

Friday Morning, November 13, 2009

Plasma Science and Technology

Room: B2 - Session PS-FrM

Plasma Science for Medical and Biological Applications

Moderator: J. Hopwood, Tufts University

8:20am PS-FrM1 Positive Streamers Propagating Inside Bubbles in Liquids, N.Yu. Babaeva, M.J. Kushner, University of Michigan

Pulsed discharges in liquids are often in the form of streamers. In most cases, streamers do not directly propagate through the liquid phase. Rather breakdown occurs inside bubbles and near gas-liquid interfaces. Often bubbles are purposely injected to facilitate breakdown. Such discharges have been extensively studied for their use in water treatment, surgery, decontamination and sterilization. Recent experiments have shown that streamers often preferentially propagate along the surface of a bubble immersed in a liquid instead of propagating along the axis of the bubble. In this talk, we discuss results from a computational investigation of the propagation of streamers inside bubbles immersed in liquids. We show that dielectric constant of a liquid determines patterns of streamer propagation. The model, *nonPDPSM*, is a 2-dimensional simulator executed on an unstructured mesh in which Poisson's equation for the electric potential, and transport equations for charged and neutral species, and electron temperature, are solved. Radiation transport and photoionization are included by implementing a Green's function propagator. A bubble of humid air, $N_2/O_2/H_2O = 55/15/30$ at atmospheric pressure is placed at the tip of a positive corona discharge immersed in a liquid of specified conductivity, σ , and permittivity, ϵ/ϵ_0 . The bubble radii are 0.45 - 0.9 mm. We found that for low values of σ and ϵ/ϵ_0 the streamer propagates along the axis of the bubble. For large values of σ and ϵ/ϵ_0 the streamer propagates along the surface of the bubble. For essentially non-conducting liquids, the transition between axial and surface-hugging streamers occurs at $4 < \epsilon/\epsilon_0 < 8$, depending on the size of the bubble and voltage. Increasing conductivity lowers the value of ϵ/ϵ_0 at which the streamer becomes surface-hugging. These trends largely result from the refraction of the electric field by the curved interface of the bubble in the presence of a diverging electric field. The final pattern of the streamer path is additionally a function of bubble size and its position relative to the tip of the electrode, applied voltage and polarity.

8:40am PS-FrM2 Atmospheric Plasma for the Degradation of Pollutants : The Promoting Effect of Water, S. Al Takriti, J.M. Giet, Université Libre de Bruxelles, Belgium, C. Pierard, ArcelorMittal Research Liege, Belgium, F. Reniers, Université Libre de Bruxelles, Belgium

Atmospheric plasmas have been used for a long time for the degradation of volatile organic compounds (VOC). In this study we focus on the degradation of non volatile organic compounds, like hexadecane and hexachloropropene, using an oxygen containing atmospheric plasma.

The kinetics of the reactions was followed by mass spectrometry, by tracking the m/z signal of the production of carbon dioxide.

The pollutants were degraded in a dielectric barrier discharge plasma chamber, operating at frequencies between 10 and 20 kHz, and at voltages between 1 and 4 kV. The plasma gas was either pure oxygen, or a helium/oxygen mixture. The promoting effect of water was studied by adding controlled amounts of water vapour to the gas mixture.

Optical emission spectrometry was used to characterize the plasma gas phase. More specifically, the oxygen emission lines, and the OH bands were followed, as a function of the plasma parameters.

It is shown that the degradation efficiency increases with the charge delivered in the plasma, as well as with the oxygen content. A correlation is established between the oxygen OES emission line and the carbon dioxide production, for plasmas containing no water. For water containing plasmas, the oxygen line decreases, whereas the carbon dioxide production increases. The decrease of oxygen is interpreted in terms of consumption of the oxygen radical by water molecules to create hydroxyl groups, which are responsible for the increase of the degradation of the organic molecules. A simple global mechanism is proposed.

