#PLATH00096
INDU / Industrial hot topics

A simple approach to transpose the deposition conditions in two different magnetron sputtering chambers: a case study of oxidation of sputter-deposited VN films

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Abstract content

Magnetron sputtering is a vacuum coating technique that enables the deposition of any metal, alloys or ceramic compounds onto a wide range of substrate materials. It is characterized by high purity films, high deposition rates, outstanding uniformity on large-area substrates, the possibility of excellent coverage of small features, and remarkably high adhesion of films. These peculiarities render this technique suitable for various applications, such as hard and wear-resistant coatings, decorative coatings, electronic thin films… [1]. Large-scale sputtering chambers are used to make possible these industrial applications. They differ from standard laboratory sputtering reactors in numerous attributes like volume, cathode dimension, pumping speed, substrate cleaning process, among others. Thereby, it is essential to establish a criterion to transpose the results from the lab standard machines to the industrial ones.

This work presents a simple approach to compare the deposition parameters between two different sputtering reactors: a semi-industrial and a laboratory-scale one. In our model, strong assumptions have been made. The difference in volume between the deposition chambers, the different pumping speeds in each machine, and the magnetron size have not been considered. We assume that the fundamental parameter that governs the growth of thin films is the energy at which the sputtered atoms arrive on the substrate surface. Hence, the criterion to have analogous films from both machines is that the sputtered atoms coming from the target arrive with the same energy at the substrate. A comparison of VN depositions and afterward oxidation of the as-deposited films is carried out to test the criterion. We fixed the deposition conditions of the semi-industrial machine. On the other hand, we conduct three sets of VN depositions with different working pressure at the same target-substrate distance in the laboratory-scale machine. The VN films of series II are deposited with the equivalent conditions of the semi-industrial chamber, series I and III with lower and higher working pressure, respectively. All films are post-oxidized in a furnace under atmospheric pressure at 550°C for up to 3.5 minutes. XRD and infrared camera show that the oxidized films from the semi-industrial chamber transform into thermochromic VO_2. For the samples from the laboratory-scale machine, only the oxidized films deposited with the analogous conditions (series II) display VO_2 with thermochromic performance. Our criterion evidence that it is possible to transpose depositions from one sputtering chamber to another (even to an industrial scale).

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#PLATH00018

NANO / Nanomaterials and nanostructured thin films

PtCu@TiO$_2$ nanoparticles by low pressure plasma

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Abstract content

Pt/Cu nanoparticles (NPs) are promising materials for catalytic application. However, those NPs are often synthesised using wet-chemical deposition procedures involving the extensive use solvents. In this work, a low-environmental impact synthesis technique based on the plasma driven decomposition of solid (powder) Pt and Cu organometallic (OM) precursors is studied. The NPs are deposited on a TiO2 powder substrate and synthesised using a low pressure inductively coupled Ar/NH3 plasma discharge. The choice of ammonia discharge limits the oxidation of the nanoparticles, without significant nitride formation. Various working pressures, treatment times, plasma powers and OM precursors ratios are tested, to form Pt, Cu and PtCu nanoparticles. The crystallinity, the size and the lattice parameters of the NPs are evaluated using X-Ray Diffraction (XRD) while the chemical states and the surface compositions are measured using X-ray Photoelectron Spectroscopy (XPS). Both chemical and crystallographic characterizations confirm the formation of metastable alloyed Pt-Cu nanoparticles. The difference of Pt and Cu concentrations in NPs measured with a volume technique (XRD) and a surface technique (XPS) suggests a Pt concentration gradient within NPs attributed to a difference in organometallics degradation kinetics.

#PLATH00082

NANO / Nanomaterials and nanostructured thin films

Local plasma-chemical etching of the silicon substrate surface by using of anodic alumina template

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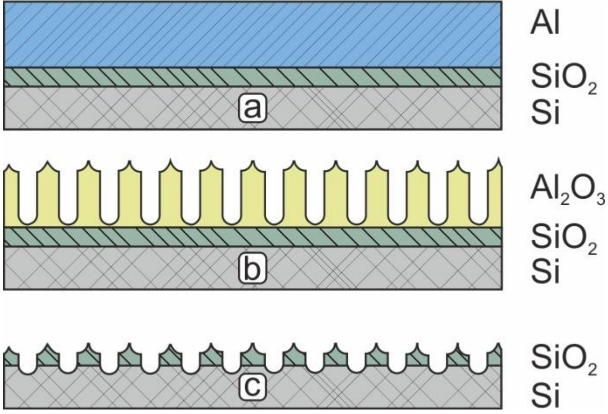
Abstract content

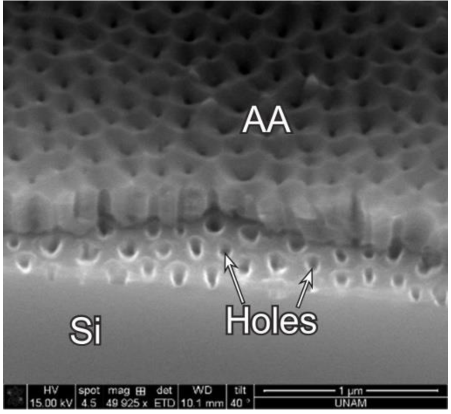
The research idea consists in forming thin functional layer on Si substrate with regularly arranged nanostructures to create on their basis efficient photovoltaic and sensor devices. The approach is to use regular nanoporous anodic alumina (AA) matrix as template to create holes arrays on Si surface, which are filled with metal oxides or sulfides by ionic layering, sol-gel method or chemical vapor deposition. In this study, the results of research on the technological processes of system nano-holes creating on the Si substrate via the porous AA matrixes are presented for the subsequent filling with the functional nanostructures. The technological sequence of samples preparation is shown in Figure 1. At first, the highly ordered AA layer with open nanopores (without so called oxide barrier layer) was formed directly on Si surface by the two-stage electrochemical anodization of Al. This condition is necessary to ensure qualitative and reproducible etching of Si surface through AA mask. Finally, a process of plasma-chemical etching (PCE) of the Si substrate surface through the modified AA porous mask has been developed. We used deep reactive ion etching (DRIE) in Ar plasma to remove the disordered AA surface layer and to reduce the oxide thickness and residues of the barrier oxide layer. CHF3 was chosen as the active gas for PCE. Optimal technological PCE modes and conditions were selected that ensure uniform selective etching of Si with satisfactory anisotropy without destroying of AA mask. Figure 2 shows SEM image of Si surface after PCE through AA mask in gas mixture Ar(100 sccm)/CHF3(5 sccm) for 20 min. at coil and platen power of 400 and 100 W, respectively. The dimensions of the holes in Si were 80 nm, with depth of 100 nm. The thickness of the mask was 250 nm, with pore diameters of about 60 nm.

References

Schematic sketch of holes arrays forming on Si



SEM image of Si wafer after PCE through AA mask



#PLATH00018

NANO / Nanomaterials and nanostructured thin films

Nitrogenation of monolayer graphene films in N_2 and N_2-O_2 flowing afterglows: analysis of incorporation-limiting mechanisms

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Abstract content

Monolayer graphene films are exposed to the flowing afterglow of a low-pressure microwave nitrogen plasma, characterized by the absence of ion irradiation and significant populations of N atoms and N2(A) metastables. Hyperspectral Raman imaging of graphene domains reveals damage generation with a progressive rise of the D/G and D/2D band ratios following subsequent plasma treatments. Plasma-induced damage is mostly zero-dimensional and the graphene state remains in the pre-amorphous regime. Over the range of experimental conditions investigated, damage formation increases with the fluence of energy provided by heterogenous surface recombination of N atoms and deexcitation of N2(A) metastable species. In such conditions, X-ray photoelectron spectroscopy reveals that the nitrogen incorporation (either as pyridine, pyrrole, or quaternary moieties) does not simply increase with the fluence of plasma-generated N atoms but is also linked to the damage generation. Based on these findings, a surface reaction model for monolayer graphene nitrogenation is proposed. It is shown that the nitrogen incorporation is first limited by the plasma-induced formation of defect sites at low damage and then by the adsorption of nitrogen atoms at high damage. Inspired by these findings, experiments were also realized in presence of oxygen impurities in the flowing afterglow. Over the range of experimental conditions investigated, the extent of damage observed by Raman is much more pronounced in the presence of oxygen. However, similar damage progression curve is observed in all cases : damage formation again increases with the fluence of energy provided by heterogenous surface recombination of N atoms. Hence, additional damage mostly results from a rise in the population of N atoms in N_2+O_2 and not to any specific role of oxygen in the plasma-graphene interaction. For comparable plasma-induced disorder levels, much lower nitrogen incorporation is observed by XPS in presence of oxygen impurities. In such conditions, nitrogen incorporation seems to compete with a surface recombination process leading to the production of NO, and therefore to a nitrogen loss. These aspects of competition between the various surface processes have been observed previously for the treatment of wooden materials in the same type of plasmas.

Thanks/Acknowledgement

This work was financially supported by the National Science and Engineering Research Council (NSERC), PRIMA-Québec, Plasmionique inc., Photon Etc., and the Fonds de Recherche du Québec – Nature et Technologies (FRQNT). L.S. and R.M. acknowledge support from the Canada Research Chair and from the Canadian Foundation of Innovation.

#PLATH00141

NANO / Nanomaterials and nanostructured thin films

Transport of sulfur species in a microwave argon plasma column for functionalization of CVD-grown graphene films

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Abstract content

Synthesis of graphene-sulfur compounds has recently been demonstrated in a two-chamber quartz ampoule with distinct temperature treatment conditions [1]. While the sulfur's chamber is heated to 200 °C for graphene atomization, the graphene's chamber is heated to 370 °C for hours for graphene functionalization. This experience is realized in an enclosed system in an argon atmosphere at around 10 Torr. While graphene-sulfur compounds show a brilliant future for the development of cheap and green energy storage devices, the original technique proposed by Martel and al. [1] produces only a limited amount of graphene-sulfur bonds. In line with the initial idea, we have examined the possibility to sustain a microwave plasma in the quartz ampoule in order to promote sulfur atomization and transport from one chamber to the other and/or to enhance graphene functionalization. The objective is to rise the process efficiency for technological applications.

As a first step, the microwave argon plasma was sustained using a surfatron at 915 MHz without sulfur, the argon plasma is always localized and contracted at the top of the discharge ampoule. In such conditions, optical emission spectroscopy mostly reveals emission lines from Ar 2p-1s transitions without any significant contribution from impurities. Detailed analysis of the broadening of the Ar 2p2-1s2 and 2p3-1s2 emission lines at 826 nm and 841 nm [2] further indicates significant neutral gas heating. This result is consistent with the relatively high electron densities in the plasma channel estimated from microwave interferometry.

Time and space-resolved optical emission spectroscopy was then used to track sulfur species with solid sulfur placed in the first-chamber quartz ampoule with the plasma on. In such conditions, significant blue emission linked to the B-X system of S_2 was seen. Such emission being a very sensitive measure of the sulfur concentration [3], it was used to probe the onset of sulfur atomization as well as its transport properties. In upcoming weeks, plasma treatments of CVD-grown graphene films with and without sulfur will be realized. Plasma-treated graphene will be characterized by hyperspectral Raman Imaging [4].

