

Tuesday Morning, October 20, 2015

Plasma Science and Technology

Room: 210A - Session PS+BI+SM-TuM

Plasmas for Medicine and Biological Applications

Moderator: Satoshi Hamaguchi, Osaka University, Japan

8:00am **PS+BI+SM-TuM1 Glow-Discharge Plasma Applications in the Biomedical Sciences: Frontiers and Horizons, Buddy D. Ratner, University of Washington** **INVITED**

Plasma treatments for biomedical applications have been explored since the early 1960's, possibly earlier than that. Plasma treatments for medical devices and for materials used in biotechnology are now widely used and have improved the performance and safety of many devices. A few advanced technologies for biomedicine exploiting plasma deposition of organic thin films will be described. These include non-fouling surfaces, thermally responsive surfaces, biodegradable surfaces, rate-limiting barriers for controlled release and surfaces that permit the growth of precision polymeric brushes by atom transfer radical polymerization (ATRP). Frontiers for plasma deposition include better control of deposition chemistry, strategies to deposit unusual chemistries and depositions that integrate biological molecules and plasma-deposited chemistries.

8:40am **PS+BI+SM-TuM3 Non-Equilibrium Plasmas in Contact with Solutions: Biological Interactions and Material Synthesis, Peter Bruggeman, University of Minnesota** **INVITED**

Non-equilibrium atmospheric pressure plasmas interacting with liquids offer a unique source of highly reactive chemistry beneficial for many applications in biology, medicine and advanced materials manufacturing. It has been shown that these plasma-liquid interactions can lead to inactivation of bacteria and virus and the synthesis of nanoparticles. Nonetheless the underpinning mechanisms are at least poorly understood. My group has been strongly involved in the study of the reactive chemistry of a well-characterized RF driven atmospheric pressure plasma jet and its interaction with liquids.

The presentation will highlight some examples of reaction pathways responsible for the inactivation of bacteria and virus in solution and the synthesis of silver nanoparticles from AgNO_3 solutions. I will illustrate the importance of reactive plasma chemistry induced by neutral gas phase reactive species such as OH, H_2O_2 , NO, O, H, O_3 and singlet oxygen. In addition, we will show that UV emission, which is often neglected as a possible mechanism, can be important in some cases.

9:20am **PS+BI+SM-TuM5 Plasma Biomedicine and Reactive Species, David Graves, University of California at Berkeley** **INVITED**

Low temperature plasma research directed towards biomedical applications such as sterilization, surgery, wound healing and anti-cancer therapy has seen remarkable growth in the last 3-5 years, but the mechanisms responsible for the biomedical effects have remained mysterious. It is known that CAP readily create reactive oxygen species (ROS) and reactive nitrogen species (RNS). Other potentially important plasma-generated species effects include charges, fields and photons. ROS and RNS (or RONS), in addition to a suite of other radical and non-radical reactive species, are essential actors in an important sub-field of aerobic biology termed 'redox' (or oxidation-reduction) biology. I will review the evidence suggesting that RONS generated by plasmas are responsible for their observed therapeutic effects. In addition, I will present several ideas about the most likely biological response mechanisms that are likely involved in therapeutic plasma biomedicine.

11:00am **PS+BI+SM-TuM10 Cold Atmospheric Plasma for the Treatment of Chronic Infected Wounds, Jennifer Granick, V.S.S.K. Kondeti, A. Truong, R.C. Hunter, P.J. Bruggeman, University of Minnesota**

Two percent of the US population suffers from chronic non-healing wounds, often complicated by antibiotic-resistant bacterial infections, and the staggering cost of wound care exceeds \$50 billion per year. Of increasing concern are multi-drug resistant bacteria, including methicillin-resistant *Staphylococcus aureus* and multi-drug resistant *Pseudomonas aeruginosa* infections. Within wounds, these bacteria adopt a biofilm-like state, and become notoriously recalcitrant to conventional antibiotic therapies. Currently approved products for the treatment of chronic wounds have not proven to be a panacea due to the complex nature of wound healing.

The ideal therapy for chronic, infected wounds would be non-painful, bactericidal without risk of resistance, able to break-up biofilms and

enhance wound healing. Recently, there has been interest in the use of cold atmospheric plasma (CAP) technology for the treatment of infections and non-healing wounds. The technology could potentially fulfill the requirements of an ideal wound healing therapy. CAP devices producing ionized gas have been developed that can operate in ambient air and that are safe to touch without any pain sensation. CAP generates a complex mixture of reactive oxygen and nitrogen species (RONS) that are able to kill bacteria, while stimulating host cell growth. CAP has the potential to combine antiseptic and wound healing capabilities in a single treatment procedure and could eliminate the risk of cytotoxicity present in many current treatment methodologies for infected wounds.

The effects of CAP on bacteria and mammalian keratinocytes and fibroblast cells have been evaluated *in vitro*. Our prototype argon CAP device produces antibacterial effects on planktonic bacterial cultures of *S. aureus* and *P. aeruginosa* at a maximal treatment duration of 20 ml/min at conditions that do not impact cell viability of fibroblasts and keratinocytes *in vitro*. We have also recently demonstrated that CAP is effective in reducing the viability of *P. aeruginosa* biofilms grown *in vitro*. When grown on the surfaces of PVC microtitre plates for 48 h, argon-air derived CAP treatment of established biofilms showed a 95% reduction in cell viability, as determined by resazurin fluorescence, relative to untreated controls, when treated at a dose of 30min/ml, which is similar to the treatment time equivalent of mammalian cell treatment.

As part of the early investigations of the use of CAP treatment as a viable therapy for chronic-infected wounds, the presentation will focus on bacterial biofilm reduction by CAP treatment *in vitro* as well as in a mouse skin wound model. The effects on mouse host cells will be examined.

11:20am **PS+BI+SM-TuM11 Humidity Effect on the Surface Modification and Bio-Deactivation of Lipopolysaccharide (LPS) by Surface Micro-Discharge (SMD), Pingshan Luan, E.A.J. Bartis, A.J. Knoll, University of Maryland, College Park, C. Anderson, D.B. Graves, University of California at Berkeley, J. Seog, G.S. Oehrlein, University of Maryland, College Park**

The surface micro-discharge (SMD), due to its scalable large area and flexibility of working gases, has great potential for many applications such as material processing and plasma medicine. The SMD normally works under ambient air conditions that contain not only N_2 and O_2 but also water vapor which can have a large impact on both the discharge behavior and plasma gas chemistry. In this study, we evaluate the effect of ambient humidity on SMD in various N_2/O_2 mixtures and the subsequent effect on the surface modification and bio-deactivation of lipopolysaccharide (LPS). Electrical behavior and optical emission spectrum (OES) of the SMD source were studied. We found that while the additional moisture did not help create strong OH (A-X) emission from SMD, it resulted in lower plasma density and extra power dissipation. We used X-ray photoelectron spectroscopy (XPS) to characterize the surface modification of LPS after treatment. We found that all SMD-treated LPS surfaces show oxygen uptake and formation of surface-bound NO_3 , while the amount of these modifications was strongly dependent on the ambient gas composition. By comparing the XPS of wet-treated (50% relative humidity at 20 °C) surfaces with their dry counterparts, we find that the water vapor reduces both the oxygen uptake and surface NO_3 formation, and that the difference between wet- and dry-treated surfaces decreases with the increasing fraction of ambient N_2 . When the N_2 fraction is up to 80% (synthetic air), the LPS surface shows comparable amount of modification with or without humidity. Among all the dry- and wet- N_2/O_2 mixtures, the dry 5% of N_2 ambient shows the greatest modification rate. We also evaluated the bio-deactivation efficiency of the SMD on LPS using enzyme-linked immunosorbent assay. Similar to surface modification, we found that the bio-deactivation rate of SMD in dry ambient is much higher than that of SMD in their wet counterparts, except the synthetic air condition which shows similar amount. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0001939) and National Science Foundation (PHY-1004256 and PHY-1415353).

11:40am **PS+BI+SM-TuM12 Plasma Diagnostics of Dielectric Barrier Discharge within a Sealed Meat Package, Vladimir Milosavljevic, Dublin Institute of Technology, Ireland, J. Lalor, P. Bourke, P.J. Cullen, Dublin Institute of Technology**

Atmospheric pressure, non-thermal plasma DBD is increasingly used in many processing applications. Despite their widespread usage, it remains largely unknown whether cold atmospheric plasma DBD maintains similar characteristics, such as gas temperatures and particle flux, when they breakdown while arcing or whether they possess different operating modes. It is essential for laboratory/industrial adoption of such plasmas that plasma diagnostics of the process are provided. Optical emission and absorption

spectroscopy have been used as diagnostics techniques with an added advantage of their non-intrusive nature.

The type of operating gas influences the stability of atmospheric plasma discharges. In this study is used a sealed meat package filled with one of two gas mixtures: O₂-CO₂ and N₂-CO₂. Different concentrations of nitrogen or oxygen and carbon-dioxide could cause the transition from a stable homogeneous discharge into a filamentary discharge. Atmospheric plasma discharges are affected by the surrounding ambient air, and for sealed packages from transfer between the package gas and the surrounding ambient atmosphere. In the vast majority of atmospheric plasma discharges, reactive nitrogen species dominates the ionic composition of atmospheric discharge and has an impact on the breakdown voltage. When N₂ is added/mixed with CO₂ plasma discharges, the CO₂ emission lines are significantly quenched. In the case of O₂-CO₂ chemistry, nitrogen is not a carrier gas but it still present in the package due to contaminant transfer with the surrounding ambient air, modifying the plasma chemistry in the package. The plasma's optical spectrum in O₂-CO₂ chemistry shows molecular oxygen, nitrogen and OH peaks. Oxygen could come from the ambient air, the O₂-CO₂ gas mixture or from humidity in the package. Electron impact excitation of molecular oxygen, at low collision energies, is of particular importance because of its role in atmospheric physics and has been objective of this study. In our study we have also recorded the O₃ band-head that belongs to the Hartley Band. Ozone plays very important role for the biological aspect of this study and shows the highest change in a concentration with the processing time. Combining the results from spectral radiation in the package provides an electron energy distribution function. The study includes a detailed experimental investigation of the spatial and temporal spectroscopic data and links them with plasma kinetics.

