due to their porous structure and high surface areas across a wide range of applications, such as gas storage, catalysis, optics, etc. In the literature, a number of studies of MOFs' functionalization have shown effectiveness of introducing specific substituent groups. It was shown that grafting functional groups, such as amino groups on the organic ligand, enhances the adsorption properties of these materials[1-2]. The pre-functionalization of MOFs' organic ligands, by grafting functional groups have been widely carried out via wet-chemical methods. A possible novel route to perform this pre-functionalization is by means of cold plasma treatments.

In this study, DBD plasma treatment in NH_3 gas has been used to investigate the efficiency of the pre-functionalization of terephthalic acid to graft the desired amino groups. During this treatment, plasma diagnostic and material characterization were carried out. The chemical species present in the plasma were identified by optical emission spectroscopy. XRD structural analysis was used in order to reveal the impact of the plasma on the structure of the organic ligand. Thermal analysis by TGA was performed to compare the thermal stability of treated and non-treated ligands. Then, the chemical composition of the samples was determined by XPS. The obtained results confirm the capability of DBD plasma treatment to graft amino groups on terephthalic acid ligand.

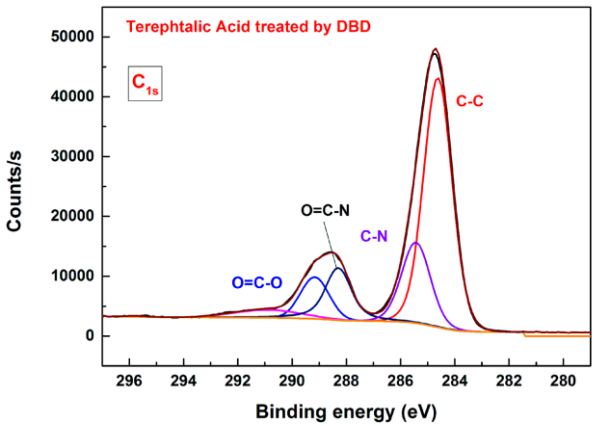
References

[1] Zana Hassan Rada et al.'' Effects of amino functionality on uptake of CO2, CH4 and selectivity of CO2/CH4 on titanium based MOFs,'', Fuel, 2015, 160, 318-327. **[2]** Olaf Hübner et al. ''On the Interaction of Dihydrogen with Aromatic Systems''. The Journal of Physical Chemistry A, 2004, 108, 3019–3023.

a DBD plasma discharge of NH3



XPS spectra of terephthalic acid treated by DBD



GROM 1 / Thin films growth and modelling

● Comprehensive PVD simulation: Application to antireflective coatings produced by OAD

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Surfaces presenting broadband antireflective (AR) properties in the visible (Vis), near- and mid-infrared (IR) regions are of great importance for the development of devices that require ultra-high optical transmission for various applications (hyperspectral cameras, detectors operating in poor lightning conditions, etc.). Elimination of Fresnel reflection over wide wavelength range can be achieved with graded-index coatings in which the refractive index progressively decreases from that of the substrate to that of the ambient medium. Because of the unavailability of optical materials with very low refractive indexes that closely match the refractive index of the air, such films are however not realizable directly using standard deposition methods. As an alternative, tuning the microstructure and the composition of multilayer films is nowadays proven as an efficient method. For that, Oblique Angle Deposition (OAD) is the dedicated technic. Controlling the angle between the substrate and the vapor flux allows obtaining tilted columnar layers with tailored refractive indexes promoted by the introduction of porosity by shadowing effect. In this study, the work publish by Lacroix et al. [1] concerning the synthesis of ITO by ion beam sputtering is fully reproduced numerically in every details of the process. The sputtered and backscattered flux is studied with SRIM [2] and SIMTRA [3], based on the phase composition of the target and the erosion profile. After the sputtering step, SIMTRA allows determining the fraction of this flux reaching the substrates after transport in the gas phase and its properties. With NASCAM [4] working in the reactive mode, the films microstructures are obtained and finally the “optic” plugin provides the transmittance of the simulated film. The obtained simulated results (morphology, composition, optical properties) are in good accordance with the experimental ones.

References

[1] B. Lacroix, “Nanostructure and Physical Properties Control of Indium Tin Oxide Films Prepared at Room Temperature through Ion Beam Sputtering Deposition at Oblique Angles”, THE JOURNAL OF PHYSICAL CHEMISTRY C, Mai 2019
[2] J.F. Ziegler, “SRIM-2003”, Nuclear Instruments and Methods in Physics Research B, Volumes 219-220, 2004, Pages 1027-1036
[3] K.V. Aeken, S. Mahieu, D. Depla, “The metal flux from a rotating cylindrical magnetron: a Monte Carlo simulation”, Journal of Physics D: Applied physics, Volume 41, 2008
[4] S. Lucas, P. Moskovkin, “Simulation at high temperature of atomic deposition, islands coalescence, Ostwald and inverse Ostwald ripening with a general simple kinetic Monte Carlo code”, Thin Solids Films, Volume 518, 2010, pages 5355-5361

GROM 1 / Thin films growth and modelling

● Experimental and modeling study on Ar/Cr high power impulse magnetron sputtering discharge

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Magnetron plasma discharges are widely used in several technological applications, especially in semiconductor manufacturing. Metallic, oxide and nitride thin film are deposited by sputtering used in different steps of device manufacturing. One of the avenues explored is the application of power in the form of very short pulses High Power Impulse Magnetron Sputtering HiPIMS. It represents an alternative to DC or RF PVD processes. Therefore, the injection of a high power about 150 Watts/cm2 during a very short pulse time allows to avoid the high heat increase during the thin film deposition process. It also allows the improvement of the ionization degree and the dissociation rate of the injected reactive gaz. To better understand about the pulsed high power discharge, a time-dependent global plasma model is developed for the ionization region in a HiPIMS discharge of Ar/Cr. The model is based on solving a nonlinear equation system composed of the continuity equations of neutral and charged species in the Ionization Region (IR) considered in the reaction scheme coupled to the power continuity equation. The advantage of our kinetic model is its ability to quantify the densities of neutrals and ions considered in the reaction scheme as well as their fluxes into the substrate. It is also possible to evaluate the electron density and temperature evolution with time. A good agreement is shown between the calculated time current evolution and that measured. The simulations results show the effects of the main machine parameters on the neutral and the ion densities evolution versus time, by varying the pressure from 5 to 30 mTorr and the pulse width from 10 to 100 µs. Also, they contribute to understand the phenomena observed experimentally and to quantify the created population from HiPIMS discharge, particularly in the IR.

GROM 1 / Thin films growth and modelling

● A multiscale modelling of thin film growth: application to sputter-deposited Cu films

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The deposition of thin films by condensation of vapor fluxes at oblique angles (oblique angle deposition (OAD)) leads to the development of columnar, tilted columns, large porosity and increased specific surface area. This route is advantageous for applications in optics, catalysis or bio-sensors. The work carried out here aims to better understand the influence of the angle of incidence and the deposition parameters (pressure P, temperature T) on the morphology of thin films of transition metal nitride (TMN) deposited by OAD. The employed methodology relies on both experimental (reactive magnetron sputter-deposition) and multi-scale computational modelling (DFT calculations and Monte Carlo codes; SRIM, SIMTRA and MODENA). The studied systems are group IVb binary TMNs (TiN, ZrN, HfN) and the ternary alloy TiAlN, promising materials for plasmonic applications. The crystal structure, texture and growth morphology are studied by X-ray diffraction, SEM and AFM imaging, and some of their properties (electrical resistivity and wettability) evaluated. The films exhibit a strongly columnar growth, and a biaxial crystallographic texture corresponding to the formation of pyramidal facets. The inclination angle of the columns b increases with the inclination angle of the substrate a and is correlated to the inclination angle y of the (111) crystal planes. The greatest variations are observed for HfN due to a more directional flux of particles. In the case of TiN, the relation b (a) shows a saturation phenomenon for a> 65 ° for high pressure , and a shift of + 10 ° when T increases from 25 ° to 500 ° C. The use of the MODENA code, based on a kinetic Monte Carlo model on a rigid lattice, and including deposition and diffusion events, makes it possible to qualitatively reproduce the trends observed experimentally, and highlights the preponderant role of the angular distribution of the particle flux on the tilt of the columns. DFT calculations are performed on ZrN and HfN systems to determine the energy landscape of (100) and (110) surfaces providing access to adsorption sites and diffusion barriers of metallic and nitrogen species, comparatively to TiN. These data show greater diffusivity on the (100) surface than on (110) one, and a different surface reactivity of nitrogen depending on the chemical and crystallographic nature of the system. The knowledge gained from these DFT calculations will subsequently improve the MODENA code by considering the specific energy barrier values for each studied system.

GROM 1 / Thin films growth and modelling

● At the edge of crystallization: a bottom-up route for the design of two-phase crystalline-amorphous nano(micro)-structured films

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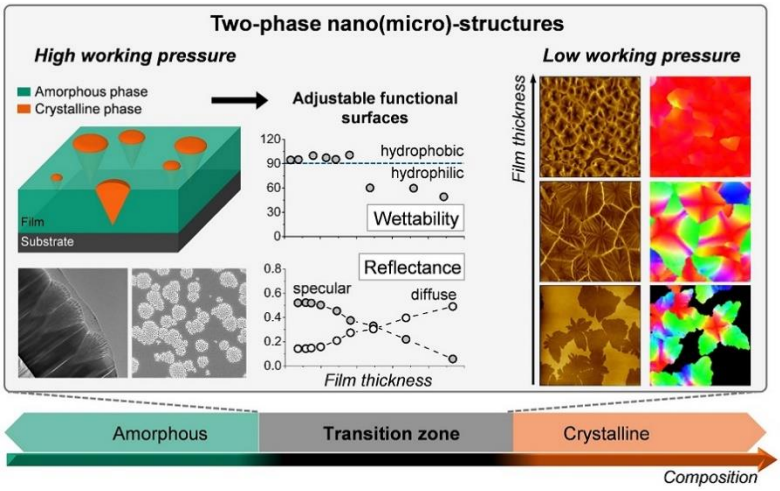
Composition-driven transition to the crystalline state is characteristic of amorphous metal alloys and is widely observed in sputter-deposited thin films. However, little is known about the nature of such transition, despite it occurs in many systems. In this work, we demonstrate that this transition offers an excellent scenario for the self-formation of original two-phase crystalline-amorphous architectures [1,2]. We show that the morphology of the obtained two-phase nano(micro)-structures strongly depends on the energy of the sputtered atoms arriving at the substrate (controlled here through the deposition pressure). Thus, at high deposition pressures (2-3 Pa), films with a microstructure consisting of a crystalline phase of feather-like morphology embedded in an amorphous matrix are obtained. The morphology of these nanostructures provides a simple bottom-up route, applicable to a broad range of alloys, for obtaining adjustable multifunctional surfaces (see Figure). In particular, we prove the feasibility of this approach as a one-step process for precise control of specular and diffuse reflectance over the visible spectrum. Further, the growth kinetics of the formed two-phase nanostructures is demonstrated equivalent to a 2-dimensional amorphous-to-crystalline phase transformation. Using Zr-W alloys as a model system, fundamental parameters of the growth process and the corresponding metastable thickness-composition phase diagram are extracted [2]. It evidences that the two-phase nanostructures, despite occurring in a wide range of compositions, can be easily hidden experimentally by growth kinetics and nucleation delay. At low deposition pressure (0.5 Pa) the microstructure of the films evolves significantly with thickness: from amorphous films in the early stage of growth to fully crystalline films formed by massive grains with lateral size larger than 1 µm, passing through a dendritic growth of the crystalline phase in the amorphous matrix for intermediate thicknesses (see Figure). These results open a new avenue on the morphology and related functional properties control in thin films.

References

[1] A. Borroto *et al.*, *Acta Materialia* **181** 78 (2019). [2] A. Borroto *et al.*, *Applied Surface Science* **538** 148133 (2021).

Amorphous-to-crystalline transition



GROM 1 / Thin films growth and modelling

● Growth of VO_2 polymorphs by radiofrequency magnetron sputtering

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anadium oxides continue to attract attention due to their outstanding properties that fulfill numerous strategic applications from telecommunications to energy harvesting. Still, the complexity of the vanadium oxide phase diagram impedes the understanding of the formation mechanisms of several VO2 polymorphs such as VO2(B), VO2(M1) and VO2(R). In this work, we investigate the growth of these polymorphs and of the neighboring vanadium oxide phases (e.g. V6O13, V2O3) on sapphire substrates by radiofrequency (RF) magnetron sputtering. The stabilization of phase-pure thin films was achieved by a precise control of the vanadium oxidation state through the oxygen partial pressure, the growth temperature and the substrate crystalline orientation. Lattice parameters, epitaxial relations, vanadium oxidation state and surface topography were systematically measured by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy, respectively. We show that for a given set of growth parameters, the epitaxial strains obtained on different oxide substrates lead to the stabilization of different VO2 polymorphs, namely, VO2(B) or VO2 (M1). We also evidence the interplay between the substrate crystalline orientation and the VO2(M1) films electrical properties, especially a narrowing of the hysteresis loop upon the metal-insulator transition.

Thanks/Acknowledgement

The authors would like to express their acknowledgement to ANRT for financial support, grant N°2018/1494.

PROC 2 / Process control

● Measurement of reactive species absolute concentrations in N_2, Ar/N_2, He/N_2 and H_2/N_2 microwave flowing afterglows at reduced pressure

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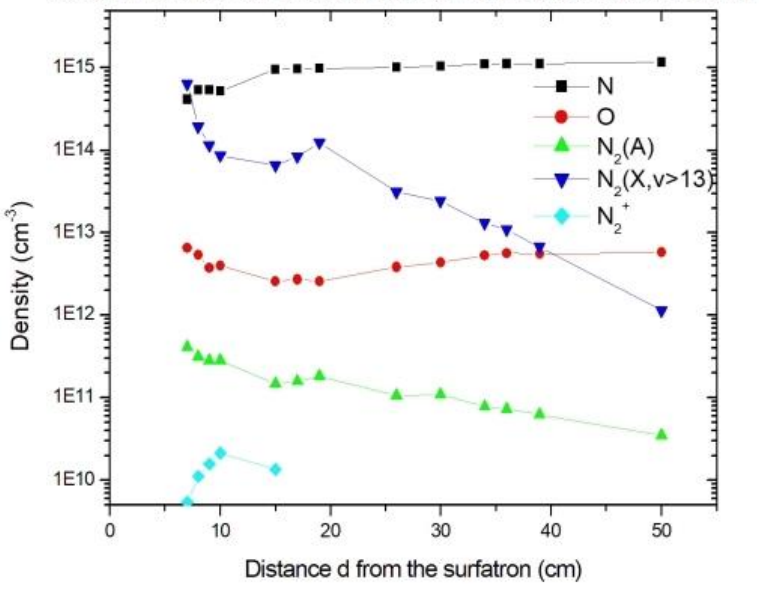
Reduced pressure (2-20 Torr) flowing afterglows initiated in N_2 and in mixtures of N_2 with rare (Ar,He) or molecular (H_2) gases generate and transport high concentrations of active species (atoms, metastable states, …) that can be used in many applications including surface sterilization or surface treatments. In the present paper, N_2, Ar/N_2, He/N_2 and H_2/N_2 microwave flowing afterglows were characterized by Optical Emission Spectroscopy (OES). The discharge was generated by a surfatron cavity (2.45 GHz) in a 5 mm i.d. quartz tube enlarging to a 50 cm in length and 18 mm i.d. tube. N_2 1+ (11-7), N_2+ 1- (0-0), N_2 2+ (1-0), NO β (0-8) and NH A-X (0-0) band intensity ratios were used to obtain absolute concentrations of N, O (oxygen been present as gas impurity) and H atoms, of N_2(A) and N_2(X,<13) metastable states and of N_2+ ions and NH molecules, assuming a simplified set of chemical reactions in the afterglow [1]. Active species densities measured up to 50 cm from the surfatron gap in a N_2 (0.5 slpm, 4 Torr) afterglow are shown Fig.1. In parallel with OES, absolute atomic densities of N and H atoms were also measured using a two-photon laser induced fluorescence technique (TALIF). In this experiment, a tunable dye laser pumped by a the second harmonic of a Nd:YAG laser was operated in the red spectral range, from 591 to 636 nm. The output beam was frequency doubled by a BBO crystal and the resulting UV beam was frequency mixed with the residual dye laser beam in a second BBO crystal. The UV laser radiations are located in the UV-C wavelength range, from 202 to 212 nm. The laser beam was focused at a constant position on the axis of the 18 mm afterglow tube while the surfatron was moved on the 5 mm tube to vary the distance between the discharge and the measuring point. Calibration of TALIF signals was performed in situ but without afterglow, using the same gas mixture containing krypton.