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#PLATH00025

PROC / Process control (including plasma diagnostics, plasma modelling)

Adaptation of SPARK to atmospheric-pressure micro-plasma jets flow conditions

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Abstract content

This work regards the adaptation to the low temperature and low speed flow conditions observed in atmospheric-pressure micro-plasma jets (APMPJs) of the Software Platform for Aerothermodynamics Radiation and Kinetics (SPARK) [1], a CFD code often used for hypersonic re-entry plasmas. Small flows require high fidelity on the calculation of dissipative processes, and low-temperature plasma chemistry requires detailed state-to-state kinetics. SPARK was adapted accordingly, facing other challenges of convergence in low-Mach conditions and the computational cost of state-to-state kinetics. A first adaptation was the inclusion of subsonic boundary conditions. Secondly, the Simple Low-dissipation AUSM solver (SLAU) [2], a low-Mach perfect-gas solver, was implemented. After validation in incompressible flow simulations, SLAU was adapted into a multi-species and multi-temperature flux solver. Inviscid, dissipative, and kinetic calculations were fully coupled with implicit time integration. Convergence was improved by including a time-step preconditioning formulated for flows with a non-equilibrium temperature for the free electrons. A reduced Argon kinetic scheme was included by applying Uniform Grouping to a state-of-the-art scheme, and run times were decreased by adopting 5th order WENO [3] reconstruction and OpenMP parallelization. The effect of the applied field was included by adding an electron energy source term. Due to the existence of streamers in our APMPJs [4], a simplified streamer model was included to improve the fidelity of this term. Benchmark simulations show a stable code, even in relatively sparse meshes, able to compute the problem in reasonable times. First tests with SLAU multispecies and multi-temperature adaptations allow for a good description of inertial effects, attributed to the low numerical dissipation during the calculation of the momentum conservation equation (see Figure 1), and flux solver adaptations prove to accelerate convergence.

Thanks/Acknowledgement

This work was partially supported by the Portuguese Foundation for Science and Technology under project UID/FIS/50010/2019 and grant PD/BD/142972/2018 (PD-F APPLAuSE).

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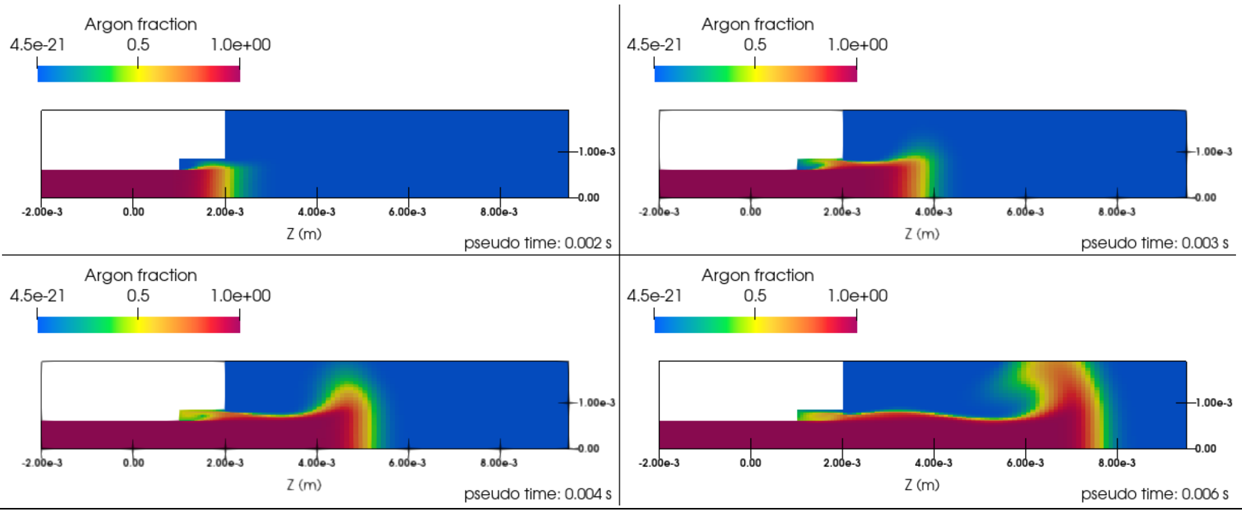
Argon mass fraction in the nozzle flow.



#PLATH00081

PROC / Process control (including plasma diagnostics, plasma modelling)

Study of the influence of a substrate on the axis of the plasma discharge by Optical Emission Spectroscopy (OES)

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Abstract content

Currently, plasma torches find applications in a wide variety of fields such as production of thin layers, surface cleaning or even sterilization [1,2,3]. The use of plasma has a significant advantage from an environmental point of view compared to processes using liquid phases which generate effluents to be reprocessed. The device used for this study is composed of a plasma torch operating at atmospheric pressure called an “Axial Injection Torch” (or TIA for “Torche à Injection Axiale”). At IRCER, the TIA is mainly used for thin layers deposition [4] and surface treatments. In this study, the plasma jet generated by the TIA is characterized by optical emission spectroscopy in order to analyze the influence of the presence of a substrate in the axis of the discharge. This study aims to be more representative of the treatment conditions by positioning the substrate at substrate nozzle distances used for the production of thin layers or for disinfection. The first measurements carried out aimed to determine the influence of the presence of a substrate and that of the nature of the substrate in the axis of the discharge onto the excitation temperature. They were conducted for different argon plasma gas flowrates [13-17slpm], at different microwave powers [250-420 W], nozzle/substrate distances [10-30 mm] and for several types of substrate (metal, silicon, Al_2O_3). The results showed that the more the distance between the nozzle and the substrate decreases the more the excitation temperature increases. When a substrate is placed in the axis of the discharge, a confinement is created therefore the excitation temperature increases in the vicinity of the substrate. Excitation temperatures ranging from 7200K to 11000K were obtained, depending on the operating conditions and the nature of the substrate exposed at the plasma. To complete this study, the gas temperature was calculated with Specair software using a mathematical adjustment of the molecular band of N_2^+.

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#PLATH00084

PROC / Process control (including plasma diagnostics, plasma modelling)

Reaction of neutral species in homogeneous phase in molecular dynamics simulation of Ar/CH_4 plasma

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Abstract content

Molecular dynamics is used to mix the majority neutral species constituting an Ar/CH_4 plasma in the homogeneous phase. The composition of this plasma and the molar fraction of each species is obtained from a 1D model. The mixing is done at temperatures of 300k, 400k, 500k and 1000.

Complex Non-Equilibrium Hydro-Carbon Plasmas are weakly ionized gases containing electrons, neutral and charged molecular species, large clusters and possibly solid particles. They are today a major tool for the elaboration of carbon materials and advanced nanostructures and several key applications in the field of microelectronics.

It is often difficult to study surface and homogeneous phase reactions experimentally because industrial processes are often established on the basis of empirical challenges and not on the basis of a thorough understanding of the physico-chemical mechanisms involved. Molecular dynamics simulations are natural methods for analyzing these phenomena because they provide insight into the mechanisms between species.

The mixing of these neutral species by molecular dynamics simulation has allowed to study the interaction between these molecules and the reaction in the homogeneous phase. This allowed to observe a conservation of the molecules C_2H_2, C_2H and the disappearance of CH_4 whatever the temperature. The formation of other species has also been observed.

MDs are carried on by mixing a total number of 519 molecules that takes into account the molar fraction, with a time step of 0.25fs. The simulation box is calculated according to the reference [1].

C-C and C-H interactions are described with the REBO potential whereas Ar-C and Ar-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)

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#PLATH00110

PROC / Process control (including plasma diagnostics, plasma modelling)

Mass spectrometric investigations in a Ar/CH_4 radio frequency low pressure discharge

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Abstract content

As with many other hydrocarbon precursors nanoparticles can be formed in low temperature plasmas from methane. It has been documented, compared to some other gases, that relatively high power densities are required [1]. It is, however, possible to form nano dust only from an argon plasma in a dirty chamber, prior conditioned with a methane plasma. In this work we study by means of mass spectrometry the gas and ion composition of a Ar/CH_4 plasma in a low temperature RF plasma. In particular, the influence of the wall and electrode condition is investigated by the comparison of the respective spectra. Additionally, with a simple rate equation model the total dissociation rate of methane is calculated for different plasma parameters.

Thanks/Acknowledgement

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

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#PLATH00159

PROC / Process control (including plasma diagnostics, plasma modelling)

NO$_x$ emissions intrinsic to water/gas hybrid DC arc plasma torch at different power levels and gas flow rates

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Abstract content

Water Hybrid plasma torches are used in a wide range of industrial applications, such as plasma spraying, spheroidization, inflight chemical synthesis, and the pyrolytic treatment of waste materials. When such applications require water hybrid plasma torches to be operated at temperatures above 2500 K, significant quantities of nitrogen oxides (NO$_x$) are produced. The main goal of the project is to investigate NO$_x$ emissions from the external plasma jet of a water hybrid plasma torch at power levels (14, 16, 20, 26 kW) and gas flow rates (12, 18, 25 slpm) which are typically used in industry. A calibrated thermochemical NO$_x$ analyzer will be used to remotely monitor NO$_x$ concentrations in the plasma jet. Together with additional thermochemical and CFD simulations, the obtained results will lead to a number of conclusions concerning the control of NO$_x$ emissions and can be used to ensure that the final NO$_x$ gases released into the atmosphere from a water hybrid plasma torch remain within regulatory limits.

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#PLATH00160
PROC / Process control

The role of energetic ions at the substrate in Thin Film plasma processing

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Abstract content

This work demonstrates the role of energetic ions in plasmas and how they affect the properties of materials deposited in thin-film plasma processing. The scope of this contribution is limited to discuss the ability to quantify the flux, energy of ions and ion-neutral fraction to optimize industrial plasma-assisted processes. For this purpose, ion energy and ion flux measurements were carried out using fully automated advanced Retarding Field Energy Analyzers (RFEA's) by Impedans Ltd [1, 2]. The *Semion Multi Sensor RFEA* measures the uniformity of ion energies and ion flux hitting a surface, negative ions, and bias voltage at any position inside a plasma chamber using an array of integrated sensors. A novel RFEA, known as the *Quantum system*, combines energy retarding grids with an integrated quartz crystal microbalance (QCM). This allows measurements of the ion energy and flux properties as well as the ion-neutral ratio and deposition rate.

A review of thin-film applications, particularly focusing on plasma-assisted Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE) processes is presented in detail [3-5]. Some of the major contributions include discussion on the impact of substrate biasing on the ion energy distribution (IED), impact of ion impingement on the chemical and microstructural properties of thin-films, tailored voltage waveforms as a technique to control the ion bombardment energy as well as for precise ion energy control. Further reported are the excellent agreements between the simulated and experimentally observed IEDs at an rf-biased electrode in a helicon plasma system, which surely gains the confidence of thin-film industries in these plasma diagnostic tools [6].

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#PLATH00007

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

Deterioration mechanism of RF-sputtered ITO films on plastic substrates

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Abstract content

Forming thin films on flexible substrates such as polymer films is an important technical issue for manufacturing portable electronic devices. In particular, transparent conductive films such as indium tin oxide (ITO) on flexible substrates are essential for the development of future portable display devices that can be bent while maintaining low resistance and high optical transmittance. However, research on the durability of such flexible transparent conductive films is still in its infancy, and there are many problems to be elucidated about the mechanism of deterioration of electrical properties. Using the RF magnetron sputtering method, we formed ITO films on PEN (polyethylene naphthalate, Theonex) substrates at room temperature to produce low resistance thin films (typically $3.8 \times 10^{-4} \Omega$ cm). This is about the same resistivity as that formed on glass substrates at high temperatures. Furthermore, we have developed a device that can measure resistance changes in realtime while bending the film inward and outward by ± 90°, and conducted 10,000 bending tests. A typical example of resistance changes during bending cycles with a bend radius R = 10 mm is shown in Fig. 1. It can be seen that as the number of bending cycle increases, the resistance of the ITO film increases accordingly. Examination with optical microscopy revealed an increase in the number of cracks perpendicular to the bending direction. The increase in crack density and resistivity showed a good correlation. We have found that bending the ITO film inward or outward reduces or increases resistance with each bend. Hall measurements in curved samples exhibited that bending changes both mobility and carrier density, as shown in Fig. 2.

