Plasma Processing
Room Naupaka Salon 1-3 - Session PS-TuP

Plasma Processing Poster Session
Moderator: Martin Nieto-Perez, CICATA Queretaro

PS-TuP2 Study of Carbon Fiber Manufacturing Process by Plasma Oxidation/stabilization and Microwave assisted Carbonization*, **Seok-Kyun Song**, B.Y. Kim, M.K. Jung,* Cheorwon Plasma Research Institute, Republic of Korea*; S. Lee,* Korea Institute of Science and Technology, Republic of Korea

Carbon fiber has a carbon content of 90~95% or more, and its strength is ten times that of steel. The manufacturing process proceeds with stabilization (chlorination), carbonization of the PAN fiber. In particular, the stabilization process is long-term treatment at high temperature which high cost is incurred. In order to low cost manufacture for carbon fiber, that is need reduction of stabilization process time. For that, we researched the oxidation/stabilization process using atmospheric pressure plasma and e-beam technology.

The atmospheric pressure plasma system developed by CPRI team suggests possibility to reduce oxidation/stabilization process time (from 120 min to 30 min, from 120 min to 10 min by add e-beam technology) and cost. Plasma oxygen radical accelerates the progress of fiber cyclization. After plasma treatment, the surface of oxidized/stabilized fiber had no damage.

In the nitrogen atmosphere, oxidated/stabilized fiber was used for low temperature carbonization of 300 ~ 1000 degrees Celsius, and energy consumption was reduced by directly supplying energy to the heating element near the fiber by the microwave assisted (MWA) method instead of the conventional resistance heating.

It has been suggested that energy can also be reduced by providing microwave assisted (MWA) energy directly to low temperature carbonized fiber for 1000 ~ 1600 degree Celsius high temperature carbonization.

PS-TuP4 Nitridation of SiO_2 by using a VHF (162 MHz) Multi-tile Push-pull Plasma Source*, **You Jin Ji**, K.S. Kim, K.H. Kim, J.Y. Byun, S.J. Lee,* Sungkyunkwan University, Republic of Korea*; A.R. Ellingboe,* Dublin City University, Ireland*; G.Y. Yeom,* Sungkyunkwan University, Republic of Korea

Nitriding processes of SiO_2 thin film have been applied in various semiconductor device manufacturing. For example, in the fabrication of nanometer scale semiconductor devices, a nitriding process of SiO_2 for a nitride layer applied to gate insulator has become an important process to prevent the penetration of p-type dopant (boron) through the thin gate oxide. Typically, plasma and thermal nitridation methods are used to meet the requirement for the nitride layer. However, the thermal method has a bad influence on the device performance due to the high processing temperatures (600-1500 ^oC), and the plasma method tends to cause damage on the treated layer due to the ion bombardment and shows a low nitridation percentage in the film due to the difficulty in dissociating nitrogen molecules having a high electron-impact dissociation energy. Very high frequency (VHF; > 30 MHz) plasma is known to dissociate nitrogen molecules more effectively with a high dissociation rate at a low temperature due to a high electron energy tail in the electron energy distribution. Therefore, in this study, the nitridation of SiO_2 was performed to obtain a uniform silicon oxynitride (SiO_xN_y) layer using a VHF (162 MHz) multi-tile push-pull plasma source at room temperature. High nitrogen incorporation (~ 24.51 %) in the SiO_xN_y layer was confirmed by the X-ray photoelectron spectroscopy (XPS) analysis at the optimized nitridation condition. In addition, the EDS in TEM showed that a SiO_xN_y layer was uniformly formed after the nitridation of SiO_2 at the optimized condition. The leakage current of the MOS capacitor that has the SiO_xN_y layer formed by using the VHF (162 MHz) multi-tile push-pull plasma source was measured to be lower than that has the SiO_xN_y layer formed by the conventional CCP (60 MHz) plasma source.

PS-TuP5 ***Fabrication of SnO Thin Films by Reducing Plasma on Atomic Layer Deposited SnO_2*****, Jaehong PARK**, *B.E. PARK, H.J. Kim,* Yonsei University, Republic of Korea

Oxide semiconductors have been intensively investigated in emerging applications, such as thin film transistor (TFT), flexible electronics and solar cell materials, owing to the added functionality using great diversity of materials and structures. There have been numerous studies on n-type semiconductors such as ZnO, SnO_2, and In_2O_3, whereas the research on p-type semiconductors is still ongoing due to the lack of synthesis technology. SnO is a representative p-type oxide semiconductor with wide band-gap and high mobility, but the poor stability of SnO limits the synthesis method to physical vapor deposition (PVD). PVD is difficult to apply in future integrated circuit process with aggressive scaling down and 3D structurization. Atomic layer deposition (ALD) is a promising technique owing to atomic-scale thickness controllability and great conformality. In this study, we synthesized p-type SnO thin film using ALD and consequent plasma treatment for reduction. We investigated the crystal structure, morphology, and electrical properties of SnO by using x-ray diffraction (XRD) and atomic force microscope (AFM). In addition, we evaluated the thermal and chemical stability of SnO film. As a result, SnO film shows highly stable SnO phase even after annealing at 400 °C with oxidation/reduction environment. This study will contribute to apply oxide semiconductor in future application by implementing various device structure, such as p-n junction, complementary metal oxide semiconductor(CMOS), and p-channel TFT.