References

[1] A. Ricard, J. Amorim, M. Abdeladim and J.P. Sarrette, Plasma Chem. Plasma Process. 40 (2020) 1351

Fig.1. Active species concentrations measured in the flowing afterglow of a N_2 discharge (0.5 slpm, 4 Torr, 100 Watt) by OES after calibration of the N atom density by NO titration



PROC 2 / Process control

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

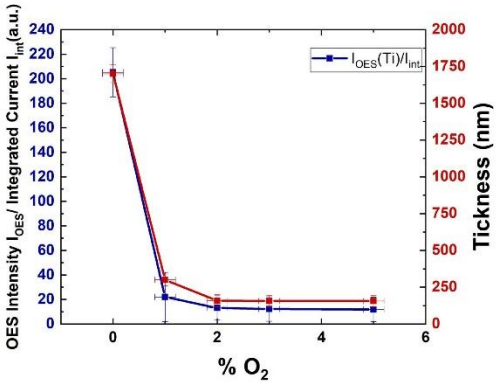
D. Boivin, A. Najah, C. Noel, G. Henrion, S. Cuynet, L. Depoucques
Univ. Lorraine, CNRS, IJL, Campus ARTEM, Nancy (FR)

Time-resolved plasma diagnostics are implemented to investigate a reactive HiPIMS (R-HiPIMS [1]) TiO2 deposition process running at duty cycle lower than 16 % and low repetition rate (1 kHz). Indeed, R-HiPIMS is the only physical process currently able to ensure optimal compliance of the coatings on complex 3D substrates. The study focuses on the influence of the gas pressure, the target to substrate distance, the duty cycle and the gas mixture composition on both the deposition rate and the hysteresis usually encountered in such PVD processes. Optical emission spectroscopy and electrical measurements are correlated with the properties of the deposits, including thickness. From these measurements, it is shown that the normalized titanium line intensity of the discharge current is a suitable parameter that reflects the deposition rate quite well as shown on the figure 1. Moreover, this parameter can also be useful to control the process in the transition regime between metallic sputtering and compound sputtering. A method is thus proposed to monitor and control the R-HiPIMS deposition process, which can be of great interest at an industrial scale.

References

[1] A. Anders, Tutorial : Reactive high power impulse magnetron sputtering (r-hipims), Applied Physics Review 121 (2017).

Correlation between the film thickness and the emi



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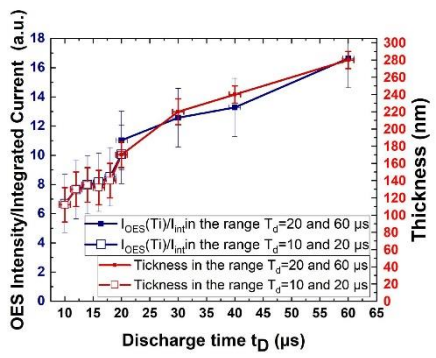

PROC 2 / Process control

- Backward-Facing Step forced flow in a nanosecond pulsed cold atmospheric pressure Argon plasma jet

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Plasma-Flow interaction in cold atmospheric pressure plasma jets (CAPJs) is of importance due to the direct influence on the reactive species production. It has been shown that, for moderate flow velocities, the effect of plasma heating and/or ionic wind in the plasma plume is too weak to explain the observed flow modification due to the plasma [1]. This work studies the argon flow modification in a CAPJ driven by nanosecond high voltage pulses [2], from single to multiple shots application. A Schlieren optical bench has been designed in order to visualize the argon flow downstream expansion in quiescent air, for moderate flow rates below 1 slm. A coupled approach is used between CCD Schlieren imaging and ICCD plasma plume imaging, both time-resolved. It is shown that the application of only one voltage pulse (*i.e*. single shot) is enough to disturb the flow, as predicted by a numerical model in helium [3]. The disturbed flow exhibits ripple propagation, on a timescale similar to the flow velocity. When operating in double shots, the second ionization wave can be used as a probe to instantly visualize the flow structure any time after the first voltage pulse application. For some flow rates, the ripple can increase in amplitude up to the point when it strongly deforms, or even stops, the plasma plume expansion, after which it is entrained by the flow and the plasma plume retrieves its full usual expansion. When a series of voltage pulses are applied, the maximal disturbance of the flow is achieved for a certain pulse repetition frequency, specific of each flow rate. It is associated with ripples alternation in the plasma plume, in a 3D helical-like arrangement. For greater pulse frequencies, the ripples progressively vanish, and the flow is clearly less disturbed. Once the ripples have vanished, increasing further the voltage pulse repetition frequency does not change the plasma plume and flow structures. We suggest that the repetitive plasma ignition mechanically forces the flow inside the capillary with consequences on the global flow structure, similarly to a forced backward-facing step flow with actuator [4].

References

[1] E.R.W. Van Doremaele et al., Plasma Sources Sci. Technol. 27, 095006 (2018)
[2] Et. Es-Sebbar et al., J. Appl. Phys. 126, 073302 (2019)
[3] A.M. Lietz et al., Appl. Phys. Lett. 111, 114101 (2017) [4] N. Benard et al., Int. J. Heat Fluid Flow 61, 158 (2016)

PROC 2 / Process control

● Oxygen atom densities in radiofrequency capacitively-coupled plasmas (RF-CCP) at intermediate pressures determined by cavity ringdown spectroscopy

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Radiofrequency capacitive discharges in the intermediate pressure range (1-10 Torr) are widely employed in many current applications including PECVD, photoresist strip and as a radical source for downstream etching[1]. However, they have been the subject of relatively few experimental studies, in part due to the difficulty of making diagnostic measurements. A key parameter characterising such discharges is the dissociation degree of the feedstock gas. In the case of a diatomic gas (such as O_2), this can be deduced from the density of atoms (O ^{3}P in this case). Several techniques have been employed for this, but each have significant drawbacks. Optical emission actinometry is widely used due to its simplicity, but the accuracy of absolute measurements is highly questionable due to the uncertainly in both the cross-sections and the energy distribution functions for specific discharges[2]. Two-Photon laser-induced fluorescence (TALIF) is also widely employed, using Xe TALIF for calibration[3]. However, the many complex calibration procedures required, and the non-linear nature of the technique, limit the achievable precision. Furthermore, the O/Xe two-photon cross section ratio is not known with high accuracy. Absorption techniques offer much better accuracy and reproducibility, but atoms generally lack transitions in convenient spectral regions. We have used the recently-developed cavity-ringdown (CRDS) technique to measure O atom densities via the forbidden ^{1}D→^{3}P transition at 630nm[4]. In addition to the atom density, these measurements can also provide the gas temperature (via the Doppler width) and information on O^- negative ion and O_3 densities from the underlying continuum absorption. Measurements were made in a 50cm-diameter, 2.5cm gap aluminium CCP reactor, operating in pure O_2 gas. The effect of gas pressure (0.5-4 Torr), excitation frequency (13.56, 27.12 and 40.68MHz) and RF power were investigated. The results observed cannot be explained by variations in the electron impact dissociation rate of O_2 alone, but are also determined by changes in the atom recombination rate at the Al surfaces induced by ion bombardment. Time-resolved measurements will allow the magnitude of these effects to be investigated.

Thanks/Acknowledgement

This project was supported by Applied Materials Corporation University Research Partnership Program.

References

[1] M.A. Hartney et al, Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena, 7, (1989) 1
[2] J-P. Booth et al, Plasma Sources Science and Technology, (2020)
[3] K. Niemi et al, Plasma Sources Science & Technology, 14, (2005) 375
[4] R. Peverall et al, Plasma Sources Science and Technology, 29, (2020) 045004

PROC 2 / Process control

● Energetics of reactions in a dielectric barrier discharge with argon carrier gas: Halocarbons

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The novel method we developed for understanding energy exchanges between argon (Ar) carrier gas and precursor molecules in a large-area (216 cm^2) dielectric barrier discharge (DBD) reactor has resulted in a series of articles, each relating to a different family of organic compounds. This communication focuses on two new groups, perfluorocarbons, C_xF_y, and perchlorocarbons, C_xCl_y, and compares results with earlier ones for hydrocarbons, C_xH_y[1] and hydrofluoromethanes, CH_xF_y[2].

The precursors (in parts per thousand concentrations) were mixed with Ar in a 20 kHz, 8 kV (peak-to-peak) DBD. For each separate compound, the energy absorbed per molecule (E_m, in eV), was determined from measurements of the time resolved discharge current, I_d, and the gap voltage, V_{gap}. Plotting E_m as a function of precursor flow rate, F_d, and also $1/F_d$, allows for the identification of the maxima, $(E_m)_{max}$, identifying the boundary between the so-called "monomer-lean" and "monomer-rich" operating regimes. It has been highly instructive to plot $(E_m)_{max}$ values as a function of atomization enthalpy (H_f) or alternatively molar mass (MM): in the case of saturated hydrocarbons, for example, this results in straight-line plots with rising MM or H_f, while the trend was not as clear cut for halocarbons.

The process generally led to thin "plasma polymer" (PP) deposits (e.g. on Si wafer substrates). Their characteristics, like their C/F or C/Cl composition ratios from XPS measurements, strongly correlated with E_m and F_d, as did PP deposition rates and water contact angles.

Thanks/Acknowledgement

The authors are grateful for financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and from the Fonds de recherche du Québec – Nature et technologies (FRQNT).

References

[1] B. Nisol et al., Plasma Process Polym, 2016;14:e201600191.
[2] S. Watson et al., Plasma Process Polym, 2020;17:e201900125.

NANO / Nanomaterials and nanostructured thin films

PL 5 ● Novel methods for tuning film properties using nanostructures

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We have developed three novel methods for tuning film properties using nanostructures: controlling nucleation in gas phase, nucleation on substrates, and nucleation under catalysts. They correspond to nanoparticle composite film deposition, inverse SK mode deposition and sputtering-assisted metal-induced layer exchange. The nanoparticle composite films are deposited using nanoparticles and radicals formed in reactive plasmas [1]. Chemical reactions on nanoparticles take place much faster than those on substrate surface, especially at low substrate temperatures, because nanoparticles of a low heat capacity become high temperature due to heating from plasma and they have a large surface to volume ratio. Utilizing this feature, we have succeeded high quality SiNx films at a low substrate temperature of 100 ^{o}C. The inverse SK mode is a new mode of hetero-epitaxial film growth, in which stress is relaxed in an atomically flat buffer layer consisted of nanocrystals aligned in-plane and out-of-plane and single crystal with a low defect density grows on the buffer layer [2]. To realize the buffer layer of this mode, we applied impurity-mediated sputtering. Nitrogen was employed as an impurity for ZnO film fabrication. We obtained single crystal ZnO on sapphire with a large lattice mismatch of 18%. The inverse SK mode opens great possibilities of single crystal hetero-epitaxy of multicomponent systems with a wide mixture range. The impurity-mediated sputtering provides an alternative method for amorphous film formation at high substrate temperatures. We applied this method to obtain amorphous ITO films with a high mobility. The metal-induced layer exchange is a well-known method of crystal film formation on glass and polymer. We reduced the processing time by 2-3 orders of magnitude and the processing temperature using a sputtering-assisted metal-induced layer exchange method [3]. By applying the method, we succeeded in crystalline Ge formation on polyamide films at 150 ^{o}C in a short processing time of 10 min. In addition to these film fabrication methods, we will show film properties and some device applications. In particular, by combining a novel inverse SK mode with a novel material of ZnInON, we demonstrated room temperature operation of an excitonic transistor, a novel ultra-low energy consumption and ultra-fast switching device with an optical input and output.

References

[1] S. H. Hwang, et al., Jpn. J. Appl. Phys. 59 (2020) 100906.
[2] N. Itagaki, et al.,Sci. Rep. 10 (2020) 1.
[3] S. Tanami, et al., Thin Solid Films 641 (2017) 59.

NANO / Nanomaterials and nanostructured thin films

- LIPSS formation by picosecond laser irradiation of magnetron sputtered gadolinium-doped ceria thin films

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The interaction between ultrashort laser beam pulses with thin films induces the formation of surface micro/nanostructures. These laser-induced periodic surface structures (LIPSS), or ripples, could improve the physico-chemical properties of thin films including their specific surface. In the case of electrochemical cells made of an assembly of thin films, they can further improve the performance of the electrode by increasing the specific contact surface by laser structuring of a wide range of materials which is an increasingly powerful technique for species active at the electrode / electrolyte interface. In this work, a picosecond Nd: YAG laser operating at its third harmonic (λ=355 nm) is used to irradiate the surface of gadolinium-doped ceria (CGO) thin films, grown by on yttria-stabilized zirconia (YSZ) by magnetron sputtering. The morphological characteristics of the thin films and their structuring were observed by high resolution scanning electron microscopy (HR-SEM). LIPSS are generally produced in a low fluence laser multi-pulse regime close to the ablation threshold. They were obtained with the period of approximately 283 nm under appropriate values of laser fluence (F from 184 to 295 mJ/cm^2) and scanning speed (0.2 mm/s to 0.4 mm/s). Exceeding the threshold leads to surface ablation. In agreement with the literature, it has been noted that these periodic structures can be classified as Low Spatial Frequency LIPSS (LSFL) or High Spatial Frequency LIPSS (HSFL). The LSFL period is generally close to the beam wavelength λ, presenting a period varying in 0.5λ-λ. On the other hand, HSFL refers to ripples having a period smaller than the beam wavelength (< 0.5λ). Our work focusses on the optimization of laser parameters to generate clear and high resolution LSFL/HSFL without ablating the CGO layer. Using numerical tools for SEM/AFM images, the enhancement of the specific surface of the CGO films will also be discussed.

