Plasma Processing
Room Naupaka Salon 5 - Session PS-ThM

Plasma Processing

Moderators: Ellen Fisher, Colorado State University, David Ruzic, University of Illinois at Urbana-Champaign

8:00am **PS-ThM1 Plasma Surface Modification: Optimizing the Positives of Plasma-Materials Interactions***, **Ellen Fisher,*** Colorado State University **INVITED**

Plasma processing represents a powerful approach to modification of a range of substrates utilizing an array of chemistries and morphologies. Unfortunately, plasmas are often given a bad rap with respect to the level of reproducibility achievable as well as the uniformity of any given treatment. Nevertheless, new applications for plasmas continue to be developed and they are employed in a vast array of industries to produce high impact, high value products. One strategy for increasing the robustness of plasma surface modification processes lies in increasing our understanding of the fundamental chemistry of the gas phase chemistry in plasmas, the resulting film chemistry and perhaps most importantly, the gas-surface interface. This talk will focus on recent work in our laboratory that explores not only the impact of the plasma on the surface, but also the effect of the substrate on the plasma chemistry. Data on systems used for plasma assisted catalysis (PAC) and plasma modification of nanostructured sensor materials will be presented. As one example, we have combined a range of spectroscopy techniques, materials characterization tools, and plasma-surface interface studies to reveal that the presence of a catalytic substrate in the plasma system results in significant changes in the plasma chemistry, most notably affecting the internal temperatures (vibrational, rotational) of various plasma species. Changes in plasma composition as well as substrate surface chemistry and morphology were also observed. Connections between these results and other trends we observe at the plasma-surface interface will be discussed.

8:40am **PS-ThM3 Super-reactive Haloester Surface Initiator for ARGET ATRP Readily Prepared by RF Glow Discharge Plasma***, **Marvin Mecwan,*** *B.D. Ratner,* University of Washington

Introduction: Surface initiated activators regenerated by electron transfer atomic transfer radical polymerization or SI ARGET ATRP is a technique that has become a powerful tool for the preparation of functional surfaces and interfaces to match the desired needs of a specific biomedical application. Glow discharge plasma polymerization has historically been used to create uniform thin polymer films that are strongly bond to surfaces. In this research, we explore ARGET ATRP surface initiators that were prepared using a novel, robust and easy synthesis method using plasma polymerization of haloesters, specifically: methyl-3-bromopropionate (M3BP), methyl-2-chloropropionate (M2CP), and ethyl-2-fluoropropionate (E2FP). Once prepared, we used the plasma polymerized haloester surface as a surface initiator for SI ARGET ATRP synthesis of HEMA as proof of concept.

Methods: Cleaned glass discs were Ar etched (40W for 10 min), followed by a CH4 layer (80W for 5 min). The monomer of choice—M3BP, M2CP or E2FP—was introduced into the reactor and plasma deposition was carried out at 150mT pressure; 80W for 1 min (adhesion), 10W for 10 mins (deposition). Plasma-treated samples were washed in methanol and ESCA was used to assess coating composition before and after washing. To grow HEMA brushes on plasma polymerized haloester surfaces, a solution prepared from HEMA, methanol, CuBr2/TPMA, and L-ascorbic acid was pipetted onto the plasma polymerized substrates and allowed to polymerize for 5, 15, 30, 60 and 120mins. ESCA, TofSIMS and ellipsometry were used to analyze the surfaces after ARGET ATRP of HEMA. Clean glass discs were used as negative controls.

Results and Conclusions: RF glow discharge plasma is a robust technique that is able to create a surface coatings that is rich in halogen species and does not delaminates; hence it can be used as a surface initiator for ARGET ATRP. Of all plasma polymerized surface coatings, M3BP showed the highest halogen content and was able to grow HEMA polymer brushes on its surface via ARGET ATRP in as fast as 15 mins. Surprisingly, E2FP, a fluoroester, was also able to grow HEMA polymer brushes despite fluorine being a poor leaving group for ARGET ATRP. The versatility of RF glow discharge plasma offers a clear advantage over other techniques previously used to deposit ARGET ATRP surface initiators.

9:20am **PS-ThM5 Practical Applications of Plasmas in Microelectronics***, **David Ruzic,*** *D.E. Barlaz, J. Mettler, G. Panici, D. Qerimi,* University of Illinois at Urbana-Champaign **INVITED**

After presenting a brief overview of the uses of plasmas to make microelectronics, the talk will focus in on metal surface wave plasmas (MSWP). These plasmas have characteristics which make them ideal for many applications. They are microwave driven, and can be launched from a number of antenna or window-like structures. If the plasma density is above cut-off, the waves are completely absorbed in the plasma sheath, spreading out along the surfaces adjacent to the launcher. In this way, a plasma can be made which hugs surfaces. This is ideal for processing of that surface. For instance, when trying to etch Sn from an EUV mirror, making a H plasma right along the mirror surface creates the active radicals which do the etching directly where they are needed.

There is a second advantage of MSWP for processing. While the first couple of mm near the surface are immersed in a higher temperature (4 eV) and density (1e12 cm^{-3}) plasma, the region many cm above the surface contains a cold (1 eV) plasma which is still fairly dense (1e11 cm^{-3}). The two distinct plasma regions created by the same source can be quite useful. If one wants to "crack' the gas used for atomic-layer processing, pass it through the surface and the dense plasma. If the desire is to not break up the molecules, inject it down stream. The advantages of having a plasma in contact with the substrate are retained in both cases. This talk will show examples of using such plasmas for both etching and deposition.