Acknowledgements : this work is funded by the IAP "physical chemistry of plasma-surface interactions - PSI" program from the Belgian Federal Government

9:00am PS-FrM3 Challenges in the Numerical Simulation of the Plasma-Biomaterial Interaction, Y. Sakiyama, D.B. Graves, University of California, Berkeley

INVITED

Nonthermal atmospheric pressure plasmas have received considerable attention in recent years. One emerging and promising application is the biomedical field. A wide variety of investigators have already demonstrated various biomedical effects of nonthermal plasmas, including sterilization/disinfection, blood coagulation, wound healing, tissue regeneration, etc.¹ The mechanisms of the plasma-biomaterial interaction are however only poorly understood. A central scientific challenge is therefore how to answer the question: "What plasma-generated species or plasma-created electric fields and currents, or any other effects of the plasma, are responsible for the observed biological effects?" Our modeling efforts are motivated by this question.

We have focused on the RF-excited plasma needle at atmospheric pressure and developed fluid models using the finite element method. Our simulation model successfully reproduced various experimental observations. For instance, our two dimensional model demonstrated that the plasma needle operates in two discharge modes: the corona-mode under low power condition and the glow-mode under high power condition.² The model showed that the plasma needle discharge strongly depends on the electrical properties of treated materials.³ Also, we found that the ring-shaped emission pattern observed during bacteria treatment⁴ was due to back-diffusion of air and Penning ionization and excitation of N_2 from He metastables.⁵ Furthermore, results from a more complete model including humid air chemistry indicate that plasma-air interaction creates various neutral species via electron impact reactions near the treated materials. Those reactive neutrals (e.g. O, OH, NO) appear to have significant effects in the inactivation processes by the plasma needle.

In this talk, we will briefly review recent progress in biomedical applications of gas plasmas. Then, our modeling results are discussed in detail.

1 G. Fridman *et al.*, Plasma Process. Polym. **5** (2008) 503.

2 Y. Sakiyama and D. B. Graves, J. Phys. D **39** (2006) 3644.

3 Y. Sakiyama and D. B. Graves, J. Phys. D **41** (2008) 095204.

4 J. Goree *et al.*, J. Phys. D **39** (2006) 3479.

5 Y. Sakiyama and D. B. Graves, Plasma Sources Sci. Technol. **18** (2009) 025022.

9:40am PS-FrM5 A Novel Way of using Plasma to Sterilize Objects for Use in Medical, Food or Pharmaceutical Applications, N.B. Koster, F.P. Wieringa, R. Koops, TNO Science and Industry, Netherlands

From literature it is known that plasma is capable of sterilizing objects. A number of the great advantages of plasma sterilization is that it is relatively cool and that it also has a cleaning action besides the sterilisation process. A disadvantage of plasma sterilization is that for a good process the object has to be placed in a reactor and after the process is completed the object has to be packed in an enclosure and sealed. This is a possible source of cross contamination due to handling and exposure to the environment. We will present a novel way of using plasma's to sterilize an object without this disadvantage. This process is called Plasma in a Bag (PiB) and has the benefit that the object is packed and sealed from the environment before the process starts and requires no handling after the sterilization process has finished. Also the way of packing enables the user to see that the enclosure is still intact and that the integrity of the object remains valid even after a long shelf life. We will show results on the efficiency of the process for several pathogens at different plasma conditions. This new process enables the use of new materials and electronics for medical applications or can replace a number of existing sterilisation techniques.

10:00am PS-FrM6 Patterned Growth of Cells and Biomolecules using a Microplasma Printing System, E. Yildirim-Ayan, Drexel University, D. Pappas, Army Research Laboratory

A versatile system called *micro-plasma integrated cell/biomolecule printing system* is described. This system enables the creation of patterned cells/biomolecules on various substrates without using any masks, master stamps or chemical treatments. The system operation is based on the integration of two techniques, namely microplasma patterning and cell/biomolecule printing. In microplasma patterning, an atmospheric pressure low-temperature microplasma is generated with a dielectric barrier discharge (DBD) plasma setup consisting of a micro-second pulsed power supply and electrode system. Through *micro-plasma integrated cell/biomolecule printing system*, we can create chemically and physically

predesigned micropatterns and print the cells/biomolecules on designed pattern with precise spatial positioning.

