Plasma Science and Technology
Room 124 - Session PS+TF-FrM

Plasma Processes for Coatings and Thin Films

Moderators: François Reniers, Université Libre de Bruxelles, **Scott Walton**, Naval Research Laboratory

8:15am **PS+TF-FrM-1 Interaction of Polycrystalline Aluminum Oxide and Sapphire Surfaces with Halogen-Containing Plasmas and Gases*, Takuya Ishihara*, *H. Tochigi,* Azbil corporation, Japan*; H. Kang,* Osaka University, Japan, Republic of Korea*; T. Ito, K. Karahashi, S. Hamaguchi,* Osaka University, Japan

In semiconductor manufacturing processes such as dry etching or chemical vapor deposition, capacitance manometers are widely used as essential vacuum pressure sensors to monitor and control the pressures of process gases. These gauges must be corrosion-resistant against process gases such as halides and their radicals generated by the plasmas. The diaphragm material of the manometer is especially important because, if its surface is altered by such corrosive gases, the sensor would send imprecise output signals possibly with the zero-point drift or pressure sensitivity shift. The errors are caused by the changes in mechanical properties of the diaphragm arising from the formation of the modified surface layer. For this reason, Ni-based alloys or polycrystalline ceramics of aluminum oxide (Al_2O_3) are typically used as the diaphragm material of capacitance manometers. More recent capacitance manometers employ sapphire (single crystal α-Al_2O_3) as their diaphragm material, which is of specific interest in this study[1]. Recent studies on the interactions of polycrystalline Al_2O_3 with fluorine-containing plasmas indicated the formation of aluminum fluoride layers on Al_2O_3 exposed to such plasmas [2-6]. In this study, ion beam experiments were performed, aiming to understand the surface modification mechanisms of Ni-based alloys and polycrystalline Al_2O_3 film by fluorine-containing plasmas. With the irradiation of energetic F^+ and Cl^+ ions, it was found that the typical etching rates of Al_2O_3 are about one-half of those of Ni-based alloys. It was also found that the fluorinated layers of Al_2O_3 were thinner than those of Ni-based alloys. In addition, surfaces of sapphire samples were exposed to xenon difluoride (XeF_2) gases for 3 and 6 months. The sapphire surface was fluorinated over the first 3 months, but the depth of the fluorinated layer did not increase much after 6 months. It indicates that a diaphragm made of pre-fluorinated sapphire may be able to prevent the signal shift of the manometer used under highly corrosive conditions in semiconductor manufacturing.

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[2] Chen Chien-Wei, *et al*, J. Vac. Sci. Technol. A Vol.41 No.1 Page.012602-012602-9 (2023)

[3] Kim Yewon, *et al*, Appl. Surf. Sci. Vol.641 Page. Null (2023)

[4] Vos Martijn F. J., *et al*, J. Phys. Chem. C Vol.125 No.7 Page.3913-3923 (2021)

[5] Chittock Nicholas J., *et al*, Appl. Phys. Lett. Vol.117 No.16 Page.162107-162107-5 (2020)

[6] Fischer Andreas, et al, J. Vac. Sci. Technol. A. Vol.38 No.2 Page.022603-022603-7 (2020)

8:30am **PS+TF-FrM-2 Development of Corrosion-Resistant, Low-ICR aC and TiN Coatings Using HIPIMS for Bipolar Plate Manufacturing for Hydrogen Fuel Cells*, Nicholas Connolly,*** University of Illinois at Urbana-Champaign*; Z. Jeckell,* University of Illinois Urbana-Champaign*; R. Paul, M. Hysick,* Starfire Industries*; M. Hossain, B. Jurczyk, D. Ruzic,* University of Illinois Urbana-Champaign

Bipolar plates (BPPs) are a critical component in proton exchange membrane fuel cells (PEMFCs) that provide conducting paths for electrons between cells, distribute and provide a barrier for reactant gases, remove waste heat, and provide stack structural integrity. Stainless steel, specifically 316L, BPPs possess high electrical and thermal conductivity, good gas impermeability, and superior mechanical properties and formability. However, stainless steel has relatively low corrosion resistance and high contact resistance in the hydrogen fuel cell stack. Additionally, to meet the Department of Energy (DOE) cost/kW target for hydrogen fuel cells, recycling of the BPPs is practically a necessity.

In order to address these challenges, we will present work on two complementary studies. The first study is deposition of conformal amorphous carbon (aC) and titanium nitride (TiN) thin films using HIPIMPS with positive cathode reversal. The interfacial contact resistance (ICR), corrosion current, and corrosion potential are reported for various aC and TiN thin films to characterize the contact resistance and corrosion resistance. The second study is etching of the previously deposited aC and TiN films in a HIPIMS system with a high-voltage cathode reversal, testing the possibility of recycling the BPP. The contact resistance and corrosion resistance are compared after the initial film deposition and then after etching of the initial film and redeposition on the same substrate.