NANO / Nanomaterials and nanostructured thin films

● Soft in hard magnetic nanocomposites by dual laser ablation approach

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With the expansion of the Internet of Things (IoT) era, the emergence of storing data has been fascinating in both applications and research. Among them, magnetic materials have great attractive attention. The current limitation in magnetic storage is practical for a single magnetic phase material[1] with the theoretical energy product-$(BH)_{max}$~516kJ/m³. Theoretical modeling suggests that the $(BH)_{max}$ could grow up to 1MJ/m³ in a soft-hard magnetic nanocomposite, for which the soft magnetic phase dimensions should be no more than twice the domain wall width of the hard phase[1]. However, the fabrication of soft-hard nanocomposites is challenging owing to insufficient control of the soft phase dimension (<10 nm). This work investigates the combination of dual laser ablation systems consisting of a Pulsed Laser Deposition (PLD-KrF laser, 248nm) coupled with a Pulsed Laser Nanoparticle Source (PLNS-Nd:YAG laser, 532 nm) to deposit thin films and nanoparticles (NPs) independently[2,3], producing soft-hard nanocomposites. The first step here is the deposition of the FePt thin films (matrix). They were deposited at room-temperature on Si/SiO_2 (100nm) and post-annealed at various rapid thermal annealing conditions (annealing temperatures, heating rates and time). Controlled annealing conditions at 750°C (heating rate of 50°C/s) allows to obtain magnetic granular films with single magnetic phase showing out-of-plane coercivity $\mu_0 H_c$~2T and remanence $\mu_0 M_r$>1T when the annealing stage is 10s and textured films with multiple phase behaviors, exhibiting $\mu_0 H_c$~4.4T and $\mu_0 M_r$>1T for longer annealing stage of 60s. In the second step, sizable NPs with a narrow size distribution of 4.1nm±0.3nm and specific compositions depending on the targets in use, are synthesized by the homemade PLNS. The flexibility of our experimental process with both PLD and PLNS allows fabricating nanocomposites with various configurations such as layer-layer, soft magnetic NPs embedded homogeneously inside hard magnetic matrix. The properties of nanocomposite are considerably affected by both the hard matrix and the soft NPs and depend on the rapid thermal annealing conditions. The remanence-$\mu_0 M_r$ increased of 16% and 24% in optimized nanocomposites with Co and $Fe_{65}Co_{35}$ inclusions, respectively, compared to single FePt matrix.

Thanks/Acknowledgement

This work is funded by the ANR-16-CE09-0019-SHAMAN project and benefited from technical supports-CARMALIM of Limoges University

References

[1] R. Skomski and J.M.D. Coey, Phys. Rev. B 48, 15812 (1993).
[2] T. Nguyen Van, I. de Moraes, N.M. Dempsey, C. Champeaux, and F. Dumas-Bouchiat, J. Magn. Magn. Mater. 520, 167584 (2021).
[3] M. Gaudin, P. Carles, E. Laborde, C. Champeaux, and F. Dumas-Bouchiat, J. Appl. Phys. 125, 054301 (2019).

NANO / Nanomaterials and nanostructured thin films

● Few-layer Graphene production graphite electrode exfoliation by nanosecond high-voltage pulsed discharge in liquid nitrogen

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Ignition of a discharge in between two electrodes in a liquid medium generates high temperature plasma containing high-energy species, and shock waves. The plasma discharge interaction can therefore be detrimental to the electrodes that erode rapidly, or beneficial in providing energy for material processing or material synthesis like the synthesis of nanoparticles for instance [1, 2]. For lamellar material, the discharge in liquid can contribute to exfoliate the material towards 2D structures. In the present work, high voltage pulsed discharges in liquid nitrogen are studied to exfoliate highly oriented pyrolytic graphite (HOPG) within various electrode configurations. The exfoliated particles were characterized by TEM,SEM and Raman to evaluate the defects, size, purity and crystallinity of the as produced nanoparticles as a function of the plasma parameters, especially, the voltage pulse frequency and width as well as the electrode configuration. Although the quantification of the actual number of layers of each particle was quite arduous, HOPG electrodes were exfoliated, thus proving that this process successfully produced few-layer graphene (FLG). From the observation of the damaged HOPG electrodes and characterization of the resulting particles, a mechanism of exfoliation is proposed and discussed. The role of the discharge parameters (e.g. voltage pulse frequency and width, electrode configuration) on the exfoliation process is pointed out. It is shown that three principal exfoliating forces are involved in the exfoliation mechanism: thermal cycles, plasma erosion and shockwave formation. Further work is needed to discriminate the more efficient among these processes.

References

[1] H. Kabbara, J. Ghanbaja, C. Noel, T. Belmonte Nano-objects synthesized from Cu, Ag and Cu28Ag72 electrodes by submerged discharges in liquid nitrogen Mater. Chem. Phys. 217 (2018) 371-378
[2] M. Trad, A. Nominé, C. Noel, J. Ghanbaja, M. Tabbal, T. Belmonte Evidence of alloy formation in CoNi nanoparticles synthesized by nanosecond-pulsed discharges in liquid nitrogen Plasma Process. Polym. 17 (2020) e1900255

PROC 3 / Process control

● Control of large-area deposition process of diamond films with versatile properties

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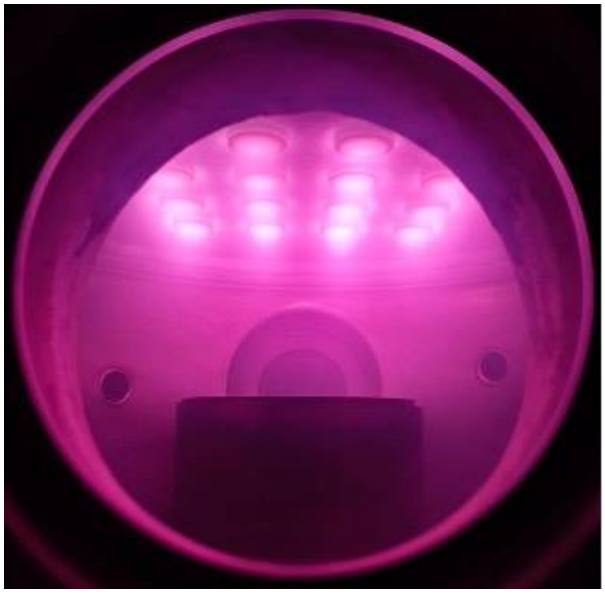
Diamond is potentially the best candidate for many applications in electronics, quantum technologies, optics, mechanics, thermal management or biomedical field, owing to its unique combination of physical and chemical properties. However, it is still incompatible with most of industrial processes because of several difficulties that have not yet been entirely overcome, especially limited synthesis areas (< 20 cm^2) in conventional reactors and non-conformal growth which restricts substrate shapes. To overcome these obstacles, new deposition reactors were designed in order to allow the synthesis of diamond films on large area (> 300 cm^2) and possibly at low substrate temperatures. Among these technologies, a distributed antenna array (DAA) microwave system [1] composed of 16 microwave plasma sources arranged in a 2D matrix and operating in $H_2/CH_4/CO_2$ gas mixture has been extensively used to produce nanocrystalline diamond films suitable for applications requiring both thermal sensitive substrates and smooth as-grown surfaces [2-4]. In this work, we investigated the capabilities of the DAA microwave system to synthesize large-area diamond films with various and controlled properties aiming at allowing a large-scale industrial production of materials compatible with high throughput fabrication processes for applications. Different forms of diamond, nano-, micro-, poly- and mono-crystalline, depending on the substrates employed and on the growth mode yielded by varying the growth parameters, were obtained. Various and controlled features in terms of grain size, surface morphology and roughness, film texture, purity and thickness were reached with satisfactory uniformity on large area (plasma size > 600 cm^2) by adjusting the process parameters. Plasma diagnostics permitted to further understand and control the effects of growth parameters through spectroscopic and electric measurements.

References

[1] L. Latrasse et al., Plasma Sources Sci. Technol. **16** (2006) 7. [2] D. Dekkar et al., Phys. Status Solidi (a) **215** (2018) 1800251. [3] D. Dekkar et al., Diam. Relat. Mater. **103** (2020) 107700. [4] D. Dekkar et al., J. Phys. D: Appl. Phys. **53** (2020) 455204.

The DAA reactor in planar matrix configuration



PROC 3 / Process control

● Atomic layer etching of Gallium Nitride (GaN) using SF_6/Ar plasmas

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The excellent electrical properties of Gallium Nitride (GaN) make it a promising semiconductor for the next generation of high-power devices, in particular the normally-off High Electron Mobility Transistors (HEMTs). Among the different etching processes, Atomic Layer Etching (ALE) of GaN is the most advantageous. It enables accurate control of the etched depth and provides less damage compared to monocyclic plasma etching process for the fabrication of GaN electronic components. Up to now and due to the high volatility of the etch by-products, notably $GaCl_3$ [1,2], the majority of the research activity carried out on GaN ALE has been performed using chlorine based chemistry for the modification step. Furthermore, fluorinated chemistries have been unequally studied. For example, Nakazawa et al used a CF_4/O_2/Ar plasma mixture to etch GaN [3] and Johnson et al studied XeF_2 molecules in the modification step of a thermal ALE process [4].
In this work, the GaN ALE process consists of cyclic SF_6 plasma chemisorption step and Ar plasma removal step. The fluorine-based plasma, enables to form a GaF_3 layer at the surface. This non-volatile etch by-product has a boiling point as high as 1000 °C at atmospheric pressure [5]. The GaF_3 modified layer is then removed during the removal step which consists of Ar plasma with a low ion bombardment to prevent any sputtering of the substrate. Self-Limiting Etching (SLE) can be achieved under such conditions.
Experiments were performed in an Inductively Coupled Plasma (ICP) reactor. This study investigates the influence of plasma parameters such as gas flow rates and the self-bias voltage. The exposure duration of ALE steps has been also investigated. AFM was used to measure the etch depth and the surface roughness.
Our first analyses show that GaN Etched depth Per Cycle (EPC) increases slowly with the SF_6 exposure time. After 100 cycles, a low etch per cycle of 0.1 nm/cycle was obtained, corresponding to a less than a monolayer of GaN.

Thanks/Acknowledgement

The authors are grateful to the European Union (IPCEI) Nano2022 project and Région Centre for their financial supporting. Most equipment is provided by CERTeM 2020 platform.

References

1. Ohba, T et al, Jpn. J. Appl. Phys. 56, 06HB06, 2017
2. Le Roux, F et al, Microelectron. Eng. 8, 2020
3. Nakazawa, K et al, DPS, 2019
4. Johnson, N. R et al, Appl. Phys. Lett. 114, 243103, 2019
5. Pearton, S. J et al, J. Appl. Phys. 86, 1–78, 1999

PROC 3 / Process control

● Active Screen Plasma Nitriding: plasma diagnostics and experiments in a laboratory reactor and an industrial one

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Plasma-assisted nitriding is a treatment usually used to improve tribological properties of metal parts. The common process consists in placing the parts in a low-pressure reactor (primary vacuum) and in connecting them to a high cathodic potential. Walls of reactor act as an anode. In this DCPN (Direct Current Plasma Nitriding) configuration, N2/H2 plasmas form directly around the load. Even if it is widely used in industry, some defects (edge effects, electric arcs) can induce inhomogeneous treatments and partial destruction of the parts. To overcome these limitations, the Active Screen Plasma Nitriding concept (ASPN) has been recently developed [1]. In this process the parts, connected to ground or to a slightly negative potential, are placed inside a metal cage to which a high cathodic potential is applied. The plasma is thus created on the screen that is a source of both nitriding species and heat.

In the laboratory, we have designed an ASPN system composed by a cylindrical stainless steel chamber containing inside a stainless steel (AISI 304 L) cylindrical mesh screen (Ø 340 mm, 220 mm in height) connected to a DC-pulse generator. Studies were also performed at IRT M2P where a semi industrial equipment (ALD Company) is capable of operating in both DCPN and ASPN mode. This reactor owns a double mesh screen in S235JR (1.0037), with 0.972 m in diameter and 1.02 m in height. The latter is connected to a DC pulse generator working in unipolar (negative potential) or bipolar mode. Both active screen plasmas were investigated by using optical emission spectroscopy (OES), voltage and current probes, fast camera and mass spectrometer. Nitrided coatings were studied by X-ray diffraction, Glow Discharge Optical Emission Spectroscopy, metallography and electronic microscopies.

Experiments showed that higher plasma reactivity is reached for a mixture N_2/H_2 of 80/20 at relatively low pressure (0.5 mbar). In these conditions, the nitrided coating has a larger thickness despite the presence of a superficial oxide layer measuring a few of tens nanometers. The properties of this layer were studied versus N_2/H_2 ratios and the results were correlated with OES in a wide spectral range (200-900 nm). Emission intensity of NO γ-band (210-290 nm) appears to be a good indicator to control the oxygen contamination. First results in bipolar mode will be also presented.

Thanks/Acknowledgement

This work was supported by IRT M2P and ANR (PIPERADE project)

References

[1] J. Georges, US patent 5 989 363 No 23 (1999)

DEPO 3 / Plasma - deposited coatings

● Fast and low-temperature atmospheric PECVD deposition of crystalline films of the system Sr-Ti-O for multifunctional applications

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Strontium titanate nanomaterials have been extensively used in a wide range of electronic and optical devices due to their high stability and suitable electrical and physicochemical properties [1]. In this context, numerous synthetic approaches have been applied for the fabrication of high quality thin films of the Sr-Ti-O system, requiring often-high temperatures and low-pressure conditions [2]. In this work, the fast and simple deposition of crystalline Sr-Ti-O films by atmospheric plasma enhanced chemical vapor deposition (PECVD) at low-temperature (< 200°C) on silicon substrates is shown. The optical, microstructural, and electrical properties of the films are discussed in detail. A thermal study of different Sr precursors (Sr isopropoxide, Sr acetylacetonate and Sr (dpm)2) has been carried out and correlations between their decomposition temperature and the crystallinity of the films have been established. Thanks to this statement, it was shown that the highest molecular weight precursor, Sr(dpm)2, exhibits a slow decomposition due to the higher energy requirements for the chain breaking, promoting a controlled film growth rate. This is beneficial for the crystallinity and the charge separation and transport efficiency in the film, which was corroborated by the superior electrical properties in the Sr(dpm)2 derived films. Furthermore, the deposition conditions were successfully applied on a variety of substrates, including quartz and FTO, facilitating the potential application of Sr-Ti-O PECVD films in optical and photoelectrochemical devices.

Thanks/Acknowledgement

A. M. H.-F. acknowledges the Luxembourg National Research Fund (FNR) and the Molecular Plasma Group (MPG) for the support on the postdoctoral position at LIST through the PLASPEROX (Industrial Fellowships/19/13711983) project.

References

[1]Phoon, B.L. et al. Vol. 43, 5151-5174, International Journal of Energy Research 2019.
[2]Baba, S. et al. Vol. 1, 211-217, Science and Technology of Advanced Materials 2000.