10:20am **PS-ThM8 From Atomic- to macro- via Nano-scales: Plasma and Ion Effects in Surface *Structuring*, *Kostya (Ken) Ostrikov,*** Queensland University of Technology, Australia **INVITED**

This presentation critically examines the effects of ions and plasmas on the formation of thin films, microscopic and nanoscale structures on the surface. Nanoscale localization of energy and matter plays a critical role in the mechanisms of ion/plasma-surface interactions that lead to the surface structuring. Examples of localization of energy and matter and plasma-specific effects in nanoscales creates specific and unique conditions not common at larger scales. Importantly, the effects of interactions of ions and other species at atomic scales (e.g., atomic bond scission, vacancy or defect creation or elimination) are intimately related to self-organization and texturing of the surface features and nanostructures at nanoscale and microscopic scales. One typical example is the formation of self-organized arrays of nanostructures on plasma exposed surfaces. Specific driving forces that lead to the creation of the textures and structures owe to the unique features of the plasma environment, prominently related to charges, electric fields, as well as mobility and reactivity of plasma-generated species. Another example is the possibility to manipulate atomic bonds in nanoporous materials to control nanopore sizes and modify the plasticity of solid materials. In particular, anodized aluminium oxide (AAO) which is normally brittle under normal conditions, can become superplastic subjected to irradiation by energetic ion beams. Examples are provided where interactions at the plasma interface lead to interesting synergistic effects. These interactions lead to several applications in nanoscale synthesis, fabrication and processing, catalytic gas conversion and biomass reforming, new sustainable industrial processes based on green chemistry. Selected examples are related to plasma-catalysis, sustainable, green-chemistry based nanomaterials and chemical processing, as well as exotic high-energy-density physical effects during nano-plasma generation using intense radiation.

11:00am **PS-ThM10 Atmospheric Plasma Synthesis of Nanoparticulates at Low Temperature and Roll-to-Roll Binder-Free Coating on Polyethylene Separator for Lithium Ion Battery with Improved Performances***, **Jing Zhang,*** Donghua University, China

The roll-to-roll atmospheric pressure plasma synthesis and coating of nanoparticulates at low temperature is the most prominent green technique to fabricate thin film on polymer substrates. It can provide a unique environment for chemical reactions and film growth, which is distinct from the ordinary condensed chemical reaction driven by single hot source. All the reactions are far from chemical equilibrium and take place at low gas temperature. Its vital role have been more and more recongnized in flexible fiber optoelectronic/electronic devices, intelligent wearable technology, lightweight fiber compositese and organic/inorganic functional composite membrane etc..

In the present study, different kinds of non-thermal reactive plasmas of HMDSO/Ar/O2 and TiCl4/Ar/O2 have applied to obtain stable discharge at atmospheric pressure and low temperature. The gas phase dissociation and nucleation process, combination of discharge modes, plasma parameter

influences on the TiO2 and SiOxCyHz films have been investigated by optical emission spectrum(OES), field scanning electron microscope (FESEM), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) etc.. P olyethylene (PE) separator for lithium-ion batteries has been tested to move through a home-made roll to roll plasma reactor and a thin film composed of well limited nanoparticulates (average size is around 100 nm) is directly deposited on its top and internal fiber surface. The nanoparticulates are tightly bound on porous PE separator top and inner surface without any other organic binders. The coated PE separator exhibits improved thermal stability, wettability to electrolyte and electrolyte uptake. LiFePO4 cells assembled with the coated PE separator display better conductivity and cycling performance. To the best of our knowledge, this is the first report on atmospheric plasma roll to roll coating of nanoparticulate film on polyolefin separators for LIBs compatible with its present online manufacture process.

11:20am **PS-ThM11 Thermo-Corrosive and Mechanical Properties of ZrO_2 based Thermal Barrier Coatings***, **Byung-Koog Jang**,* Kyushu University*; H.-T. Kim,* Korea Institute of Ceramic Engineering and Technology

Thermal barrier coatings (TBCs) have received a large attention because they increase the thermal efficiency of gas turbine engines by increasing the gas turbine inlet temperature and reducing the amount of cooling air required for the hot section components. Electron beam-physical vapor deposition (EB-PVD) or plasma spray coatings is a widely used technique for depositing thermal barrier coatings (TBCs) on metal substrates for high temperature applications, such as gas turbines, in order to improve the thermal efficiency. High temperature capability of TBCs used in a gas turbine is often degraded by deposits of calcium-magnesium-alumino-silicate (CMAS). The CMAS melts are produced when siliceous minerals (volcanic ash, dust and sand) are ingested with the intake air and deposited on the hot surface of TBCs.

This work describes the thermal conductivity and corrosive properties of 2~8mol%Y_2O_3-stabilized ZrO_2 (YSZ) coatings by EB-PVD and plasma sprayed coatings. The hot corrosion between YSZ coatings and volcanic ash was examined by isothermal heating at 1200°C in air between 10 min and 100hrs. The thickness of corrosive region at top surface of TBCs by the reaction between YSZ coating and volcanic ash was increased with increasing the oxidation time. In addition, the mechanical properties of YSZ TBCs were evaluated by nano indentation.

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