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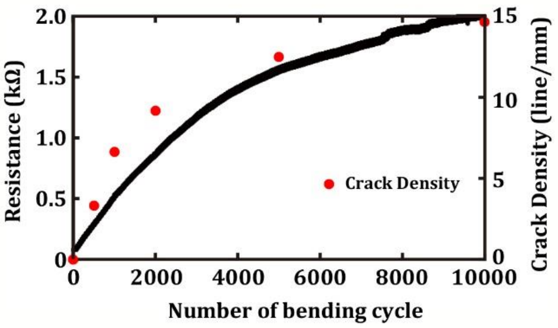
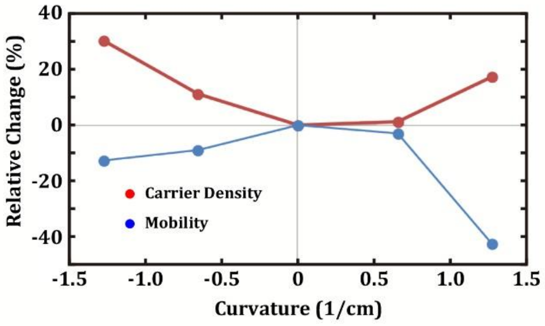
Resistance change by bending cycle



Carrier Density and Mobility change by bending



#PLATH00019

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

Dual-functionality multilayer coating compatible with IML for automobile applications using reactive DC magnetron sputtering

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Abstract content

Nowadays, there is a great interest on the part of the automotive industry in the development of new coatings that can transform a car's interior, increasing the appeal, comfortability, and safety while also, minimizing the manufacturing cost and increasing the quality of the car-user interface, becoming more suitable for every driver. One way to achieve this goal has been to utilize polymeric materials, so, in this context, the future of lightweight automotive parts relies on the use of plastic components, such as ABS, Polypropylene, Polycarbonate, among others. Therefore, a necessity for higher performance materials assured by improved coatings, providing not only good chemical resistance, UV resistance, anti-fingerprint ability among others is the desired features[1, 2,3]. In this context, the present study aims to the development of a multi-layer coating with anti-reflective and other properties on a polymeric substrate label. Using Reactive DC Magnetron Sputtering technology, it is attained that the use of materials such as TiO2 and Al2O3 to build a multi-layer, as well as other materials such as SiO2 and ZnO can be used to improve the optical performance of the base polymer materials. Finally, it is intended that this label with anti-reflective coating is compatible and easily integrated with IML (In-Mould Labelling) technology. To guarantee the quality and specificities of the coating, morphological tests such as Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) will be carried out, as well as, optical tests throughout the analysis of spectrophotometry.

Thanks/Acknowledgement

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#PLATH00118

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

Effects of the operating parameters on aerosol-assisted atmospheric pressure plasma thin film deposition

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Abstract content

Non-thermal atmospheric pressure plasmas are used for a wide range of applications. Recently efforts have been made to couple an aerosol injection of liquid precursor(s) with atmospheric plasmas in order to elaborated thin films. The dispersion of liquid droplets and their interaction with the plasma and/or the post-discharge lead to different issues. In this study, a non-thermal atmospheric pressure plasma torch from AcXys Plasma Technologies is used. This process offers an easy and robust solution to generate low temperature post-discharge in air or nitrogen. It is suitable for thin film deposition on flat or 3D complex substrates for in-line production. The influence of discharge and process parameters (gas process, gas and precursor flow rates, discharge power, distance between nozzle and substrate ...) on the thin film properties are investigated. The shape and velocity of the droplets are obtained by rapid imaging the aerosol. Morphology and roughness of the coatings determined by Atomic Force Microscopy (AFM) are discussed as well as the images obtained from Scanning Electron Microscopy (SEM). The thin film properties can be tailored by both the aerosol characteristics and the plasma process parameters. Dense thin films or porous films with high roughness can be elaborated from the same precursor depending on the process parameters. The comprehension of these phenomena, through further investigation, can improve the optimization of aerosol-assisted plasma.

Keywords: thin film coating, aerosol, plasma deposition, aerosol-assisted atmospheric pressure plasma

#PLATH00136

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

How to allow adhesion of powder paint on insulating substrates?

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Abstract content

Powder paint is of great interest compared to liquid paint because it is environmentally friendly since no solvent is used and also affordable since just one layer is needed. However, the adhesion of this paint is based on electrostatic interactions with the substrate, which needs then to be conductive. So the objective of this work is to be able to apply powder paint onto insulating substrates, particularly polymer ones such as polycarbonate (PC) and polyamide-6 (PA6). In order to achieve this goal, we have deposited on these substrates a thin layer of a conductive polymer by plasma polymerization of different monomers (aniline, pyrrole, acetylene and thiophene). The plasma polymer is then doped by iodine vapours in order to create charge carriers. We have studied the adhesion and the homogeneity of the coat of paint according to the nature of the plasma polymer, its thickness, its doping duration and its chemical structure depending on plasma parameters. As an example of result, figure 1 presents the homogeneity and the adhesion of the coat of paint according to the nature of the plasma polymer. They are better when the conductive polymer used is pp-aniline which is directly linked to its higher doping efficiency (the layer is darker in colour after doping). It means that a greater amount of charge carriers is created allowing a higher electrical conductivity. It can be explained by the chemical structure of the plasma polymers studied using FTIR and UV-Visible spectroscopies.

Plasma polymer	pp-aniline	pp-pyrrole	pp-acetylene
Plasma polymer after doping (I_2, 1h)			
After painting			
Paint thickness	159±17 µm	125±22 µm	
Adhesion test			
Class of adhesion on PA6	0 or 1	0 or 1	5

Figure 1..Results of painting of PA6 substrates according to the nature of the plasma polymer

#PLATH00154

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

Magnetron co-sputtered TiO_2/Ag/Cu antimicrobial coatings

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Abstract content

The aim of this study was to utilize the advantages of the magnetron co-sputtering as a dry technology for the fabrication of TiO2/Ag/Cu composite coatings with controlled characteristics correlating to the antimicrobial activity of the coated medical devices. Elemental composition and distribution, surface morphology, wettability, surface energy and its component were estimated as a surface characteristics influencing the bioadhesion. Well expressed, specific, Ag/Cu concentration depending antimicrobial activity in vitro was demonstrated toward Gram-negative and Gram-positive standard test bacterial strains (both, by diffusion tests and Most Probable Number of survived cells). Direct contact and eluted silver/coper nanoparticles and ions mediated killing were experimentally demonstrated as a mechanism of the antimicrobial activity of the studied TiO2/Ag/Cu thin composite coatings. It is expected that they would ensure broad spectrum bactericidal activity during the indwelling of the coated medical devices, maintaining their performance for at least 12 h, and suggesting that benefits of their use can be obtained over longer time.

Thanks/Acknowledgement

Nation Scientific Fund, Bulgaria is gratefully acknowledged for its financial support of this investigation (Grant KP-06-COST/20/2019) that is a part of the activities of COST Action CA 16217 ENIUS.

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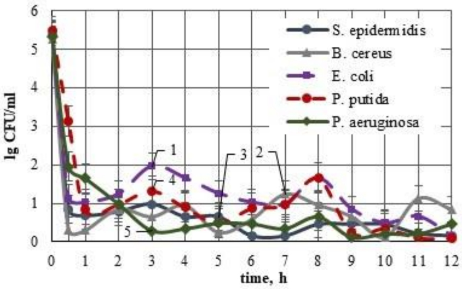
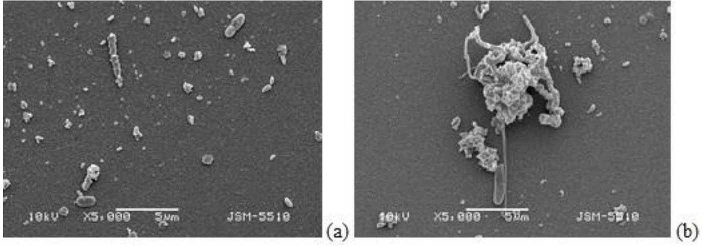
E. coli (curve 1), B. cereus (curve 2), S. epiderm



SEM images of significantly damaged E. coli cells



#PLATH00030

GROM / Thin films growth and modelling

High temperature oxidation resistance of metallic materials by PVD coatings: influence of the initial substrate roughness

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Abstract content

The application of a coating to the surface of metallic materials can improve some properties, such as high temperature (800-1000 °C) resistance. The preparation of the substrate and its initial surface state play a major role in the continuity and conformity of the deposited PVD layer. Long open porosities can be present and will affect diffusion phenomena, leading to a loss of the high temperature protective properties of the PVD layer. In this study, steel substrates were prepared with different surface finishing grades from grinding to mirror polishing. They were then coated by sputtering and finally oxidized at high temperature. Surface topography and cross section morphology analyses were performed by optical profiler and SEM on the bare substrates, after coating and after oxidation. In order to understand the role of the surface morphologies PVD simulation are performed with SIMTRA [1] for the transport and NASCAM [2] for the growth.

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#PLATH00097

GROM / Thin films growth and modelling

Microstructure and properties control in sputter-deposited Zr-Cu thin film metallic glasses

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Abstract content

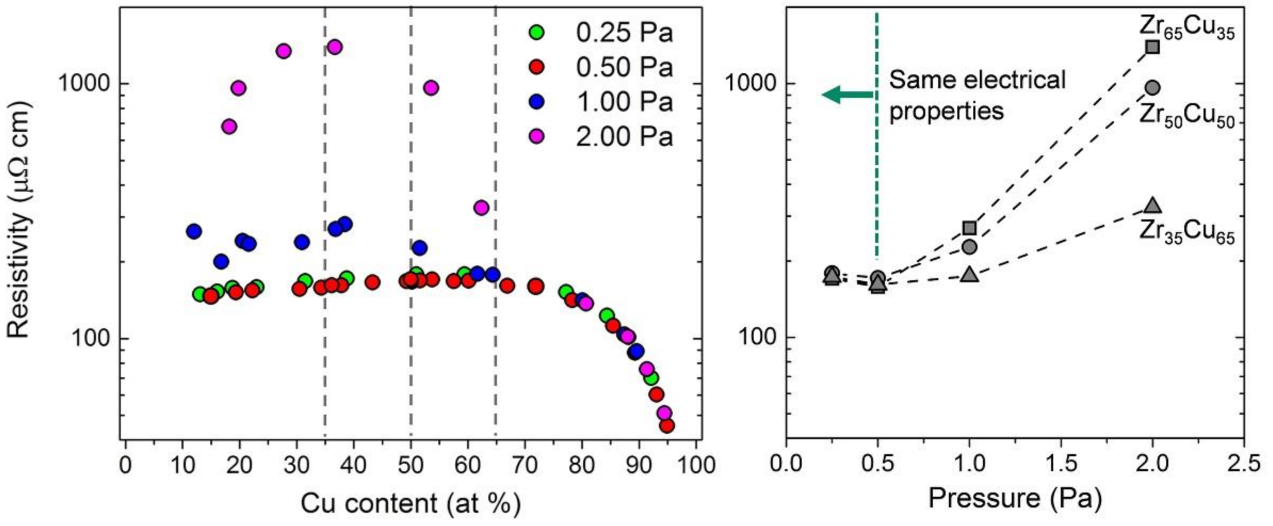
Owing to their amorphous structure, metallic glasses (MGs) have emerged as a new class of materials with remarkable properties compared with their crystalline counterpart. Using physical vapor deposition methods such as sputtering, MGs can be prepared in the form of thin film metallic glasses (TFMGs). Thus, the microstructural control inherent to the sputtering process can be exploited to tailor the properties of TFMGs. In this work, we report on the influence that the energy of the sputtered atoms arriving at the substrate (controlled here through the deposition pressure) has on the structure, microstructure, and properties of the deposited films. Zr-Cu alloys, largely known for their good glass forming ability, were used as a model system and studied over a wide range of compositions. We demonstrate that by increasing the deposition pressure, a composition-dependent transition from a denser to a columnar microstructure occurs. This microstructural transition directly affects the residual stress state as well as the electrical and optical properties of the deposited TFMGs. In particular, we show that there is a threshold in the deposition pressure below which the resistivity of the films remains constant (see Figure).