The research leading to these results has received funding from the European Union's Seventh Framework Programme managed by REA Research Executive Agency (FP7/2007-2013) under Grant Agreement number 605125.

12:00pm PS+BI+SM-TuM13 Low-Temperature Plasma Surface Modification of Porous Polymeric Materials for Environmental and Medical Applications, Michelle Mann, A. Pegalajar-Jurado, E.R. Fisher, Colorado State University

Three-dimensional (3D) porous polymeric materials are widely used in biomedical and environmental applications, such as wound healing and water filtration. Polymers used for these applications are chosen for their mechanical properties and porosity, yet the surface properties, such as hydrophobicity, limit their use in aqueous environments. For example, polymeric ultrafiltration membranes typically require pretreatment before use and tend to foul due to adsorption of biomolecules in the watercourse. Bioresorbable polymeric scaffolds used for wound healing are prone to attachment of bacteria, leading to prolonged infection at the wound site. These issues can be addressed with two simultaneous approaches. To prevent bacterial attachment and proliferation, antibacterial properties can be introduced into the materials via incorporation of biocidal agents or antibacterial coatings. Moreover, surface modification can be used to create more compatible polymeric materials by increasing wettability. Through plasma processing, tailored surface modification can be achieved while retaining the morphology and bulk properties of the material. Here, we will describe the modification of ultrafiltration polysulfone (UPS) membranes and poly(ϵ -caprolactone) (PCL) scaffolds to create low-fouling materials with enhanced wettability. H₂O_(g) plasma treatment of UPS membranes and PCL scaffolds results in materials with significantly enhanced wettability while scanning electron microscopy (SEM) images demonstrate porous morphology is maintained. X-ray photoelectron spectroscopy (XPS) data show an increase in surface oxygen content throughout the membrane cross-section after plasma treatment, and modified UPS membranes demonstrate a significant increase in initial water flux. In addition, the performance of modified UPS membranes in the filtration of biological solutions will also be discussed. Furthermore, the biological performance of PCL scaffolds incorporated with various biocidal agents will be presented along with biocidal agent leaching studies.

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. Vandencastele, 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 C₆F₁₂ or C₆F₁₄ in argon or helium onto surfaces previously decorated with SiO₂ or TiO₂ 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 CF₂ and CF₃ moieties in the final coating. Similarly, the nature of the oxide nanoparticles has a strong influence on the chemistry of the coating: whereas SiO₂ particles do not modify the CF_x films, the TiO₂ 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 andToF-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

2D Materials Focus Topic

Room: 212C - Session

2D+EM+MG+NS+SE+SM+SS+TF-ThM

Emergent 2D Materials

Moderator: Paul Sheehan, Naval Research Laboratory

8:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM1 CVD Growth and Characterization of 2D MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, and MoS₂-_xSe_{2-x} Alloys**, David Barroso, T. Empante, A. Nguyen, V. Klee, I. Lu, E. Preciado, C. Lee, C. Huang, W. Coley, S. Naghibi, G. von Son, A. Brooks, J. Kim, L. Bartels, University of California, Riverside

Transition Metal Dichalcogenides (TMDs) have been of increasing interest over the past years due to their exciting semiconducting properties. In the bulk, TMDs possess a native indirect bandgap and transition to a direct bandgap as they approach the monolayer limit. The bandgaps range from 1.15 eV to 1.95 eV depending on composition. Using organic liquids and/or inorganic powders as precursors, CVD growth techniques have been realized for MX₂ TMDs (M = Mo, W; X = S, Se, Te) and their alloys at tunable compositions. We achieved consistent synthesis of these TMDs materials. The films can either be made homogeneous in bandgap or exhibiting a linear bandgap gradient. Characterization of the films include Raman and photoluminescence spectroscopy, as well as AFM. Device fabrication allows for transport measurements. Depending on the composition, the materials show n- or p-doping in a consistent fashion.

8:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM2 Investigation of Manganese Dioxide Nanosheets by STM and AFM**, Loranne Vernisse, S. Afsari, S.L. Shumlas, A.C. Thenuwara, D.R. Strongin, E. Borguet, Temple University

Interest in ultrathin two-dimensional nanosheets has grown exponentially thanks to their unique and diverse electronic properties. As they possess atomic or molecular thickness and infinite planar dimension, they are expected to have different properties than the bulk of the material from which they originate. This offers opportunities for the development of devices in various areas, ranging from catalysis to electronics. Using the exfoliation approach, it is possible to investigate 2D nanosheets of different materials in search of new phenomena and applications. Bearing this mind, we focused on manganese dioxide (MnO₂), and more specifically δ-MnO₂ (Birnessite). This mineral has the advantage to present a low surface enthalpy [1], which results in weak water binding. Moreover, the presence of defects, e.g., oxygen vacancies has a dopant effect on water oxidation. These properties make MnO₂ a perfect candidate as a catalytic surface for water splitting and pave the way to the design of clean and renewable energy system. Furthermore, MnO₂ can be easily exfoliated into ultrathin nanosheets owing to the layered structure of the manganese oxide precursors.

Our goal is to investigate the catalytic activity of ultrathin MnO₂ nanosheets using scanning probe microscopy techniques, especially atomic force microscopy (tapping mode) and scanning tunneling microscopy (ambient and electrochemical conditions). In this perspective, we have first improved the deposition processes and find the imaging conditions to observe MnO₂ nanosheets with an average thickness of one or two layers. We have also showed that MnO₂ single layer nanosheets exhibit an expected hexagonal atomic pattern and present some defects. We will now resolve and identify the different defects and investigate the evolution of the conductivity as a function of the defect concentration and the number of layers.

This work was supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575.

[1] M. M. Najafpour, E. Amini, M. Khatamian, R. Carpentier, S. I. Allakhverdiev, Journal of Photochemistry and Photobiology B: Biology (2014), 133, 124.

8:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM3 Two-Dimensional Early Transition Metal Carbides and Carbonitrides "MXenes": Synthesis, Properties and Applications**, Michael Naguib, Oak Ridge National Laboratory

INVITED

Ternary layered carbides and nitrides with formula of M_{n+1}AX_n (M stands for early transition metal, A for group A element, X is carbon or nitrogen, and n=1, 2, or 3), so called MAX phases, are known for their unique combinations properties of ceramics and metals. It was found recently that etching atomically thin layers of aluminum from the MAX phases results in

forming weakly bonded stacks of two-dimensional (2D) layers of early transition, coined as MXenes. The etching was carried out in fluoride contained aqueous systems. Thus MXenes surfaces are terminated with a mixture of groups including OH, O, and F. Sonicating MXenes in water results in delaminating few layers of MXenes from each other. However, to achieve a large-scale delamination, intercalation of a large compound between the layers prior to delamination is needed. MXenes were found to be a very interesting family of 2D materials since they are electrically conductors and hydrophilic. They also showed an excellent performance as electrodes for electrochemical super capacitors and Li-ion batteries. Here the recent progress in MXenes research from the synthesis to properties and applications will be covered, and in more details, large-scale delamination of MXenes will be discussed. Also, light will be shed on the performance of MXenes as electrode materials for electrochemical energy storage systems.

9:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM5 Molecular Beam Epitaxy of Large area HfSe₂(ZrSe₂)/MoSe₂ van der Waals Heterostructures on AlN(0001)/Si substrates**, Athanasios Dimoulas, P. Tsipas, E. Xenogiannopoulou, D. Tsoutsou, K.E. Aretouli, J. Marquez-Velasco, S.A. Giamini, N. Kelaidis, NCSR DEMOKRITOS, Greece

Two dimensional (2D) semiconductor van der Waals heterostructures (HS) made of group IVB (Zr, Hf) and group VIB (Mo, W) metal dichalcogenides are predicted [1] to have type II or type III band alignments mainly because of a large difference in their workfunctions and band gaps, which makes them candidates for novel 2D staggered, or broken gap tunneling field effect transistors (TFET). We use molecular beam epitaxy (MBE) to grow high quality large area HfSe₂ [2,3], ZrSe₂ [4] and MoSe₂ [5] films directly on AlN(0001)/Si(111) substrates. We confirm by RHEED and HRTEM that atomically thin layers (1-6 ML) are grown in single crystal form with a well-defined in-plane orientation on AlN. The films are continuous with smooth surface morphology (0.6 nm RMS roughness) and abrupt interfaces with no detectable reaction as verified by in-situ XPS and HRTEM. Micro Raman mapping for all layers confirms their structural integrity down to one monolayer and reveals very good uniformity on a cm-scale wafer and excellent stability of MoSe₂ over a period of at least two weeks in air. Strong room temperature PL signal of 1 ML MoSe₂ indicate high quality direct gap semiconductor in agreement with valence band structure details imaged by our in-situ ARPES [3, 5]. In a second step, MoSe₂/HfSe₂ [3] and MoSe₂/ZrSe₂ [4] HS were grown. Despite the large lattice mismatch, all layers are grown epitaxially as evidenced by RHEED with no detectable defects at the interfaces as confirmed by HRTEM suggesting good quality vdW epitaxy [6]. Using UPS the workfunctions (WF) were estimated to be 5.2, 5.5 and 5.4 eV for MoSe₂, HfSe₂ and ZrSe₂ respectively [3,4]. The last two differ substantially from theoretical values (~ 6 eV). Based on our STM and DFT calculations [3], we conclude that this difference is due to an ordered Se adlayer which lowers the HfSe₂ and ZrSe₂ WF bridging the WF gap between them and MoSe₂. As a result, small valence band offsets of 0.13 and 0.58 eV were found for the HfSe₂/MoSe₂ and ZrSe₂/MoSe₂ HS, respectively leading to type II band alignments. The availability of low cost wide-gap-AlN/Si wafers in 300 mm wafer sizes defines a manufacturable route for single crystal 2D semiconductor technology.

