

Advanced Surface Engineering

Room: 212A - Session SE+PS+SM-TuM

Atmospheric Pressure Plasmas, CVD and Other Deposition Methods

Moderator: Hana Barankova, Uppsala University, Sweden, Michael Stueber, Karlsruhe Institute of Technology

8:00am **SE+PS+SM-TuM1 Synthesis of Hybrid Nanoparticles - Fluorinated (Super)Hydrophobic Coatings by Atmospheric Plasma : Possibilities and Challenges**, *J. Mertens, J. Hubert, N. Vandecasteele, François Reniers*, Université Libre de Bruxelles, Belgium

In order to obtain superhydrophobic coatings, one has to combine a low surface energy surface with a specific roughness. We propose a simple method to obtain such coatings by depositing by atmospheric plasma fluorinated coatings starting from C_6F_{12} or C_6F_{14} in argon or helium onto surfaces previously decorated with SiO_2 or TiO_2 nanoparticles. The loading (concentration) and size of nanoparticles were varied, as well as the plasma parameters (nature of the process gas and precursor, plasma power, deposition time). Depending on the experimental parameters, coatings exhibiting water contact angles from 110° to more than 160° could be obtained. The mechanisms for the polymer synthesis have been studied by a combination of atmospheric mass spectrometry and X-ray photoelectron spectroscopy, and the influence of the process gas on the final chemical structure of the coating is evidenced and explained. A higher fragmentation pattern is shown for Argon, due to the higher electron density and the higher energy available in the filamentary discharge. This is responsible for a change in the CF_2 and CF_3 moieties in the final coating. Similarly, the nature of the oxide nanoparticles has a strong influence on the chemistry of the coating: whereas SiO_2 particles do not modify the CFX films, the TiO_2 nanoparticles contribute to a significant degradation of the chemistry of the coating. This method can easily be implemented on any industrial process line, provided a good adhesion of the final coating on the substrate is obtained.

8:20am **SE+PS+SM-TuM2 Deposition of Antifouling PMOXA-like Coatings using Atmospheric Pressure Helium Plasma Jet**, *Sameer Al-Bataineh, A. Cavallaro, M. Ramiasa, K. Vasilev*, University of South Australia

Antifouling interfaces are important in a wide range of applications such as food packaging, water purification, marine biofouling and biomedical devices.^{1,2} In recent years, poly(2-oxazoline)s have attracted much attention due to their numerous biological applications as antifouling polymers.^{3,4} Poly(2-methyl-2-oxazoline)(PMOXA) has antifouling properties comparable to the gold standard PEG, and has better stability in a range of aqueous solution and biological media.⁵ Atmospheric pressure plasma (APP) is an emerging technology with a wide range of applications including material processing.⁶ The advantage of using APP for surface modification is that it eliminates the use of expensive vacuum equipment and enables continuous surface modification processes. This study aims to develop PMOXA-like coatings using atmospheric pressure helium plasma jet.

The plasma jet system used in this study consisted of a glass capillary tube with an internal diameter of 1mm that was surrounded by two external hollow electrodes separated by 4mm. The carrier helium gas was sent through a glass container at a flow rate of $1L.min^{-1}$ and carried the oxazoline monomer (2-methyl-2-oxazoline, MOXA) vapour into the glass tube. The plasma jet was operated at an applied voltage of 5.5 kV_{pk-pk} and a frequency of 10 kHz. Deposition of the plasma coatings was carried out under static deposition conditions with 3mm separation distance between the end of the capillary tube and the substrate. To enhance stability of the coatings, substrates were heated during plasma deposition process.

Surface elemental composition and molecular structure of oxazoline plasma polymer coatings were thoroughly characterised using XPS and ToF-SIMS. Stability of the plasma coatings were examined by incubation in PBS buffer solution at room temperature overnight. The antifouling properties of the plasma coatings are now under investigation towards resisting protein adsorption and bacterial cell adhesion. In addition, the surface chemistry and functionality of the coatings produced in this study will be briefly compared to those prepared with an RF low pressure plasma.⁷

This study offers a convenient alternative single step strategy for preparation of oxazoline-based antifouling coatings.