8:45am **PS+TF-FrM-3 Evolution of Graphene Nanoflake Size and Morphology in Atmospheric Pressure Microwave Plasma*, Parker Hays*,** *D. Patel, D. Qerimi,* University of Illinois at Urbana-Champaign*; M. Stowell,* LytEn*; D. Ruzic,* University of Illinois at Urbana-Champaign

Graphene was synthesized using an atmospheric pressure microwave plasma system, employing argon/nitrogen mixtures as carrier gases and methane as the carbon precursor. This study investigates the effects of varying methane flow rates and plasma power on graphene growth, including the role of gas temperature. The process involves the decomposition and subsequent reorganization of carbon radicals into graphene sheets. To collect the synthesized graphene, tungsten carbide rods were strategically positioned at three distinct points along the plasma column.

The variations in particle diameter were systematically analyzed using Dispersive Light Scattering (DLS) and Scanning Electron Microscopy (SEM). Results indicate that particle diameter generally decreases along the plasma column until reaching a critical power threshold. Beyond this threshold, the diameter increases, particularly at the middle collection port, suggesting the presence of an optimal "Goldilocks zone" for graphene growth. This zone, located at the juncture between the bulk plasma and its afterglow, exhibits a significant temperature gradient, potentially ideal for graphene formation.

Further, an increase in methane flow rate correspondingly reduced the particle diameter across all ports, attributed to enhanced plasma quenching effects. Conversely, an escalation in plasma power led to an increase in particle diameter, likely due to the extension of the plasma field.

These findings demonstrate that manipulating methane flow rates and plasma power can significantly influence graphene particle size, optimizing growth conditions within the identified Goldilocks zone. This study provides a deeper understanding of the thermodynamic and chemical mechanisms governing graphene synthesis in microwave plasma systems, offering a pathway to tailored graphene production for advanced material applications.

9:00am **PS+TF-FrM-4 Gentle Processing of Graphene and Diamond in a Low Temperature Magnetized Plasma*, Yevgeny Raitses,*** Princeton Plasma Physics Laboratory*; F. Zhao,* Fermi Lab*; C. Pederson, K. Fu,* University of Washington*; A. Dogariu,* Princeton University

In this work, we present results of the use of a low temperature plasma in applied magnetic field for graphene hydrogenation and hydrogen passivation of diamond. The chemical functionalization of two-dimensional materials is an effective method for tailoring their electronical and chemical properties with encouraging applications in energy, catalysis and electronics. Experiments on graphene hydrogenation [1] revealed that with the applied magnetic field of 10-50 Gauss, a plasma generated by a DC-RF source of non-thermal electrons at a hydrogen pressure of about 10 mtorr is capable to achieve a high (~ 36%) hydrogen coverage without damage on monolayer graphene. Plasma measurements utilizing electrostatic probes for measurements of plasma properties, optical emission spectroscopy for characterization of plasma chemical composition and two-photon absorption laser-induced fluorescence (TALIF) for measurements of absolute hydrogen density revealed that with the applied magnetic field, the plasma density and the density of hydrogen atoms are much larger than without the magnetic field. The latter explains a high converge observed in the treated 2D material [1]. In more recent experiments, the same plasma source was applied for hydrogen passivation of diamond for quantum defect charge state control [2]. Measurements indicate that in this novel plasma treatment hydrogen terminates the surface with no observable damage to diamond.

References

[1] F. Zhao, Y. Raitses, X. Yang, A.Tan, and C. G. Tully, "High hydrogen coverage on graphene via low temperature plasma" **177**, 244 (2021)

[2] C. Pederson, et al., "Optical tuning of the diamond Fermi level measured by correlated scanning probe microscopy and quantum defect spectroscopy" Phys. Rev. Mater. **8**, 036201 (2024)

9:15am **PS+TF-FrM-5 A Plasma-Based Anodization Process for the Production of AlF_3 Layers***, **Scott Walton**, J. Murphy,* US Naval Research Laboratory*; L. Rodriguez de Marcos, J. Del Hoyo, M. Quijada,* NASA*; V. Wheeler, M. Sales, M. Meyer, D. Boris,* US Naval Research Laboratory