We acknowledge financial support from ERC Advanced Grant SMARTGATE-291260. We thank IMEC for providing the AlN/Si substrates.

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9:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM6 Surface Investigation of WSe₂ Atomically Thin Film and Bulk Crystal Surfaces**, Rafik Addou, H. Zhu, University of Texas at Dallas, Y.-C. Lin, S.M. Eichfeld, J.A. Robinson, Penn State University, R.M. Wallace, University of Texas at Dallas

Heterogeneous fabrication of semiconducting two-dimensional layered materials presents a promising opportunity to develop highly tunable electronic and optoelectronic materials. (1-2) An example of crystalline monolayer of WSe₂ grown by chemical vapor deposition on epitaxial graphene (EG) grown from silicon carbide had been investigated at nanoscale level. The WSe₂ surface was characterized using atomic force microscopy (AFM) scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS). (3,4) AFM and

large STM images show high-quality WSe₂ monolayers. The sharpness of the W 4f and Se 3d core levels confirms the absence of any measurable reaction at the interface and oxide formation. The photoemission measurements of WSe₂-Graphene interface suggest p-type doping due to charge transfer (EG withdraws electrons from WSe₂) at the interface and formation of Schottky-type contact,(5) suggesting possible applications of such heterostructures as diodes and photodetectors. High-resolution STM images reveal atomic-size imperfections induced by Se vacancies and impurities. Additionally, the investigation of bulk WSe₂(0001) surface shows spatial variation attributed to the presence of two components in W 4f_{7/2} core level attributed to the presence of both n- and p-type behavior. STM images exhibit also various types of defect induced by vacancies and dopants. The STS spectra reveal two main characteristics i) expected p-type conductivity where the Fermi level located at the valence band edge, and ii) zero conductivity at negative bias explained by defect-induced band bending as reported on geological MoS₂ crystal surfaces.(4) In conclusion, the spatial variation (topography and electronic structure) is more noticeable in bulk WSe₂ grown by chemical vapor transport than in CVD thin films.

This work was supported in part by the Southwest Academy on Nanoelectronics sponsored by the Nanoelectronic Research Initiative and NIST and the Center for Low Energy Systems Technology, one of six centers supported by the STARnet phase of the Focus Center Research Program, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

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11:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM10 A Kinetic Study on the Adsorption of Polar (Water) and Non-Polar (Benzene) Molecules on CVD Graphene, Nilushni Sivapragasam, U. Burghaus, North Dakota State University**

The adsorption kinetics of water and benzene at ultrahigh vacuum conditions were studied. Two different chemical vapor deposited graphene samples (graphene/SiO₂ and graphene/Cu) were utilized. Different surface analytical techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy) were used to characterize the surface. Subsequently, a kinetics study - to understand the adsorption of water and benzene- using thermal desorption spectroscopy (TDS) was conducted. The TDS results revealed the hydrophobicity of water on graphene. However, the adsorption kinetics of water on graphene did not mimic the bare substrate, i.e., graphene is non-transparent for water adsorption. In contrast, graphene was transparent for benzene adsorption. Furthermore, the adsorption kinetics of both, water and benzene were substrate dependent.

11:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM11 Epitaxial Ultrathin MoSe₂ Layers Grown by Molecular Beam Epitaxy, Ming-Wei Chen, M.B. Whitwick, O. Lopez-Sanchez, D. Dumcenco, A. Kis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

Two-dimensional transition metal dichalcogenides (TMDs) have attracted widespread attention recently, and the focus is specifically on ultrathin layers due to the strong spin-orbit coupling and direct band-gap transition of single-layers. The unique properties of various TMDs also enable the possibilities for future optoelectronic applications. However, the synthesis of TMDs with uniform large-area and high-quality still remains challenging. While chemical vapour deposition has been demonstrated as a promising technique, the complexity of chemical precursors and the lacking of *in-situ* observation technique strongly hinder the progress.

Here, We propose to use ultra-high vacuum molecular beam epitaxy (MBE) to grow MoSe₂ ultrathin layers, down to single-layer in a controllable way. Epitaxial MoSe₂ layers were successfully grown on different crystalline substrates via van der Waals epitaxy mechanism, benefited from the weak interlayer interaction and the lacking of dangling bonds. Reflection high energy electron diffraction (RHEED) was used to *in-situ* monitor the initial growth stage and revealed a clear transition of the streaks, demonstrating the formation of MoSe₂ layer. Sharp streaks were obtained in the growth end, with the streak spacing corresponding to MoSe₂ lattice constant, and no significant strain effect was observed. In order to demonstrate the validity of van der Waals epitaxy, different crystalline substrates with lattice mismatch up to 30 % have been tested. The epitaxial layers showed a smooth and uniform surface in atomic force microscopy, and the quality was further confirmed in Raman spectrum and transmission electron

microscopy. Furthermore, photoluminescence of the single-layer MoSe₂ showing a sharp peak of ~1.58 eV at room temperature demonstrates the direct band-gap feature and indicates the potentials of photovoltaic applications. In the end, the growth of two-dimensional van der Waals heterostructures has also been addressed and the results pave way for heterostructure studies.

In summary, molecular beam epitaxy has been proved to be a reliable route to grow large-area and high-crystalline transition metal chalcogenides, and is promising to facilitate the integration of other two-dimensional materials in the future.

11:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM12 A Two-Dimensional Oxide Quasicrystal, Stefan Förster, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J.I. Flege, Institute of Physics, University of Bremen, Germany, K. Meinel, R. Hammer, M. Trautmann, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J. Falta, Institute of Solid State Physics, University of Bremen, Germany, T. Greber, Physik-Institut, University of Zürich, Switzerland, W. Widdra, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany**

INVITED

With the recent discovery of the first oxide quasicrystal (QC) aperiodicity is entering the field of two-dimensional materials [1]. Aperiodicity means that the system exhibits long-range order as expressed by sharp diffraction spots but since the ordering follows an aperiodic function the system is lacking translational symmetry. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from BaTiO₃ thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelve-fold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. In addition to this dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found on $(2+\sqrt{3})$ and $(2+\sqrt{3})^2$ larger scales indicating the characteristic self-similarity of an ordered QC [1]. The high-resolution STM measurements allow furthermore to identify atomic flips in the structure indicating lattice excitations in the quasicrystal called phasons. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3DBaTiO₃ islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. This wetting process can be reversed by annealing in an oxygen atmosphere. In-situ LEEM measurements show that under these conditions the QC decays into small BaTiO₃ islands. The observed interface-driven formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon.

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Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic

Room: 211D - Session SM+AS+BI+PS-ThM

Plasma Processing of Biomaterials

Moderator: Deborah O'Connell, University of York, UK, Satoshi Hamaguchi, Osaka University, Japan

8:00am **SM+AS+BI+PS-ThM1 Potential of Low Temperature Plasma Sources in Cancer Treatment, Jean-Michel Pouvesle, GREMI CNRS/Université d'Orléans, France, G. Collet, CNRS, E. Robert, GREMI CNRS/Université d'Orléans, France, L. Ridou, CNRS-CBM, France, S. Dozias, T. Darny, GREMI CNRS/Université d'Orléans, France, B. El Hafni-Rahbi, C. Kieda, CNRS-CBM, France**

INVITED

The last decade has seen an impressive increase of the research dedicated to the biomedical applications of low temperature Non Thermal Plasmas (ltNTP), especially with plasma sources working at atmospheric pressure. Medical applications of ltNTP now concern a very wide range of domains including cancer treatment. The antitumor effect of ltNTP has been clearly shown *in vivo* on murine models with various cancer types (bladder, colon, glioblastoma, melanoma, ovary, pancreas). Although the involved mechanisms are far from being fully understood, the therapeutic effect is now totally admitted and the first clinical study (head and neck) has been reported [1]. In case of plasma jet experiments, the observed effect are most of the time attributed to the very rich chemistry generated by the interaction of the rare gas plasma plume with the surrounding environment constituted

either from the ambient air, or this latter in complex interaction with liquids at the interface with the targeted organ. Our recent experiments performed on tissue oxygenation[2] or breast cancer treatments on immunocompetent mice [3] lead to the conclusion that probably the involved chemistry couldn't, alone, completely allow describing the observed phenomena. This, especially under very soft treatment conditions, is suggesting possible triggering of some immune system chain processes and also possible modifications in the microenvironment of tissue and tumors. In this context, there is still an unknown role of the electric field associated with the ionization front or generated in the environment of the plasma plume tip. Taking into consideration the recent vessel normalization based-cancer treatment, the ltNTP effect should be further investigated in view of blood vessels structure and function (blood flow) as well as tumor hypoxia compensation to confirm a possible ltNTP-based adjuvant approach for cancer treatments. These results suggest new ways, especially combined therapy, to consider the plasma and its therapeutic delivery in ltNTP-based tumor therapy. In this talk, after a presentation of the context and the plasma devices, we will go through the specific case of cancer treatment with what have been already demonstrated *in vitro* and *in vivo*, what can be directly linked with the produced discharges, including recent results on electric field measurements in plasma biological application conditions.

This work is supported by the APR Region Centre PLASMEDNORM.