Thanks/Acknowledgement

This work was supported by the ANR MEGALIT project (grant ANR-18-CE08-0018) of the French Agence Nationale de la Recherche

References

Electrical properties of Zr-Cu TFMGs



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#PLATH00126

GROM / Thin films growth and modelling

Epitaxial growth of $(ZnO)_X(InN)_{1-X}$ films by magnetron sputtering: effects of surface polarity of ZnO substrates

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Abstract content

We have recently developed novel semiconductors, $(ZnO)_x(InN)_{1-x}$ (called “ZION” hereinafter), which are pseudo-binary alloys of ZnO and InN. ZION have high exciton binding energy of 30–60 meV making ZION promising materials for various kinds of optoelectronic devices[1,2]. Here, we demonstrate epitaxial growth of ZION films on ZnO substrates by magnetron sputtering. Since substrate surface polarity often affects the film growth[3], we prepare ZION films on both Zn- and O-polar ZnO substrates and discuss the effects on the film quality.

ZION films were deposited on Zn- and O-polar ZnO substrates by radio-frequency magnetron sputtering. O_2, N_2 and Ar gases were used. The total pressure was 0.50 Pa. ZnO and In targets were used. The substrate temperature was 450°C.

High-resolution TEM images show that the heteroepitaxial growth of ZION films with atomically sharp interfaces on both Zn- and O-polar ZnO surfaces, however, a significant difference in the lattice relaxation process between the films is also observed. Figure 1 shows distance between Zn or In atoms as a function of ZION film thickness. On Zn-polar ZnO surfaces, relaxation occurs at the beginning of the film growth, whereas on O-polar surfaces, the ZION films are fully coherent with the 1.6%-lattice-mismatched ZnO substrates at least for 15 mono layers. The differences in the film quality are probably attributable to differences in the surface migration of Zn/In atoms between on Zn- and O-polar surfaces.

Thanks/Acknowledgement

This work was supported by JSPS KAKENHI JP18H01206, JP19K21978, NTT collaborative research, and Samco Science and Technology Foundation.

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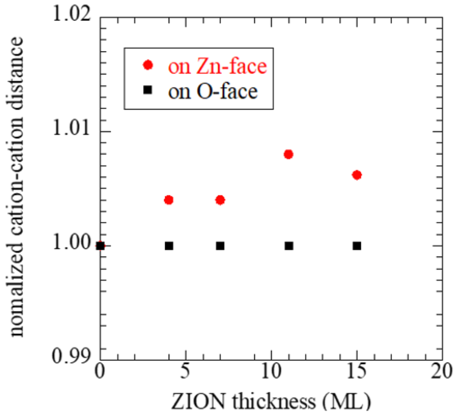
Fig. 1. Cation-cation distance along the a-axis as



#PLATH00146

HELI / Health and life science

Investigation of the chemical stability of plasma-activated solutions

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Abstract content

Plasma pharmacy concerns the production, optimization, and stabilization of plasma-activated solutions. To be considered as efficient anti-cancer drugs, plasma-activated solutions should be easily produced and stored, and it is essential that they maintain their anti-cancer properties over time. Given that among the variety of plasma-generated RONS, H_2O_2 and NO_2^- have been established as the main anti-cancer drivers of plasma-activated solutions [1,2], the cytotoxic activity of these liquids is highly dependent on the stability over time of these two reactive species. The purpose of this work was to assess the chemical stability of plasma-treated PBS(Ca_2^+/Mg_2^+), in terms of H_2O_2, NO_2^- and NO_3^- degradation, as a function of storage time and temperature. An atmospheric-pressure plasma jet of coaxial electrode configuration driven by high-voltage pulses in the kHz range was used to produce the plasma [3]. PBS(Ca_2^+/Mg_2^+) solutions were treated by the plasma, and then stored at 4 different temperatures: ~+20°C (room temperature), +4°C, –20°C and –80°C. Alongside, untreated PBS(Ca_2^+/Mg_2^+) containing ad-hoc concentrations of H_2O_2, NO_2^- and NO_3^- (i.e. mimicking solutions) were stored at the same temperatures. The absolute concentrations of H_2O_2, NO_2^- and NO_3^- were measured in these stored solutions after 1, 7, 14, 21 and 75 days of storage. Thus, the degradation of those reactive species, in respect to their initial concentration measured just after the plasma treatment, was determined. The influence of the freezing rate (for solutions stored at –20°C and –80°C) was also studied by comparing fast and slow freezing. Finally, the actual effect of storage time and temperature on the viability and permeability of cancer cells treated *in vitro* by the solutions was also assessed. Our results show that, for both plasma-treated and mimicking solutions, the reactive species considered remain stable for 21 days at room temperature or at +4°C. On the contrary, significant degradation is observed at –20°C and –80°C, even for the first days of storage. We conclude that both plasma-treated and mimicking solutions can preserve their cytotoxic activity, at least for 21 days, if stored at +20°C or +4°C, providing a basis for their practical application in cancer therapy.

Thanks/Acknowledgement

This work was financially supported by the PLASCANCER project (INCa-PlanCancer N°17CP087-00) and performed in the framework of the CNRS network GdR 2025 HAPPYBIO.

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#PLATH00056

ENER / Renewable energies

Optical performance of high temperature air-stable solar absorber coatings based on W/SiCH plasma multilayers

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Abstract content

CSP technologies (Concentrated Solar Power) are growing strongly in the global energy mix. Improving their performance, an essential solution to intermittent solar radiation, requires the development of highly absorbent coatings aimed at increasing the temperature of heat transfer fluids and lowering the cost of receivers whose surface converts the concentrated solar flux into heat. Innovative spectrally selective thermo-optical structures maximise solar absorption while minimising radiative heat loss (low reflectance in the solar region of the spectrum (0.25 - 2.5 µm) and high reflectance in the infrared (>2.5 µm)), and must withstand temperatures (up to 800°C) in air while maintaining their optical properties.

This paper presents the metal-dielectric multilayer stacks based on W and SiCH materials developed in various projects: ANR ASTORIX (2014-2019), French Region Occitanie PLASMECO (2018-2021), ANR NANOPLAST (2019-2023). They are deposited using low pressure plasma techniques: magnetron sputtering PVD for W and PECVD microwave for SiCH. Solar absorptance, thermal emittance and heliothermal efficiency, corresponding to the materials optical performance, were studied on a reference stack and stacks annealed for 500°C in filtered air (without H2O and CO2) for 12h, 24h, 48h and 96h. The results showed that, on one hand, the samples were not degraded after annealing and, on the other hand, after 12h, there was an increase in solar absorption up to 92% and a reduction in thermal emittance of 14 points, leading to an increase in heliothermal efficiency of 14 points. For longer aging, optical properties remain stable. SEM, EDS, RBS and FTIR characterisations show thickening and oxygen incorporation into the material due to aging. This may reflect the formation of a protective SiO layer on the surface of the coatings during the early stages of aging which protects the material from further oxidation.

#PLATH00004

LIQU / Plasma and liquids

Bi_2O_3 nano-sheets and nanotubes synthesized by discharges in liquid nitrogen

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Abstract content

Bismuth oxide has a narrower band gap than TiO_2 [1]. It is an excellent photocatalyst for water photolysis and organic pollutants degradation under visible light. As an important type of layer-structured p-type semiconductor, the photocatalytic behaviour of Bi_2O_3 is pretty different from N-type TiO_2. It is also dependent on the allotropic phase as Bi_2O_3 adopts many polymorphic forms, the most common being monoclinic α-phase, tetragonal β-phase, body-centered cubic γ-phase, and face centered cubic δ-phase. In this work, we show how it is possible to synthesize easily Bi_2O_3 nanoparticles by nanosecond pulsed discharges in liquid nitrogen. By creating high-voltage (10 kV) discharges between Bismuth electrodes separated by a distance of 100 µm typically, Bismuth nanoparticles are produced with three size distributions. Oxidation occurs in a second step, after nitrogen evaporation. Therefore, a part of the nanoparticles exhibit a core-shell structure if oxidation is incomplete. When the applied voltage is lowered to 4-5 kV, ultra-thin nano-sheets and nanotubes also form. The mechanisms responsible for the growth of these new structures are still under investigation but in the case of nanowires, self-catalyzed vapor–liquid–solid route seems highly probable [2, 3]. The microstructure and composition of the nano-objects are characterized by X-ray diffraction, high-resolution TEM (HRTEM) and electron energy loss spectroscopy (EELS). If Bi_2O_3 nanoparticles are amorphous, nano-sheets are cubic, which opens interesting perspectives for their use as active photocatalysts.

Thanks/Acknowledgement

The authors acknowledge the French PIA (programme d'investissements d'avenir) project Lorraine Université d’Excellence (Ref. ANR-15-IDEX-04-LUE) for financial support.

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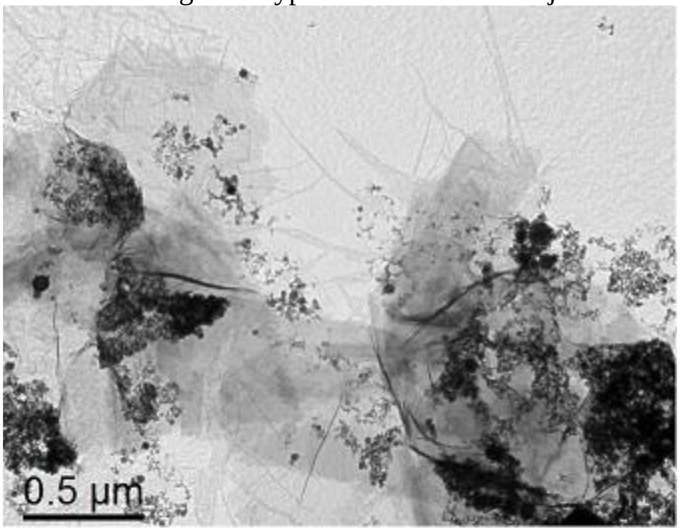
Picture showing the 3 types of Bi2O3 nano-objects



#PLATH00032

LIQU / Plasma and liquids

Efimov physics and few-body approximation in nuclear, atomic and molecular physics

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Abstract content

The main difficulties in the research of few-body problems are bounded with the really many-channels and multidimensional nature of the these problem, impossible applied many well-known theories such as adiabatic, impulse, coupled channels, etc.

For this reason we proposed new method for the investigation of the different few-body processes used the mathematically rigorous for-malism based on the treatment of collision processes as many body processes, using Faddeev-Yakubovsky equations [1] (FYE) in integral and differential forms. In particular techniques based on FYE have been used successfully in studies of the dynamics of few-particle systems (bound-state properties and elastic, reactive and breakup scattering) [2]. That is why we applied this formalism for the theoretical investigation of the dynamics of the different processes in atomic and chemical physics. [2].

Calculation of low-energy characteristics in scattering processes like scattering length, effective range parameter, amplitude, cross section etc. The investigation the theory of quasimolecule (electron + molecule), the ionization mechanism in quasimolecule and the main characteristics of quasimolecule autoionization states, determination of the bound between these states, the resonance states, potential energy surface (PES) and dynamics of the chemical reaction.

The scattering atoms with two (O + CS, H + H_2 , O + N_2 , O + O_2) and few atomic (O + CF_3J, O + CS_2 , O + OSC, HCl + HCl) molecules, the many particles interactions, orientations of the reacting molecules etc. on the reactions dynamic, the confection between the interactions in FYE and PES, the investigation of the resonances, virtual states and threshold phenomena in chemical reactions.

The studding the unusual dynamical thresh old phenomena in chemical reactions such as Efimov states based on FYE. This research may be obtain the information of the reaction mechanism, PES etc. and may have a strong influence on the scattering observable. Hence the careful studding of these states may be provide better understanding of the control and management of the chemical reaction processes.

