Plasma Science and Technology Division
Room 104A - Session PS+PB-MoA

Plasma and Polymers: 'The Legacy of Riccardo d'Agostino and Beyond'

Moderators: Ankur Agarwal, KLA-Tencor, Mohan Sankaran, Case Western Reserve University

1:20pm **PS+PB-MoA-1 Foreword/introduction to the session: "Reflections on the Legacy of Riccardo d'Agostino"**, *P Favia,* University of Barii, Italy

In this contribution I will review the career of Prof. d'Agostino and reflect on his scientific achievements, his extensive network in the field of plasma chemistry, plasma processing of materials and applications, and his role as mentor for several generations of M.Sc. students as well as PhD and postdocs.

1:40pm **PS+PB-MoA-2 Atmospheric Pressure PE-CVD of Drug-containing Nanometric Capsules**, ***Pietro Favia,*** *C Lo Porto, A Treglia,* University of Bari, Italy; *F Palumbo,* CNR Institute of Nanotechnology NANOTEC, Italy

Plasma Enhanced Chemical Vapor Deposition Processes have been investigated by Riccardo d'Agostino and co-workers, and by many of his colleagues, in the late 80s and early 90s, mainly at low pressure, resulting in a large number of publications on the deposition kinetics and on the applications of coatings of different composition and properties. Many other PE-CVD approaches have been developed since then, and the deposition processes have been or are going to be deeply investigated, following the legacy of Riccardo d'Agostino in this field.

In this talk we present a set of data on the direct PE-CVD of nanometric capsules in the plasma phase resulting from Aerosol Assisted (AA) Atmospheric Pressure (AP) PE-CVD processes fed with Helium (carrier), Ethylene (film precursor) and aerosol droplets of solutions of drugs (nancomicyn, gentamicyn, etc). This approach [1, 2, 3] can lead, in certain conditions, to the deposition of thin coatings directly on the droplets of the aerosol, thus leading to the synthesis of drug-containing nanometric capsules, of potential interest for biomedical applications, e.g., as anti-bacterial surfaces [4].

The influence of various plasma parameters on the AA-AP-PE-CVD processes is discussed, as well as some properties of the coatings.

acknowledgements

The mentorship of Prof. d'Agostino is acknowledged by the authors of this contribution, as well as the recognition of his legacy in the field of plasma processing of materials.

references

1. A. Heyse et al, Plasma Proc. Polym. 8, 965 (2011)
2. Palumbo et al, Plasma Proc. Polym. 12, 1302 (2015)
3. Lo Porto et al, Polym. Chem. 8, 1746 (2017)
4. Sardella et al, *Materials* 2017, 9, 515

2:00pm **PS+PB-MoA-3 Ultrathin Metal-Organic Covalent Networks by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD) for Gas Separation Membranes**, ***Karen Gleason,*** *M Wang,* MIT; *N Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg; *M Creatore, A Perrotta,* Eindhoven University of Technology, The Netherlands, Netherlands; *K Heinze,* Johannes Gutenberg-Universität, Mainz, Germany

Metal-Organic Covalent Networks (MOCN) were synthesized as ultrathin (<100 nm), defect-free and mechanically flexible layers by initiated Plasma Enhanced Chemical Vapor Deposition (iPECVD). The low substrate temperature used for iCVD allowed use of thermal sensitive porous poly[1-trimethylsilyl)-1-propene] (PTMSP) as a substrate. Uniform layers were grown over 150 nm diameter substrates and did not delaminate upon mechanical deformation. The resulting robust MOCN/PTMSP composite membranes exhibiting outstanding gas separation performance for multiple pairs of gases. Using zinc (II) meso-tetraphenyl porphphyrin (ZnTPP) as the monomer and tert-butyl peroxide as the initiator, film deposition was achieved at low plasma excitation powers. The nearly unchanged intensity of the Soret bands in the UV-vis spectra confirmed the retention of the 18 pi e- conjugation of the monomer units incorporated into the films. The gas selectivity for the separation of H_2/CH_4 or H_2/N_2 is small (<3) for either the PTMSP base membrane or for thin films of evaporated ZnTPP. However, the gas selectivity for both H_2/CH_4 or H_2/N_2 rises to >500 for the PTMSP/iPECVD ZnTPP composite membrane, exceeding the performance of commercial membranes. Ellipsometric Porosimetry and Density Functional Theory Calculations are consistent with a pore size of ~0.4 nm in the MOCN film. Additionally, iPECVD layers derived from a metal-free porphyrin and from porphyrins containing magnanese (III) and cobalt (III) will be described.