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8:40am **SM+AS+BI+PS-ThM3 Plasma Polymerized Polypyrrole Thin Films and Their Use in Drug Release Control**, C. Li, National Yang Ming University, Taiwan, Republic of China, *Yung Te Lee*, National Central University, Taiwan, Republic of China, *J.H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China

Polypyrrole thin films were deposited using a plasma polymerization process. During deposition, power input (between 30W to 70W), monomer (pyrrole) flow rate (30 sccm to 50 sccm), and Ar flow rate were varied. Optical emission spectroscopy (OES) was used to study the plasma characteristics under each deposition condition. After deposition, these films were characterized using FTIR, AFM, ellipsometry, ultraviolet-visible (UV-vis) spectroscopy, and surface profilometer. Eventually, these films were applied to control drug release rate under different thickness and structure. The results were correlated with the process parameters and plasma conditions.

9:00am **SM+AS+BI+PS-ThM4 Thin Film Metallic Glass: A Novel Coating for Various Biomedical Applications**, *Chia-Chi Yu, Y. Tanatsugu, S. Chyntara, C.M. Lee, W. Diyatmika, J.P. Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China, *M.J. Chen, S.H. Chang, W.C. Huang*, Mackay Memorial Hospital Tamsui Campus, Taiwan, Republic of China

Thin film metallic glasses (TFMGs) exhibit unique properties such as high strength, smooth surface as well as good wear- and corrosion-resistances due to their amorphous atomic structure. The biocompatibility and antibacterial property of TFMGs can also be obtained, which show great potential for biomedical applications. In addition, the low surface free energy of TFMGs in certain compositions can be achieved and leads to the relatively high hydrophobicity and the low friction coefficient.

In this presentation, various applications of TFMG are discussed, including the property enhancements of dermatome blade and syringe needle, thrombosis reduction for intravenous catheter, and the suppression of cancer cell attachments. A Zr-based TFMG is coated on substrates by using magnetron sputtering. The TFMG-coated dermatome blade show a great enhancement of durability and sharpness, compared with those of the bare one. For the syringe needle, significant reductions in insertion and retraction forces for TFMG-coated needle are achieved due to the non-sticky property and relatively low coefficient of friction. For thrombosis reduction, less platelet aggregations are observed on the TFMG than that on the bare glass in platelets adhesion test, suggesting TFMG-coated catheters is potentially useful to be placed into vessels for long periods of time with reduced numbers of the aggregation of blood platelets. For cancer cell attachment suppressions, TFMG exhibits the least cancer cell attachment among other control groups. Thus, anti-proliferation and anti-metastasis of medical tools can be achieved with TFMG coating.

9:20am **SM+AS+BI+PS-ThM5 Plasma Surface Functionalization of Nano-structured Materials for Biomedical Applications**, *Masaaki Nagatsu, H. Chou, A. Viswan, T. Abuzairi, M. Okada, M.A. Ciolan*, Shizuoka University, Japan, *N.R. Poespawati, R.W. Purnamaningsih*, University of Indonesia, *A. Sakudo*, University of the Ryukyus, Japan, *S. Bhattacharjee*, Indian Institute of Technology, Kanpur, India **INVITED**

In this study, we will present the recent experimental results on plasma surface functionalization of nano-structured materials for bio-medical applications.

First, with the graphite-encapsulated magnetic nanoparticles(MNPs), we studied the surface functionalization by using the Ar plasma pre-treatment followed by NH₃ plasma post-treatment, to introduce the amino groups onto the surface of the nanoparticles.¹⁾ The amino group population of each nanoparticle with a typical diameter of 20 nm was evaluated by using the conventional chemical technique using SPDP and DTT solutions and we obtained about 8 x 10⁴ amino groups per nanoparticle.²⁾ Immobilization of the antibody of influenza virus onto the surface of amino-modulated magnetic nanoparticles was then performed for aiming at studying the feasibility of collection and condensation of virus. After magnetic separation, we succeeded in a significant concentration of the influenza virus number compared with that of the initial sample.³⁾ Using the same method, we also demonstrated a higher concentration of Salmonella about 70 times higher than that of initial sample by the magnetic separation.⁴⁾ The present results suggest the feasibility of the proposed plasma surface functionalized MNPs for rapid concentration of influenza virus or various bacteria.

As the second topic, the selective ultrafine surface modification of functional groups onto the polymeric substrate or vertically aligned CNT dot-array with a dot size of several μm was investigated using the atmospheric pressure plasma jet with a nano/micro-sized capillary. The micro-sized surface modification of amino or carboxyl groups introduced onto the CNT dot-array were confirmed by the fluorescence labelling technique.⁵⁾ With fluorescence-labeled avidin molecules, we also confirmed efficient capturing of avidin molecules by the biotin-immobilized CNT dot array through strong biotin-avidin binding process. The present result supports the feasibility of future biochip sensor to detect specific protein, virus or bacteria. In addition to these results, the other experimental results will be presented and discussed at the conference.

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11:00am **SM+AS+BI+PS-ThM10 Tailoring Biomaterials-cell Interaction through Reactive Surface Modification**, *Salvador Borros*, Institut Químic de Sarrià, Ramon Llull University, Barcelona, Spain **INVITED**

The immobilization of biologically active species is crucial for the fabrication of smart bioactive surfaces. For this purpose, plasma polymerization is frequently used to modify the surface nature without affecting the bulk properties of the material. Thus, it is possible to create materials with surface functional groups that can promote the anchoring of all kinds of biomolecules. Different methodologies in protein immobilization have been developed in recent years, although some drawbacks are still not solved, such as the difficulties that some procedures involve and/or the denaturalization of the protein due to the immobilization process. However, along with the chemical signals, the mechanical forces are critical for many tissues, since they are constantly suffering tension, shear, loading, etc. Essentially, the cell signaling exerted by forces is transduced through receptors that are in intimate contact with the matrix. Therefore, the main consequence of this receptor-matrix interaction is that cells and matrix are mechanically coupled, so that matrix deformation is considered the main cause of the mechanical signaling. By mimicking these mechanical forces in the surface of a material, it would be possible to obtain more physiological environments and thus a more physiological cell response. Again, the use of plasma polymerization techniques can help to design surfaces that can be tailored in terms of mechanical properties and chemical compositions and thus have a high potential for cells signaling.

This paper reports the work that we have developed in the last 10 years in the design, synthesis and characterization of thin films that can be a platform for studying the interaction between cells and separate influences

of physical and chemical cues of a matrix on the adhesion, growth and final phenotype of cells.

11:40am **SM+AS+BI+PS-ThM12 Analysis of Amino Group Formation on Polystyrene Surfaces by Nitrogen-Hydrogen-Based Plasma Irradiation**, *Kensaku Goto, D. Itsuki, M. Isobe, S. Sugimoto, S. Miyamoto, A. Myoui, H. Yoshikawa, S. Hamaguchi*, Osaka University, Japan

Polystyrene is a widely used cell-culture plate material. Currently cell culture plates on the market include those whose inner surfaces are covered with amino and/or carbonyl groups for a better control of cell adhesion to the plate surfaces. Such functional groups on a cell culture plate surface may immobilize glycoproteins or other biopolymers that function as extracellular matrices (ECM) and thus affect the environments where the cells are cultured. The goal of this research is to understand how such functional groups, especially amino groups, are formed on a polystyrene surface, depending on the deposition methods. Of particular interest are plasma-based methods of surface functionalization. In this study, we have observed experimentally how exposure of N_2/H_2 or N_2/CH_3OH plasmas to polystyrene surfaces form amino-group-like structures and also examined using molecular dynamics (MD) simulation how a polystyrene surface interacts with incident energetic ions such as NH_3^+ as well as abundant low-energy radicals such as NH_2 under conditions similar to our experiments. In the experiments, we used parallel-plate discharges with an inverter power supply whose peak-to-peak voltage was about 3kV and frequency was 20kHz at a relatively high gas pressure of 250 - 2,500 Pa. In MD simulation, we used a simulation code with interatomic potential functions that had been developed in-house based on quantum mechanical calculations of atomic interactions involved in this system. Results of MD simulations under the conditions similar to plasma enhanced chemical vapor deposition (PE-CVD) by ammonia plasmas or cyclopropylamine (CPA) [1] suggest that, with energetic ion bombardment, amino groups tend to be broken to form new covalent bonds by ion bombardment. Preliminary results of cell culture experiments with plasma-treated polystyrene cell plates will be also reported.

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12:00pm **SM+AS+BI+PS-ThM13 Tailoring the Surface Properties of Three-Dimensional, Porous Polymeric Constructs for Biomedical Applications Using Plasma Processing**, *Morgan Hawker, A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Utilizing bioresorbable polymers to fabricate constructs with three-dimensional (3D), porous architectures is desirable as these constructs mimic the extracellular matrix—a critical characteristic for many biomedical applications including tissue engineering, controlled-release drug delivery, and wound healing. Although the bioresorbability and architecture of these materials are suitable for such applications, the surface properties (i.e., chemical functionality and wettability) must often be customized depending on the desired function. Plasma processing is an attractive tool for surface modification of these delicate polymeric materials as it provides a low-temperature, sterile environment with a variety of precursor choices. The presented work will highlight the plasma modification of a variety of 3D, porous polymeric constructs. Specifically, we fabricated scaffolds via electrospinning and porogen leaching techniques using both poly(ϵ -caprolactone) (PCL) and polylactic acid (PLA) to develop a repertoire of native polymer constructs with differing bulk properties. We evaluated the efficacy of plasma-modifying 3D constructs using contact angle goniometry, X-ray photoelectron spectroscopy, and scanning electron microscopy to assess changes in wettability, chemical functionality, and scaffold architecture. The interactions of plasma-modified scaffolds with different biological species, including human dermal fibroblasts and *Escherichia coli* were explored, specifically to assess scaffold bioreactivity. Notably, we demonstrate that scaffold properties, and thus bioreactivity, can be customized depending on the choice of plasma precursor. We show that plasma treatment using fluorocarbon and hydrocarbon precursors (i.e., octafluoropropane, hexafluoropropylene oxide, and 1,7-octadiene) results in hydrophobic and bio-non reactive scaffolds. Additionally, precursors with nitrogen and oxygen functionality (i.e., allylamine, allyl alcohol, water, and ammonia) can be used to fabricate scaffolds that are hydrophilic and bio-reactive. Altogether, this work illustrates the comprehensive tunability of biologically-relevant polymeric constructs in terms of their bulk properties, surface properties, and cell-surface interactions.