DEPO 3 / Plasma - deposited coatings

● Comparison of dual ECR/RF-Magnetron/ Tetramethylsilane (TMS) and RF-Magnetron/TMS plasmas used for SiCN:H thin films deposition in Ar/N_2 gaz mixture

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SiCN materials have very interesting properties that can be modulated by changing the chemical composition. The most remarkable are the mechanical properties with high Young's modulus and hardness, modulation of the Tauc's bandgap and the optical index, high temperature resistance to oxidation, anti-reflective coating for photovoltaic applications, passivation of electronic contacts, low-k value to reduce the interconnect resistance-capacitance application in the integrated circuits, and so on. We have developed a new plasma-assisted chemical vapour deposition process. This involves in combining two types of plasmas excitations. The first plasma is excited at electronic cyclotronic resonance (ECR) at 2.45 GHz and the second one is a RF magnetron (13.56 MHz) plasma with a silicon target. The gas mixture used is Ar/N2/Tetramethylsilane (TMS). The control of the process is carried out by in-situ optical diagnostics in the visible range by reflectometry and in the infrared by FTIR spectroscopy in transmission and in reflection mode. In this study, we compare the efficiency of coupling the magnetron/TMS, or ECR/Magnetron/TMS, in order to qualify the right process for SICN:H thin film deposition. The two coupling processes allow obtaining a growth rate of about 2 µm/h greater than in the conventional ECR process (about 50 nm/h). In the dual RF magnetron/TMS process, we obtain very dense films for large autopolarisation voltages. The optical index is around1.85 at a wavelength of 633 nm, the Tauc's bandgap is about 3.0 eV. This is explained by the low chemical composition variation from the FTIR measurements. In the dual ECR/Magnetron RF/TMS process, we obtain a large modulation of the chemical composition with the autopolarisation voltage of the silicon target. This is also accompanied by a good modulation of the optical index in the visible range, and the Tauc's bandgap. The optical index varies linearly between 1.55 and 1.97 at a wavelength of 633 nm and the Tauc's gap decreases linearly between 4.7 to 3.2 eV. This results are in good agreement with the FTIR spectra finger print deconvolution. The apparition of columnar structure depending on the applied autopolarisation voltage is discussed. The dual ECR/Magnetron RF/TMS process appears very attractive for large variety of SiCN:H thins films applications due to the modularity of the films properties.

DEPO 3 / Plasma - deposited coatings

• Photocatalytic and electrical properties of Ti-W oxide thin films deposited by low temperature PECVD

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The interest in depositing functional thin films of metal oxide at low temperature has been increasing over the past decades, notably to allow the processing of heat-sensitive substrates. The use of polymers could be beneficial to applications such as flexible electronic, photovoltaics or photo-catalyzed wastewater treatment. While many techniques enable the deposition at low temperature (<150°C), only a limited number of them allow to obtain decent crystallization of the as-deposited metal oxide thin films, which is a key feature for many functional properties. Among these techniques, most of which being plasma-assisted, Plasma Enhanced Chemical Vapour Deposition appears particularly suitable as it has been shown to deposit crystallized TiO_2 thin films at temperatures below 130°C. Moreover, pulsing the plasma power allowed reducing the temperature increase to less than 80°C while maintaining anatase crystallization at the surface of the film, provided that sufficient thickness was reached. [1] In this work, thin films of titanium and tungsten oxide have been deposited at low temperature by PECVD, using a rf inductively coupled oxygen plasma. Titanium Tetraisopropoxide and Tungsten ethoxide were used as precursors of Ti and W, respectively. The composition of the oxide film was tuned by varying the precursor flowrates and was assessed by X-Ray Photoelectron Spectroscopy (XPS). The film structure was investigated using X-Ray Diffraction, Raman Spectroscopy, in situ spectroscopic ellipsometry and Scanning Electron Microscopy. Their photocatalytic activity was studied by measuring methylene blue degradation kinetics in aqueous solution under UV exposure and their conductivity was probed using four-point measurements. $Ti_{1-x}W_xO_z$ thin films have been deposited with x ranging from 0 to 1. A columnar structure is found for all compositions, consistently with morphologies of pure oxides thin films. TiO_2 and WO_3 thin films were found to exhibit crystallization in the anatase and monoclinic phase respectively. It is found that the insertion of W in the TiO_2 thin film hinders its crystallization and affects the crystal structure. However, it should be noted that anatase crystallization is maintained up to x=0.15. Moreover, XPS revealed energy levels in the band gap of the materials, whose population and energy depend on composition. The photocatalytic and electrical properties of the thin films are discussed as a function of W content in the oxide film.

Thanks/Acknowledgement

ANR-17-CE08-0045

References

[1] D. Li, N. Gautier, B. Dey, S. Bulou, M. Richard-Plouet, W. Ravisy, et al. Applied Surface Science 2019;491:116–22

DEPO 3 / Plasma - deposited coatings

● Wafer edge and bevel encapsulation by localized SiO_2 and Si_3N_4 plasma enhanced chemical vapor deposition

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As 3D integration schemes move forward new process challenges arise. One of them is to manage contamination issues of multiples stacked wafers. Particularly, wafers edge and bevel are known to be the source of delamination or defects, as metals or particles contaminations [1-3]. This is even more critical when, after bonding, back-end of line wafers are reprocessed on front-end tools [4]. In this paper, we present a strategy consisting in encapsulating the bevel area in a single process step. SiO2 and Si3N4 are deposited on standard or bonded Si wafers in a 300mm PECVD reactor at 350°C. We study the influence of pressure, RF power, and single or dual frequency plasma excitation on deposition rate and refractive index. No deposition occurs on most of the top surface since the gap between the wafer front side and the top grounded electrode remains below 1 mm. On the wafer edge and bevel, where plasma and deposition take place, films wet etch rates and FTIR spectras confirm oxide and nitride excellent qualities. The radial deposition profiles is characterized by ellipsometry and scanning electron microscopy cross section. Profiles toward the wafer center or inside the gap formed by edges of bonded wafer are compared. Below a gap typically in the order of the plasma Debye length, diffusion like profiles are observed. We discuss these results against literature models [5-7].

References

[1] C.Bunke, T.F. Houghton, K. Bandy, G. Stojakovic, and G. Fang, IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, VOL. 26, NO. 4, NOVEMBER 2013
[2] A.Vert, et.al., 2015 26th Annual SEMI Advanced Semiconductor Manufacturing Conference, ASMC 2015, 7164420, pp. 362-366
[3] M.C. Silvestre, et.al., 2016 27th Annual SEMI Advanced Semiconductor Manufacturing Conference, ASMC 2016, 7491136, pp. 124-128
[4] L. Brunet, et. al., Technical Digest - International Electron Devices Meeting, IEDM, 2018-December,8614653, pp. 7.2.1-7.2.4
[5] L.S. Hong, Y. Shimogaki, and H. Komjyama, Thin Solid Films 365 (2000) 176±188
[6] A.J. Knoll, A.Pranda, H.Lee, and G.S. Oehrlein, J. Vac. Sci. Technol. B 37, 031802 (2019)
[7] N. Babaeva, and M.J. Kushner, J. Appl. Phys. 101, 113307 (2007)

DEPO 3 / Plasma - deposited coatings

● Vanadium-doped TiO_2 synthesised by metal organic Plasma Enhanced Chemical Vapour Deposition for photocatalytic applications

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In the field of TiO_2 thin films, Plasma Enhanced Chemical Vapour Deposition have been investigated. However, if low deposition temperatures are reached, the deposited films remain, usually, amorphous. Recently, we developed a pulsed plasma assisted deposition process enabling the deposition of anatase TiO_2 at temperature below 115°C[1]. Using an Electron Cyclotron Wave Resonance (ECWR) plasma source in a remote configuration opens the possibility of a roll to roll process on polymeric ribbons.

The non-toxicity, good chemical stability, high availability and low price of TiO_2 make it a reference for today's and tomorrow's photocatalysts. Nonetheless, the wide band gap (3.2 eV) of its most photocatalytic polymorphs (anatase) is still an impediment to overcome in order to make a better harnessing of visible part of sunlight. As alternative, cationic doping with transition metals appears to be a promising way. Therefore, Vanadium triisopropoxide (VTOP) and Titanium(IV) isopropropoxide (TTIP) were co-injected into the chamber via two different injection rings (Fig. 1).

We focused on the vanadium concentration, tuned by varying the (VTOP)/(TTIP) vapour ratio, in the gas phase. The cristallinity, morphology and composition of the V-doped titania layers were characterized by Scanning Electron Microscopy, Raman Spectroscopy, XRD and XPS. UV/Visible spectroscopy and ellipsometry allow to monitor the impact of the dopant concentration on the optical properties. The photocatalytic performance was evaluated through their ability to decompose stearic acid under 365 nm UV-light and visible light. The photocatalytic behavior was further investigated through charge carriers generation, transport in the bulk and injection at the interface to the external medium under AM1.5G simulated sunlight. Photoelectrochemical measurements also provided insightful information on the effect of doping PECVD TiO_2 with vanadium toward photocatalytic applications. An anodic photocurrent of 80 $\mu A.cm^{-2}$ was obtained with the best V-TiO_2 sample, without using sacrificial agents, opening the path to further optimizations for enhanced performance.

Thanks/Acknowledgement

French Agence Nationale de la Recherche (ANR) and Luxembourgish Fonds National de la Recherche (FNR) through the FNR-ANR-INTER (ANR-17-CE08-0045-01 and INTER/ANR/16/11565003/PATIO/Choquet).

References

[1] Dey, B. et al. Anatase TiO_2 deposited at low temperature by pulsing an electron cyclotron wave resonance plasma source. Sci. Rep. 1–11 (2020). doi:10.1038/s41598-020-78956-1

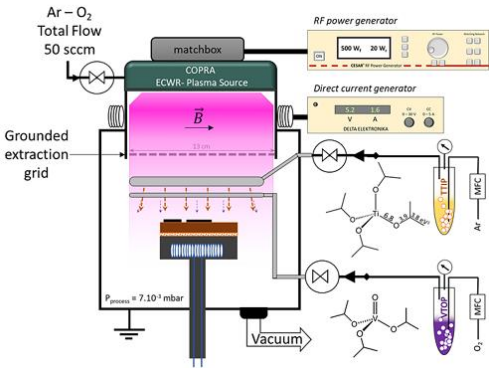

Fig. 1 : Remote ECWR process used at LIST

GROM 2 / Thin films growth and modelling

- Pulsed aerosol assisted deposition of pp-HMDSO thin film in a Dielectric Barrier Discharge

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Aerosol-assisted plasmas can be used to produce a wide variety of thin films, including homogeneous, nanotextured and/or nanocomposite coatings. For example, the nebulization of colloidal solutions, i.e. liquid solutions containing nanoparticles, in plane-to-plane dielectric barrier discharge (DBD) at atmospheric pressure has been used for nanocomposite thin film deposition [1]. However, nanoparticles-loaded droplets in the aerosol lead to the deposition of aggregated nanoparticles embedded in the matrix [1]. Recently, a new process of nanoparticles injection in plasmas has been developed [2]. This method consists in synthesizing the nanoparticles prior to their injection in the plasma in a low frequency pulsed injection regime. However, the impacts of the pulsed aerosol injection on the DBD physics are still opening questions. This work aims to study a pulsed-aerosol-assisted DBD deposition process. In contrast with the continuous nebulization of solutions, pulsed injection causes a sudden increase of the quantity of precursor as droplets in the inter-dielectric space – the average velocity being in the 10 m.s-1 range. We observed that depending on the process parameters (injection times, pulse frequency, continuous gas flow rate, etc.), the discharge stability is modified. These parameters are also critical for transport and evaporation of the droplets and so on the thin film deposition (here ppHMDSO). For example, by varying the different parameters of the pulsed-aerosol-assisted DBD, we observe that the deposit can consist in different phases (liquid and solid) as a function of the time residency of the aerosol and the thickness of the deposited layer.

Thanks/Acknowledgement

The authors gratefully acknowledge Erika Loranger and Guillaume Carnide for their contribution to this work.

References

[1] J. Profili, O. Levasseur, J.-B. Blaisot, A. Koronai, L. Stafford, and N. Gherardi, “Nebulization of Nanocolloidal Suspensions for the Growth of Nanocomposite Coatings in Dielectric Barrier Discharges,” Plasma Process. Polym., vol. 13, no. 10, pp. 981–989, Oct. 2016.
[2] M. Khan, Y. Champouret, R. Clergereaux, C. Vahlas, and A.-F. Mingotaud, “Process for the preparation of nanoparticles,” EP 16305977.7, 2016.

GROM 2 / Thin films growth and modelling

- Role of H_3^+ ions in deposition of silicon thin films from SiH_4/H_2 discharge: modeling and experiments

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A 1D fluid model [1,2] including a detailed chemistry for silane-hydrogen discharges as well as surface reactions to account for deposition and etching processes has been implemented to study the effects of gas pressures (1 to 3.5 Torr) and silane concentration (2 to 10%) on the deposition rate of silicon thin films in a standard RF-PECVD reactor [3]. The thickness of the films and their deposition rate as functions of the process conditions were determined from the optical modelling of UV-visible spectroscopic ellipsometry measurements. The experimental values of the deposition rate were compared with results from the 1D fluid model. SiH_3 radicals are found to be the main contributor to the computed deposition rates, while H_3^+ ions play the main role in the etching process. The study reveals that etching by hydrogen ions must be taken into account to reproduce properly the experimental deposition rate. In particular etching by H_3^+ ions must be taken into account to achieve a good agreement between the experimental and modelled values of the deposition rate as a function of the total gas pressure and the silane fraction in the discharge.

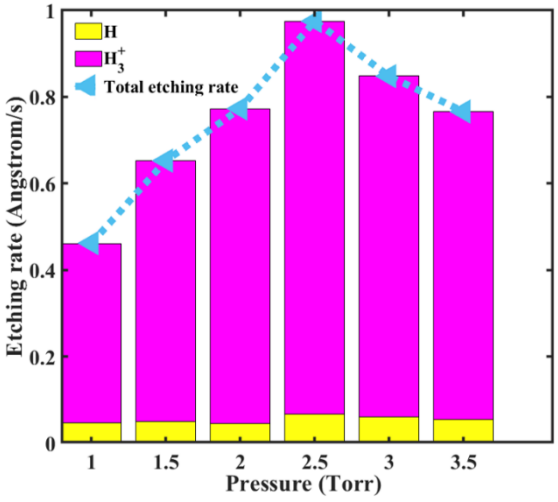
Thanks/Acknowledgement

This work got financial support from the Ecole Polytechnique and CNRS. Tinghui Zhang's fellowship is supported by China Scholarship Council.

References

[1] Orlac'h J. M., Novikova T., Giovangigli V., Johnson E. and Roca i Cabarrocas P. 2019 Plasma Sources Science and Technology 28 055003 [2] Giovangigli V. 2012 Science China Mathematics 55 285 [3] Roca i Cabarrocas P. , Kim K. H., Cariou R., Labrune M., Johnson E. V., Moreno M., Torres Rios A., Abolmasov S. and Kasouit S. 2012. MRS Online Proceedings Library Archive 1426 319

The etching rate as a function of gas pressure



GROM 2 / Thin films growth and modelling

- A parametric study for the PECVD from Ar/CH_4

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Representing the simplest hydrocarbon, being of low cost and non-hazardous, methane is an ideal candidate as a case study for the growth of carbonaceous films. Because the gas kinetics and surface chemistry can vary from one process to another, a typical capacitively coupled RF discharge of parallel plate type has been applied for different Ar/CH_4 gas mixtures. The focus of this study is the use of a quartz crystal microbalance in order to monitor the growth speed and density of the grown thin films for various plasma parameters, eg. pressures, gas mixtures and powers. Film densities for different substrate positions have been measured by the comparison to SEM acquisitions. Furthermore, coupling the microbalance data to the characteristics of the discharge current allows to monitor the onset of nanoparticle formation and mass spectrometric data help to understand the gas kinetics.