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#PLATH00033

LIQU / Plasma and liquids

Resonances in electron scattering by molecules

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Abstract content

The methods of the quantum theory few-body scattering based on the Faddeev-Yakubovsky equations [1] in momentum and configuration space are present [1,2].

Scattering states properties of three-body resonantly interacting particles are considered and are shown to be independent of a form of two-body forces, being determined only presence of resonances. The resonances produce an effective long range interaction between three particles [3].

This methods are applied to the calculation of the dissociative electron attachment to hydrogen and hydrogen-halide diatomic initial rovibrational exiting molecules H_2, N_2, Li_2, Na_2, HCl, DCl, HBr, DBr, HJ, DJ, HF, DF.

The results of this calculations are compered with available experimental data [5] and other calculation [2-4].

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#PLATH00061
LIQU / Plasma and liquids

Synthesis of bismuth-based nanoparticles into an imidazolium ionic liquid by reactive magnetron sputtering

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Abstract content

Sputtering deposition over liquid substrates is considered as one of the most promising methods for synthesizing and stabilizing original nanostructured materials. Recently, room temperature ionic liquids, referred to as ‘designer green solvents,’ have attracted exceptional attention in obtaining nanoparticles of high purity and controlled size. However, to our knowledge and up to now, only metallic nanoparticles have been synthesized by sputtering. Therefore, the scope of our study is to synthesize semiconductor nanoparticles by injecting different reactive gases. By sputtering a bismuth target onto 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [BMIM][TFSI] ionic liquid in an Ar, Ar/O_2, and Ar/O_2/CF_4 plasmas, we succeeded in obtaining metallic bismuth, bismuth oxide, and bismuth oxyfluoride nanoparticles respectively. Directly after synthesis, transmission electron microscopy showed the formation of non-agglomerated spherical nanoparticles with a size smaller than 20 nm. Various analytical techniques as XRD, Raman, UV-Vis, and IR spectroscopy were employed to characterize the nanoparticles. First, sputtering bismuth in an Ar plasma allowed obtaining a dark color solution containing metallic bismuth nanoparticles. Thereafter, the influence of target power, sputtering time, and aging on the nanoparticles’ concentration and suspension was explored. Secondly, by injecting O_2 and CF_4 reactive gases, the solution stays transparent. The different techniques confirmed the formation of bismuth oxide and oxyfluoride nanoparticles. Moreover, the variation of the O_2 and CF_4 flow rates enabled tuning the composition depending of reactive gas ratio. The following nanoparticles are favorable for photocatalytic applications. Finally, the interaction of the ionic liquid with the different plasmas, without target sputtering, was investigated by optical emission spectroscopy to verify if the created radicals modify chemically the ionic liquid.

#PLATH00128
LIQU / Plasma and liquids

Viscous droplet in a nonthermal plasma: microflow at plasma-liquid interface

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Abstract content

We study the interactions of microplasma with a viscous liquid droplet in a narrow gap [1]. We show that local change of properties at their interface caused by actions of plasma can induce radial viscous fingering. The system is investigated experimentally employing synchronized optical and electrical time-resolved measurements. Temporal development of the destabilization, stretching, and fragmentation of the plasma-liquid interface is studied for the whole event lifespan. The perturbation wavelength and temporal development of fingering speed, plasma-liquid interface length, dissipated power, and fractal dimension of the pattern are determined. Recorded changes in the dissipated mean power show a strong correlation to subsequent stretching of the interface. Our extensive parametric study shows that oil viscosity and applied voltage amplitude both have a significant impact on the interface evolution. Notably, at relatively high voltages the destabilized interface featured properties noticeably diverging from the theoretical prediction of a known model. We propose an explanation based on the change of the liquid viscosity with increased heating at high applied voltage amplitudes. Furthermore, the introduced methodology enables spatially resolved quantification of the dissipated power density, i.e. the main cause of the process, and of the unstable plasma-liquid interface velocity, i.e. the main result of the process. We demonstrate how the irregular distribution of these parameters leads to the observed microflow. The viscous fingering process and the secondary droplets pinch-off are investigated for two power scenarios.

Thanks/Acknowledgement

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#PLATH00024

NANO / Nanomaterials and nanostructured thin films

Synthesis and characterization of plasmonic composites (Fe/La)/Au for enhanced optical properties

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Abstract content

Metallic nanoparticles based on gold (Au) attract more and more attention due to their ability to enhance optical extinction by excitation of Surface Plasmon Resonance (SPR) that manipulates light-matter interaction. Mixing gold with magnetic materials like Iron (Fe) can lead to enhanced magneto-optical effects [1-3]. As Iron is sensitive to oxidation, the transformation of the non-noble metal in the nanoalloy will be studied, as well as its properties evolving upon oxidation between those of Fe/Au and those of Fe_2O_3/Au. $LaFeO_3$ can substitute Fe_2O_3. Both oxides are semiconductors but the former adopts a perovskite structure and it is considered as a promising photocathode material. Adding a gold buffer layer to perovskite affects the optical properties of the plasmonic oxide/Au composite, as shown by Wang et al. [4], in a way that is still to be investigated. In this work, we aim to apply femtosecond and nanosecond laser ablation to Fe/Au and $LaFeO_3$/Au thin films deposited by PVD technique on a quartz substrate to synthesize the NPs made of a mixture of these elements. Presently, we are working on deposition of Fe/Au and $LaFeO_3$/Au bi-layers by PVD in order to control their thickness, composition and structure before laser ablation. This second step is expected to melt both phases and form by quenching of the melt a composite. Thus-formed nanoparticles will be investigated by different techniques to correlate their composition and structure to their optical properties. Raman analyses, electron transmission microscopy, and emission spectroscopy will be used in that purpose.

Thanks/Acknowledgement

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#PLATH00057

NANO / Nanomaterials and nanostructured thin films

Nanocomposite cermet coatings for CSP technologies deposited by RF reactive PVD assisted with microwave ECR sources

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Abstract content

Improving the performance of Concentrated Solar Power technologies requires the development of optically efficient and thermally stable absorber materials. To achieve this, our objective is to develop spectrally selective coatings using plasma technology, i.e. absorbent in the visible and near infrared and lowly emissive in the infrared. These coatings must also be resistant to high temperatures in air and high thermomechanical stress. Among suitable solutions are ceramic-metal composites (cermets) based on Tungsten and SiCH materials. Compared to more classical multilayer selective solar, allow the diffusion of oxygen in the coating to be limited by eliminating grain joints and improving mechanical properties (e.g. crack blocking, resistance to deformation).

First of all, thermo-optical properties of cermets including various metals, embedded in a SiCH reference matrix from our laboratory, were simulated and optimized with a homemade optical modelling tool. This study revealed that metal-SiCH composites presented a high thermo-optical efficiency to convert concentrated solar flux into heat for real CSP operating conditions. W-SiCH was found to be well adapted for such applications. W containing SiCH materials were then synthesized on silicon and steel substrates by two direct plasma methods: reactive radiofrequency (RF) magnetron sputtering PVD, with and without the assistance of microwave ECR sources.

Study of the reactive PVD processes to control the formation of cermet layers was carried out by Optical Emission Spectroscopy (OES) coupled with films characterizations. OES showed an attended increase in electron concentration and a decrease in the mean electron temperature. Addition of ECR sources to reactive RF PVD allows for plasma parameters to be modified and favors the production of powders. The crossing of various material characterizations (XPS/AFM/KFM/EDS/RBS) reveal that nanograins containing tungsten were enclosed into the material coating deposited on steel substrates. Thermo-optical characterizations of these cermets show that they are optically selective, and that their insertion in multilayers containing tungsten IR-reflective sublayer and silicon carbide antireflective top layer could lead to good optical performance as solar absorbers.

#PLATH00088

NANO / 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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Abstract content

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

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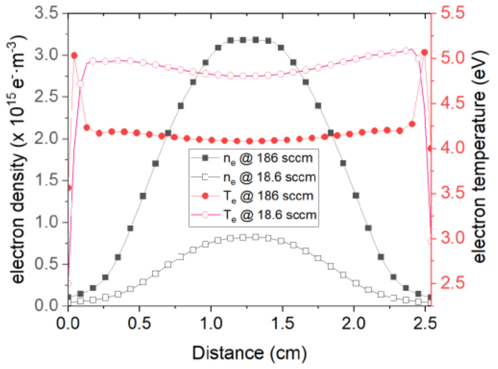
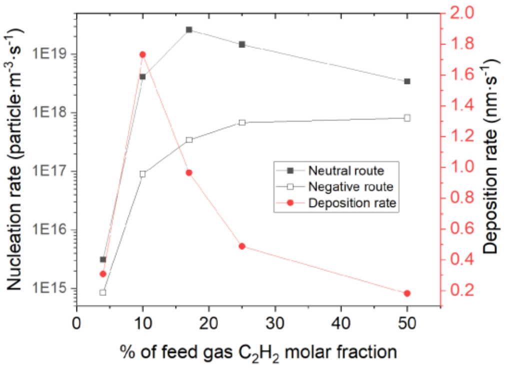
I Stefanovic et al 2017 Plasma Sources Sci. Technol. 26 065014

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





#PLATH00101

NANO / Nanomaterials and nanostructured thin films

Investigation of the mechanisms involved in one-step nanocomposite thin films synthesis by direct pulsed liquid injection of a colloidal solution in a low-pressure plasma

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Abstract content

Nanocomposite thin films, consisting of nano-objects imbedded in a thin film matrix, have raised growing attention in recent years, due to the great tunability of their properties. Several attempts have been made to provide a reliable process for the growth of nanocomposite thin films. A number of these attempts involve the injection of a liquid nanoparticles-containing colloidal solution in a plasma environment, 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 and direct liquid injection of a nanoparticles-containing colloidal solution[2]. In this hybrid process, a TiO_2 colloidal solution is injected as droplets in an O_2/HMDSO inductively coupled RF plasma, employed for the growth of the SiO_2 matrix of a nanocomposite thin film. The sudden pressure increase (typically from 3 to 15 mTorr) and new chemical environment brought by the pulsed injection of liquid (pulses of 1 ms with a frequency of 1 Hz) leads to abrupt changes in the plasma parameters, which in turn affects the droplets' evaporation. However, the influence of the different interactions between plasma, solvent and nanoparticles on droplets evaporation is yet to be understood. The aim of the present work is to gain insight on the modifications of the plasma composition upon the injection of the colloidal solution. For this purpose, the plasma is monitored by in situ time-resolved optical emission spectroscopy (OES), actinometry is used to track the time variation of concentration of some of the plasma species (O, H, CO, OH), and film growth is followed through in situ spectroscopic ellipsometry. We investigate the effect of colloidal and solvent-only solutions on interactions involved in the hybrid process, depending on various injection parameters: quantity of liquid injected, frequency of injection, solvent volatility, and concentration of nanoparticles in the colloidal solution. Preliminary results show that injection-induced pressure increase hinders HMDSO fragmentation and therefore SiO_2 deposition, which creates alternating deposition periods for SiO_2 and TiO_2-NP. In addition, the use of solvent of higher volatility seems to favor faster evaporation of the droplets in the plasma.

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#PLATH00102

NANO / Nanomaterials and nanostructured thin films

Optimization of nanostructured TiAlBN coatings deposited by HiPIMS

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Abstract content

The ever-increasing demands for longer tool life in high-speed machining require multifunctional coatings that display several interlinked characteristics such as high thermal stability, hot hardness and toughness. For this purpose, hard nitride (Ti, Al)N-based nanocomposites coatings have been developed [1–3], but they still suffer from low fracture resistance. In this work, a series of high Al-fraction multilayered TiAlBN nanocomposite coatings deposited by HiPIMS is presented and compared with another TiAlN series (an industrial standard) deposited under the same conditions. The effect of the variation of bias voltage, relative multilayer thickness or the layer composition in the microstructure and the mechanical properties was also studied. TiAlBN coatings exhibit a refined grain structure with individual layer thickness down to 2 nm, which translates into improved fracture toughness over TiAlN while maintaining hardness values up to 40 GPa. The results demonstrate the advantages of TiAlBN multilayered coatings over monolayer TiAlN coatings in terms of thermal stability, hardness and fracture toughness. More recently, the application of positive pulses after the HiPIMS main pulse have shown to enhance the coatings properties [4] and were also applied to TiAlBN materials.