2:20pm **PS+PB-MoA-4 Influence of Energetic Conditions on the Plasma Polymerization of Cyclopropylamine in Capacitively Coupled Discharges**, ***Lenka Zajickova,*** *M Michlicek,* Masaryk University, Czech Republic; *S Hamaguchi,* Osaka University, Japan

Thin films prepared by plasma polymerization of cyclopropylamine (CPA) in capacitively coupled discharges demonstrated their attractive functional properties as a matrix layer in immunosensors or surface modification of synthetic polymers used for a cell cultivation. These bioapplications required tuning the concentration of amine and other bio-active groups together with the film stability in aqueous media. Since the final plasma polymer composition is influenced by the discharge power and the polymer cross-linking can be modified by ion energy flux towards the growing film the investigation of bulk plasma and plasma-surface interactions with respect to the energetic conditions are necessary for fundamental understanding of the overall process. This work puts together the results on the plasma polymer properties with the plasma diagnostics by mass and ion spectrometry, optical emission spectroscopy and retarding field energy analyzer placed at the substrate position. The experiments are complemented by the molecular dynamic simulations of the film growth.

2:40pm **PS+PB-MoA-5 Electrochromic Investigation of PEDOT Film Deposited by Plasma Radicals Assisted Polymerization *via* CVD**, ***Bianca Rita Pistillo,*** *G Lamblin, J Polesel-Maris, K Menguelti, D Arl, D Lenoble,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Quite recently conducting polymer have been introduced into a broad range of organic electronic devices in place of analogous inorganic semiconductors, owing to their numerous merits as flexibility, low cost and lightweight over their forerunners. Similarly to inorganic material, also conducting polymer display electrochromism. The oxidation or reduction of these films is usually associated with reversible ion insertion and extraction across an electrochromic material/electrolyte interface with complementary electron transfer across the electrochromic material/electrode interface. In the last years, the study and implementation of organic electrochromic materials (OEM) into devices had a tremendous growth also because of their relatively narrow absorption band in displaying diverse and clear colour. [T.T. Steckler et al. J. Am. Chem. Soc. 2014, 136, 1190] There are many interesting applications of OEM such as smart windows, flexible displays, electrochromic fibres, etc. One of the most attractive ones is Poly(3,4-ethylenedioxythiophene) (PEDOT) with its derivatives. PEDOT changes its colour from dark blue/purple, in its reduced state, to light blue, in the oxidised state with very low applied switching potential. Plasma Radicals Assisted Polymerization via Chemical Vapour Deposition (PRAP-CVD) has been developed at Luxembourg Institute of Science and Technology as an efficient alternative to conventional vapour-based processes of conductive thin films as PEDOT. [D. Lenoble, Controlled radical assisited polymerization, Lux. 91934, 2013] This process is based on the concomitant but physically separated injection of low-energy oxidative radical initiators and vaporized monomer species into a reactor where temperature and pressure are finely controlled. [B.R.Pistillo et al. J. Mater. Chem. C 2016, 4, 5617] A few advantages of making the process completely dry include the possibility of processing solvent-sensitive substrates such as paper, overcoming the effects of rinsing on the underlying films in the case of multilayer structures. Moreover, PRAP-CVD allows the deposition of highly conformal coatings, which accurately follows the geometry of the underlying substrate independently from its nature, enlarging the application of PEDOT as OEM. In this work, we present the investigation of electrochromic properties of PRAP-CVD PEDOT films. The behaviour of films was compared with the data in the literature revealing a faster switching time compared to other vapour-based processes reported. The range of switching potential with limited electrochemical degradation of the thin electrochromic film was also investigated by the means of UV-visible spectroelectrochemistry.