Thin Film

Room: 114 - Session TF+EM+NS+PS+SM-ThM

Plasma ALD and Nano-applications

Moderator: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, Richard Vanfleet, Brigham Young University

8:00am **TF+EM+NS+PS+SM-ThM1 Atomic Layer Deposition of Silicon Dielectrics: Precursors, Processes, and Plasmas**, *Dennis Hausmann*, Lam Research Corporation **INVITED**

As the dimensions of modern semiconductor devices continue to shrink below the current 14 nm technology node, novel processes for the deposition of highly conformal, low temperature, silicon based dielectrics will be needed for applications that include sidewall spacers, barriers, and patterning layers. Atomic layer deposition (ALD) is an ideal method for achieving the high conformality and has been used in high volume manufacturing (HVM) to deposit high-k dielectric materials (HfO_2 , ZrO_2 , etc.) for several technology generations. Plasma assisted ALD is the best known method to meet low temperature ($<500^\circ C$) requirements and is now being used for depositing conformal silicon dielectrics such as silicon oxide (SiO_2) and silicon nitride (Si_3N_4).

In this presentation, we discuss the current state of the art of precursors, plasmas, and process conditions required to deposit conformal silicon dielectrics by plasma ALD. Theoretical and experimental data will be presented in order to explain the observed reaction characteristics for the plasma ALD of silicon oxide (SiO_2), silicon nitride (Si_3N_4), and the lack (so far) of silicon carbide (SiC). Generic to all ALD processes is the high cost of the precursors relative to traditional chemical vapor deposition (CVD); in the case of silicon dielectric ALD, this is exacerbated by the relative low “reactivity to cost ratio” of available silicon precursors. Although plasmas enable low temperature deposition, they pose challenges for achieving isotropic film properties over the complex topography on today’s semiconductor devices.

8:40am **TF+EM+NS+PS+SM-ThM3 ALD Dielectrics for Power Electronics**, *Veena Misra*, NCSU **INVITED**

Owing to a high critical electric field and high electron mobility, wide band gap materials such as GaN and SiC are being sought for high voltage power electronics applications. In the case of GaN devices, the reliability continues to be a challenge to must be addressed before successful commercialization. In our work, different dielectrics deposited by Atomic Layer Deposition (ALD) have been investigated for improving the threshold voltage stability and dynamic reliability of AlGaN/GaN based MOSHFETs. A novel pulsed-IV-based methodology was developed and demonstrated to be applicable for detecting both shallow and deep traps and implemented on evaluating different high-k and low-k ALD dielectrics. Using physics-based simulation models and experimental data, it was demonstrated that the leakage at the surface of the AlGaN, whether through the passivation dielectric bulk or the dielectric/AlGaN interface, must be minimized to restrict the formation of a “virtual gate” and minimize current collapse. It was also found that an optimal passivation dielectric must create a high density of shallow interface donor traps to quicken the de-trapping of electrons from the “virtual gate” and the recovery of the channel underneath. Combining simulation and experimental results, an optimal set of ALD dielectrics for a reliable gate stack and access-region passivation regions, respectively, was determined and will be discussed. In the area of SiC devices, low inversion channel mobility, caused high density of interface states (Dit) at SiO_2/SiC interface, limits the wide adoption of SiC MOS devices. Atomic Layer Deposition offers key advantages in the area of gate dielectrics such as good film quality, low substrate damage, superior uniformity, precise thickness control, and low process temperature. Additionally, deposited SiO_2 enables interface engineering to independently control the interface properties. To enhance the channel mobility and maintain good overall gate dielectric properties, a thin layer of a different dielectric material can be inserted to improve interface properties and high quality deposited SiO_2 can be used as the bulk gate dielectric. We have demonstrated a novel interface engineering technique utilizing ultra thin lanthanum silicate ($LaSiO_x$) at the SiC/dielectric interface and ALD SiO_2 as the bulk gate dielectric. The lanthanum silicate interface engineering dramatically improves the mobility of 4H-SiC metal oxide semiconductor field effect transistors (MOSFETs) and is attributed to the large driving force of La_2O_3 to react with SiO_2 .

9:20am **TF+EM+NS+PS+SM-ThM5 Pb(Zr,Ti_{1-x})O₃ Magnetoelectric Tunnel Junctions for Magnetoelectric RAM (MeRAM) Memory Applications**, D. Chien, X. Li, K. Wong, P. Khalili, K. Wang, Jane P. Chang, University of California at Los Angeles

As existing memory systems approach fundamental limitations, ultra-thin uniform conformal PZT films are needed for next-generation ultralow-power voltage-controlled non-volatile magnetoelectric RAM (MeRAM) memory devices. By utilizing the magnetoelectric effect, where an electric field or voltage can be used to control the magnetization switching (instead of current), the writing energy can be reduced, resulting in increased memory density (Amiri, P.K. et al., Journal of Applied Physics, 2013). Previous research has shown that the voltage-controlled magnetic anisotropy (VCMA) effect increases with the capacitance of the stack (Kita, K. et al., Journal of Applied Physics, 2012). Therefore, integrating an ultra-thin PZT film (having a dielectric constant 1-2 orders of magnitudes higher than currently used MgO) into the tunneling oxide layer will enhance the VCMA coefficient, allowing for a lower voltage to switch the magnetization of the free magnetic layer and thus decreasing the write energy.

Using atomic layer deposition (ALD), a surface-reaction controlled process based on alternating self-limiting surface reactions, an ultra-thin film of PZT can be synthesized with precise control of the film thickness and elemental composition (Zr/Ti = 52/48). ALD PZT thin films were synthesized by depositing alternating layers of PbO, ZrO₂, and TiO₂ layers using Pb(TMHD)₂, Zr(TMHD)₄, and Ti(Oi-Pr)₂(TMHD)₂ as metal precursors and H₂O as the oxidant. The number of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. The bottom layers of Ta/CoFeB (free magnetic layer)/MgO were sputtered, the PZT film with thickness of 1.7 nm was deposited by ALD, the top layers of MgO/CoFeB (fixed magnetic layer)/Ta/Pt were sputtered, and the entire stack was annealed at 200°C for 30 minutes in order to fabricate PZT magnetoelectric tunnel junctions (MEJs).

The perpendicular magnetic anisotropy (PMA) of the bottom free magnetic CoFeB layer was verified via superconducting quantum interference device (SQUID) magnetometer, confirming that the ALD PZT deposition process is a viable method for synthesizing PZT MEJs. The tunnel magnetoresistance (TMR) was measured to be 50%, demonstrating a promising read-out process. Due to the integrated ALD PZT layer in the tunneling barrier, the VCMA coefficient of PZT MEJ devices is expected to be double that measured for CoFeB/MgO/CoFeB devices ($\xi = 37$ fJ/Vm) (Zhu, J. et al., Physical Review Letters, 2012).

9:40am **TF+EM+NS+PS+SM-ThM6 Plasma-Assisted ALD of High-Quality Molybdenum Oxide Films**, Martijn Vos, B. Macco, N.F.W. Thissen, A.A. Bol, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

In this contribution we present a novel plasma-assisted atomic layer deposition (ALD) process to deposit high-quality molybdenum oxide films, with a high growth per cycle (GPC) over a wide temperature range of 50 °C to 350 °C. This process complements existing (thermal) ALD MoO_x processes, which are less suited for deposition at low temperature, due to low GPC and contamination. A decent deposition process is of importance as MoO_x films have received great interest due to their remarkable optoelectronic and catalytic properties and find their use in many applications, including solid state lithium batteries, gas sensors, and more recently solar cells.

A variety of deposition techniques exists for the deposition of MoO_x, such as evaporation, sputtering, chemical vapor deposition and ALD. While many of the applications of MoO_x films can benefit from the merits of ALD, i.e. conformality and digital thickness control, only few ALD processes are known from literature [1, 2]. Recently bis(tert-butylimido) bis(dimethylamido) molybdenum ((NtBu)₂(NMe₂)₂Mo) appeared as a promising precursor for ALD of MoO_x films, using O₃ as oxidant [2].

The plasma-assisted ALD process we report on uses (NtBu)₂(NMe₂)₂Mo and O₂ plasma and shows a relatively high GPC between 0.70 Å and 0.93 Å for amorphous films deposited at temperatures up to 250 °C. In comparison, the analogous O₃ process is featured by a low GPC of 0.17 Å at 150 °C. For deposition temperatures above 250 °C polycrystalline growth was observed, accompanied by an increase in GPC to 1.88 Å for 350 °C. From Rutherford backscattering measurements it was determined that the C and N content in the films is below the detection limit (3 at.% and 2 at.% respectively) for all deposition temperatures, which demonstrates the high-quality of the films (while the aforementioned O₃ process resulted in 9.2 at.% N). Furthermore the O/Mo ratio was found to be just below 3, indicative of oxygen vacancies, which are common for MoO_x films and can lead to an increased conductivity, which is beneficial for many applications. Additional material properties such as band gap, work function and surface morphology will also be discussed and finally an outlook to the application of this ALD process in silicon solar cells will be given.

[1] M. Diskus *et al.*, J. Mater. Chem. **21** (2011) 705

[2] A. Bertuch *et al.*, J. Vac. Sci. Technol. **32** (2014) 01A119

11:00am **TF+EM+NS+PS+SM-ThM10 Status and Prospects of Plasma-Assisted Atomic Layer Deposition**, Harm Knoops, Oxford Instruments Plasma Technology, UK, W.M.M. Kessels, Eindhoven University of Technology, Netherlands **INVITED**

Plasma-assisted atomic layer deposition (ALD) or plasma ALD has established itself as a prominent branch in ALD processing and a wide range of plasma ALD processes are currently available. Due to the complexity of plasmas, plasma ALD is different from thermal ALD in various aspects. Even though the main relevant species in plasmas have been identified,¹ the effects of plasma chemistry and plasma-surface interaction need further study. In this contribution an overview on the status of plasma ALD is given and the key prospects for plasma ALD are highlighted.

