iPlasmaNano-IX August 26-29, 2018 Marina Grand Resort New Buffalo, Michigan, USA

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David Ruzic (druzic@illinois.edu)	Jozef Stefan Institute
University of Illinois Urbana-Champaign	Chairman, iPlasmaNano steering committee

Sunday, August 26th, 2018

2:00-5:00 pm	Registration
5:00-5:20 pm	Conference Opens and Welcome
5:20-7:20 pm	Session S1: Plasmas and liquids for environmental, biomedical, and agricultural applications
7:20 pm	Opening Reception
Monday, August 27 th , 201	8

7.20 0.40 am	Dra alterat
7:30-8:40 am	Breaklast
8:40-10:20 am	Session M1: Plasma synthesis of nanoparticles in the gas phase
10:20-10:50 am	Coffee break
10:50-11:50 am	Session M2: Plasma synthesis of nanoparticles/nanomaterials in the liquid phase
11:50 am-1:30 pm	Lunch
1:30-3:30 pm	Session M3: Plasma physics
3:30-4:00 pm	Coffee break
4:00-5:40 pm	Session M4: Thin film deposition and modification
6:30 pm	Dinner
	Special Talk: Kostya "Ken" Ostrikov, "Plasma nanoscience: two decades of research – centuries of joy"

Tuesday, August 28th, 2018

7:30-9:00 am	Breakfast
9:00-10:40 am	Session T1: Plasma sources
10:40-11:10 am	Coffee break
11:10 am-12:10 pm	Session T2: Energy applications
12:10-1:50 pm	Lunch
1:50-3:30 pm	Session T3: Plasma-based manufacturing
3:30-4:00 pm	Coffee break
4:00-5:40 pm	Session T4: Plasma catalysis
6:30 pm	Depart for excursion and dinner

Wednesday, August 29th, 2018

7:30-9:00 am	Breakfast
9:00-10:40 am	Session W1: Plasma diagnostics and modeling
10:40-11:10 am	Coffee break
11:10 am-12:10 pm	Session W2: Multicomponent, multidimensional, multifunctional materials
12:10-12:30 pm	Concluding remarks and departure

Sunday August 26th

5:00-5:20 pm Welcome by David Go and David Ruzic

- 5:20-7:20 pm Session S1: Plasmas and liquids for environmental, biomedical, and agricultural applications (Chair: David Go, University of Notre Dame)
- 5:20-5:40 pm John Foster, University of Michigan, "Plasma self organization in atmospheric pressure dc glows and its role in the modification of metal and liquid anode properties"
- 5:40-6:00 pm Paul Rumbach, University of Notre Dame, "Understanding the chemistry of the plasmaliquid interface through experiment and theory"
- 6:00-6:20 pm Selma Thagard, Clarkson University, "A plasma-based process for treatment of perfluoroalkyl substances (PFASs) in ion exchange brine regenerant solution: reactor design challenges and physiochemical processes at the plasma-liquid interface"
- 6:20-6:40 pm Jacob Shelley, Rensselaer Polytechnic Institute, "Atmospheric-pressure glow discharges as tools for the detection and identification of elemental, molecular, and biopolymeric species"
- 6:40-7:00 pm Michael Keidar, George Washington University, "Adaptive plasma for cancer therapy: physics, mechanism, and applications"
- 7:00-7:20 pm Michael Kong, Old Dominion University "Broad-spectrum inhibition of cancer metabolism with cold atmospheric plasma"

Monday August 27th

8:40-10:20 am Session M1: Plasma synthesis of nanoparticles in the gas phase (Chair: Abbas Semnani, Purdue University)

- 8:40-9:00 am Lorenzo Mangolini, University of California, Riverside, "Low temperature plasmas for nanoparticle synthesis: fundamentals and applications"
- 9:00-9:20 am Jan Benedikt, University of Kiel, "Atmospheric plasmas for generation of nanostructured materials or nanoparticles"
- 9:20-9:40 am Rebecca Anthony, Michigan State University, "Plasma-based synthesis and surface modification for photoluminescent nanocrystals"
- 9:40-10:00 am Yevgeny Raitses, Princeton Plasma Physics Laboratory, "Arc-based synthesis of carbon nanoparticles and nanostructures
- 10:00-10:20 am Souvik Ghosh, University of Minnesota, "Fundamental studies of agglomeration of nanoparticles generated in a dc microplasma"

10:20-10:50 am Coffee break

10:50-11:50 am Session M2: Plasma synthesis of nanoparticles/nanomaterials in the liquid phase (Chair: Ken Hara, Texas A&M University)

10:50-11:10 am Angela Capece, The College of New Jersey, "Synthesis of silver nanoparticles in ionic liquids by electron irradiation"