In this study, the authors patterned mouse osteoblast cells on ultra high molecular weight polyethylene films. An O₂/He mixture was used as the working gas for the ignition of a micron-sized discharge. The microplasma nozzle with a tip of 30 μm was navigated on a straight line with a 2mm/s speed to create the micropattern. The physicochemical properties of the microplasma patterned surface were examined by Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS). The SEM data showed that the dynamic microplasma treatment results in an increase of the surface roughness. The surface morphology was changed along the microplasma treated line while the rest of the substrate remained unaffected. The XPS data showed that the atomic concentration of oxygen increased from 5% for the as-received polyethylene film to 18% for the center of the microplasma treated line. Following the micropatterning, mouse osteoblast cells were deposited uniformly on the substrate to determine the effect of microplasma patterning on cell attachment. The biological characterization has been done by live/dead assay where mouse osteoblast cells were labeled and imaged using fluorescence microscopy. The data showed the attachment and survival of the cells strictly along the plasma activated line. With these observations, it is viable to print the cells and dictate their shapes in predetermined locations and arrays through *micro-plasma integrated cell/biomolecule printing system*.

10:20am **PS-FrM7 How Does the Chemical Equilibrium in the Vaporous Phase Influence the Surface Properties of Poly-Parylenes?**, T.H.T. Huber, F. Schamberger, G. Franz, Munich University of Applied Sciences, Germany

The properties of deposited polymeric films strongly depend on the density and the state of excitation of the species in the vaporous phase which determine the degree of consecutive reaction paths covering the bandwidth between volume polymerization and surface polymerization. According to Yasuda, the former reaction mainly causes roughened fine-grain deposits, whereas smooth and shiny layers can be generated easily by the latter one [1]. For chemical vapor deposition, the main parameters are gas flow, number density (degree of rarefaction) and gaseous temperature which are extended by a row of additional parameters in plasma-activated processes, beginning with the (absorbed) plasma power and terminating with the delicate parameters obtained by diagnostic tools. These changes in the reaction mechanism were extensively studied for the biocompatible molecule parylene (*p*-xylylene) which is already deposited on stents for tribological purposes and is intended to cover the inner surface of artificial bladders [2]. We investigated the deposition two types of pure parylene (type N: non-substituted, and type C: substituted by one Cl atom), diluted with different amounts of argon, and a reactive alternative by adding oxygen [3]. The *in-situ* methods are energy-dispersive mass spectrometry and Langmuir probe analysis which have been correlated with *ex-post* measurements of the film quality: contact angle (surface energy) and the morphology, but most prominent the content of the aromatic species in the volume of the layer which goes down not unexpected with growing plasma power. Adding oxygen opens the window to a hydrophilic response of the surface. With the knowledge of densities of the dimeric precursor, the monomeric species, and the electron density, we modeled the chemical equilibrium of dissociation, and from the density of the aromatic compounds in the layer, we could follow the track of "safe" polymerization and could also describe the ranges for volume polymerization and surface polymerization [4].

[1] H. Yasuda: *Plasma polymerization*, Academic Press, New York (1985)

[2] G. Franz, F. Rauter, S. Dribinskiy, JVSTA, to be published

[3] K.G. Pruden, K. Sinclair; J. Polymer Sci. **A41**, 1486 (2003)

[4] G. Kokkoris, V. Constantoudis, P. Angelikopoulos, G. Boulousis, E. Gogolides; Phys. Rev. **B76**, 193405 (2007)

10:40am **PS-FrM8 Synthesis of Polystyrene and Sulfonated Polystyrene Thin Films by Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition**, D. Merche, Université Libre de Bruxelles (ULB), Belgium, C. Poleunis, P. Bertrand, Université Catholique de Louvain (UCL), Belgium, M. Sferrazza, F. Reniers, Université Libre de Bruxelles (ULB), Belgium

Thin coatings of pp-PS and pp-sulfonated PS were synthesized by "Plasma Enhanced Chemical Vapour Deposition" (PECVD) in a home-built "Dielectric Barrier Discharge" (DBD) system near atmospheric pressure. Styrene (C₈H₈) and trifluoromethane sulfonic acid (CF₃SO₃H) monomers were used as precursors and were introduced in the discharge using a flux of Ar or He. An atmospheric RF plasma torch was also used for PS deposits. It consists of two closely spaced perforated metallic electrodes. The process gas is Ar. The precursor (styrene vapour) was introduced into the plasma downstream of the electrodes (afterglow). The polymers were deposited on various substrates (PTFE, HDPE, stainless steel, glass, and silicon wafer)

and were characterized by FTIR, XPS, SSIMS, WCA, AFM and optical microscopy. The plasma phase was studied by OES.