Regarding the current understanding of plasma ALD, three subjects will be treated. First the basic plasma species (i.e., radicals, electrons, ions, and photons) and their role in plasma ALD will be discussed. For instance, potential damage to the surface from photons, but also cases where plasma species can repair defects (e.g., N₂ plasmas on GaN surfaces).² Second plasma chemistry and potential poisoning or inhibition processes will be treated, which can play a big role in the ALD of nitrides and conductive films. Third, dissociation in the plasma of reaction products can lead to redeposition effects which can have a large influence on for instance SiN_x and TaN_x ALD.

Several topics will be discussed regarding the prospects for plasma ALD. Even though plasma ALD provides additional possibilities, many cases exist where material properties or cycle times are still unsatisfactory and advances in reactor design such as the capability to provide additional energy in the form of a controlled ion bombardment are needed. In addition, advanced processing schemes such as 3-step ABC ALD cycles can be beneficial as shown by ALD of noble metals at low deposition temperatures (e.g., Pt ALD).³ Whether metal films initially grow as continuous films or as nanoparticles (as well as the particle size), will depend on the chemistry, the surface energy, and the growth temperature. Recently, plasma ALD has shown to allow ALD of Ag by spatial ALD at high pressure.⁴ This case shows that more understanding of the plasma is needed because of an unexpected decreased growth at long plasma exposures (presumably caused by NH₃ poisoning). In general, increasing control of the plasma and understanding of the relevant processes at the surface and in the plasma will be key to further develop plasma ALD.

¹ Profijt *et al.*, *JVST A29*, 050801 (2011)

² Chen *et al.*, *Phys. Status Solidi A* (2014) / DOI 10.1002/pssa.201431712

³ Mackus *et al.*, *Chem. Mater.* **25**, 1769 (2013)

⁴ Van den Bruele *et al.*, *JVSTA33*, 01A131 (2015)

11:40am **TF+EM+NS+PS+SM-ThM12 A Novel Plasma-Enhanced ALD Process for HfO₂ using HfCp(NMe₂)₃ and O₂ Plasma**, Akhil Sharma, V. Longo, A.A. Bol, W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

In atomic layer deposition (ALD) the associated precursor chemistry has a large effect on the quality and properties of the deposited thin films. The most commonly used hafnium precursor for ALD of HfO₂ is HfCl₄. This precursor is not ideal for all applications due to possible chlorine contamination and the generation of corrosive by-products during the ALD process. Organometallic precursors such as Hf(NtMe)₄ promise to be a better choice but they typically suffer from a limited thermal stability. In this context, HfCp(NMe₂)₃ might offer a better alternative because of its higher thermal stability. However, while using H₂O as oxygen source in a thermal ALD process it yields a low growth rate¹. This creates an opportunity for studying this precursor in combination with other oxygen sources. In this work, we report on the development of a novel plasma-enhanced ALD (PE-ALD) process using HfCp(NMe₂)₃ in combination with an O₂ plasma to deposit HfO₂ thin films. To our knowledge, to date, the PE-ALD for this precursor has not been reported in the literature.

Our results show that the PE-ALD process offers significant advantages over the reported thermal ALD process such as a high growth rate, reduced deposition temperature, shorter cycle time and good control over composition of the deposited films. In contrast to the thermal ALD process using HfCp(NMe₂)₃ and water¹, the PE-ALD process has resulted into a wide ALD temperature range (150-400°C) with significantly higher growth per cycle values (1.1Å/cycle) and shorter cycle times which ultimately improves the wafer throughput. The level of impurities were found to decrease with increasing the deposition temperature as concluded from XPS and ERD analyses. The concentrations of residual carbon and hydrogen reduced from 1.0 at% to 0.2 at% and 3.4 at% to 0.8 at%, respectively, by increasing the deposition temperature from 200°C to 400°C. Moreover,

RBS studies showed an improvement in stoichiometry of HfO₂ thin films with increase in deposition temperature resulting in a Hf/O ratio of ~0.5 at 400°C. Furthermore, GI-XRD measurements detected a strong transition from amorphous (300°C) to fully crystallized films (400°C), consisting of a mixture of monoclinic, tetragonal and cubic phases. These results therefore have demonstrated that PE-ALD using HfCp(NMe₂)₃ and O₂ plasma is a promising and viable alternative to the thermal ALD process producing high quality HfO₂ thin films over a wider temperature range and with faster cycle times.

1. Consiglio et al, J. Vac. Sci. Technol. A 30(1), 2012

12:00pm **TF+EM+NS+PS+SM-ThM13 Conductive Hafnium Nitride Layers By Plasma-Assisted Atomic Layer Deposition, Saurabh Karwal, B.L. Williams, W.M.M. Kessels, M. Creatore**, Eindhoven University of Technology, The Netherlands

Transition metal nitrides (TMNs) have gained much attention in the semiconductor industry due to their characteristics such as copper and lithium diffusion barriers, metal-like behaviour (i.e. low resistivity) and high hardness, mechanical strength and chemical inertness. Among TMNs, hafnium nitride exhibits a low bulk resistivity of 33 μΩcm and highest negative Gibbs free energy of formation (HfN: -88.2, TiN: -80.4, TaN: -60.3 kcal/mol) and hence could serve as novel material for several applications, such as diffusion barrier and gate electrode in microelectronics, and reflective back contact for CIGS solar cells.

Conductive hafnium nitride thin films were deposited by inductively coupled plasma (ICP)- assisted atomic layer deposition using a heteroleptic metalorganic hafnium precursor, tris(dimethylamino)cyclopentadienylhafnium CpHf(NMe₂)₃ [TDMACpH] and H₂-or N₂- fed plasmas serving as co-reactants. The effects of the substrate temperature, plasma chemistry and plasma exposure time have been investigated in terms of growth-per-cycle (GPC), chemical, electrical and morphological properties of the deposited layer. It has been observed that highly resistive (0.75 Ωcm) Hf₃N₄ thin films are obtained via an A-B type ALD cycle (TDMACpH/N₂ -fed plasma) with a GPC of 0.035 nm/cycle. Furthermore, a limited abstraction of the ligands leads to a residual carbon content in the layer of 7%.

Instead, conductive films (1.8 x 10⁻³ Ωcm) are achieved upon the application of an A-B-C ALD cycle where an intermediate H₂- fed plasma exposure step is included between the TDMACpH exposure and the N₂-fed plasma step, with a GPC of 0.045 nm/cycle. This intermediate step is found to be responsible for a more efficient removal of the precursor ligands and for the reduction of Hf⁴⁺ state to Hf³⁺ state, essential for guaranteeing electron conductivity. This transition of chemical and electrical properties of the deposited thin films is also accompanied by a change in crystallographic properties from amorphous (A-B ALD cycle) to conductive cubic HfN (A-B-C ALD cycle), as revealed by grazing incidence X-ray diffraction.

Contact: s.karwal@tue.nl

Thursday Afternoon, October 22, 2015

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic

Room: 211D - Session SM+AS+BI+PS-ThA

Plasma Processing of Biomaterials and Biological Systems

Moderator: David Graves, University of California, Berkeley, Jean-Michel Pouvesle, GREMI CNRS/Université d'Orléans

2:20pm **SM+AS+BI+PS-ThA1 Matching Plasma Sources with Intended Biomedical Outcomes: Open Questions in Modeling of Plasma Surface Interactions**, *W. Tian*, University of Michigan, *S.A. Norberg*, US Military Academy - West Point, *A.M. Lietz*, University of Michigan, *N.Yu. Babaeva*, Joint Institute for High Temperatures, **Mark Kushner**, University of Michigan **INVITED**

Plasma surface modification of materials for biomedical applications typically involves atmospheric pressure plasmas in the form of dielectric barrier discharges (DBDs) or atmospheric pressure plasma jets (APPJs). In many cases, APPJs operate similarly to DBDs with an ionization wave (IW) propagating through a rare-gas dominated gas channel. The intersection of the IW with the surface being treated, for example tissue, in both DBDs and APPJ produces locally large fluxes of ions, UV/VUV photons and electric fields onto the surface. These fluxes are collectively *hard fluxes* due to the higher levels of activation energy they represent. Remote DBDs and APPJs where the plasma plume does not intersect the surface produce *soft fluxes*, dominated by neutral reactants. The character and ratios of *hard-to-soft fluxes* and their compositions are functions of flow dynamics, ambient conditions (e.g., humidity) and pulse power waveforms. In many biomedical applications, the tissue is covered by a liquid (or the intended surface is liquid as in plasma activated water). In these cases, plasma produced activation energy, radicals and ions must penetrate through the plasma-liquid interface, where liquid phase mechanisms then determine the reactants to the tissue. From one perspective, significant advances have been made in modeling these processes and furthering our understanding. From another perspective, there are still significant open questions that models need to address, including the manner of coupling of the gas phase plasma and liquid, gas induced fluid dynamics, long term evolution of the liquid chemistry, reactions at the surface of the tissue and control schemes to minimize variability. A brief overview of progress in modeling plasma modification of biomaterials will be provided followed by examples of the authors' modeling works for APPJs and DBDs intersecting with model tissues and liquids.