Efficient ultraviolet (UV) mirrors are essential components in space observatories for UV astronomy. Aluminum mirrors with fluoride-based protective layers are commonly the baseline UV coating technology; these mirrors have been proven to be stable, reliable, and with a long flight heritage. However, despite their acceptable optical performance, it is still insufficient for future large telescopes in which several reflections are required. Recently, a readily scalable, plasma-based passivation process was developed to produce a thin AlF3 layer on the surface of aluminum. The passivation process uses an electron beam generated plasma produced in a fluorine-containing background (SF6 or NF3), to simultaneously remove the native oxide layer while promoting the formation of an AlF3 layer with a tunable thickness. Interestingly, this process has the characteristics of classic aluminum anodization – either electrochemical or plasma – where oxygen is replaced by fluorine. The process takes advantage of the ability for electron beam driven plasmas produced in electronegative gas backgrounds to generate substantial densities of negative ions, which are utilized to grow the fluoride layer. In this presentation, we will discuss the process using operating parameter studies, plasma diagnostics, and materials characterization, with an eye on understanding the growth mechanisms and the potential for better process control. This work partially supported by the Naval Research Laboratory base program.

9:30am **PS+TF-FrM-6 One-Step Synthesis of Spatially Differentiated Crystalline Vanadium Oxide Coatings Using Atmospheric Pressure Dielectric Barrier Discharge***, **Marie Brabant**, A. Demaude, D. Petitjean, F. Reniers,* Université libre de Bruxelles, Belgium

Initially perceived as a limitation, the presence of inconsistencies in DBDs presented obstacles to achieving uniform plasma treatments and coatings. However, recent breakthroughs in immobilizing filaments within DBDs have demonstrated effective control over these irregularities.[1,2] This development has now enabled the deposition of innovative patterned inorganic coatings that were previously unexplored. Vanadium oxide coatings, in particular, hold promise for diverse applications, including catalysis,[3] memory compounds,[4] or as practical solutions for smart windows.[5]

This study introduces a pioneering method for locally depositing dense crystalline inorganic coatings (V_2O_5) without requiring annealing and utilizing atmospheric pressure DBDs, marking a significant advancement in the field. Vanadium oxide coatings with spatial variation were successfully deposited in a single step using an atmospheric pressure dielectric barrier discharge featuring immobilized filaments. Initial findings indicate fast deposition rates beneath the filament regions and low deposition rates between them. Moreover, differences in the oxidation states of vanadium beneath the filaments and between them were also observed, suggesting different reactivities.[6]

Through the incorporation of a patented inductive heating device into the reactor,[7,8] coupled with a pulsed signal, crystalline coatings were obtained by heating the substrate at 473 K, occasionally resulting in crystal needles measuring up to 50 µm in length. This crystallinity was confirmed by XRD analysis.

While further optimization is necessary to refine gas and reactive species distribution, this feasibility study demonstrates the potential for locally depositing crystalline coatings using a DBD with immobilized filaments and an appropriate substrate heating system, paving the way for new applications.

Acknowledgements

This work is funded by the FNRS (Belgian fund for research) under the Instream and Streamcoat projects.

References :

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6. M. Brabant, et al. JVST A, 42, 023008 (2024).
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8. A. Remy, F. Reniers. patent EP3768048A1 (2019).

9:45am **PS+TF-FrM-7 Biofilm Decontamination in an Endoscope-Like Setup Using a Cold Atmospheric Plasma***, **Juliette Zveny**,* Université libre de Bruxelles, Belgium*; F. Reniers, A. Remy,* Université Libre de Bruxelles, Belgium*; T. Serra,* université libre de Bruxelles, Belgium*; A. Bourgeois,* Erasme Hospital, Belgium*; A. Nonclercq, D. Lakhloufi, A. Botteaux,* université libre de Bruxelles, Belgium*; A. Delchambre,* Université Libre de Bruxelles, Belgium*; J. Deviere,* Erasme Hospital, Belgium

Endoscopes are essential medical devices used to detect, prevent and cure many diseases. Well-established cleaning and decontamination procedures allow them to be used safely on multiple patients every day. However, cases of cross-contamination still occur, demonstrating that the decontamination process is flawed.[1] Here, we propose a novel decontamination method using an Ar/H_2O Cold Atmospheric Plasma (CAP).

In this research, we investigate the effect of CAP not only on bacteria, but also on biofilm.Biofilm is a matrix made by bacteria to increase their resistance to external stress.[2] Pseudomonas aeruginosa biofilms were grown during 24 hours in a PTFE tube mimicking the operating channel of an endoscope before being subjected to plasma treatment. The plasma was generated in a DBD setup with the high voltage applied between a metal wire passing through the contaminated tube and a metal mesh surrounding the tube.