The pp-sulfonated PS films obtained by plasma copolymerization could present interesting properties as electrolyte membrane for miniaturized fuel cell applications (Polymer Electrolyte Membrane Fuel Cell- PEMFC) using H₂ or CH₃OH (Direct Methanol Fuel Cell-DMFC). CF₃SO₃H allows introduce the sulfonic acid groups for proton conductivity in the membrane whereas the styrene constitutes the backbone of the membrane.

The major features that characterize PS are present in the FTIR, XPS and SSIMS spectra, although some differences between pp-PS films and their conventionally polymerized counterparts are observed (like oxygenation during or after deposition due to the atmosphere environment, branching, degree of cross-linking, and unsaturations). According to the WCA and XPS results, the pp-PS films deposited by the RF plasma torch (placed in a plexiglass chamber) are more oxygenated than those deposited by the DBD operated in a much more controlled atmosphere [1]. The chemical structure of the deposited coatings was investigated by FTIR and TOF-SSIMS as a function of the nature of the carrier gas. The pp-PS films synthesized in the presence of Ar (for both processes) exhibit more branching, more unsaturations, a higher degree of cross-linking, and a lower density of aromaticity than pp-PS synthesized with He as the main plasma gas.

The influence of the nature of the carrier gas, and of the discharge voltage and the ratio of the partial pressures of the monomers on the sulfonic content (therefore on the degree of fragmentation of the CF₃SO₃H monomer) for both carrier gases was investigated for pp-PS sulfonated by XPS, SSIMS and FTIR.

[1] D. Merche, C. Poleunis, P. Bertrand, M. Sferrazza, F. Reniers, *IEEE Transactions on Plasma Science* (2009), Under Press, Available online on <http://www.ieeetps.org/>

11:00am **PS-FrM9 Functionalization of Wood Surfaces in the Afterglow of an Atmospheric Pressure Dielectric Barrier Discharge**, J. Prigent, Université de Montréal, Canada, F. Busnel, Université Laval, Canada, V. Blanchard, FPNnovations-Division Forintek, Canada, L. Stafford, Université de Montréal, Canada

The use of wood products in architectural or exterior applications is often limited by the short durability of these products and the fast deterioration of their appearance. Several waterborne coatings aimed at preserving the wood properties have been developed but these coatings are often characterized by poor adhesion on wood surfaces. To improve adhesion, we investigated modification of the surface properties of wood samples following their exposition to the afterglow of an atmospheric pressure dielectric barrier discharge in N₂/O₂ mixtures. The surface energy divided into a dispersive (non-polar) part, γ_{DS}, and a polar part, γ_{PS}, was determined by means of contact angles measurements. For polar sugar maple samples, γ_{PS} decreased from 78.5 mJ/m² before treatment to 59.0 mJ/m² after N₂ plasma exposure. γ_{PS} further decreased with the introduction of O₂, reached a minimum value of 31.2 mJ/m² at 85%N₂-15%O₂, and then increased until it reached its untreated value in a pure O₂ plasma. The dispersive component showed the opposite behavior, going from 3.3 mJ/m² before treatment to 24.4 mJ/m² after exposure to the 85%N₂-15%O₂ plasma. On the other hand, no modification was observed for black spruce, probably because untreated samples already had a large dispersive component. Optical emission spectroscopy (OES) was used to understand the change in plasma properties leading to the observed variation of γ_{PS} and γ_{DS}. The gas temperature determined using the second positive system of N₂ (C³Π_u v''=0 - B³Π_g v''=2) was 320 ± 20 K and showed no trend with O₂ concentration, thus ruling out variations due to thermal effects. Significant NO (A²Σ⁺ - X²Π) emission in the 225-305 nm range was observed in pure N₂ plasmas. However, these bands disappeared with the introduction of O₂, indicating that UV photons are not the prominent species driving the observed decrease in surface polarity. We also observed a strong increase of the N₂⁺ (B³Σ_u v''=0 - X²Σ_g⁺ v''=0) to N₂ (C³Π_u v''=0 - B³Π_g v''=2) bandhead intensity ratio with increasing O₂ concentration. Such behavior is usually ascribed to an increase signature of the early afterglow and thus to an increase in the erosion rate of polymer surfaces [1]. In pure N₂ plasmas, one expects N grafting to form nitrogen-containing groups which are likely to promote non-polar bonding [2]. As only a moderate decrease of γ_{PS} was observed in pure N₂ and no change was observed in pure O₂, it is believed that a combination of N grafting and surface erosion by oxygen atoms is required to achieve maximum modification of the surface polarity.