1. Lowe S, et al., *Polym. Chem.*, 2015, 6, 198.

2. Zou L, et al., *J. Membr. Sci.*, 2011, 369, 420.

3. Luxenhofer R, et al., *Macromol. Rapid Commun.*, 2012, 33, 1613.

4. Sedlacek O, et al., *Macromol. Rapid Commun.*, 2012, 33, 1648.

5. Konradi R, et al., *Langmuir*, 2008, 24, 613.

6. Merche D, et al., *Thin Solid Films*, 2012, 520, 4219.

7. Ramiasa MN, et al., *Chem. Commun.*, 2015, 51, 4279.

8:40am **SE+PS+SM-TuM3 Antibacterial Silicon Oxide Thin Films Doped with Zinc and Copper Grown by Atmospheric Pressure Plasma Chemical Vapor Deposition**, *E. Jäger*, Montanuniversität Leoben, *J. Schmidt, A. Pfuch, S. Spange, O. Beier*, INNOVENT e.V., *O. Jantschner, R. Daniel*, Montanuniversität Leoben, *Christian Mitterer*, Montanuniversität Leoben, Austria

Zn- and Cu-doped SiO_x films were applied by atmospheric pressure plasma chemical vapor deposition to study their antibacterial efficiency against Gram-negative *Escherichia coli* and their cytotoxic effect on the growth of mouse cells. ZnO_x and CuO_x particles were found to be homogeneously embedded within the SiO_x films. For both doping elements, bacteria are killed already within the first three hours after exposure to the film surface. In contrast, mouse cells grow well on the surfaces of both film types, with a slight inhibition effect present only after the first day of exposure, due to the more pronounced release of zinc and copper. The obtained results indicate that the films show a high potential for use as effective antibacterial surfaces for medical applications

9:00am **SE+PS+SM-TuM4 Carbon Bridge Incorporation in Organic-Inorganic Hybrid Coatings using Atmospheric Plasma Deposition in Ambient Air**, *Linying Cui*, Stanford University, *G. Dubois*, IBM Almaden Research Center, *R.H. Dauskardt*, Stanford University

Atmospheric plasma deposition in ambient air has a huge potential for large-scale coating synthesis at reduced cost for energy, display, and aerospace applications. However, the abundant oxygen in air poses significant oxidation challenge for incorporating specific oxygen sensitive components in the coating. In this work, the oxygen sensitive carbon bridge structure was successfully incorporated into the inorganic silicate network in the oxygen-helium atmospheric plasma in ambient air. The mechanism of incorporating the specific carbon structure in an oxidative species rich environment was elucidated by a kinetics model which takes into account the probability of oxidation, adsorption, and desorption of different precursor species during gas transport and on the substrate surface. The key tuning knobs were identified as the precursor chemistry and the precursor delivery rate. The resulting carbon bridged organo-silicate coatings exhibited significantly improved plasticity, more than doubled adhesion, and up to four times increase of moisture resistance in terms of the driving energy threshold for debonding in humid air, compared to plasma silica coatings and commercial sol-gel polysiloxane coatings. In order to further improve the interfacial bonding of the coating to oxygen sensitive substrate in an oxidative atmospheric plasma environment, other deposition parameters were also investigated in order to fully activate but not over-oxidize the substrate. The resulting carbon bridged, highly adhesive coating showed remarkably enhanced hydrothermal stability, a key requirement for application in exterior coatings and functional membranes. As an example for application, the carbon-bridged coating was deposited between hard scratch-resistant coatings and oxygen-sensitive polymer substrate to enhance the adhesion of hard coatings for airplane window protection.

9:20am **SE+PS+SM-TuM5 Atmospheric Plasma in Liquids**, *Ladislav Bardos, H. Barankova*, Uppsala University, Sweden **INVITED**

Experiments using spark discharge above the water level were reported already in 1784 by Henry Cavendish after his study of air. His results inspired in 1894 Lord Rayleigh and William Ramsay and led to an important discovery of argon present in air. Studies of water electrolysis and interactions of a glow discharge with water solutions were described in 1887 by J. Gubkin and followed in 1952 by R.A. Davies and A. Hickling. The first type of plasma discharge submerged directly into water was an arc. The arc discharges are used for the underwater welding already since 1930. A number of applications of submerged arcs have already been tested and reported. Rapid developments of non-thermal (cold) atmospheric plasma sources during last century led to new studies of plasma in liquids. Studies of the plasma-assisted electrolysis and different phenomena observed on surfaces of electrodes during electrolysis in water electrolytes enhanced an interest in different types of submerged discharges. New processes were developed like the plasma electrolytic oxidation (PEO), formation of nanoparticles and nanotubes, novel plasma-chemical reactions, plasma cleaning, disinfection and "activation" of water or water solutions. This

presentation summarizes several interesting systems and results on the submerged plasma in liquids. Examples of the experimental systems and the results of tests of cold plasma discharges in water using different power generators and an efficient low power production of hydrogen from the mixtures of water with ethanol will be presented and discussed in more details.