3:00pm **PS+PB-MoA-6 Initial ZnO Crystallite Formation by Plasma Enhanced ALD**, ***Alberto Perrotta,*** *J Pilz, A Coclite,* Graz University of Technology, Austria

ZnO is a wide direct bandgap semiconductor, extensively studied as thin film because of its unique optical, electrical, and piezoelectric properties. Its crystalline structure and degree of crystallinity have a crucial impact on the material characteristics and a particular crystallographic texture may be beneficial for gaining optimized piezoelectric properties or enhanced velocities in surface acoustic wave devices. Therefore, the possibility to control the preferred crystallographic orientation in ZnO thin films has been often investigated.

Atomic layer deposition (ALD) offers the possibility to study in detail the growth of ZnO, due to its layer-by-layer nature and sub-nm thickness control. The initial growth of ZnO adopting diethylzinc (DEZ) and water and its impact on the crystallographic texture of the resulting thin films shed light on the growth mechanisms and the influence of the substrate nature on the in-plane and out-of-plane crystal orientations.

However, thin films deposited with plasma enhanced ALD are known to show several differences when compared to thermal ALD. Therefore, for ZnO thin films the growth mechanism and initial crystallite formation may be greatly influenced by the use of plasma. In this contribution, the initial growth of direct plasma ALD ZnO grown on Si (100) is investigated. DEZ and pure oxygen plasma are adopted during the process. The first 20 cycles of growth are analysed using synchrotron light grazing incidence X-ray diffraction (GIXD), X-ray reflectivity (XRR), and spectroscopic ellipsometry (SE). The influence of substrate temperature ranging from 25 °C to 250 °C on the crystal growth and crystal orientation are studied. A closed layer was obtained within 7 cycles as measured by XRR for all the temperature explored, suggesting island growth of the ZnO. However, GIXD showed no crystalline texture forming at this stage. An amorphous intermixed interface between the native SiO_2 and the growing layer was found, with a density in between pure SiO_2 and ZnO. Irrespective of the deposition temperature, the first crystal structure was measured at around 3 nm, with a preferential out-of-plane orientation transiting from (100) at room temperature to (002) at 250 °C. The first crystallographic seeds were found to largely determine the final microstructure of thicker films.

3:40pm **PS+PB-MoA-8 On Fluorocarbons and Fish: Creating a Global Impact on Generations of Plasma Chemists***, **Ellen Fisher,*** Colorado State University

Plasma processing represents a powerful approach to modification of a range of substrates with an array of chemistries and morphologies. One of the most useful plasma processing tools is that of plasma polymerization for thin film formation. Arguably, the work of Riccardo d'Agostino and his coworkers over numerous decades, especially in the arena of fluorocarbon film deposition, has significantly enhanced our understanding of plasma polymerization and influenced countless additional studies around the globe. Here, we will detail how d'Agostino's work based in Bari, Italy inspired a range of studies of various fluorocarbon systems that have been performed over more than 2 decades in one laboratory nearly 6000 miles away. Despite the foundational data provided by d'Agostino's early examination of plasma polymerization processes, the remaining paucity of data regarding the fundamental, molecular-level mechanisms that drive fluorocarbon and hydrocarbon plasma polymerization begged further examination. Combining a range of spectroscopy techniques, materials characterization tools, and plasma-surface interface studies has yielded another generation (or two) of insight. This presentation will focus on film deposition studies utilizing multidimensional substrates (e.g. membranes, scaffolds, nanomaterials), and the connections between d'Agostino's pioneering plasma polymerization work and our more recent studies relevant to a range of value added products, including blood-contacting devices, sensors, tissue engineering, and separation technologies.

4:00pm **PS+PB-MoA-9 DIRECT and Remote Surface Functionalization using Atmospheric Pressure Dielectric Barrier Discharges***, **Francesco Fracassi,*** University of Bari, Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; F Fanelli,* Institute of Nanotechnology (NANOTEC), NRC, Italy, Italia*; V Armenise, A Uricchio, R d'Agostino,* University of Bari, Italy, Italia

The utilization of atmospheric pressure dielectric barrier discharges (DBDs) for the surface modification of materials is a very interesting and actual topic. In recent years, efforts have been directed toward the development of a large variety of processes which exploit different DBD configurations and electrode geometries. This contribution describes DBD-based deposition and treatment processes which are potentially of interest also for environmental applications. The processes are performed on polyurethane (PU) foams, i.e., three-dimensional porous substrates which can be quite uniformly surface functionalized by DBDs, since, under suitable experimental conditions, the discharge ignites both outside the foam and throughout its entire porous structure. Three experimental strategies are utilized: i) direct treatment and deposition in parallel plate DBD; ii) direct aerosol-assisted deposition in parallel plate DBD; iii) remote deposition of thin films containing carboxylic acid groups with DBD jet.