The decontamination process consisted of a 30 min plasma in a water-saturated argon atmosphere. The chemical activity of the discharge was optimized by the presence of water, which allowed the production of hydroxyl radicals (OH) and hydrogen peroxide (H_2O_2), powerful oxidant species. Other parameters, such as the voltage, made it possible to increase the concentration of these species without increasing the power.

Plasma treatments showed effective decontamination capacities, with no bacteria found in the tube after regrowth for various treatment times (5 to 30min). It also shows promising results in terms of biofilm destruction, with up to 79% of the original biofilm destroyed. The biofilm destruction is dependent on the position inside the tube as well as on its own humidity. OES measurements also highlight the voltage dependency on OH radical formation and biofilm destruction.

Acknowledgements:

This work is funded by the ARC project COSMIC (ULB) and by the Cremer Foundation.

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[2] U. Beilenhoff &al, Endoscopy. 49 (2017). https://doi.org/10.1055/s-0043-120523.

10:00am **PS+TF-FrM-8 Nonthermal Plasma Jet Integrated Aerosol-Based 3D Printing with Machine Learning Optimization***, **Jinyu Yang**, Y. Du, K. Song, Q. Jiang, Y. Zhang, D. Go,* University of Notre Dame

Aerosol-based printing has emerged as a versatile technique to fabricate functional devices with complex structures, offering high throughput and microscale resolution, along with capabilities unattainable with traditional approaches. Despite these promises, the printing of conductive films often requires post-printing sintering to remove surfactants from the nanoparticle-containing inks and promote the sintering and densification to form a continuous film with desired electrical conductivity, which conventionally demands thermal processing at elevated temperatures. Herein, we report a novel aerosol jet printing method that integrates a nonthermal, atmospheric pressure plasma jet to enable *in-situ* sintering during aerosol deposition. The impacts of various processing parameters on printing quality and *in-situ* sintering efficiency are investigated. A machine learning algorithm is incorporated to provide online, real-time defect detection and parameter control, enhancing the yield of high-quality films via automatic *in-situ* compensation whenever a region-specific anomaly is detected. Our method achieves low temperature sintering of silver nanoparticles with electrical conductivities comparable with those sintered through other plasma treatment approaches. Because the films require no post processing, the overall manufacturing time can be reduced by more than tenfold. This method holds significant potential for technological advances in printed electronics, wearable devices, and biomanufacturing.

10:30am **PS+TF-FrM-10 Fluorine Plasma Assisted Remediation of Single Crystal Diamond Surfaces**, ***Michael Mathews,*** National Research Council Postdoctoral Fellow at U.S. Naval Research Laboratory; *J. Levine-Miles, B. Pate,* US Naval Research Laboratory

The extreme material properties of diamond present unique opportunities for the development of novel high-power electronic devices. Achieving these advances are, however, not without challenges. In particular, the generation of unwanted defects in diamond homoepitaxial films is known to depend on the surface preparation of the diamond seed. Most notably, the nucleation of threading dislocations from sub-surface defects of mechanically prepared diamond surfaces prevent the realization of high-quality chemical vapor deposited diamond epi-layers. Once formed, these threading dislocations propagate into the newly formed homoepitaxial layer, degrading physical properties and impacting device performance.

This work introduces a four-step process to mitigate surface preparation challenges in single crystal diamond. In the first step, an isotropic fluorine-based reactive ion etch is used to remove damaged material below the diamond surface. This yields a surface with both adsorbed and chemisorbed fluorine corresponding to one- to several monolayers of fluorine coverage with some graphitic carbon arising from ion bombardment. The second step exposes the fluorinated surface to a rapid thermal anneal designed to remove non-sp^3 carbon species. Step three is a radical-dominant etch that addresses damage from ion bombardment intrinsic to typical reactive ion etch methods, and provides further surface smoothing. This etch exploits the aggressive surface chemistry of fluorine radicals and yields a surface that has some adsorbed and significantly less chemisorbed fluorine, with no increase in sp^2 (graphitic) carbon. This surface is then exposed to the same rapid thermal anneal (Step 4) described in the second step, yielding a smoother, higher quality diamond surface. Chemical and morphological changes of the surface in each step are characterized using x-ray photoelectron spectroscopy and atomic force microscopy.