Thanks/Acknowledgement

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#PLATH00105

NANO / Nanomaterials and nanostructured thin films

Enhanced resonance Raman scattering of spin-coated silver nanoparticles by treatment in a microwave argon plasma jet open to ambient air

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Abstract content

This work investigates the treatment of thin films made of spin-coated silver nanoparticles with dimensions in the 60-80 nm range by an open-to-air microwave argon plasma jet characterized by neutral gas temperatures of 2200 ± 200 K. Scanning Electron Microscopy reveals a consumption of small nanoparticles to produce micrometer-scale aggregates with sharp edges. Similar features with rounder edges are obtained after conventional thermal annealing. In both conditions, Auger Electron Spectroscopy and X-ray Diffraction analysis indicate an oxidation of silver nanoparticles. However, only plasma-exposed samples exhibit a rise in the surface-enhanced resonance Raman scattering (SERS) signal. By combining 58 58 µm2 mappings of Hyperspectral Raman IMAging (RIMA) with multivariate curve resolution by log-likelihood maximization, it is shown that SERS enhancement is controlled by aggregated domains.

#PLATH00064

SOUR / Plasma sources and electrical discharges

Power balance in microwave microplasmas generated in capillary tubes

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Abstract content

Over the last years, we have designed and tested several launchers able to generate microwave microplasmas in dielectric capillary tubes. Advantages of microwaves are numerous: plasmas can operate over a large range of pressures (from 10^{-4} mbar to atmospheric pressure), with very low power (a few W to a few tens of W), in continuous mode, and electrodeless. The obtained microplasmas turn out to produce high electron and ion densities (10^{14} cm^{-3} range), high power density (up to 10 $kW.cm^{-3}$), high amount of active species (10^{12} cm^{-3} range for argon metastable states) and high amount of photons, all of them interesting for a large panel of potential applications. Motivation to our study comes from the fact that the power balance in microwave microplasmas is almost never discussed. In the best cases, authors only report input and reflected measured powers and suppose that the difference is coupled to the plasma. The current work is thus dedicated to determine the microwave power really coupled to the plasma. It requires a complete power balance study taking into account all the power loss possibilities. Our measurements put into evidence the negligible nature (<1 %) of a large part of the loss channels: microwave field leakage, optical radiation from the plasma, chemistry and post-discharge heating. The power balance will therefore be made solely from measurements of incident and reflected powers, heating of the microwave coupling elements and heating of the external walls of the capillary tube. These balances will be presented without plasma, with an argon plasma at low pressure, and at atmospheric pressure and/or in a reactive argon/air mixture. Our measurements show that without plasma, almost all the incident microwave power is back reflected (> 90%) and about 5% is lost in heating of the microwave coupling elements. With plasma, overall, the reflected power becomes lower (25-60% of the incident power), the heating of the microwave coupling elements higher (15-30%) and the power transmitted to the plasma, measured via capillary heating, is relatively low (5-20%). This is striking different compared to numerous studies considering only the incident and reflected measured powers, giving power transmitted to the plasma of the order of 90 % of the incident power. A strong conclusion remains from this study: the real power coupled to the plasma is, in the best case, lower by a factor of 2 to 3 compared to what is traditionally reported in the literature.

#PLATH00140

SOUR / Plasma sources and electrical discharges

The DC gas breakdown in tubes of arbitrary length

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Abstract content

The dc gas breakdown in tubes of arbitrary length V.A. Lisovskiy, E.Ya. Bannikova, S.V. Dudin, R.O. Osmayev, V.D. Yegorenkov *V.N. Karazin Kharkiv National University, 4 Svobody Sq., Kharkiv, 61022, Ukraine E-mail: lisovskiy@yahoo.com* This paper has investigated the dc discharge breakdown between flat electrodes in a long tube. Two experimental techniques have been employed: 1) the breakdown voltage U has been measured in the broad range of gas pressure p, the inter-electrode distance L being kept fixed; 2) with the gas pressure fixed the breakdown voltage has been measured for different values of the inter-electrode distance . With the first technique we have found that at small inter-electrode distance values ($L < 5$ см) the gas breakdown is well described with Paschen's law, i.e. on the $U(pL)$ graph breakdown curves practically match each other. At larger L values one observes a shift of breakdown curves to the lower pressure range as well as to the range of higher breakdown voltages. The breakdown curves measured with the first technique possess an important feature that their minima are located on the straight line corresponding to the maximum ionization ability of electrons (Stoletow's constant) and the right-hand branches of all curves approach one another. When one fixes the gas pressure and registers the breakdown voltage $U(L)$ for different values of the inter-electrode distance L, then the $U(L)$ curves possess an U-shaped pattern and with the gas pressure increasing they are displaced down and to the left, with the minimum breakdown voltage of the curves $U(L)$ decreases. The left-hand branches of the $U(pL)$ curves measured according to the second technique match for all pressure values because they refer to narrow gap values when Paschen's law holds. But increasing the inter-electrode distance L leads to the increase of diffusion loss of electrons on the tube walls which area also increases. Therefore the right-hand branches of such breakdown curves at low pressure run in the region of higher breakdown voltage values in contrast to respective branches of the curves obtained according to the first technique. That is, on decreasing the gas pressure the breakdown curves $U(pL)$ are shifted to the range of higher breakdown voltage values and lesser pL product values. At the minima of such breakdown curves the ionization ability of electrons is not maximum as a result of a considerable diffusion loss of electrons and non-uniform axial distribution of electric field strength.

#PLATH00047

SURF / Plasma - surface interactions

Atmospheric pressure plasma microfluidic chips wettability treatment

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Abstract content

Microfluidics technologies are nowadays under the spotlight in many fields such as biomedical, pharmacology, and chemistry. These allow the manipulation of very small volumes of fluids thanks to miniaturized hydraulic systems obtained using advanced microfabrication techniques. Recently, geosciences have also jumped in the microfluidics revolution. Indeed, the ability of microfluidics to design well-controlled porous structures on chips and to isolate the overlapping hydro-bio-chemical phenomena occurring in the soils and the subsurface enables unprecedented visualization and characterization of the dynamic processes in geological porous materials. Despite all the recent progress, however, microfluidics for geosciences is still in its infancy. Geosciences microfluidic applications require hydrophilic sidewalls to mimic environmental subsurface behavior. These chips are basically made of polydimethylsiloxane (PDMS) that is natively hydrophobic and made hydrophilic during oxygen plasma activation/bonding. However, the wettability is not stable over time. In this work, we used an Atmospheric Pressure Plasma Jet (APPJ) for the treatment of the microchannels. This device is commonly used in plasma medicine and has the singular feature to generate a plasma that propagates away from the confinement of electrodes on several meters in a capillary tube. We explored the influence of a neon APPJ propagation along the microchannels in order to modify the wettability from hydrophobic to hydrophilic behavior. We succeeded to inject and propagate the plasma into PDMS-glass microchip (figure 1: Neon plasma propagating along a homemade PDMS on glass microfluidic chip). Depending on the treatment time, a significant change in the channel wettability was observed for blue-colored water circulation (figure 2: Flow front characterization at the inlet of the microchip a) before and b) after a plasma treatment - scale bar is 200µm).

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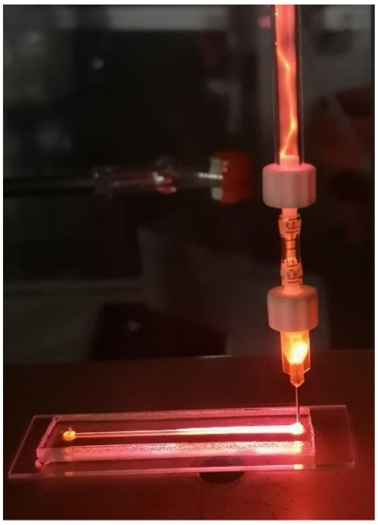

Figure 1

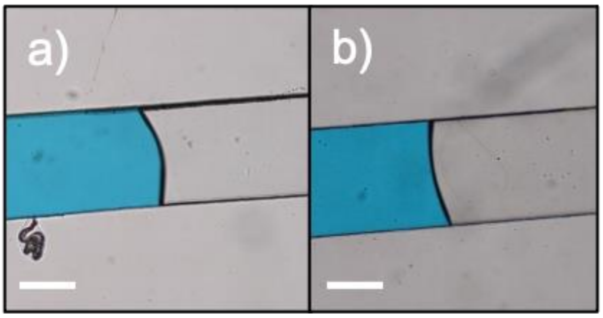

Figure 2

#PLATH00080

SURF / Plasma - surface interactions

Cryo-ALE of Si based on SF_6 physisorption

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Abstract content

Cryogenic Atomic Layer Etching (Cryo-ALE) has been presented in the previous PLATHINIUM conference (2019) as a different approach to achieve ALE of SiO_2. In this process, C_4F_8 is used as a precursor in the “modification” step in order to physisorb on a cooled SiO_2 surface between -120°C and -90°C [1,2]. The “etching” step is then achieved by using an Ar plasma with a low energy ion bombardment. However, C_4F_8 injection at cryogenic temperatures does not allow high etching selectivity of SiO_2 over Si and Si_3N_4 as the deposited CF_x passivation layer is not thick enough to efficiently passivate Si and Si_3N_4 surfaces. Nevertheless, self-limiting etching was achieved and a very stable process of SiO_2 etching was obtained.

In 1996, Royer *et al.* studied the chemisorption of fluorine and sulfur on Si during a simultaneous exposure to SF_6 gas and Ne^+ ion beam. In this study, they showed by XPS measurements that the fluorine amount at the Si surface increases as the temperature decreases in a process window between 20°C and -130°C [3]. Moreover, SF_6 is a well-known gas used in Si plasma etching. Therefore, cryo-ALE based on SF_6 physisorption was studied to extend the use of this new type of process to other materials and to characterize its etching properties.

This work was carried out using a cryogenic ICP reactor equipped with in-situ diagnostics. Mass spectrometry measurements enabled to characterize the SF_6 physisorption and its surface residence time at different temperatures. Spectroscopic ellipsometry was used to monitor the etching rate and to characterize the sample surface at the nanoscale during the three process steps: SF_6 physisorption, pumping and Ar plasma etching. Tests were performed on SiO_2, Si_3N_4 and p-Si coupons glued on SiO_2 6” carrier wafers.

SF_6 physisorption experiments will first be studied and presented notably to find the optimal temperature and purging time for the process. Then, cryo-ALE test results on Si, SiO_2 and Si_3N_4 will be shown. These results will finally be compared to the ones obtained using C_4F_8 physisorption.

Thanks/Acknowledgement

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#PLATH00089

SURF / Plasma - surface interactions

Plasma surface activation of CFRP substrate to enhance adhesion of PVD/PECVD coatings

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Abstract content

Polymer composites materials such as Carbon Fibres Reinforced Polymer (CFRP) are increasingly employed in aircraft industry as replacement of metallic components because of their higher specific resistance. In order to increase the durability of these materials, it could be interesting to deposit metallic or ceramic thin films. PVD and PECVD processes can be considered to coat thermally sensitive substrate. But, adhesion of such films is known to be low on polymer substrates [1].

Surface pre-treatments are therefore required to improve the adhesion of coatings on CFRP substrate. Nowadays, it is commonly accepted that the enhancement of the adhesion of a coating is related to the density of nucleation sites at the polymer surface [2-3]. In order to get films with the highest level of adhesion, plasma treatment have to be optimized for the chemical composition of the substrate. Surface energy measurements can then be used to quantify the surface activation.