[1] M.K. Boudam et al., J. Phys D. **40**, 1694 (2007)

[2] S. Vallon et al., J. Adhes. Sci. Technol. **10**, 1287 (1996)

11:20am **PS-FrM10 Combination of Bio-template and Ultimate Top-down Etching Processes for Defect-free, High Density, Size-controlled and Excellent Uniform Si-Nanostructure for Ideal Quantum Effect Devices**, *M. Igarashi, C. Huang*, Tohoku University, Japan, *M. Takeguchi*, NIMS, Japan, *S. Horita*, JAIST, Japan, *Y. Uraoka, T. Fuyuki*, NAIST, Japan, *I. Yamashita*, Panasonic Co., Ltd. and NAIST, Japan, *S. Samukawa*, Tohoku University, Japan

Nanometer-scale structures such as quantum dots (QDs) have been widely studied because they have potential applications to the development of quantum effect devices, such as single electron transistors, quantum dot lasers and quantum dot solar cells. To realize quantum dots, the fabrication of defect-free, size-controlled and uniform sub-10-nm-scale structures is needed. However, it is difficult for conventional optical lithography and plasma etching processes to satisfy these requirements.

In this study, we proposed a novel nanofabrication process for the fabrication of nanostructures, which combines a biomaterial template, radical etching and neutral beam etching (NBE). We fabricated silicon nanodisks (disk-shaped silicon nanostructures with diameters of about 10 nm on a very thin silicon oxide film) by using a ferritin iron core as etching mask and Cl NBE. Additionally, we succeeded in precisely controlling the nanodisk diameter by using surface treatment of NF_3 gas + hydrogen radicals (NF_3 treatment). The surface oxide thickness and its removal conditions greatly affected the fabricated nanodisk diameter. It was notable that the coulomb staircases of nanodisk structures were obtained with a conducting AFM probe at room temperature. The successful fabrication of Si nanodisk should be attributed to the defect-free etching process that involved our neutral beam. Our new process is very useful to fabricate defect-free and size-controlled nanostructure for ideal quantum effect devices.

Authors Index

Bold page numbers indicate the presenter

— A —

Al Takriti, S.: PS-FrM2, 1

— B —

Babaeva, N.Yu.: PS-FrM1, **1**

Bertrand, P.: PS-FrM8, 2

Blanchard, V.: PS-FrM9, 2

Busnel, F.: PS-FrM9, 2

— F —

Franz, G.: PS-FrM7, **2**

Fuyuki, T.: PS-FrM10, 3

— G —

Giet, J.M.: PS-FrM2, 1

Graves, D.B.: PS-FrM3, 1

— H —

Horita, S.: PS-FrM10, 3

Huang, C.: PS-FrM10, 3

Huber, T.H.T.: PS-FrM7, 2

— I —

Igarashi, M.: PS-FrM10, **3**

— K —

Koops, R.: PS-FrM5, 1

Koster, N.B.: PS-FrM5, **1**

Kushner, M.J.: PS-FrM1, 1

— M —

Merche, D.: PS-FrM8, **2**

— P —

Pappas, D.: PS-FrM6, **1**

Pierard, C.: PS-FrM2, 1

Poleunis, C.: PS-FrM8, 2

Prégent, J.: PS-FrM9, **2**

— R —

Reniers, F.: PS-FrM2, **1**; PS-FrM8, 2

— S —

Sakiyama, Y.: PS-FrM3, **1**

Samukawa, S.: PS-FrM10, 3

Schamberger, F.: PS-FrM7, 2

Sferrazza, M.: PS-FrM8, 2

Stafford, L.: PS-FrM9, 2

— T —

Takeguchi, M.: PS-FrM10, 3

— U —

Uraoka, Y.: PS-FrM10, 3

— W —

Wieringa, F.P.: PS-FrM5, 1

— Y —

Yamashita, I.: PS-FrM10, 3

Yildirim-Ayan, E.: PS-FrM6, 1