The direct treatment is performed by feeding the DBD with He-O_2 mixtures in order to form carboxyl groups on the polyurethane surface. The treated foams are able to adsorb heavy metals from water solutions and can be regenerated (release of adsorbed heavy metals) through immersion in concentrated sodium chloride solution. However, the treated foams suffer ageing in water and, therefore, at the second reuse the amount of adsorbed metals decreases. A water-stable surface containing carboxyl groups is obtained with the DBD jet fed with helium-acrylic acid-ethylene mixtures (remote thin film deposition). No morphological and chemical modifications of the deposits are detected also after 72 h of immersion in water.

When the parallel plate DBD is fed with He-C_3F_6 mixtures, the deposition of fluoropolymer thin films occurs on both the exterior and interior of the foam. The treated foams are superhydrophobic and oleophilic, simultaneously, with potential application for the separation of oil from polluted water, since they selectively adsorb oil, while repelling water.

The direct aerosol-assisted deposition in parallel plate DBD is utilized to prepare hybrid organic-inorganic nanocomposite coatings composed of a hydrocarbon polymer and ZnO or TiO_2 nanoparticles. Under appropriate deposition conditions, it is possible to obtain multifunctional coating characterized by superhydrophobicity, superoleophilicity as well as by the peculiar photocatalytic properties of the utilized nanoparticles. The application of the treated foams for oil-water separation and for the photocatalytic degradation of organic pollutants in water is currently under investigation.

4:20pm **PS+PB-MoA-10 Quest for Durable Low-index Optical Coatings: From Plasma Polymerized Fluorocarbons to Hybrid Organic-inorganic and Nanostructured Films***, L Martinu,* ***Jolanta Klemberg-Sapieha****, O Zabeida,* Ecole Polytechnique de Montreal, Canada

Low (n less than about 1.55@550nm) and ultra-low refractive index materials (n less than 1.38@550nm) are of particular interest in the context of enhanced optical performance of interference filters (IF, including anti-reflective coatings). In addition, for many years now, there has been a lot of effort to develop such low and ultra-low index films with multifunctional characteristics making them suitable for the applications of IF on plastic and flexible substrates. This includes a necessity to better understand and optimize the thermo-mechanical properties (hardness, Young's modulus, adhesion, thermal expansion coefficient), surface energy (hydrophobicity), and possibly provide complementary functionalities (color, electrical conductivity, etc.). This presentation provides an overview of the progress in the field outlined above, starting with the work performed jointly with Professor Riccardo d'Agostino. In the first part, we describe the main optical, mechanical and dielectric characteristics of plasma polymerized fluorocarbons and related metal-doped plasma polymers. In the second part, we introduce hybrid organic-inorganic (SiOCH) materials that are shown to combine high mechanical resistance of ceramics with high elasticity of polymers. We demonstrate, that the refractive index of such films can vary from 1.50 to 1.53, while the extinction coefficient is kept below 10-4. At the same time, the hardness-to-Young's modulus ratio, H/E, is substantially increased (to 0.16) compared to 0.08 for pure SiO2), a result that is well correlated with the increased resistance to crack formation and propagation. Such layers, incorporated in multilayer structures on plastic substrates, provide significantly enhanced optical and mechanical stability in environments involving large temperature and humidity excursions. In the third part, we explore the characteristics of a new category of hybrid SiOCH thin films prepared by glancing angle deposition (GLAD) using electron beam evaporation of SiO2, in the presence of an organo-silicone precursor. The resulting layers are shown to exhibit n as low as 1.2, high elastic rebound and high hydrophobicity, and better mechanical properties than their inorganic counterparts. Their performance is discussed in terms of their anisotropy assessed by the nanostructure-based spectroscopic ellipsometry model. Finally, we demonstrate successful implementation of the ultra-low index material in a complete IF stack.

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