In this way, the purpose of this work is to study the effect of low pressure Ar and N_2 plasmas on the surface energy of CFRP. Various plasma conditions are tested by changing parameters like partial gas pressure, gas mixture and bias voltage. These measurements are complemented by chemical analysis (XPS, FTIR) and surface morphology observations (Profilometer, SEM) to clarify the involved mechanisms.

Finally, the best conditions for plasma activation are tested previous the deposition by magnetron sputtering of pure titanium thin film . The resulting adhesion evaluated using scratch test and pull-off test methods, is improved thanks to plasma activation.

Thanks/Acknowledgement

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#PLATH00109

SURF / Plasma - surface interactions

Contributions of grain boundaries in plasma-modified graphene

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Abstract content

Raman spectroscopy is an efficient method to characterize the graphene structure. The technique gives distinctive features for pristine, damaged and even doped graphene. Raman is however limited by its intrinsic microscopic nature, only being able to probe the area exposed to the laser beam (~ 1 µm). Hyperspectral Raman Imaging (RIMA for Raman Imaging) is a powerful method developed by Photon etc. in collaboration with the group of Prof. Martel [1] in order to obtain qualitative as well as quantitative data on a macroscopic scale. Such instrument enable the study of defects engineering located in grains or at grain boundaries, central to the development of functional materials. Although there is a surge of interest in the formation, migration and annihilation of defects during ion and plasma irradiation of bulk materials, these processes are rarely assessed in low-dimensional materials and remain mostly unexplored. Here, we use a hyperspectral Raman imaging scheme providing high selectivity and diffraction-limited spatial resolution to examine plasma-induced damage in a polycrystalline graphene film. Measurements conducted before and after very low-energy (11–13 eV) ion bombardment show defect generation in graphene grains following a zero-dimensional defect curve, whereas domain boundaries tend to develop as one-dimensional defects. Damage generation is slower at grain boundaries than within the grains, a behaviour ascribed to preferential self-healing [2]. This evidence of local defect migration and structural recovery in graphene sheds light on the complexity of chemical and physical processes at the grain boundaries of two-dimensional materials. Furthermore, evidence of preferential doping at grains boundaries or domains is observed with either Boron or Nitrogen linked with their different migration energy compared to carbon’s.

Thanks/Acknowledgement

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#PLATH00137

SURF / Plasma - surface interactions

Atmospheric pressure plasma for surface engineering applications

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Abstract content

Plasma processing allows extremely accurate alterations of a substrate and is widely used when manufacturing transistors for computer chips[1, 2] and precise lenses[3, 4], however very limited results have been published for the atmospheric plasma etching of metals. Current techniques such as: laser modification, vacuum plasma etching, CVD/PVD (Chemical/Physical Vapour Deposition), SPDT (Single Point Diamond Turning) or Electrolysis based methods all have drawbacks when processing high value metal parts, such as: high running costs, expensive tool replacements, long processing times or involve the use of harmful chemicals. We report here the development of an atmospheric pressure plasma technique for the fast, cost-effective finishing of metal surfaces. Atmospheric reactive atom plasma(RAP) has previously shown good results with optical (Si based) materials, providing nanometre roughness and form accuracy over large areas[5]. Extending this approach to metal parts provides new challenges to the chemistry and physics involved. Using two different plasma systems, a number of compounds and their mixtures have been investigated as reactive species for plasma etching of Ti64 (Ti-6Al-4V) plates. The initial results demonstrate volatile products are formed and can be removed from the surface. Combining various characterisation techniques, the underlying surface chemistry and physics are explored. Initial work shows promising results for a number of applications such as finishing of turbine blades for aerospace engines

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#PLATH00142

SURF / Plasma - surface interactions

Effect of plasma sources on the surface modification of carbon reinforced epoxy by atmospheric pressure plasma treatment

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Abstract content

The bonding and adhesion properties of polymer composites is an important consideration in manufacturing processes. A key challenge in polymer adhesion is the need for adhesive pretreatment to improve the wettability properties of the surface. Often three sequential steps are needed: contaminant removal, physically induced surface modification and chemical treatment. Atmospheric plasma treatment (APT) has been shown to either achieve, or eliminate the need for, one or more of these steps[1,2]. The effects of APT on the surface properties of thermoplastics and thermosetting polymers have been reported recently[3], but the report on the effect of different plasma sources on the APT of polymers has been limited. This report presents a study of the effect of dielectric barrier discharge (DBD) plasma sources on the surface modification of Carbon reinforced epoxy. 50% carbon fibre epoxy samples were subjected to either microwave or dielectric barrier discharge (DBD) plasma sources with either argon, nitrogen or oxygen under atmospheric conditions. The surface energy of the polymers and composites were determined using liquid contact angle analysis. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and coherent probe scanning interferometer techniques were used to characterise the surface changes. The underlying mechanisms for the observed change of surface properties will be discussed.

Thanks/Acknowledgement

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#PLATH00065

TRIB / Plasma - deposited protective and tribological coatings

Structure, stress and mechanical properties of Mo-Al-N sputter-deposited thin films: role of point defects

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Abstract content

In this work, the structural and mechanical properties of ternary Mo-Al-N alloys are investigated by combining thin film growth experiments and density functional theory (DFT) calculations. $Mo_{1-x}Al_xN_y$ thin films with various Al fractions ranging from x = 0 to 0.5 and nitrogen-to-metal ratio ranging from y = 0.78 to 1.38, were deposited by dc reactive magnetron cosputtering from elemental Mo and Al targets under $Ar+N_2$ plasma discharges. The elemental composition, mass density, crystal structure, residual stress state, and intrinsic (growth) stress were examined by WDS, XRR, XRD (including pole figure and $\sin^2\psi$ measurements), and real-time *in situ* wafer curvature. Nanoindentation tests were carried out to determine film hardness *H* and elastic modulus E_{IT}, while the shear elastic constant C_{44} was measured selectively by surface Brillouin light spectroscopy.

All deposited $Mo_{1-x}Al_xN_y$ films have a cubic rock-salt crystal structure and exhibit a fiber-texture with a [001] preferred orientation. The incorporation of Al is accompanied by a rise in nitrogen content from 44 to 58 at. %, resulting in a significant increase (2%) in the lattice parameter when x increases from 0 to 0.27. This trend is opposite to what DFT calculations predict for cubic defect-free stoichiometric $Mo_{1-x}Al_xN$ compounds and is attributed to variation in point defect concentration (nitrogen and metal vacancies) when Al substitutes for Mo. Increasing substrate temperature from 350 to 500 °C has a minimal effect on the structural properties and phase composition of the ternary alloys but concurs to an appreciable reduction of the compressive stress from −5 to −4 GPa.

A continuous increase and decrease in transverse sound velocity and mass density, respectively, lead to a moderate stiffening of the shear elastic constant from 130 to 144 GPa with increasing Al fraction up to x = 0.50, and a complex and nonmonotonous variation of *H* and E_{IT} is observed. The maximum hardness of ~33GPa is found for the $Mo_{0.81}Al_{0.19}N_{1.13}$ film, with nitrogen content close to the stoichiometric composition. The experimental findings are explained based on structural and elastic constant values computed from DFT for defect-free and metal- or nitrogen-deficient rock-salt MoAlN compounds [1].

Thanks/Acknowledgement

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#PLATH00072

TRIB / Plasma - deposited protective and tribological coatings

Enhanced tribomechanical performance of metal-doped DLC coatings deposited by HiPIMS with positive pulse technology

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Abstract content

Diamond-like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its many properties, DLC stands out for a good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear. Nevertheless, a factor limiting the widespread application of DLC coatings is their thermal stability. DLC is very temperature-sensitive since its sp3-sp2 structure undergoes a graphitization process at high temperatures that deteriorates both hardness and coefficient of friction. In order to overcome this limitation, new ways to modify DLC coatings for acceptable high temperature performance have been explored. In this work, we investigated the deposition of hard DLC coatings doped with various elements (W, Cr and Si) using HiPIMS technique with the novel incorporation of positive pulses. Highly ionized plasma discharges were obtained during HiPIMS deposition. The high ion energy bombardment allowed reaching higher sp3 bonding levels. EELS spectroscopy was used to evaluate sp3 content and Raman was used for sp2 structural characterization of the films. Enhanced mechanical properties (hardness up to 35 GPa) were observed with nanoindentation for doped DLC coatings. High temperature nanoindentation tests were also performed from room temperature to 500ºC in order to evaluate the evolution of hardness and Young Modulus with temperature. The results shows that the mechanical properties at high temperature mainly depend on the sp3 content. Pin-on-disk tests were carried out in order to assess the tribological performance of the coatings both at room and high temperature. The increased toughness and reduced compressive stress that doping provides to the carbon matrix together with a high sp3 bonding structure obtained with HiPIMS deposition improves the stability of DLC coatings for high temperature tribological applications. The application of metal-doped DLC coatings has proven highly effective in machining high silicon content aluminium alloys.

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#PLATH00122

TRIB / Plasma - deposited protective and tribological coatings

Resonant nuclear reaction analysis investigation of nitrogen and oxygen diffusion processes involved in plasma assisted multi-interstitials surface hardening of Ti6Al4V alloy

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Abstract content

Widely employed in industrial applications including aeronautics turbines and biomedical prosthesis, titanium alloys are presenting highly interesting properties, like low density, high strength or excellent oxidation or corrosion resistance. However, their uses are often restricted by their poor tribological behaviour. Hence, several treatments are proposed to improve the wear resistance, for instance by depositing a hard surface layer (like titanium nitrides or carbides). Without any substrate preparation, these hard and often fragile layers may lead to the “eggshell” effect when the wear solicitation is important and the damages induced by the wear debris on the “soft” substrate may be worse than with untreated titanium alloys. In order to remedy this weakness, multi-interstitials (N, O) diffusion surface treatments of the titanium alloy substrate can provide a thick and strong mechanical support to the top hard layer or can directly be the wear resistant layer. For this purpose, low-pressure plasma assisted diffusion thermochemical treatments, using sequential Oxygen and Nitrogen atmosphere, were applied on Ti6Al4V samples: nitriding was operated at 850°C and working pressure of 5 Pa (60%vol. N_2 + 40%vol. H_2); oxidations were operated at 750°C and working pressure of 5 Pa (100% O_2 or 100% CO_2).. In order to study the potential influence of each interstitial (N, O) on the diffusion of the other one, various sequential treatments (nitriding + oxidizing or oxidizing + nitriding) were performed with isotopic ^{15}N or ^{18}O elements in the reactive atmosphere and the resulting composition profiles were analysed by resonant nuclear reaction analysis (NRA). Microstructure of the modified surfaces were also characterized by optical microscopy and scanning electron microscopy (SEM) and the crystallographic structure was determined by X-Ray Diffraction (XRD); Glow Discharge Optical Emission Spectroscopy (GDOES) and Energy Dispersive X-Ray Spectroscopy (EDS) provided depth profiles of the treated surface chemical composition and were compared to the NRA results. To investigate the potential improvement in wear resistance, Vickers microhardness profiles were measured on cross section. Improved microhardness profiles were obtained over few tens of micrometres by combining nitriding + oxidizing treatments of few hours, corresponding to incorporation of O and N interstitials in the α-Ti matrix.

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#PLATH00077

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

DIRECT OBSERVATION OF TWINNING DOMAINS IN COPPER IODIDE THIN FILM SYNTHESIZED BY MAGNETRON SPUTTERING OF CU THIN LAYERS AT LOW TEMPERATURE AND IODINE VAPOR

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Abstract content

Copper iodide (CuI) is attracting much attention for thin film applications, due to promising properties for optoelectronic devices and wide band-gap semiconductors. This non-toxic material is composed of earth abundant elements. Recently, it has been shown that CuI can be bonded with organic ligands used in perovskite solar cells. Depending on the temperature, copper iodide can crystallize in three structures named α, β, and γ-CuI. At room temperature, the more stable phase is the γ-CuI one (F-43m, a = 6.054 Å) that is very promising as p-type transparent material. In this work, thin films of CuI have been synthesized by the iodination of sputtered Cu coatings with iodine vapor to investigate the film properties and their optoelectronic performance. The structural, electrical, and optical properties of CuI thin films deposited on glass and silicon substrates were studied by X-ray diffraction, Hall effect, UV-visible spectrometry and photoluminescence. We obtained transparent p-type semiconductors films crystallizing in the γ-phase with wide bandgap ($E_g \approx 3.1$ eV). Copper iodide films exhibit a strong preferred orientation in the [111] direction. Thin film morphology, examined by scanning electron microscopy, shows a variation of crystal size depending on the iodination conditions. Crystallographic twin domains in CuI grains have been observed by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) through which the twin geometry and orientation can be understood, This information is crucial for further improvements of perovskite solar cells.