Thanks/Acknowledgement

This work was partly supported by the French National Research Agency (ANR) through the MONA project (ANR-18-CE30-0016).

GROM 2 / Thin films growth and modelling

- Helium-charged aluminum and silicon films deposited by Direct Current Magnetron Sputtering

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The study of helium behavior in metals has drawn significant attention in the materials science community. The insolubility and high mobility of He atoms in the materials make them easily trapped by vacancies, having a strong tendency to precipitate into bubbles [1,2]. Sputtering with He gas has been little investigated. However, previous researches have reported the formation of either porous metallic coatings or He bubbles containing films using pure He plasma [3,4]. In the present work, we study the deposition of aluminum and silicon films with thickness in the range of 1-3 µm by direct current magnetron sputtering in various He/Ar atmospheres. The plasma is analyzed by mass spectrometry. Our results reveal that the variation of He to Ar flow rate ratio influences remarkably the plasma composition as well as the composition and the morphology of the deposited films. The amounts of Al/Si and He into the films are determined by Rutherford Backscattering Spectroscopy (RBS) and Proton Elastic Backscattering Spectroscopy (PEBS), respectively. Moreover, Slow Positron Beam analysis (SPB) is performed to investigate the possible formation of vacancy-type defects. SEM images demonstrate that Al films deposited with low He percentage show the typical columnar structure. After that, the grain size decreases as the helium concentration increases inside the film until completely nanoporous films are obtained with the 100% He plasma. The experimental results (plasma diagnostic and film characterization) realized with Al and Si films are compared to the growth process simulation obtained from molecular dynamics. This approach helps to understand the mechanisms leading to He insertion and the formation of He bubbles or porous structure.

References

[1] L. Yue, D. Ai-Hong, Z. Yu-Lu, Z. Bing, W. Kang, H. Qing, S. Li-Qun, Q. Xiu-Bo, W. Bao-Yi, Helium-related defect evolution in titanium films by slow positron beam analysis, Chin. Phys. Lett. 29 (2012) 047801.
[2] L. Pentecoste, P. Brault, A.-L. Thomann, P. Desgardin, T. Lecas, T. Belhabib, M.-F. Barthe, T. Sauvage, Low Energy and low fluence helium implantations in tungsten: Molecular dynamics simulations and experiments, J. Nucl. Mater. 470 (2016) 44-54.
[3] B. Lacroix, V. Godinho, A. Fernández, The nanostructure of porous cobalt coatings deposited by magnetron sputtering in helium atmosphere, Micron. 108 (2018) 49-54.
[4] R. Schierholz, B. Lacroix, V. Godinho, J. Caballero-Hernández, M. Duchamps, A. Fernández, STEM-EELS analysis reveals stable high-density He in nanopores of amorphous silicon coatings deposited by magnetron sputtering, Nanotechnology. 26 (2015) 075703.

GROM 2 / Thin films growth and modelling

- The effect of nitrogen on the stress and morphology evolution during growth of thin silver films

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The development of stress in vapor-deposited thin films is strongly correlated with the film morphological evolution. Metal films grown on weakly-interacting substrates at conditions of high atomic mobility exhibit a pronounced 3D growth as a result of liquid-like coalescence step [1], and develop a compressive-tensile-compressive (CTC) stress evolution with increasing thickness [2]. In a recent study [3], we showed that addition of minority N_2 species in the growth atmosphere leads to incomplete island coalescence and promotes substrate wetting . However, the effect of these morphological changes on the stress response remains to be explored.

We report here a systematic study on the stress generation and evolution in thin polycrystalline Ag films grown by magnetron sputtering in mixed Ar-N_2 gas atmospheres. The stress evolution was measured *in situ* and real-time using wafer curvature technique and was complemented by *ex situ* chemical and microstructural analyses using XRD, XPS, AFM, EBSD and TEM.

We uncover significant changes in the stress evolution of Ag films when N_2 is added to the working gas for N_2-to-total pressure ratio *p* up to 25%. The tensile peak is shifted to lower thickness (from ~13 nm in pure Ar to ~7 nm for *p*=25%), and confirms that film continuity occurs earlier in the presence of N_2. This is followed in the next stage by larger compressive stress due to the formation of smaller grain sizes. More notably, a compressive-to-tensile turnaround is observed with further film thickening, with a transition thickness decreasing from 310 to 40 nm when *p* increases from 3 to 25%. Simultaneously, surface roughness emerges in the form of surface undulations with a nearly constant period of 50 nm. The origin of this stress turnaround is attributed to extensive grain growth which is accompanied by a change in preferred orientation from (111) to (100), as revealed by EBSD and TEM. The overall results of our study provide critical insights for controlling stress in films grown in complex gas compositions

Thanks/Acknowledgement

Authors acknowledge financial support from the French Government program “Investissements d’Avenir” (LABEX INTERACTIFS, reference ANR-11-LABX-0017-01), the Åforsk foundation (contract ÅF 19-137) and the Hungarian National Research, Development and Innovation Office (OTKA NN112156 project).

References

[1] P. B. Barna, M. Adamik, Thin Solid Films 317 (1998) 27-33.
[2] A. Jamnig, N. Pliatsikas, K. Sarakinos, G. Abadias, J. Appl. Phys. 127 (2020) 045302.
[3] A. Jamnig, N. Pliatsikas, et al., ACS Appl. Nano Mater. 3 (2020) 4728–4738.

HELI / Health and life science

PL6 ● A cocktail of active ingredients – benefits and challenges for plasma medicine

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Low-temperature plasma discharges in or in contact with air produce a variety of reactive oxygen and nitrogen species (RONS). The reactive species produced by plasmas are the same molecules that the human body generates for signaling or antimicrobial effects. Plasma treatment of eukaryotic cells can thus cause a similar effect as an innate immune system oxidative burst and plasma at low doses can mimic an immune response to tissue damage, wounds or infection which could initiate a natural healing response. Utilizing plasma-generated RONS for plasma-aided wound healing or plasma oncology is therefore a promising alternative to conventional treatments and the effectiveness of plasma for wound healing and cancer treatment has been shown in vitro and in vivo. Yet, the mechanisms of action and the delivery of RONS to the target are currently still under investigation.

In this contribution we will explore the cocktail of active ingredients; the generation and transport of the reactive species O and OH from the gas phase through a liquid to a biological sample and investigate the role that the biological sample plays as part of the reaction pathway. Using the model biological sample cysteine, which is often found in proteins that play a key role in signaling, the differences between a more OH/H_2O_2-dominated chemistry and a more O-dominated chemistry is explored. The results indicate that the modifications caused by a OH/H_2O_2-dominated chemistry are similar to those that can be found in context of redox biology, whereas modifications caused by O-dominated chemistry differ significantly. Atomic oxygen is unknown in nature whereas OH and H_2O_2 are well known and produced by organisms. The cocktail of active ingredients in a plasma and the variety of different plasma sources available makes it thus difficult to assess and generalize the impact of plasma on cells. On the other hand, the tunability of plasma and the possibility to tailor RONS production to certain outcomes provides a promising and powerful tool to aid the healing of chronic wounds or to develop new strategies in cancer treatment.

NANO 2 / Nanomaterials and nanostructured thin films

- Thermal evolution of bilayers composed of fcc nanoparticles prepared by gas aggregation cluster source

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In the presented work, we investigated thin films consisting of face-centered cubic metallic nanoparticles. First, copper, silver and gold nanoparticle layers were studied individually, subsequently, bilayers of these nanoparticles were deposited and analyzed.

Studied nanoparticles were prepared by Haberland type gas aggregation cluster sources, which are using magnetron sputtering of single metallic targets. This physical preparation method is environmentally friendly, scalable to industrial demands and provides high cleanness of the process.

Copper, silver and gold nanoparticles belong to plasmonic nanoparticles, in which it is possible to couple electromagnetic field with the collective oscillations of conduction electrons - plasmons. These nanoparticles have a great application potential because for all of them the localized surface plasmon resonance is in the region of visible light.

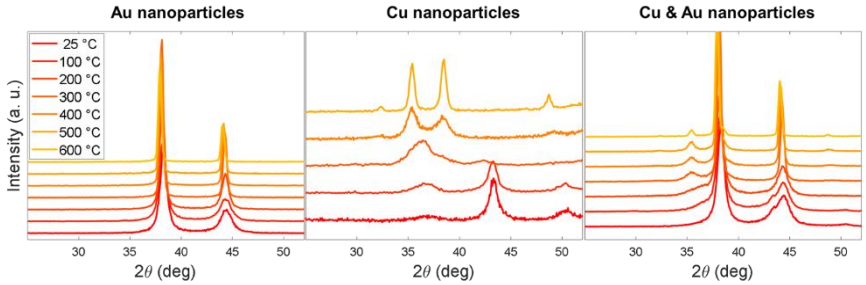
Our study is focused on the thermal stability of described nanoparticle layers and temperature changes in their optical properties. The thermal evolution of morphology, chemical and phase composition, size distribution and microstructure of Cu, Ag and Au nanoparticles was determined by combining in-situ x-ray scattering methods (XRD, SAXS) and ex-situ scanning electron microscopy (SEM). Optical properties of the layers were analyzed by UV-Vis spectroscopy and ellipsometry.

Copper nanoparticles are not stable in the air atmosphere, the oxidation process starts immediately after removal from the deposition chamber and core-shell Cu@Cu_2O nanoparticles are formed. Cu nanoparticles further oxidize during the heating process, but the size of nanoparticles is almost constant up to 200 °C. Additional layer of Au/Ag nanoparticles at the top of copper nanoparticles slows down the oxidation. In contrast to copper nanoparticles, no oxidation was observed during annealing of silver and gold nanoparticles up to 800 °C. SAXS and SEM measurements showed that silver nanoparticles are less stable than the gold ones, Ag nanoparticles start to coalesce around 100 °C. During annealing, the size of the crystallites increases and the amount of microstructural defects (microstrain, stacking faults) is reduced for all types of layers. The film properties further depend on the bilayers sequence order.

Thanks/Acknowledgement

This study was financed by the Grant Agency of Charles University (grant 1546119) and by the project NanoCent, Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

XRD patterns measured during the sample annealing



NANO 2 / Nanomaterials and nanostructured thin films

- One-step nanocomposite thin films synthesis by direct liquid injection of a colloidal solution in a low-pressure plasma: optimization of the nanoparticles distribution

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Nanocomposite thin films are attracting increasing interest due to the enhanced properties they exhibit. Their particularly high surface-to-volume ratio compared to traditional composite materials allows nanocomposites to combine more efficiently the properties of their constituents. More specifically, incorporating TiO_2 nanoparticles in an SiO_2 amorphous matrix could lead to quality high-κ insulators, self-cleaning coatings, or optical thin films. A reliable, versatile and tunable process is still needed for the growth of nanocomposite thin films with controlled morphology and nanoparticles distribution. One strategy consists in the use of direct liquid injection of a nanoparticles-containing colloidal solution in plasma deposition systems, like atmospheric pressure DBD[1]. Previous research in our lab led to the development of a safe-by-design one-step process coupling low-pressure PECVD for the SiO_2 matrix and direct liquid injection of a TiO_2 colloidal solution for the nanoparticles[2]. One of the main challenges with this kind of approach is the control of droplet evaporation during their transport from the injector to the substrate. Indeed, droplets impacts on the substrate can lead to either pollution of the sample by solvent residue, or nanoparticles agglomeration in so-called “coffee-ring” shapes. This phenomenon can reduce the surface-to-volume ratio and thus be detrimental for the targeted properties. The aim of the present work is to reduce the impact of slow evaporation on the final distribution of TiO_2 nanoparticles in the films. The strategy to achieve this goal involves: 1) the use of a low-flow injector to limit the quantity of liquid entering the reactor per injection, 2) the use of solvents of higher volatility for the colloidal solution, and 3) biasing the substrate up to -100 V, which is expected to have a significant influence on charged droplets trajectory, and therefore on their evaporation during transport. To study the effect of these parameters, the plasma is monitored by in situ time-resolved optical emission spectroscopy (OES) and film growth is followed through in situ spectroscopic ellipsometry. The chemical composition of the films is investigated by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Coffee-ring shapes size and distribution are studied using optical microscopy. Preliminary results have shown that biasing the substrate during deposition and using a highly volatile solvent both induced a notable decrease in the size of droplet imprints.

References

[1] Profili et al. 2016 Plasma Process. Polym. 13, 981 [2] Mitronika et al. 2021 J. Phys. D: Appl. Phys. 54 085206

NANO 2 / Nanomaterials and nanostructured thin films

- Nanoparticles and self-assembled nanotrusses generated through hollow cathode pulsed sputtering

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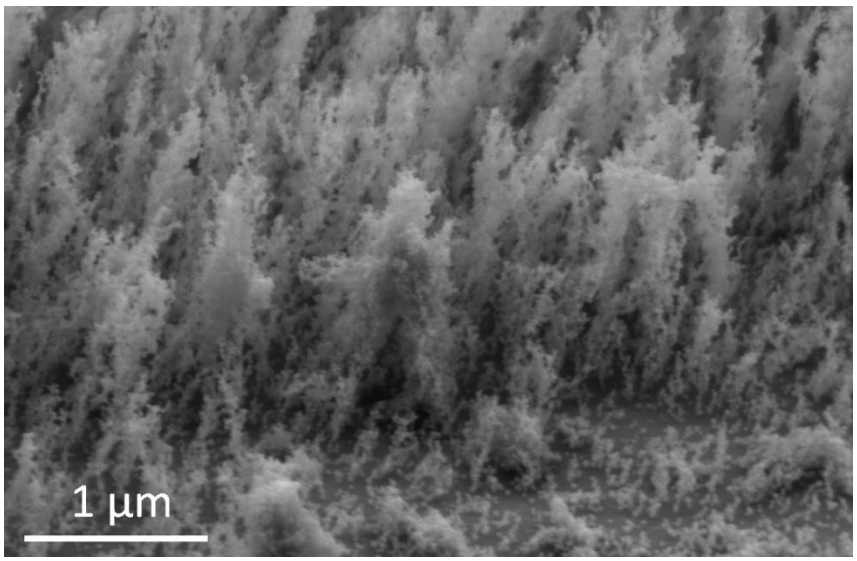
Nanoparticles in a plasma attains a negative potential due to the higher mobility of electrons as compared to ions. This open up interesting possibilities in synthesis of the nanoparticles as well as in guiding and assembling the nanoparticles into nanostructures. In this work, we use hollow cathode sputtering in combination with high-power pulsing to ensure close to full ionization of the sputtered source material. The trapping of positive ions on growing nanoparticles have been shown to be at least two orders of magnitude more effective than trapping neutral atoms, which promotes rapid growth of the nanoparticles to desired sizes.[1] The negative charge of the nanoparticles also makes it possibility to guide nanoparticles for assembly and collection on desired positions, by applying a positive electrical voltage to the collection site. For ferromagnetic nanoparticles, we also demonstrate generation of nanowires as well as nanowires cross-linked into trusses as seen in Fig. 1. Since the magnetic nanoparticles are generated under pure conditions, they assemble into wires without oxides in the interfaces.[2] Nanowires and trusses assembled on conducting substrates can potentially be competitively used as low-cost, large area electrodes, which we have demonstrate by using Pt diluted PtNi-alloys for the hydrogen generating electrode in electrocatalysis of water.