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10:45am **PS+TF-FrM-11 Noncapillary Liquid Surface Waves Generated by Self-organized Plasma Patterns**, *O. Dubrovski,* University of Notre Dame, Israel; *J. Yang,* University of Notre Dame, China; *F. Veloso,* Pontificia Universidad Católica de Chile, Instituto de Física, Chile; *H. Chang, D. Go,* ***Paul Rumbach,*** University of Notre Dame

Direct current (DC) plasmas are known to self-organize into a patterned state on a resistive anode surface. This phenomenon is commonly observed in plasma-liquid interactions, where plasma will self-organize into concentric rings or spots on the liquid surface, which then move and oscillate at frequencies of ~100 – 1000 Hz [1]. We propose that a Turing-like autocatalytic reaction-diffusion mechanism drives pattern formation in the plasma, and the size (wavelength) of the pattern structures is dictated by the reaction-diffusion wavelength of plasma electrons [2]. Electro-hydrodynamic (EHD) coupling at the interface creates liquid surface waves of the same wavelength as the pattern, resulting in dynamic motion (rotation and oscillation) of the plasma pattern. Increasing the viscosity of the solution causes the pattern motion to slow down, as predicted by viscous wave theory. Interestingly, the observed characteristic frequency of the plasma-liquid waves is much slower than predicted by capillary wave theory, indicating that EHD effects dominate, and surface tension effects are negligible [3].

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[2] P. Rumbach *et al.*, PSST 28 (2019).

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11:00am **PS+TF-FrM-12 Dielectric Barrier Discharge Configurations for Effective Biofilm Decontamination in PTFE Tubes**, ***Antoine Remy***, *J. Zveny, T. Serra, D. Lakhloufi, J. Devière, A. Botteaux, A. Delchambre, F. Reniers, N. Antoine,* Université libre de Bruxelles, Belgium

Biofilms are extracellular protective barriers produced by bacteria, enabling their growth and proliferation in otherwise inhospitable environments. Endoscopes are particularly susceptible to bacterial contamination and biofilm development. As a result, a single endoscope that has been thoroughly decontaminated can potentially transmit disease between multiple patients. The current solution in development, single-use endoscopes, while solving the contamination problem, may lead to an expansion of the environmental and technological dependence that is already a significant concern. This study investigates the potential of cold atmospheric discharge for endoscope sterilization. The study focused on two configurations of atmospheric pressure dielectric barrier discharge (DBD), generating a plasma in a long polytetrafluoroethylene (PTFE) tube. In order to generate reactive nitrogen and oxygen species (RONS), the discharge was generated in air, helium, water-saturated argon, and water-saturated helium. The first configuration uses two discharges, one upstream from the tube and another inside it, while the second configuration generates a single discharge directly within the tube. Prior to the decontamination tests, tube samples were contaminated by 24-hour grown *Pseudomonas aeruginosa* biofilm. We employed titration with $TiOSO_4$ to quantify the production of H_2O_2, while infrared absorption spectrometry was used to analyze the presence of gaseous species, including NO, N_2O, NO_2, HNO_3, and O_3. The efficacy of the bacterial decontamination and biofilm removal was evaluated through regrowth assays of the bacteria and crystal violet assays, respectively. Among the various gases used, helium/water and argon/water were identified as the most active, demonstrating complete bacterial decontamination of the tube after a 5-minute treatment. However, the biofilm remained largely unaffected. Future research will focus on optimizing the discharge composition and duration for biofilm removal, with the aim of developing a single-step endoscope decontamination process.

11:15am **PS+TF-FrM-13 Plasma Nanocoatings for Surface Passivation of Silver Nanowires**, ***Qingsong Yu***, *Y. Liao, G. Zhao, Y. Ling, Z. Yan,* University of Missouri-Columbia

Low-temperature plasma processing is a unique technique in thin film deposition and surface modification of various materials. Plasma deposition can produce nano-scale coatings that are highly conformal to substrate surface topography, free of voids, and have robust adhesion to various substrates, including metallic substrates. Silver Nanowires (AgNWs) have found applications in strain sensors, transparent flexible conductors, light emitting diodes, e-paper, self-healing electronic devices, liquids crystal displays, artificial skins, and solar cells [1]. The unique properties of AgNWs make them promising candidates for various technological advancements, offering advantages over traditional materials in terms of flexibility, cost-effectiveness, and optical transparency.

In this study, trimethylsilane (TMS) plasma nanocoatings with controllable thickness of 10 – 100 nm were applied onto AgNWs to examine their passivation effects and electrical conductivity stability. Our experimental results showed that application of TMS plasma nanocoatings onto AgNWs induced < 25% increase in their electrical resistance, but effectively protected them from degradation due to surface oxidation/corrosion and, as a result, significantly improved their electrical stability under various environments with different humidity levels and temperatures. It was also observed that TMS plasma nanocoating changed AgNWs surfaces from hydrophilic to hydrophobic but did not affect much in their optical transparency, which is critical for use as transparent electrodes. Detailed experimental results will be presented and discussed in the conference.

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