#PLATH00119

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

EELS STUDY OF $SMNIO_3$ THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING WITH A SOFT AIR ATMOSPHERE POST-ANNEALING

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Abstract content

A large number of functional oxides crystallize in the structure of the perovskite family. Among these, rare earth nickelates ($ReNiO_3$) exhibit a reversible metal-insulator transition (MIT) at a critical temperature. The latter can be modified according to the stoichiometry and the nature of the rare earth. Because of this, $ReNiO_3$ has an increasing research interest due to the tunability of its remarkable structural, electronic, magnetic and optical properties. In this work, we focus on samarium nickelate ($SmNiO_3$) thin films. This kind of perovskite has a MIT of around 120°C, whereby it looks like a great candidate for a new generation of thermochromic solar absorbers. In previous works, $SmNiO_3$ was classically obtained by oxidation of metallic mixtures at high oxygen pressures with the aim to stabilize the metastable Ni^{3+} oxidation state. Nevertheless, we show that $SmNiO_3$ thin films can be grown as the habitual orthorhombically distorted perovskite structure under atmospheric pressure. These layers were synthesized by a confocal magnetron sputtering deposition system and subsequently annealed under a soft air atmosphere for crystallization. EELS analysis were performed to study the degree of oxidation of the elements. Structural characterization was made by XRD and HRTEM techniques, while electrical and optical properties were determined by four-point probe and FTIR, respectively.

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#PLATH00124

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

PE-CVD with organometallic precursors: contribution of aerosol assisted processes

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Abstract content

PE-CVD is widely used to deposit inorganic thin films. For example, a lot of different precursors (Tetraethyl orthosilicate - TEOS, Hexamethyldisiloxane - HMDSO, Hexamethyldisilane - HMDS, Tetramethylsilane - TMS, etc.) has been used for organosilicon or silica-like coatings. In contrast, only few studies are using organometallic precursors. Indeed, such molecules are generally unstable, pyrophoric and highly reactive with air and/or oxygen. Aerosol-assisted processes are able to avoid these problems. Indeed, diluted in organic solvents, it enables to inject droplets of organometallic precursor charged liquids. This contribution aims to report first results obtained with nickel- or zinc-based organometallic precursors. Using a pulsed injection of the liquid solution, it enables to deposit DLC matrices doped with Ni or Zn. Depending on the aerosol composition, the plasma behaviours as well as the film structures and properties will be discussed.

#PLATH00125

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

Plasma polymer for enhancing adhesion bonds of metal/elastomer assembly

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Abstract content

Plasma-enhanced chemical vapor deposition has been used to deposit polymeric films on metal or polymers whose properties can be adjusted by optimizing deposition parameters. Multilayers or single plasma layers with chemical composition gradient in thickness are credited with providing outstanding properties such as the adhesion between the plasma polymer and the substrate [1,2]. The multilayer plasma deposit is applied to different precursors (acetylene, acrylic acid, maleic anhydride) in the aim of adhesion for metal / elastomers assembly. In addition to the thermodynamic aspects of wetting, the adhesion mechanisms are based on various interactions such as the establishment of chemical bonds and the diffusion of the macromolecular chains of the adhesive and the polymeric materials. Therefore, here, four model plasma layers, representative of these mechanisms were synthesized by combining the pulsed or continuous wave for the plasma polymerization of these three precursors. Pulsed wave deposits carried out under conditions less degrading and preserving the chemical groups of each precursor should promote the chemical adhesion. Opposite continuous wave deposits with less reactive group retention play on the thickness of the deposit, i.e on duration without providing targeted chemical functionality and are in favor of the interdiffusion of macromolecular chains. The last experiment (CW + PW) is intermediate to the other methods. A thick layer about several 10 nm is first deposited on the substrate under continuous wave; then at the extreme surface the chemical functionalization is provided by the deposition in pulsed wave under optimal retention conditions. This experimental path should combine the effects of chemical anchoring and interdiffusion with a chemically controlled surface and a relatively thick film to facilitate the creation of an interphase during further adhesive vulcanization. After a full characterization of each plasma layer, the validation of these model layers is illustrated by measuring the mechanical strength of two assemblies (aluminum - poly(acrylonitrile butadiene) rubber (NBR) and stainless steel - fluoroelastomer (FKM)). It appears that the thermodynamic criteria, the hydrophobicity or the thickness depending of the plasma polymer and elastomer properties enhance the yield stress.

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#PLATH00155

DEPO / Plasma - deposited coatings for optical, electronical and other functionalities

Fabrication and characterization of magnetron co-sputtered $TiO_2/SiO_2/Ag$ coatings inhibiting bacterial adhesion and biofilm formation

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Abstract content

Aim of this study was the development of antimicrobial coatings for medical devices, employing the advantages of magnetron co-sputtering as a dry technique to deposit $TiO_2/SiO_2/Ag$ nanocomposite thin films. Their biological activity was correlated to surface characteristics influencing the bio-adhesion and biofilm formation: elemental composition, morphology, surface energy and its polar and disperse parts. Dispersing effect of SiO_2 was observed lidding to a formation of a submicron grain structure of the coatings. Strong inhibitory effect toward Escherichia coli growth was found: viable bacterial cells number, approaching to zero at the first 30 min - 1 h, depending on the Ag content (Fig. 1). Biofilm formation in urine flow at 48 h was reduced down to 92 % compared to a control glass surface (Fig. 2). Direct contact and eluted silver mediated killing were experimentally demonstrated as a mechanism of antibacterial action. The $TiO_2/SiO_2/Ag$ coatings are promising candidate for antimicrobial protection of urinary tract devices for at least 48h, suggesting benefits over longer time.

Thanks/Acknowledgement

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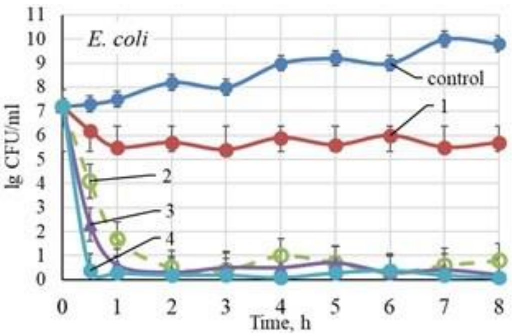
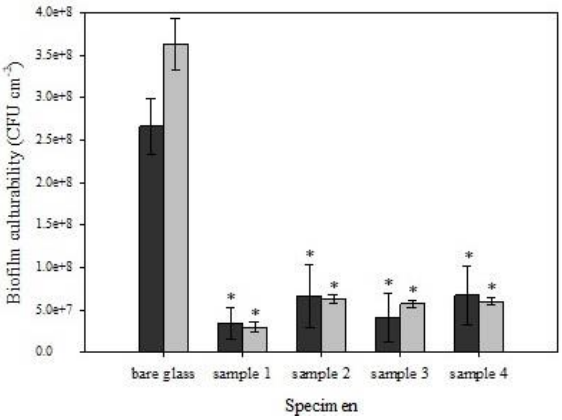
E. coli growth inhibition by studied coatings



E. coli biofilm formation in urine flow



#PLATH00063

GROM / Thin films growth and modelling

Multi-scale modelling of sputtered deposited TiN, ZrN, HfN and TiAlN thin films at oblique angle incidence

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Abstract content

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.

#PLATH00087

GROM / Thin films growth and modelling

Optimization of the anti-reflective coating (SiC_XN_YH) / Silicon interface to improve silicon photovoltaic cell performance

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Abstract content

Thin dielectric films are nowadays widely used in the photovoltaic field (PV), for which both passivation of surfaces and anti-reflective properties are sought. Hydrogenated silicon carbonitride thin films (a-SiC_xN_y:H) recently attracted great interest because of their physico-chemical intermediate of those of silicon carbide (SiC) and silicon nitride (Si_3N_4). The most useful behavior concerns the optical constant tunability of a-SiC_xN_y:H films which are promising as antireflective coatings for silicon photovoltaic cells. However, the interface between the Si substrate and antireflective films plays a key role on the yield of PV cells. Thus, a surface passivation method, consisting of a nitridation process performed using N_2 plasma (ECR and GDS) sources implemented in an ultra-high vacuum chamber, was set up. This aims to minimize the dangling bonds and therefore to reduce the interface state density. Various experimental parameters (substrate temperature, nitridation time, N_2 pressure, substrate crystallographic orientation) have been varied to create a very thin SiN film (less than 10 nm) studied by X-ray Photoelectron Spectroscopy measurements combined with surface models which allow the determination of the composition and the thickness of the nitride layer formed. Having optimized the SiN layer structure, a-SiC_xN_y:H film is elaborated by a reactive deposition process using non-toxic gases (CH_4, N_2, O_2) involving radio-frequency plasma. Electrical measurements were carried out to estimate the improvement of the elaborated interface.

Thanks/Acknowledgement

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#PLATH00132

GROM / Thin films growth and modelling

Effect of the deposition rate on competitive growth between amorphous and crystalline phases in sputtered Zr-Cr thin films

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Abstract content

Here, we report a one-step bottom-up approach to synthesize Zr-Cr thin films at the transition between amorphous and crystalline state, allowing a self-separation of the two phases to occur during deposition. In this work, Zr-Cr thin films were synthesized by magnetron co-sputtering of Zr and Cr targets. It is shown scanning electron microscopy and X-ray diffraction that changing the composition of the film between the amorphous and the crystalline compositions enables discovering a competitive self-separation of the two phases, leading to competitive growth between amorphous and crystalline phases. The crystalline phase becomes predominant with increasing thickness, until it covers the whole surface. This process is similar to what we have reported in Zr-W and Zr-Mo systems [1, 2]. Yet, the deposition rate is shown here to change the geometrical characteristics of crystalline regions during growth. This competitive growth enables tuning surface-related functional properties (i.e. surface roughness, reflectivity, wettability, …) with a one-step process.

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#PLATH00121

HELI / Health and life science

The application of Cold Atmospheric Plasma (CAP) in medicine

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Abstract content

Over the past few years, the application of cold atmospheric plasma (CAP) in medicine has developed into an innovative field of research of rapidly growing importance. One promising new medical application of CAP is cancer treatment.

The therapeutic effects of CAPs are related to reactive oxygen and nitrogen species (ROS and RNS) present in the plasma. Experiments are currently showing that CAP can selectively kill cancer cells and less damage to healthy cells, but the underlying mechanisms remain unclear. Using computer simulations, we try to shed light on the mechanism of selectivity, based on Voltage dependent anion channels (VDACs). These protein channels are located on the cell membrane that carries H2O2 and other active oxygen species to the inner part of the cell.

Specifically, we perform molecular dynamics simulations for the permeation of H2O2 through hvdac1 (one of the members of the VDAC family) on the dioleoylphosphatidylcholine (DOPC) phospholipid bilayer (PLB). The free energy barrier of H2O2 across hvdac1 is lower than for the DOPC PLB. This indicates that the delivery of H2O2 into the cell interior more easily through the hvdac1 channel. Due to the abundance of this channel in cancer cells compared to healthy cells, plasma is more likely to affect cancer cells. This study gives a better insight into the role of VDACs in the selectivity of CAPs for treating cancer cells.