References

1. Pilch *et al*., Fast growth of nanoparticles in a hollow cathode plasma through orbit motion limited ion collection, *Appl. Phys. Lett.* **103**, 193108 (2013)
2. Ekeroth *et al*., Catalytic Nanotruss Structures Realized by Magnetic Self-Assembly in Pulsed Plasma, *Nano Lett.*, **18**, 3132-3137 (2018).

Nanotrusses from self-assembled PtNi-nanoparticles



NANO 2 / Nanomaterials and nanostructured thin films

- Charge gas and discharge parameters influence on kinetic and nucleation in RF Ar/C_2H_2 plasmas

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Low pressure Ar/C2H2 CCRF plasma with a showerhead electrode inlet gas configuration has been studied with a 1D fluid model. This model coupled a 13.56MHz RF discharge module and a long time scale module for describing chemistry and molecular growth kinetics. The flow influence on the discharge equilibrium and the surface processes is analyzed. Such plasmas are characterized by a strong coupling between electron-impact and argon metastable quenching on acetylene. This leads to the formation of hydrocarbon ions and radicals by ionization and dissociation reactions which result in molecular growth through neutral and ionic routes. A study over the discharge and the feed gas parameters has been performed in order to understand their impact on the plasma dynamic, the different nucleation routes and the surface deposition. Figure 1 shows the effects of the flowrate on the electron density, ne, and temperature, Te, for a 96:4 Ar:C2H2 discharge at 10 Pa. At high flowrate, the discharge is dominated by C2H2+ as the acetylene is easier to ionize. One can see that the decrease of the flowrate leads to a smaller electron density and an Ar+ dominated plasma due to a higher depletion of C2H2. The composition of the gas also affects the plasma and the chemistry. The influence of the percentage of acetylene in the feed gas on the kinetics of neutral and negative nucleation and of surface deposition on the electrode is presented in figure 2 for a flowrate of 18.6 sccm and a pressure of 10 Pa. This work also underlined the key-role of Argon metastable in the kinetics of carbon materials (films or dusts) production in non-equilibrium discharges.

Thanks/Acknowledgement

This work was partly supported by the French National Research Agency (ANR) through the MONA project (ANR-18-CE30-0016)

References

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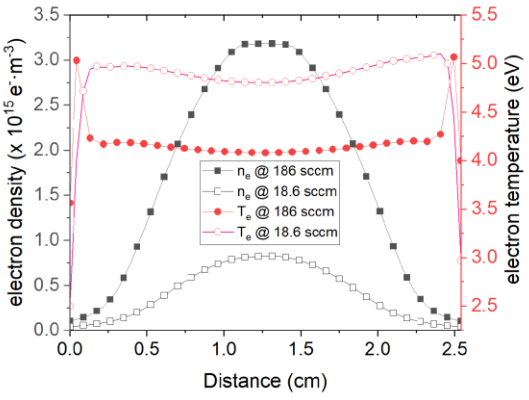
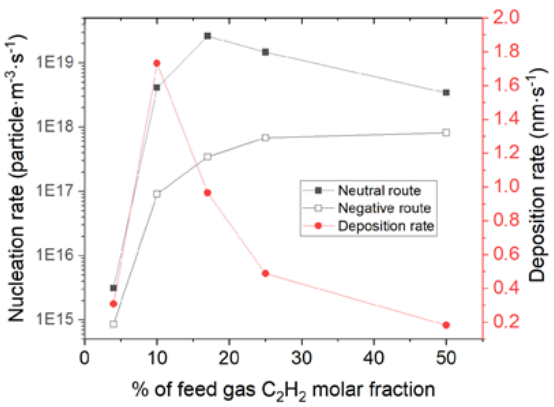
ne and Te in a 4:96 Ar:C2H2 10 Pa RF plasma



Rates for different compositions at 18.6sccm



NANO 2 / Nanomaterials and nanostructured thin films

- Pulsed aerosol assisted plasma deposition: influence of the injection parameters on ZnO/DLC nanocomposite thin films

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Aerosol-assisted processes enable to deposit thin films, homogeneous [1,2] or nanocomposite [3,4,5,6]. For example, the nebulization of colloidal solutions, i.e. liquid solutions containing nanoparticles, in different plasma processes has been widely used for nanocomposite thin film deposition. However, nanoparticles loaded droplets in the aerosol lead to the deposition of aggregated nanoparticles embedded in the matrix. Recently, a new process of nanoparticles injection has been developed [7]. This method, called reactor-injector of nanoparticles, consists in synthesizing nanoparticles prior to their injection in the plasma in a pulsed injection regime. It enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in the matrix [7]. This work aims to study the deposition of ZnO/DLC nanocomposite thin films in a low-pressure RF plasma. The main challenge of this process is to find the best compromise between the parameters for an efficient synthesis of ZnO nanoparticles and an optimal behaviour of low-pressure RF plasmas in a pulsed regime. It is shown that the operating window enables to deposit nanocomposite thin films with an extended range of volume fraction.

References

[1] Hou, X., & Choy, K. L. (2006). Processing and applications of aerosol-assisted chemical vapor deposition. Chemical vapor deposition, 12(10), 583-596.
[2] Palumbo, F., Porto, C. L., Fracassi, F., & Favia, P. (2020). Recent advancements in the use of aerosol-assisted atmospheric pressure plasma deposition. Coatings, 10(5), 440.
[3] Palgrave, R. G., & Parkin, I. P. (2006). Aerosol assisted chemical vapor deposition using nanoparticle precursors: a route to nanocomposite thin films. Journal of the American Chemical Society, 128(5), 1587-1597.
[4] Mitronika, M., Profili, J., Goullet, A., Gautier, N., Stephant, N., Stafford, L., ... & Richard-Plouet, M. (2020). TiO2–SiO2 nanocomposite thin films deposited by direct liquid injection of colloidal solution in an O2/HMDSO low-pressure plasma. Journal of Physics D: Applied Physics, 54(8), 085206.
[5] Profili, J., Levasseur, O., Blaisot, J. B., Koronai, A., Stafford, L., & Gherardi, N. (2016). Nebulization of nanocolloidal suspensions for the growth of nanocomposite coatings in dielectric barrier discharges. Plasma Processes and Polymers, 13(10), 981-989.
[6] Fanelli, F., Mastrangelo, A. M., & Fracassi, F. (2014). Aerosol-assisted atmospheric cold plasma deposition and characterization of superhydrophobic organic–inorganic nanocomposite thin films. Langmuir, 30(3), 857-865.
[7] Khan M.L., Champouret Y., Clergereaux R., Vahlas C., and Mingotaud A.-F., “Process for the preparation of nanoparticles,” EP 16305977.7, 2016.

LIQU / Plasma and liquids

- Magnetron sputtering of copper, silver and gold onto oils for nanoparticle synthesis.

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Magnetron Sputtering (MS) onto liquids allows obtaining high purity dispersions of nanoparticles (NPs - Fig.1). We studied the sputtering of Cu, Ag, and Au onto castor and rapeseed oil (and its polymers) as these vegetable oils are low cost and non-toxic, can be stored in air, and withstand vacuum. The effect of sputtering time and power, Ar pressure, type of sputtering plasma (dcMS vs Bipolar HiPIMS), and viscosity of host liquid are studied. The formation of a cloud of particles underneath the oil surface is observed (Fig.2) while films form for high viscosity oils. The scenario of NPs formation is inferred from experimental and theoretical analyses. Cu NPs oxidize rapidly in castor oil with formation of stable copper oxide NPs (3-10 nm for dcMS). Au NPs (2.4 - 3.2 nm for dcMS) have higher stability in castor oil than Ag NPs (1 - 4 nm for dcMS [1]) but secondary growth processes take place (Fig.1). Bipolar HiPIMS plasma promotes the formation of NPs twice larger than those obtained in dcMS mode.

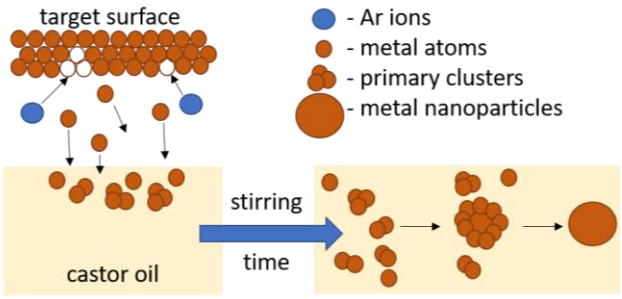
Thanks/Acknowledgement

S.K. and J.C. are senior research associate and research director of the National Fund for Scientific Research (FNRS, Belgium), respectively. S.K. and A.S. thank the FNRS for the financial support through the "SOLUTIoN" project No T.0134.19. The DFT calculations were supported by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the FNRS under Grant No. 2.5020.11. J.D.W. is grateful to the FNRS for the acquisition of the Waters QTof Premier mass spectrometer. A.C. acknowledges financial support from the project "Nanomaterials centre for advanced applications", Project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

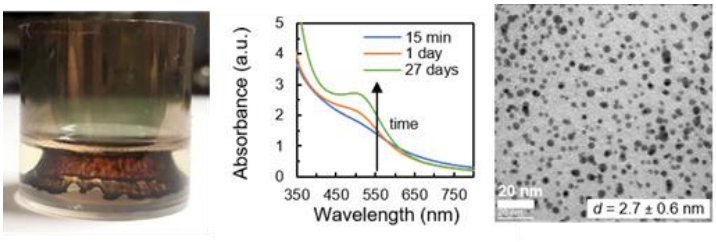
References

[1] A. Sergievskaya, A. O'Reilly, A. Chauvin, J. Veselý, A. Panepinto, J. De Winter, D. Cornil, J. Cornil, and S. Konstantinidis, Colloids Surfaces A Physicochem. Eng. Asp. 615, 126286 (2021).

Scenario of Au-NPs formation in castor oil



Characterization of Au-NPs



LIQU / Plasma and liquids

- Plasma-liquid interaction: a novel route to exfoliate graphite flakes and functionalize graphene.

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Graphene nanoparticles were produced by a nanosecond plasma discharge ignited at atmospheric pressure between a metal electrode and the surface of distilled water containing suspended graphite flakes. It is shown that the discharge was able to both functionalize the graphite particles in the liquid and to provide enough energy to break the Van der Waals bonds between the graphene planes, thus producing graphene flakes, depending on the surrounding atmosphere. Transmission electron microscopy confirmed the hexagonal structure of graphene sheets, and showed that they were monocrystalline and contamination-free. Meanwhile, the interaction of the discharge with the liquid also produced reactive species, especially OH radicals that functionalized the graphene flakes to make them less hydrophobic.

LIQU / Plasma and liquids

- Statistical analysis of the temporal evolution of spark discharges under various conditions of electrode configuration, liquid composition, and pulse magnitude and width

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Production of nanoparticles is one of the promising applications of spark discharges in liquid. The synthesis mechanisms are strongly related to plasma-surface and plasma-liquid interactions. On the other, the main barrier that limits further developing these discharges is related to reproducibility. Indeed, due to external uncontrolled factors, such as impurities, presence of low-density regions, microscopic state of the electrode surface, etc., the breakdown moment can significantly evolve within the pulse period. Therefore, discharges occurring at the beginning of the pulse and at the end of it exhibit very different characteristics, which may influence the characteristics of the synthesized nanomaterial. In this paper, we aim to put forward a statistical study of the influence of various discharge parameters (e.g. applied voltage, pulse width, nature of liquid, and electrode geometry) on the discharge characteristics, such as the discharge probability, the breakdown voltage, the discharge current, and others. These characteristics are monitored as a function of time, by letting them naturally evolve, until the moment when no discharges occurred. The time evolution of the discharges is mainly due to electrode erosion that induces i) an increase of the interelectrode gap, ii) a modification of the electrode geometry, iii) and a change in liquid properties. Each experiment lasted between 400 and 38 000 discharges, depending on the four parameters mentioned previously. By reporting the variation of the discharge characteristics, information of important nature are revealed and will be discussed. The findings can be further utilized in the context of the production of nanoparticles, where a control of the discharge characteristics is required.

Thanks/Acknowledgement

We would like to thank the Fonds de Recherche du Québec – Nature et Technologie (FRQ-NT) and the Canada Foundation for Innovation (CFI) for funding the research infrastructure. We would also like to thank Pr. Paul Charbonneau and Luc Turbide from the University of Montreal, for allowing us to use their servers to perform our data analysis. We would like to thank Léonard Sauvé for his guidance.

References

Hamdan, A., Profili, J. and Cha, M.S., 2020. Microwave plasma jet in water: effect of water electrical conductivity on plasma characteristics. Plasma Chemistry and Plasma Processing, 40(1), p.169-185. Beroual, A., 2016. Pre-breakdown mechanisms in dielectric liquids and predicting models. Institut of Electrical and Electronics Engineers, Conference paper. T. J. Lewis et al., 1962. A Statistical Interpretation of the Electrical Breakdown of Liquid Dielectrics. Proc. R. Soc. Lond. A 1962 269, 233-248

- Investigation of the streamer propagation at air-water interface: influence of water conductivity and other discharge conditions.

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Non-thermal plasmas produced by nanosecond discharges is a novel field of plasma physics that have huge interest for many applications. Although this field is under investigation since more than one decade, our understanding of the fundamental mechanisms is still at an embryonic level. Moreover, when such a plasma is coupled with a dielectric surface (solid or liquid), novel processes are identified. Here, we present a study on the dynamics of pulsed nanosecond discharges, produced by a positively polarized voltage in air in contact with water. The gap distance between the anode and the water surface was 10 µm . The investigated parameters are the voltage applied and the conductivity of the water. The voltage was adjusted from 9 to 20 kV, while the volume of water was adjusted at 20, 60, and 160 ml. These different volumes produce a water film that has a thickness of 6, 17, and 45 mm, respectively. The discharge dynamics on the water surface was monitored using ICCD camera and the acquired images were integrated during 1ns. We observed that the streamer ignites in air at the anode tip and propagates towards the water surface. Initially, it has a disk-like shape that evolves (after a few nanoseconds) to a ring who breaks into dots that propagate on the water surface. Automated statistical analysis performed on a large number of images as well as on their electrical characteristics allowed us to identify the position of the dots and to establish their temporal evolution. As for the influence of the voltage amplitude, we observed that its augmentation leads to an augmentation of the propagation velocity of the dots; this can be explained by the increase of the electric field intensity at water surface. This latter depends not only on the applied field but also on that produced by the space charge at the streamer heads, i.e. the plasma dots. Because the plasma dynamics as well as the electric field at water surface are highly sensitive to water electrical conductivity, the influence of this latter will be also investigated, and the results will be communicated during the conference.