3:00pm **SM+AS+BI+PS-ThA3 Plasma Processing of Biomimetic and Sintered Calcium Phosphates for Bone Regeneration and Repair**, *Cristina Canal*, Technical University of Catalonia, Spain **INVITED**

Large bone defects caused by trauma, osteoporotic fractures, infection and tumour or cysts resection pose a great clinical and socio economic problem. Bone grafting materials respond to the need generated by over 2 million bone grafting procedures that are performed every year worldwide. As an alternative to autografts or xenografts, different biomaterials have been proposed, yet with partial success since different aspects remain yet to be improved.

In this context, the use of low pressure (LP) and atmospheric pressure (AP) plasmas opens new opportunities in the field of bone biomaterials. It is the aim of this talk to provide an overview on the strategies undertaken in our group to enhance diverse features of bone biomaterials and to enhance bone therapies.

The examples discussed here include biomimetic hydroxyapatite (HA) and β -tricalcium phosphate (β -TCP) as the most clinically used calcium phosphate (CaP) ceramics for bone regeneration. Some of the points of improvement include increasing their mechanical strength, or using them as local dosage forms for the delivery of drugs, to aid in different therapies, such as combating infection or fighting cancer.

For instance, we have investigated LP plasmas with the aim of expanding the use of biomimetic CaPs to load-bearing sites. Although composites have been defined, their performance is not yet optimal, possibly due to insufficient adhesion between the matrix and the reinforcing agent. Oxygen and argon plasmas have been employed in the surface modification of polylactide fibers to improve the adhesion at the interface between them and biomimetic CaPs with interesting results.

In a different approach we have focused on modulating drug delivery from bone biomaterials. Both AP and LP plasmas are of interest with views on different medical applications and in the design of advanced biomaterials with controlled drug release properties. Different strategies are considered with that aim, such as using either plasma functionalization with AP plasma jet to modulate the interactions of the drug with the CaP surface or employing LP plasma polymerization on CaP scaffolds as a strategy to control the drug release. Lastly, AP plasmas are in the limelight due to their wide potential in the medical field, and here we will discuss some recent findings for application in bone therapies and regeneration.

Acknowledgements

Spanish Government is acknowledged for support through Project MAT2012-38438-C03-01, co-funded by the EU through European Regional Development Funds, and Ramon y Cajal fellowship of CC. The European Commission is also acknowledged through funding in FP7/2007-2013 under the Reborne project (no. 241879).

4:00pm **SM+AS+BI+PS-ThA6 Plasma Processing of Biomaterials and Biomedical Devices**, *H.J. Griesser*, *T.D. Michl*, *S.S. Griesser*, *M. Jasieniak*, *H.H. Mon*, *Bryan Coad*, University of South Australia **INVITED**

Gas plasmas have attracted considerable attention over more than 40 years as a convenient method for changing the surface chemical composition of biomaterials and thereby alter and control the interfacial interactions between biomedical devices and contacting "biology" such as protein solutions, blood, cells and tissue, and bacterial biofilm growth. Plasma technologies are already in use on a large industrial scale in several biomedical device companies; for example 30-day contact lenses use a thin plasma coating to confer wettability and low fouling to silicone-based contact lens materials. Bio-interfacial interactions are very short range, and hence it is sufficient to apply ultrathin coatings (< 20 nm thick). Plasma techniques are ideally suited because process control is straightforward and the resultant surface modifications or coatings tend to have a high degree of uniformity and reproducibility compared with other, solution based coating methods. On the other hand, the complex chemical composition of plasma gas phases prevents fine control of chemistry to the extent achievable by conventional chemical approaches. Detailed surface analysis is essential.

Plasma approaches are useful to produce coatings designed to combat the problem of bacterial and fungal biofilm growth on biomedical devices, which leads to infections and delayed healing. One approach is the use of organochlorine plasma polymer coatings, which are highly effective at contact killing. Other, cytocompatible approaches comprise the use of plasma polymer coatings that release NO or available antibiotics such as levofloxacin. A different approach entails the covalent immobilization of a monolayer of antimicrobial molecules onto a thin plasma polymer interlayer whose function is to provide good adhesion and reactive surface chemical groups that can be used to attach antibiotics. Such covalently grafted monolayers have given excellent deterrence of attachment and biofilm formation of bacteria and pathogenic fungi.

4:40pm **SM+AS+BI+PS-ThA8 Organs on a Chip – Biointerfaces in Stem Cell Research**, *Kevin Healy*, University of California at Berkeley **INVITED**

Highly regulated signals in the stem cell microenvironment such as ligand adhesion density, matrix stiffness and architecture, and growth factor presentation and concentration have been implicated in modulating stem cell differentiation, maturation, tissue formation, and ultimately function. My group has developed a range of materials systems and devices to study and control stem cell function and their self-organization into three-dimensional microtissues (e.g., 'organs on a chip'). These systems are being developed for screening molecular therapies and patient specific medicine via *in vitro* disease specific tissue models. Examples of how biointerface science is important in these applications will be highlighted. The benefits of our approach include: 1) robust and reproducible platform embodiments precision microengineering to create better microtissue environments; 2) precise delivery of molecules (e.g., drugs) in a computationally predictable manner; 3) ability to model human cardiomyopathy; and, 4) cost efficient and high content characterization of cardiac tissue drug response.

5:20pm **SM+AS+BI+PS-ThA10 Effect of the Radical Species for Gene Transfection by Discharge Plasma Irradiation**, *Yoshihisa Ikeda*, *M. Jinno*, Ehime University, Japan

Gene transfection is a technique of deliberately introducing nucleic acids into cells in order to give them specific characteristics. In practice, this can be achieved in three different ways: chemical method, physical method and the viral vector method.

One of the physical methods that uses discharge plasma irradiation was invented by Satoh, who is one of the authors, and his group in 2002. Since this technique is free from adverse effect associated with viruses, there are no risks as the others mentioned above. The plasma irradiation on genes and cells induces the transfection process in which the genes and cells are exposed to discharge current, charged particles and chemically reactive species.

The authors investigated the factors for plasma gene transfection by changing protocols and looked at the time periods the factors become effective. The results is that transfection rate drops to 1/10 of the standard protocol when the charged particles and chemically reactive species genes are washed out from the wells by PBS solution 60s after plasma irradiation. Since the life times of the charged particles delivered from plasma to the plasmid solution is less than 60s, the direct effect of the charged particles causing transfection finishes before wash out process. This means that nearly 1/10 of transfections occur during plasma irradiation and that the last 9/10 of transfections occur after plasma irradiation is stopped. This second stage transfection is mainly caused by the residual chemically reactive species, however, plasma irradiation stress to cells and plasmids also induces transfection., i.e. possibly charging effect and oxidation stress induce bio-chemical process of the cells in addition to the chemical reactions on the cell membrane and plasmid induced by chemically reactive species such as radicals.

5:40pm **SM+AS+BI+PS-ThA11 Nonlinear Optical Spectroscopic Observation of Plasma-Treated Bio-Specimen, Kenji Ishikawa, R. Furuta, K. Takeda, Nagoya University, Japan, T. Nomura, T. Ohta, Meijo University, Japan, H. Hashizume, H. Kondo, Nagoya University, Japan, M. Ito, Meijo University, Japan, M. Sekine, M. Hori, Nagoya University, Japan**
Applications of nonequilibrium atmospheric pressure plasma (NEAPP) to the medical field have been reported in recent years. However, a mechanism of interactions between NEAPP and living cells has not been yet elucidated comprehensively. Our strategy for elucidation of plasma-biomaterial interactions is to observe reactions *in situ* at real time. By applying nonlinear optical spectroscopic techniques, the vibrational sum-frequency-generation (SFG) and multiplex coherent anti-Stokes Raman scattering (CARS) microscopy, which are a beneficial tool for addressing best sensitivity at surface and interface, have been used in this study. By using SFG, we have explored topmost surface modification after the interaction between plasma and biopolymeric materials. For the NEAPP-induced reactions on budding yeasts as an eukaryotic cell model, a two-dimensional mapping of budding yeasts treated by the plasma using the CARS microscopy was observed with fluorescence label-free contrasts of chemical vibrational nature. The biomedical imaging of cell membranes, intracellular organelles, nucleus and so forth, was revealed to decompose intracellular membrane by exposure of plasma-generated chemically reactive species, especially for induction of lipid peroxidation. These results will be useful for understanding the plasma induced reactions in the plasma medicine.

Thursday Evening Poster Sessions

**Surface Modification of Materials by Plasmas for
Medical Purposes Focus Topic
Room: Hall 3 - Session SM-ThP**

**Surface Modification of Materials by Plasmas for
Medical Purposes Poster Session**

SM-ThP1 Replacing Self-Assembled Monolayers by Functional Plasma Polymers in Fabrication of Immunosensors, *Lenka Zajickova, A. Manakhov, E. Makhneva, D. Kovar*, Masaryk University, Czech Republic, *G. Dorozinsky, O. Shynkarenko, G. Beketov*, Lashkaryov Institute of Semiconductor Physics, Ukraine, *P. Skladal*, Masaryk University, Czech Republic

Plasma polymerization is an efficient way to the modifications of various surfaces by desired functional groups. It finds potential applications in tissue engineering or fabrication of biosensors. This work reports on the plasma polymerization of two functional coatings that were used as a replacement of self-assembled monolayers (SAMs) in the fabrication of immunosensors. Amine-based coatings were deposited from cyclopropylamine mixed with argon in low pressure capacitively coupled discharge whereas carboxyl-based coatings were prepared by copolymerization of maleic anhydride and acetylene in atmospheric pressure dielectric barrier discharge. The coatings were prepared on gold surfaces of either quartz crystal microbalance or surface plasmon resonance sensors. Their performance was tested on a model system, monoclonal antibody (Ab AL-01) against human serum albumin (HSA) interacting with the corresponding HSA antigen. The immobilization of antibodies and inactivation of free non-reacted groups was realized in buffers with various pH. A crucial point was the stability of the prepared plasma polymers in liquids that was studied by time-varying sensor response and also by physical characterization methods (X-ray photoelectron spectroscopy, infrared spectroscopy, atomic force microscopy, ellipsometry) in the dry state. The performance of the immunosensors with the plasma polymer layers were compared to the sensors prepared using the standard procedure using SAM.