11:00am **SE+PS+SM-TuM10 Study of Polymer Confinement Effects in Nanocomposite Thin Films Synthesized by Initiated Chemical Deposition**, *Chia-Yun(Sharon) Hsieh, K.K.S. Lau*, Drexel University

Initiated chemical vapor deposition (iCVD) is a liquid-free polymer synthesis technique that simultaneously deposits the polymers as thin films on supporting substrates. It produces well-defined polymers that are spectroscopically identical to corresponding polymers synthesized in the liquid phase. A wide range of polymers have been produced by iCVD, including hydrophilic polyglycidol (PGL), hydrophobic polytetrafluoroethylene (PTFE), semicrystalline polyethylene oxide (PEO), and amorphous poly (methyl methacrylate) (PMMA). In addition, iCVD is an effective approach for integrating polymers within porous 3D inorganic nanostructures to produce polymer nanocomposite thin films. By utilizing inorganic nanostructural templates such as mesoporous TiO₂ nanoparticle networks, good dispersion of the nanoparticles can be ensured by adopting well-established dispersion procedures. Conformal and uniform polymer growth within the pore space can be achieved by operating under reaction-limited iCVD conditions that allow efficient delivery of reactive precursors by gas and surface diffusion. Quantitative measurements using thermogravimetric analysis has shown that 90–100% of the available pore space can be filled in porous layers of up to 12 μm in thickness with 10–20 nm diameter interconnected pores. As a result, we are able to achieve polymer nanocomposite thin films with high inorganic content (>80 wt%) that are well-dispersed. This ability provides an ideal platform for studying polymer confinement effects that lead to significantly altered polymer properties compared to its bulk 2D planar film counterpart with no inorganic filler. For example, iCVD PGL-TiO₂ nanocomposite thin films has shown a significant increase of 50–60°C in the polymer glass transition temperature (a transition between the glassy, brittle state to the rubbery, pliable state) compared with bulk PGL. This has been attributed to the strong hydrogen bonding interactions between the polar oxygen groups on PGL with the hydroxyl groups on the TiO₂ surface. Here, we will detail the iCVD approach in making different polymer nanocomposite thin films and discuss the resulting nanoscale confinement effects on polymer properties as a result of different polymer-substrate interactions. This knowledge has critical implications in applying polymers in the design of nanostructured devices as bulk polymer properties might not be followed in these systems.

11:20am **SE+PS+SM-TuM11 Persistent Superhydrophilicity of Polycarbonate Surfaces via Nanoimprint Lithography and Atomic Layer Deposition**, *Xue Li*, Institute of Materials Research and Engineering (IMRE), Singapore, *K.S.L. Chong, M.S.M. Saifullah, R.B. Yang, C.S. Lee, Y.C. Loke*, Institute of Materials Research and Engineering (IMRE), *A.Y. He*, Loke

Superhydrophilic surfaces are often exploited for their anti-fog ability and typically rely on coatings which modify the surface energies of the materials to create such effects. Such traditional coatings are often applied wet and are not long lasting. A persistent superhydrophilic coating with both anti-fog and anti-UV properties have been fabricated on polycarbonate (PC) surfaces *via* a combination of nanoimprint lithography and atomic layer deposition (ALD) process. Nanoimprint lithography was used to pattern anti-reflection (AR) structures on to a PC surface. These samples were then coated with a thin layer titanium dioxide (TiO₂) layer *via* a low temperature ALD process (<80 °C). The PC sample with AR patterns demonstrated enhanced visible light transmittance upto 94% and reduced transmittance in the UV wavelengths (<400 nm). The TiO₂ layer is superhydrophilic and the resultant samples showed a persistent superior anti-fog effect. More importantly, the superhydrophilicity can be recycled *via* rinsing in an oxidant solution, and had demonstrated stability upto 4 months.

11:40am **SE+PS+SM-TuM12 Enhanced CO₂ Permeation Characteristics Performance On A Crack-Free Nanostructured Ceramic Membrane**, *Ngozi Nwogu, E. Gobina*, Robert Gordon University, UK

Carbon capture from point source emissions have been acknowledged as one of numerous strategies required for alleviating unrestricted release of greenhouse gases (GHGs) into the atmosphere. To keep greenhouse gases at controllable levels, large drops in CO₂ emissions through capturing and separation will be necessary. Reduction and manipulation of materials at nanometre scale are key experiments in nano-science and nanotechnology. In this work, an experimental study is made on the preparation, the morphological characterization and the gas permeation of ordered ceramic

multilayer membranes with silica top layer. We developed and manufactured a crack-free thin film membrane on a fresh tubular alumina ceramic membrane with pore diameter of 6000nm. By using a hybrid material of appropriate proportion, the nano-fabrication conditions are then controlled with extremely high carbon dioxide permeance due to the membrane immersion in a silica solution. Results obtained from the experiments show that the nanostructured silica membranes have potential applications in the treatment of large gas streams under low pressure conditions like carbon dioxide separation from flue gases.

Keywords: Carbon capture, CO₂ Permeation, nanostructured ceramic membrane & flue gases

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