LIQU / Plasma and liquids

- The dependance of the selective anti-cancer nature of plasma-activated solutions on short- and long-lived reactive oxygen and nitrogen species

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Cancer has been one of the leading causes of death over the last decades. Cancer treatment involves surgery, radiation, and drugs such as chemotherapy. The anti-cancer drugs inhibit cell division and proliferation and, usually, their effects are not selective towards cancer cells. Cold atmospheric-pressure plasmas (CAPPs) have been extensively studied over the last years as a potential cancer treatment, alone or in combination with the other conventional treatments mentioned above. In this study, we assessed the anti-tumour capacity of direct and indirect plasma treatments, using two models of head & neck cancer cells, i.e. CAL27 and FaDu, and three normal cell lines (primary human fibroblasts, primary gingival keratinocytes, and epithelial cells), in terms of metabolic cell activity, cell viability, lipid peroxidation, intracellular ROS production and caspase 3/7 induction. We show that during indirect plasma treatments (plasma off), plasma-activated solutions induce cell death selectively to cancer cells, as the normal cells are barely affected. On top of that, we provide evidence that this anti-cancer effect of plasma-activated solutions is mainly due to the combination of its composition in H2O2 + NO2– + NO3– with its acidic pH. On the other hand, direct plasma treatment is more effective in reducing cell viability in vitro than indirect plasma treatment, especially towards normal cells. This hypersensitivity of normal cells to direct plasma treatment is a result of the synergistic effect of the plasma treatment time (plasma on) and the incubation time in the plasma-activated solution (plasma off). It should be noted that normal cells are very resistant to these treatment modes when applied separately. We demonstrate that this synergy is due to the action of short-lived reactive species, that can operate during the plasma treatment and the first seconds/minutes of incubation in the plasma-activated solution immediately after the plasma being switched off. To conclude, we show that normal and tumour cells respond differently to plasma-activated liquids, whether we consider the direct or indirect plasma treatments, providing a basis for practical application in cancer therapy of plasma-activated solutions or even of mimicking solutions containing H2O2 + NO2– + NO3– and slightly acidic pH.

Thanks/Acknowledgement

This work was financially supported by the LabEx LaSIPS (project PHeCell3d) and the Université Paris-Saclay (Strategic Research Initiative NanoTheRad), and performed in the framework of the CNRS network GdR 2025 HAPPYBIO.

References

[1] P.-M. Girard et al., Sci. Rep. 6, 29098 (2016)
[2] K. Sklias et al., Cancers 13, 615 (2021

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DEPO 4 / Plasma - deposited coatings

- Influence of lanthanum stoichiometry in La_xFeO_y perovskites on their photocatalytic performances in hydrogen production by water splitting.

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The transition from a civilization that is fossil-fuel dependent to one that is solar-powered, and which uses ubiquitous and abundant molecules as feedstocks in a circular manner is one of the grandest scientific and technological challenges of our times. In this context, hydrogen is a promising energy carrier, albeit current technics of its production are pollutant and/or exhibit a lack of efficiency. Photoelectrochemical (PEC) water splitting is one of the most promising processes to generate H_2 but the PEC efficiency is limited by the semiconductor photocatalyst performances. Lanthanum ferrite ($LaFeO_3$) is a suitable material for photocatalytic applications due to its high visible light absorption, stability and low cost. However, its performances are limited by a high charge recombination rate due to the modest electron transport. In recent years, various methods have been developed to improve the light absorption and the charge transport in photocatalysts. For instance, we showed that $LaFeO_3$/g-C_3N_4 heterostructured thin films led to an increased amount of produced hydrogen by 74% compared to pure $LaFeO_3$ [1].

Another strategy is the development of non-stoichiometric materials. **In this work, the influence of the stoichiometry of La_xFeO_y thin films on their photocatalytic activity for H_2 production was investigated.** Thin films were deposited on electrodes by magnetron co-sputtering. The composition was controlled by adjusting the power applied on the metallic targets. The highest photoactivity was observed for $La_{0.43}FeO_y$ films. The crystallization of these films and their photocatalytic activity were further improved by oxidation in an external furnace at 650 °C for 2 h. TEM analyses confirm the formation of $LaFeO_3$ crystallites in the film and show a continuous polycrystalline Fe_2O_3 layer at the surface. The presence of Fe_2O_3 at the upper surface originates from an exsolution mechanism typically observed for non-stoichiometric perovskites [2]. The improvement of the photocatalytic properties by adjusting stoichiometry, oxidation temperature and film thickness was confirmed by H_2 production measurements. We observe an increase of the H_2 production rate of 103% by comparison with a stoichiometric $LaFeO_3$ thin film. **The increase in catalytic performances for these non-stoichiometric films composed of earth abundant, low-cost and non-toxic elements, make them of high interest materials for photoelectrodes in PEC water splitting systems.**

Thanks/Acknowledgement

This work was supported partly by the French PIA project « Lorraine Universite d'Excellence », reference ANR-15-IDEX-04-LUE.

References

[1] V. Guigoz et al., International Journal of Hydrogen Energy 45 (2020) 17468-17479.
[2] O. Kwon et al., Nature Communications 8 (2017) 15967.

DEPO 4 / Plasma - deposited coatings

- Enhancement of high-temperature oxidation resistance and thermal stability of hard and optically transparent Hf-B-Si-C-N films by Y or Ho addition

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Multielement ceramic coatings are appropriate candidates for high-temperature applications due to their excellent behavior at temperatures exceeding 1000°C. When a very high oxidation resistance is combined with the thermal stability of a high optical transparency, they can be considered for high-temperature passive protection of optical and optoelectronic devices. Therefore, this work focuses on a systematic investigation of high-temperature behavior of Hf-B-Si-Y/Ho-C-N films with a high hardness and optical transparency [1]. The films were deposited using pulsed dc magnetron co-sputtering of a target consisting of a B_4C plate overlapped by Hf, Si and Y or Ho stripes with the fixed 15% Hf + 50% Si + 5% Hf/Y/Ho fractions in the target erosion area in an argon-nitrogen gas mixture (25% N_2 fraction) onto Si and SiC substrates heated to 450°C and held at a floating potential. The oxidation resistance of the films in air (up to 1500°C) and the thermal stability of their structure in inert gases (up to 1600°C) were investigated by high-resolution thermogravimetry and differential scanning calorimetry. Other analytical techniques were employed to characterize changes in the structure and properties of the films after their heat-treatment. All as-deposited films were amorphous, highly optically transparent, electrically non-conductive and possessed a sufficiently high hardness (around 22 GPa) and low compressive stress (< -1.5 GPa). Very low mass changes (around 25 μg/cm^2) were detected upon heating to 1500°C in air. $Hf_6B_{12}Si_{29}Y_2C_2N_{45}$ and $Hf_5B_{13}Si_{25}Ho_3C_2N_{48}$ films exhibited a lower thickness of a protective surface oxide layer (194 nm and 202 nm, respectively) compared to a $Hf_6B_{10}Si_{38}C_2N_{44}$ film (243 nm). The oxide layer was composed of HfO_2 nanocrystallites of different structures embedded in an amorphous matrix. Heating of the films in helium up to 1100°C resulted in an increase of their hardness while retaining optical transparency. In case of the $Hf_6B_{12}Si_{29}Y_2C_2N_{45}$ film, the hardness increased even up to 1300°C and the film remained optically transparent up to 1400°C. It was also found that the transformation of the amorphous structure to the crystalline one starts in all cases around 1400°C at the film/substrate interface. The lowest thickness of the crystallizing zone was observed for the $Hf_6B_{12}Si_{29}Y_2C_2N_{45}$ film confirming its highest thermal stability among the films investigated. Multielement Hf-B-Si-Y/Ho-C-N films were proven to have a high potential to be good candidates as high-temperature protective coatings for optical and optoelectronic devices.

References

[1] M. Kotrlová et al., J. Non-Cryst. Solids, 553 (2021), 120470.

DEPO 4 / Plasma - deposited coatings

- $MgSnN_2$ a new semiconductor material for optoelectronic applications

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III-N materials are commonly used as active layers in LEDs, transistors, solar cells and mechanical devices[1, 2]. The main spinneret is based on the use of InGaN alloys. However, such layers contain indium and gallium. Significant volatility in their price and supply over the last years has led to considerable concern given their critical roles and their use in a wide range of large-scale electronic devices. Moreover, at present the crystalline III-N materials require the use of epitaxial growth techniques with high cost and high complexity. It is important to study and develop new earth abundant materials with optimized properties for the realization of innovative optoelectronic devices that could be competitive cost for mass production. In this work, we aim at developing a new kind of inexpensive, indium/gallium-free, nitride material that could be the basis of new way for optoelectronic applications. The study of such very innovative material is an ambitious goal but has already started in various countries (Japan, USA). The studies are focusing on $MgSnN_2$ thin films (bandgap energy ≈ 2 eV) that is a good candidate for green emitters in LEDs and an absorber material in tandem photovoltaics[3]. $MgSnN_2$ thin films have been deposited by magnetron co-sputtering at different substrate temperatures (up to 500 °C). The Mg/Sn atomic ratio has been controlled by the current applied to the Mg and Sn targets. The structure of the films has been studied by X-ray diffraction. Whatever the deposition temperature, the films crystallize in a wurtzite-like structure with a strong preferred orientation in the [002] direction. The columnar microstructure of $MgSnN_2$ thin films have been studied by transmission electron microscopy. The optical band gap deduced from UV-visible spectroscopy is ranging in the 2.1 – 2.4 eV range. The electrical resistivity, carrier concentration, type and carrier mobility have been measured by Hall effect. Finally, the chemical environment of the Sn atoms has been investigated using Mössbauer spectrometry.

References

(1) Nakamura, S. et al. InGaN/GaN/AlGaN-Based Laser Diodes with Modulation-Doped Strained-Layer Superlattices Grown on an Epitaxially Laterally Overgrown GaN Substrate. Appl. Phys. Lett. 1998, 72 (2), 211–213. https://doi.org/10.1063/1.120688.
(2) Amano, H. et al. Metalorganic Vapor Phase Epitaxial Growth of a High Quality GaN Film Using an AlN Buffer Layer. Appl. Phys. Lett. 1986, 48 (5), 353–355. https://doi.org/10.1063/1.96549.
(3) Yamada, N. et al. Composition-Dependent Properties of Wurtzite-Type Mg1+xSn1–XN2 Epitaxially Grown on GaN(001) Templates. ACS Appl. Electron. Mater. 2021. https://doi.org/10.1021/acsaelm.0c01115.

SOUR / Plasma sources and electrical discharges

PL7 ● Electrical diagnostics for Dielectric Barrier Discharges: from integrated measurements to spatially resolved measurements. Benefits for plasma processes at atmospheric pressure?

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Dielectric Barrier Discharges (DBDs) can be used in many processes as thin-film coating, sterilization, treatment of gases, aerodynamic flow control, and lighting devices [1]. Depending on the gas, electrical operation parameters and discharge geometry, the plasma operates in the classical filamentary mode or in a homogeneous regime [2]. Electrical measurements are a more convenient than optical measurements to characterize the discharge regime and to study the discharge behavior. However, and because of the dielectric presence, it is not possible to directly measure the electrical parameters of the discharge. Usually, the electrical parameters are calculated from the measured quantities under usage of an electrical equivalent circuit [4]. The key parameter for this approach is the determination of the discharge area, which is usually considered to be equal to the electrode surface as long as the discharge is homogeneous. However, even if the plasma seems to cover the electrodes uniformly, its electrical properties (current density, breakdown voltage, duration of discharge, …) are not exactly the same at any time and at any point of the surface. For example, when a gas flow is injected from one side of the planar DBD arrangement, tthe species densities are not the same along the gas flow because of the kinetic processes and chemical reactions in the discharge [4]. Thus, the discharge current and the gas voltage are not uniform along the spatial DBD dimensions. Therefore, determination of discharge current and gas voltage from macroscopic parameters of the DBD is often inacurrate.

In order to have a more accurate characterization of the discharge behavior, a measurement of the local current density is required. To get a 2D mapping of the discharge electrical parameters, the ground electrode is prepared as a segmented electrode with 64 equally spaced square segments. The high voltage electrode still remained full. This electrode is a 3x3 cm^2 square, while each square of the segmented electrode has a 3.44 mm side length, a distance of 350 mm spaced each segments. A prototype, using a ground electrode divided into 64 identical squares and a data acquisition system has been developed [5]. This system can be used to study the spatial electrical behavior of a DBD. It has been successfully validated on planar DBD by the comparison with short exposure time photos taken by a camera from above the discharge cell [5]. It has been used to study the diffuse discharge (APTD) and shows the effect of a gas flow on the local electrical behavior of the discharge. In the case of diffuse DBDs with sinusoidal voltages at frequencies from 1 to 20 kHz, the temporal and spatial resolutions are high enough to characterize the behavior of the discharge with sufficient spatial information.

This electrode arrangement and measuring systems allows a 2D mapping of the discharge electrical parameters (discharge current, power dissipated, gas voltage, etc.) of Townsend but also for Glow discharges, hybrid or patterned regimes. Concerning the plasma processes for surface coatings, this system can be used to monitor the evolution of the local discharge power which defines the local deposition rate. If we use this segmented electrode as the high voltage electrode with adequate power supply, we could reconfigure the electrode and the power transfer to the discharge. Then this system could be used to realized patterns. All of this opens up new directions which will be discussed during the presentation.

References:

1. U. Kogelschatz, Plasma Chem Plasma P 23 (1), 1-46 (2003).
2. R. Brandenburg, Plasma Sources Science and Technology 26 (5), 053001 (2017).
3. A. V. Pipa, J. Koskulics, R. Brandenburg and T. Hoder, Rev Sci Instrum 83 (11), 115112 (2012).
4. C. Tyl, X. Lin, M. C. Bouzidi, S. Dap, H. Caquineau, P. Segur, N. Gherardi and N. Naudé, J Phys D Appl Phys 51 (35) (2018).
5. C. Tyl, S. Martin, C. Combettes, G. Brillat, V. Bley, A. Belinger, S. Dap, R. Brandenburg, N. Naudé, Rev Sci Instrum 92 (5), 053552 (2021).

NANO 3 / Nanomaterials and nanostructured thin films

- Effect of exit-orifice size on Cu nanoparticles produced by gas-aggregation source

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In nanoparticle production by magnetron sputtering and subsequent gas aggregation, there are many parameters influencing the process of nanoparticle formation. One of the key parameters is the pressure of the background working gas. The pressure is usually controlled by adjusting the flow rate, which however leads to an undesirable simultaneous change of two important parameters, both influencing the formation of the nanoparticles. In this work, we introduce an additional parameter influencing the pressure of the working gas. Changing the aggregation chamber exit-orifice diameter allows us to isolate and investigate the effect of the working-gas flow rate at a given constant pressure. The experimental results show that the conventional approach of changing pressure by adjusting the flow rate (at a constant orifice diameter) does not significantly influence the nanoparticle size or their deposition rate. However, when the pressure is held constant, changing the flow rate has a notable effect. We suggest that the determining parameter which needs to be considered is the pressure to flow rate ratio. This ratio determines the residence time of the nanoparticles inside the aggregation chamber (and therefore the time available for them to grow) and is constant for a constant orifice diameter. Decreasing the orifice diameter, however, increases the pressure to flow rate ratio, gives the nanoparticles longer time inside the aggregation chamber and allows them to grow larger. Apart from their size, the orifice diameter also influences the deposition rate and its angular distribution.