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ThM11, 6

— E —

Eichfeld, S.M.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM6, 5
El Hafni-Rahbi, B.: SM+AS+BI+PS-ThM1,
6
Empante, T.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5

— F —

Falta, J.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
Fisher, E.R.: PS+BI+SM-TuM13, 2;
SM+AS+BI+PS-ThM13, 8
Flege, J.L.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
Förster, S.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, **6**
Furuta, R.: SM+AS+BI+PS-ThA11, 12

— G —

Giamini, S.A.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM5, 5
Gobina, E.: SE+PS+SM-TuM12, 3
Goto, K.: SM+AS+BI+PS-ThM12, **8**
Granick, J.L.: PS+BI+SM-TuM10, **1**
Graves, D.B.: PS+BI+SM-TuM11, 1;
PS+BI+SM-TuM5, **1**
Greber, T.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
Griesser, H.J.: SM+AS+BI+PS-ThA6, 11
Griesser, S.S.: SM+AS+BI+PS-ThA6, 11

— H —

Hamaguchi, S.: SM+AS+BI+PS-ThM12, 8
Hammer, R.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
Hashizume, H.: SM+AS+BI+PS-ThA11, 12
Hausmann, D.M.: TF+EM+NS+PS+SM-
ThM1, **8**
Hawker, M.J.: SM+AS+BI+PS-ThM13, **8**
He, A.Y.: SE+PS+SM-TuM11, 3
Healy, K.E.: SM+AS+BI+PS-ThA8, **11**
Hori, M.: SM+AS+BI+PS-ThA11, 12
Hsieh, C.Y.: SE+PS+SM-TuM10, **3**
Hsieh, J.H.: SM+AS+BI+PS-ThM3, 7
Huang, C.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
Huang, W.C.: SM+AS+BI+PS-ThM4, 7
Hubert, J.: SE+PS+SM-TuM1, 2
Hunter, R.C.: PS+BI+SM-TuM10, 1

— I —

Ikeda, Y.: SM+AS+BI+PS-ThA10, **11**
Ishikawa, K.: SM+AS+BI+PS-ThA11, **12**
Isobe, M.: SM+AS+BI+PS-ThM12, 8
Ito, M.: SM+AS+BI+PS-ThA11, 12
Itsuki, D.: SM+AS+BI+PS-ThM12, 8

— J —

Jäger, E.: SE+PS+SM-TuM3, 3
Jantschner, O.: SE+PS+SM-TuM3, 3

Jasieniak, M.: SM+AS+BI+PS-ThA6, 11
Jinno, M.: SM+AS+BI+PS-ThA10, 11

— K —

Karwal, S.: TF+EM+NS+PS+SM-ThM13,
10
Kelaidis, N.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM5, 5
Kessels, W.M.M.: TF+EM+NS+PS+SM-
ThM10, 9; TF+EM+NS+PS+SM-
ThM12, 9; TF+EM+NS+PS+SM-
ThM13, 10; TF+EM+NS+PS+SM-
ThM6, 9
Khalili, P.: TF+EM+NS+PS+SM-ThM5, 9
Kieda, C.: SM+AS+BI+PS-ThM1, 6
Kim, J.: 2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
Kis, A.: 2D+EM+MG+NS+SE+SM+SS+TF-
ThM11, 6
Klee, V.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
Knoll, A.J.: PS+BI+SM-TuM11, 1
Knoops, H.C.M.: TF+EM+NS+PS+SM-
ThM10, **9**
Kondeti, V.S.S.K.: PS+BI+SM-TuM10, 1
Kondo, H.: SM+AS+BI+PS-ThA11, 12
Kovar, D.: SM-ThP1, 13
Kushner, M.J.: SM+AS+BI+PS-ThA1, **11**

— L —

Lalor, J.: PS+BI+SM-TuM12, 1
Lau, K.K.S.: SE+PS+SM-TuM10, 3
Lee, C.: 2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
Lee, C.M.: SM+AS+BI+PS-ThM4, 7
Lee, C.S.: SE+PS+SM-TuM11, 3
Lee, Y.T.: SM+AS+BI+PS-ThM3, 7
Li, C.: SM+AS+BI+PS-ThM3, 7
Li, X.: SE+PS+SM-TuM11, 3;
TF+EM+NS+PS+SM-ThM5, 9
Lietz, A.M.: SM+AS+BI+PS-ThA1, 11
Lin, Y.-C.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM6, 5
Loke, Y.C.: SE+PS+SM-TuM11, 3
Longo, V.: TF+EM+NS+PS+SM-ThM12, 9
Lopez-Sanchez, O.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM11, 6
Lu, I.: 2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
Luan, P.: PS+BI+SM-TuM11, **1**

— M —

Macco, B.: TF+EM+NS+PS+SM-ThM6, 9
Makhneva, E.: SM-ThP1, 13
Manakhov, A.: SM-ThP1, 13
Mann, M.N.: PS+BI+SM-TuM13, **2**
Marquez-Velasco, J.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM5, 5
Meinel, K.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
Mertens, J.: SE+PS+SM-TuM1, 2
Michl, T.D.: SM+AS+BI+PS-ThA6, 11
Milosavljevic, V.: PS+BI+SM-TuM12, **1**
Misra, V.: TF+EM+NS+PS+SM-ThM3, **8**
Mitterer, C.: SE+PS+SM-TuM3, **3**
Miyamoto, S.: SM+AS+BI+PS-ThM12, 8
Mon, H.H.: SM+AS+BI+PS-ThA6, 11
Myoui, A.: SM+AS+BI+PS-ThM12, 8
— N —
Nagatsu, M.: SM+AS+BI+PS-ThM5, 7

- Naghibi, S.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
- Naguib, M.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM3, 5
- Nguyen, A.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
- Nomura, T.: SM+AS+BI+PS-ThA11, 12
- Norberg, S.A.: SM+AS+BI+PS-ThA1, 11
- Nwogu, N.C.: SE+PS+SM-TuM12, 3
- **O** —
- Oehrein, G.S.: PS+BI+SM-TuM11, 1
- Ohta, T.: SM+AS+BI+PS-ThA11, 12
- Okada, M.: SM+AS+BI+PS-ThM5, 7
- **P** —
- Pegalajar-Jurado, A.: PS+BI+SM-TuM13, 2;
SM+AS+BI+PS-ThM13, 8
- Pfuch, A.: SE+PS+SM-TuM3, 3
- Poespawati, N.R.: SM+AS+BI+PS-ThM5, 7
- Pouvesle, J.-M.: SM+AS+BI+PS-ThM1, 6
- Preciado, E.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
- Purnamaningsih, R.W.: SM+AS+BI+PS-
ThM5, 7
- **R** —
- Ramiasa, M.: SE+PS+SM-TuM2, 2
- Ratner, B.D.: PS+BI+SM-TuM1, 1
- Reniers, F.A.B.: SE+PS+SM-TuM1, 2
- Ridou, L.: SM+AS+BI+PS-ThM1, 6
- Robert, E.: SM+AS+BI+PS-ThM1, 6
- Robinson, J.A.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM6, 5
- **S** —
- Saifullah, M.S.M.: SE+PS+SM-TuM11, 3
- Sakudo, A.: SM+AS+BI+PS-ThM5, 7
- Schmidt, J.: SE+PS+SM-TuM3, 3
- Sekine, M.: SM+AS+BI+PS-ThA11, 12
- Seog, J.: PS+BI+SM-TuM11, 1
- Sharma, A.: TF+EM+NS+PS+SM-ThM12, 9
- Shumlas, S.L.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM2, 5
- Shynkarenko, O.: SM-ThP1, 13
- Sivapragasam, N.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM10, 6
- Skladal, P.: SM-ThP1, 13
- Spange, S.: SE+PS+SM-TuM3, 3
- Strongin, D.R.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM2, 5
- Sugimoto, S.: SM+AS+BI+PS-ThM12, 8
- **T** —
- Takeda, K.: SM+AS+BI+PS-ThA11, 12
- Tanatsugu, Y.: SM+AS+BI+PS-ThM4, 7
- Thenuwara, A.C.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM2, 5
- Thissen, N.F.W.: TF+EM+NS+PS+SM-
ThM6, 9
- Tian, W.: SM+AS+BI+PS-ThA1, 11
- Trautmann, M.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
- Truong, A.: PS+BI+SM-TuM10, 1
- Tsipas, P.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM5, 5
- Tsoutsou, D.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM5, 5
- **V** —
- Vandencastele, N.: SE+PS+SM-TuM1, 2
- Vasilev, K.: SE+PS+SM-TuM2, 2
- Vernisse, L.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM2, 5
- Viswan, A.: SM+AS+BI+PS-ThM5, 7
- von Son, G.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM1, 5
- Vos, M.F.J.: TF+EM+NS+PS+SM-ThM6, 9
- **W** —
- Wallace, R.M.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM6, 5
- Wang, K.: TF+EM+NS+PS+SM-ThM5, 9
- Whitwick, M.B.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM11, 6
- Widdra, W.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM12, 6
- Williams, B.L.: TF+EM+NS+PS+SM-
ThM13, 10
- Wong, K.: TF+EM+NS+PS+SM-ThM5, 9
- **X** —
- Xenogiannopoulou, E.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM5, 5
- **Y** —
- Yang, R.B.: SE+PS+SM-TuM11, 3
- Yoshikwa, H.: SM+AS+BI+PS-ThM12, 8
- Yu, C.: SM+AS+BI+PS-ThM4, 7
- **Z** —
- Zajickova, L.: SM-ThP1, 13
- Zhu, H.:
2D+EM+MG+NS+SE+SM+SS+TF-
ThM6, 5