PS-TuP6 Plasma-Surface Interactions in Atmospheric Pressure Plasmas: In situ Measurements of Electron Heating in Materials*, S. Walton,* Naval Research Laboratory*; B. Foley,* Pennsylvania State University*; J. Tomko,* University of Virginia*; D.R. Boris, E.D. Gillman, S.C. Hernandez,* Naval Research Laboratory*; A. Giri,* University of Virginia*; T.B. Petrova,* Naval Research Laboratory*; **Patrick Hopkins**,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physico-chemical changes that occur during plasma-based materials synthesis and processing. Indeed, the energy delivered to the surface, via a flux of particles and photons, in concert with a flux of reactive species serves to chemically modify, etch, and/or deposit materials, with an efficacy that depends on the plasma processing environment. A unique feature of plasma synthesis and processing is that most of the delivered energy is absorbed at or very near the surface over short (picosecond) time scales. The dissipation of thermal energy proceeds through electron-electron and/or electron-phonon interactions as they propagate through the material, with relaxation time scales that can be orders of magnitude slower. Typically then, the surface is not in thermal equilibrium with the bulk material. Fast, surface-sensitive techniques are thus required to fully appreciate the dynamics of the plasma-surface interaction. In this work, we employ pump-probe Time-Domain Thermoreflectance, a surface sensitive technique typically used to measure thermal properties of thin films, to determine electron heating of thin metal films during exposure to an atmospheric pressure plasma jet. The results, in conjunction with current measurements, are used to develop a first order understanding of plasma jet-surface interactions. The results show that the energy delivered by the plasma jet causes a localized increase in electron energy within the thin film over an area commensurate with the plasma jet radius. More details of this work an be found in the following recently published paper: Walton, S.G., Foley, B.M., Tomko, J., Boris, D.R., Gillman, E.D., Hernandez, S.C., Giri, A., Petrova, Tz.B., Hopkins, P.E., "Plasma-surface interactions in atmospheric pressure plasmas: In situ measurements of electron heating in materials," *Journal of Applied Physics* **124**, 043301 (2018).

PS-TuP9 Origin of Plasma Damage during Sputtering of Ultrathin ITO Contact Layer on p-GaN for InGaN/GaN LEDs*, T.K. Kim, Y.-J. Cha, **Joon Seop Kwak**,* Sunchon National University, Republic of Korea

We systematically examined the origin of plasma-induced damage on *p*-GaN surface during the sputtering of ITO transparent conductive electrodes (TCE) and its effects on the forward voltage and the light output power (LOP) of InGaN/GaN LEDs. Firstly, we investigated the effect of direct current (DC) power in radio frequency (rf) superimposed DC sputtering (RF+DC sputtering) of ITO on the forward voltage and and LOP of InGaN/GaN LEDs and found that the plasma-induced damage was sensitive to the DC power. The forward voltages of the LEDs at 20 mA drastically decreased from over 5 V to 3 V and the LOP of the LEDs was greatly enhanced by more than 20% at 250 mA, when the DC power was changed from negative to positive values. Secondly, electron flux as well as ion flux during the RF+DC sputtering of ITO with the various DC power were calculated based upon the plasma discharge parameters measured by cutoff probe and Langmuir probe. Changing the DC to positive power drastically reduced the electron flux in plasma, suggesting that plasma electrons play an important role in plasma-induced damage of *p*-GaN surface. Furthermore, the significant increase in forward voltage of the LEDs was observed, when electron-beam irradiation on *p*-GaN surface was employed. This confirms that the plasma electrons, not ions, can cause the plasma-induced damage on *p*-GaN during the sputtering of ITO. Lastly, physical mechanism for the generation of plasma-induced damage on *p*-GaN by the plasma electrons was suggested. The plasma electrons can compensate the deep level defects (DLDs) in the *p*-GaN surface and reduce the density of DLDs, which increase the effective barrier height at the ITO/DLD band of *p*-GaN. Furthermore, the plasma electrons yielded the energetic ad-atoms of ITO on *p*-GaN during sputtering by energy transfer of the electrons to the ad-atoms and increased the plasma-induced damage on *p*-GaN. We successfully demonstrated the plasma-induced-damage-free ITO TCE on the InGaN/GaN LEDs by sputtering, which showed 20 % improved LOP of the LEDs with comparable forward voltage of 2.9 V at 20 mA to the LEDs with conventional e-beam-evaporated ITO.

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.

Author Index

Bold page numbers indicate presenter