NANO 3 / Nanomaterials and nanostructured thin films

- In situ plasma pre-treatments of Silicon for ALD of Al_2O_3

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One common drawback of the Atomic Layer Deposition (ALD) is the phenomenon of discrete nucleation on the initial surface, which lead to a non-continuous growth of very thin layers. For instance, on conventionally cleaned silicon, it is impossible to grow a continuous layer of Al2O3 thinner than 3nm by ALD using Trimethylaluminum (TMA) and water (H2O) [1].

In this work, we study the influence of in-situ plasma treatments in an ALD equipment just before Al2O3.

First part studies the creation of an interfacial layer by nitridation/oxidation of the silicon using an Inductively Coupled Plasma of N2, NH3 and/or O2. We show that it allows in any case a strong enhancement of the density of the nucleation site, leading to an apparent linear kinetic of deposition versus the number of ALD cycles. Material characterizations at the atomic scale allow the comparison of the Si3N4, SiON and SiO2 interfaces and their combination with the deposited Al2O3. They emphasize the importance of in-situ processing, in order to avoid oxidation in air.

Second part studies the effect of the in-situ cleaning/etching of the silicon by SF6 or H2 plasmas. In both cases, we show that pressure, plasma power and time parameters lead to a strong decrease of the nucleation density. For instance, with SF6 plasma, the deposition kinetic exhibits a delay of growth of about 60 cycles, instead of about 5 in case of conventionally cleaned silicon. This phenomenon can be simulated by a decrease of the nucleation density by a factor of 200, i.e. a relative density of nuclei of about 2.5x 10-5. AFM characterizations confirm the existence of these nuclei, which are revealed by performing hundreds of ALD cycles. Also the deposition kinetic of Al2O3 in the first cycles is a marker of the silicon surface cleanness, and that in-situ plasma etching can be useful for the optimization of this property.

The combination of in-situ plasma cleaning and plasma nitridation of silicon seems then a promising solution for the realization of <3nm films with good insulating properties.

Thanks/Acknowledgement

This work was supported by LAAS-CNRS micro and nanotechnologies platform member of the French RENATECH network.

References

[1] G.P. Gakis, C. Vahlas, H. Vergnes, S. Dourdain, Y. Tison, H. Martinez, J. Bour, D. Ruch, A.G. Boudouvis, B. Caussat, E. Scheid, Investigation of the initial deposition steps and the interfacial layer of Atomic Layer Deposited (ALD) Al2O3 on Si. (2019) Applied Surface Science, 492. 245-254. ISSN 0169-4332

NANO 3 / Nanomaterials and nanostructured thin films

- Pulsed Laser Deposition for the fabrication of Gold nanoparticle arrays and Gold nanoparticles-Vanadium dioxide nanocomposites

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Since its discovery, Pulsed Laser Deposition (PLD) has gradually become relevant in the deposition of thin films with complex stoichiometry and for the manufacturing of nanostructures. By controlling the laser parameters, deposition environment (vacuum or gas: O_2, etc.), temperature of the substrate, PLD is also relevant for the deposition of metals and mainly of oxides and as proposed in this work to nanocomposites based on metallic arrays embedded in a thin film matrix. First, we develop arrays of Gold nanoparticles on a sapphire substrate. The nanoparticles are defined using combined colloidal lithography and PLD. The colloidal lithography is performed with a Langmuir Blodgett system, using polystyrene spheres of 3 µm in diameter deposited on c-sapphire. Then, a metallic film is deposited on the spheres by PLD with KrF laser (fluence: 2-3 J/cm^2). After removing the spheres, organized metallic quasi-triangular nanoplatelets (QTP) arrays are revealed. The formation of QTPs are possible due to the high directionality and low reactivity of ablated material given by PLD. Then, nanocomposites are fabricated by embedding the QTPs into a 200 nm epitaxial VO_2 matrix made by PLD. The morphological and structural characteristics of the nanocomposites are studied by local Raman spectroscopy mapping, H-R X-ray diffraction, FTIR spectroscopy, Scanning electron microscopy. The optical properties of the nanoparticles arrays and of the nanocomposites are investigated and demonstrated their ability to tune the transmission of light through the generation of localized surface plasmon resonances (LSPR). Particularly, due to the reversible metal-to-insulator (MIT) transition of VO_2 (TMIT ~ 68 °C), an active modulation (of more than 500 nm) of the LSPR is achieved. A theoretical approach (finite difference time domain method) correlated to the experimental data allows to attribute the modulation of the LSPR characteristics of the nanocomposite to the creation of a core-shell structure consisting of gold-QTP surrounded by metallic VO_2 and embedded into dielectric VO_2 evolving with temperature during the MIT of VO_2 matrix.

Thanks/Acknowledgement

This work is realized at the IRCER laboratory, France under financing supports from the French MESRI Ministry and the Labex – S_LIM (ANR-10-LABX-0074-01) Corresponding Author e-mail address: adrian.bercea@unilim.fr, corinne.champeaux@unilim.fr and frederic.dumas-bouchiat@unilim.fr

References

References: Packed colloidal spheres for thin film structuration; towards modulation and tunability of surface plasmon resonance A. BERCEA, C. CONSTANTINESCU, F. DUMAS-BOUCHIAT, C. CHAMPEAUX, PLUMEE 9 (1) (2019), http://pubs.ub.ro/?pg=revues&rev=plumee&num=201901&vol=9&aid=4970

- 2D electric field measurements in Ar plasmas using a fine particle trapped with optical tweezers

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High-precision nanofabrication based on plasma processing has been one of the main technology drivers of modern information society. Development of highly sensitive diagnostic methods in processing plasmas is imperative for understanding and controlling interactions between the materials and plasma. A diagnostic method using a fine particle in plasma is a possible solution. Here, we have measured two-dimensional profile of electric field strength in Ar plasmas using a fine particle trapped with laser tweezers. A plasma reaction vessel with a quartz window on the top and a sapphire window on the bottom was used in the experiments. The vessel was set up in an epi-illumination microscope. A metal mesh grounded electrode was placed in the center of the vessel, and a ring electrode with an inner diameter of 15mm and an outer diameter of 25mm was placed on the bottom of the vessel. The ring electrode was connected to a 13.56MHz rf power source through a matching box. When an acrylic particle of 20μm in diameter was introduced into the plasma, it was levitated in the plasma/sheath boundary region above the powered ring electrode. A single particle was trapped in plasma with optical tweezers[1]. Then it was moved horizontally with the laser. Figure1 shows that the levitation positions of the laser-trapped fine particle in Ar plasma at 60Pa for each laser power. At the levitation position, the electrostatic force and the force of lazser on the particle are balanced with the gravity. The force of the laser on the particle was obtained from an ray optical model[2], and a particle charge was deduced from Orbit motion limited(OML) model[3]. Therefore, we deduced vertical electric field strengths E_z from these derivations. These results of fig.1 give 2D profile of E_z with a range of 3×10^3 and 4×10^3[V/m] in plasma from the force balance of an optically trapped particle.

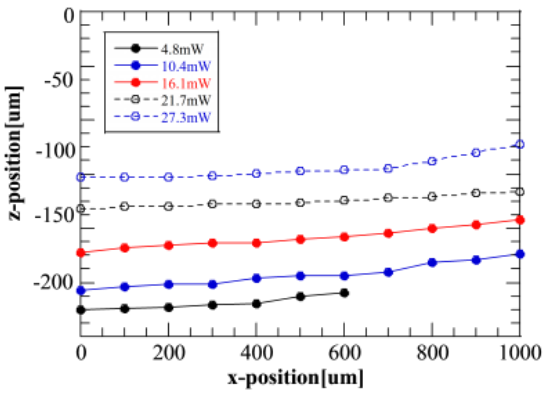
Thanks/Acknowledgement

This work was partly supported by JSPF KAKENHI(Grant No.JP19K03809 and JP20H00142).

References

[1] A. Ashkin, Biophys. J. 61(1992) 569. [2] Philip h. jones, et al., Optical Tweezers Principles and Applications, 22(Cambridge university press, 2015). [3] G. Paeva, Sheath phenomena in dusty plasmas, (Technische Universiteit Eindhoven, 2005).

Positional change in laser-trapped fine particles



PROC 4 / Process control

- Detection of trends in ground-state densities from optical emission spectroscopy data obtained during a controlled high-power impulse magnetron deposition of ZrO_2 films

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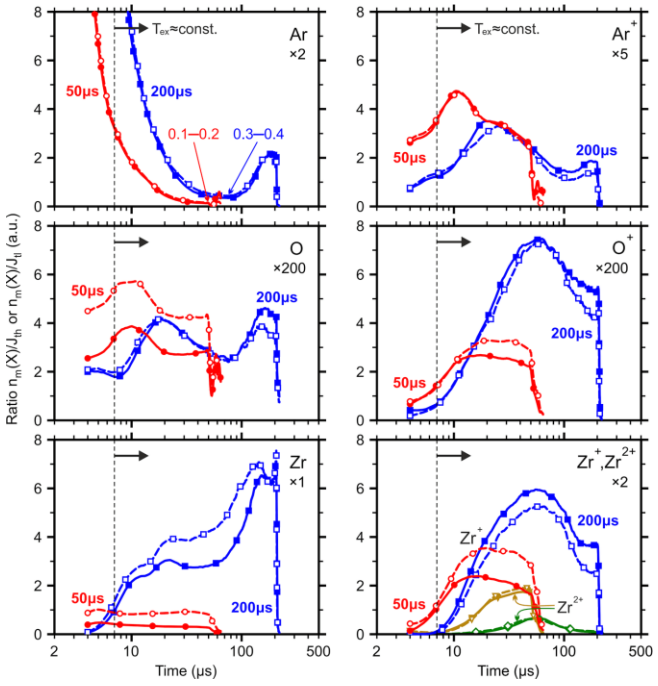
At our department, a feedback pulsed reactive gas flow control (RGFC) system had been developed to utilize exclusive benefits of the high-power impulse magnetron sputtering in a high-rate reactive deposition of stoichiometric films [1,2]. During depositions of ZrO_2 films, oxygen was admitted directly into a high-density plasma in front of the target and the O_2 flow rate was adjusted by the pulsed RGFC system according to the average discharge current in a period that oscillates in compliance with the instantaneous O_2 partial pressure, p_{ox}. The repetition frequency of the voltage pulses with a duration of t_{on}=50 and 200μs was 500Hz at the deposition-averaged target power density of 52–53Wcm^{-2} (peak target power density was 3.1kWcm^{-2} at t_{on}=50μs and 1.1kWcm^{-2} at t_{on}=200μs). The Ar partial pressure was 2Pa. The deposition rate of densified stoichiometric ZrO_2 films up to 120nm/min was achieved at t_{on}=200μs on a floating substrate 100mm from the target. From the excited-state populations, $n_m(X)$, of the atoms (X=Zr, Ar, and O) and ions (X=Zr$^+$, Zr^{2+}, Ar$^+$, and O$^+$) determined from the optical emission spectroscopy data, and from the constancy of the excitation temperature, T_{ex}, the trends in the time evolution of the local ground-state densities, $n_1(X)$, can be derived [4,5] according to relation $n_1(X)$~$n_m(X)/J_t$, where J_t is the target current density. The resulting trends of $n_1(X)$ near the target are shown in the appended figure for max. (full lines) and min. (broken lines) p_{ox}. The increased peak target power density leads to more intense Ar density reduction (owing to momentum transfer, heating, and ionization), the decrease of O_2 diffusion back to the target against the much stronger sputtering wind, and very intense ionization of the sputtered Zr atoms to Zr$^+$ and Zr^{2+} ions near the target.

References

[1] J. Vlcek, J. Rezek, J. Houska, R. Cerstvy, and R. Bugyi, *Surf. Coat. Technol.* **236** (2013) 550. [2] J. Vlcek, J. Rezek, J. Houska, T. Kozak, J. Kohout, *Vacuum* **114** (2015) 131. [4] A. D. Pajdarova, J. Vlcek, and J. Rezek, *J. Appl. Phys.* **121** (2017) 171908. [5] A. D. Pajdarova and J. Vlcek, *J. Vac. Sci. Technol. A* **37** (2019) 061305.

Trends in ground-state densities of particles.



PROC 4 / Process control

- Kinetic mechanisms in CO_2-N_2 plasmas

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This contribution reports the comparison of simulation results from a 0D self-consistent kinetic model with recent experimental data obtained in low-pressure DC discharges. This comparison allows the development of a new reaction mechanism (i.e., a set of reactions and rate coefficients validated against benchmark experiments) for CO_2-N_2 plasmas.

Investigating the impact of N_2 on the overall CO_2 conversion is relevant as N_2 can be present as an impurity in industrial CO_2 emission and can be used to promote CO_2 vibrational excitation. The system of election is a DC glow discharge, operating at pressures in the range p=0.1-10 Torr and discharge currents I=10-50 mA, in a Pyrex tube of radius R=1 cm, which is stable, axially homogenous, and easily accessible to a variety of diagnostics. The set of measurements provides the gas temperature, vibrational temperatures of CO_2, reduced field E/N, and densities of O(3P), NO, NO_2, CO($X^1\Sigma^+$) and CO2($X^1\Sigma^+_g$). The simulation results are obtained with the LoKI (LisbOn Kinetics) [1] simulation tool solving a Boltzmann-chemistry global model.

The admixture of N_2 has a beneficial impact on CO_2 decomposition [2,3]. Several reasons can be assigned to it, one of them being the transfer of vibration quanta from the first vibrational level of N_2 to the asymmetric mode of CO_2 and the fact that vibrationally excited CO_2 can undergo molecular dissociation through the so-called ladder climbing mechanism or by electron impact stepwise processes. The dilution with N_2 can also limit the influence of back reaction mechanisms producing back CO_2 from CO. These mechanisms will be discussed in the detail at the conference. Understanding the impact of the different processes on the overall kinetics, along with the validation against experimental data, will contribute to further develop the existing models [3-5] and to better control and enhance CO_2 conversion.

Thanks/Acknowledgement

Acknowledgments: This work was partially supported by the European Union's Horizon 2020 research and innovation programme under grant agreement MSCA ITN 813393, and by Portuguese FCT-Fundação para a Ciência e a Tecnologia, under projects UIDB/50010/2020 and UIDP/50010/2020.

References

[1] A. Tejero-del-Caz et al, Plasma Sources Sci. Technol. 28 (2019) 073001
[https://nprime.tecnico.ulisboa.pt/loki]
[2] M. Grofulović et al, Plasma Sources Sci. Technol. 28 (2019) 045014
[3] L Terraz et al, J. Phys. D: Appl. Phys. 53 (2020) 094002
[4] A F Silva et al, Plasma Sources Sci. Technol. 29 125020 (2020)
[5] S. Heijkers et al, J. Phys. Chem. C 119 (2015) 12815−12828