11:10-11:30 am	ı	Thierry Belmonte, Institut Jean Lamour, "Synthesis of alloy nanoparticles by discharges in liquids: a short review"
11:30 am-11:50) pm	Daniel Jaramillo, University of Louisville, "Low pressure plasma Interactions with molten metals for materials processing"
11:50-1:30 pm	Lunch 8	Poster Session
1:30-3:30 pm	Sessior (Chair: (n M3: Plasma physics Carles Corbella, Ruhr University, Bochum)
1:30-1:50 pm		Venkatt Ayyaswamy, University of California, Merced, "A general-purpose computational framework for plasma physics and chemistry"
1:50-2:10 pm		Yangyan Fu, Michigan State University, "Gas breakdown in microgaps with electrode surface protrusions: Paschen's curve, non-uniformity of electric field, and breakdown mode transitions"
2:10-2:30 pm		Allen Garner, Purdue University, "Gas breakdown at microscale and smaller gaps: Theoretical unification of mechanisms and experimental assessment of surface roughness"
2:30-2:50 pm		Matthew Goeckner, North Carolina State University, "The physics of pulsed and level-to- level discharges used for material processing"
2:50-3:10 pm		Sergey Baryshev, Michigan State University, "Field emission to glow discharge transition in nanodiamond vacuum diode"
3:10-3:30 pm		Sung-Jin Park, University of Illinois, "Microplasma Technology in Nanoscale Processes and Environmental Science: Future for the Social Impact,"
3:30-4:00 pm		Coffee break
4:00-5:40 pm	Sessior (Chair: F	n M4: Thin film deposition and modification Rebecca Anthony, Michigan State University)
4:00-4:20 pm		Erwin Kessels, Eindhoven University, "Ion-surface interaction during plasma-enhanced atomic layer and how it can be used to tailor film properties"
4:20-4:40 pm		Carles Corbella, Ruhr University, "Plasmas and the nanoscale: from surface nanotexturing and plasma-surface interactions towards the synthesis of nanomaterials"
4:40-5:00 pm		J. P. Allain, University of Illinois, "Controlling soft matter nanotopography with directed plasma nanosynthesis resulting in bioinspired antibacterial properties"
5:00-5:20 pm		Holger Vach, Centre National de la Recherche Scientifique, "From aromatic silicon nanoclusters to 2D silicene layers"
5:20-5:40 pm		Eitan Barlaz, University of Illinois, "Micro- and nanotexturing of metal surfaces by femtosecond laser exposure for controllable wettability"

Tuesday August 28th

9:00-10:40 am	Session T1: Plasma sources (Chair: Angela Capece, The College of New Jersey)
9:00-9:20 am	Steve Shannon, University of Texas at Dallas, "Advances in source design to extend process to the atomic scale"
9:20-9:40 am	Abbas Semnani, Purdue University, Microwave microplasma: From destructive power- limiting effects to promising high-power tuning applications
9:40-10:00 am	Gary Eden, University of Illinois, "Microcavity plasmas and their macro-impact"
10:00-10:20 am	Jeffrey Hopwood, Tufts University, "Plasma-reconfigurable metamaterials and photonic crystals"
10:20-10:40 am	Sergey Macharet, Purdue University, "Nanoscale spatial and temporal manipulation of plasmas for RF electronics"
10:40-11:10 am	Coffee Break
11:10-12:10 pm	Session T2: Energy applications (Chair: Sergey Baryshev, Michigan State University)
11:10-11:30 am	Uwe Kortshagen, University of Minnesota, "Nonthermal plasma synthesis of semiconductor nanocrystals for energy applications and electronic materials"
11:30-11:50 am	Zheng Bo, Zhejiang University, "Plasma-enabled growth of vertical graphenes for energy storage"
11:50-12:10 pm	Michael Gordon, University of California, Santa Barbara, "Microplasma spray deposition of micro-supercapacitors for on-chip energy storage"
12:10-1:50 pm	Lunch
1:50-3:30 pm	Session T3: Plasma-based manufacturing (Chair: Elijah Thimsen, University of Washington-St. Louis)
1:50-2:10 pm	Luis Velasquez-Garcia, Massachusetts Institute of Technology, "Plasma microsystems for sensing and additive manufacturing"
2:10-2:30 pm	Christian Zorman, Case Western Reserve University, "A novel, low temperature inkjet printing technology based on non-thermal plasma conversion of metal-salt based inks"
2:30-2:50 pm	Sang Han, University of New Mexico, "From materials engineering to device applications: Testing our understanding of nature"
2:50-3:10 pm	Timothy Fisher, University of California, Los Angeles, "Roll-to-roll plasma chemical vapor deposition for scalable graphene production"
3:10-3:30 pm	Remi Dussart, University of Orleans, "Cryogenic etching for advanced processing"
3:30-4:00 pm	Coffee Break
4:00-5:40 pm	Session T4: Plasma catalysis (Chair: Souvik Ghosh, University of Minnesota)

4:00-4:20 pm	Chris Hadacre, University of Manchester, "In situ investigation of non-thermal plasma driven catalytic reactions"
4:20-4:40 pm	Angel Barranco, Consejo Superior de Investigaciones Cientificas, "Remote plasma deposition and processing of oxide and metal supported nanostructures for multifunctional applications"
4:40-5:00 pm	Richard van de Sanden, Dutch Institute for Fundamental Energy Research (DIFFER), "Plasma dissociation of CO2 using a vortex stabilized microwave plasma flow reactor: new insights in the plasma chemistry"
5:00-5:20 pm	Yannick Engelmann, University of Antwerp, "Plasma catalysis at the nanoscale: A generic Monte Carlo model for the investigation of the diffusion and the chemical reactions of plasma species at porous catalyst surfaces"
5:20-5:40 pm	David Go, University of Notre Dame, "Developing catalysts for plasma systems: Breaking the scaling of conventional catalysis"

Wednesday August 29th

9:00-10:40 am Session W1: Plasma diagnostics and modeling

(Chair: Eitan Barlaz, University of Illinois)

9:00-9:20 am	Chris Hogan, University of Minnesota, "Utilization of aerosol analytical approaches in the examination of non-thermal plasma synthesis reactors"
9:20-9:40 am	Holger Kersten, University of Kiel, "Spatiotemporal diagnostics and extraction of nanoparticles during particle growth cycles in an acetylene plasma"
9:40-10:00 am	David Pai, Centre National de la Recherche Scientifique, "Plasma-fluid-surface diagnostics of nanosecond pulsed plasmas"
10:00-10:20 am	David Boris, U.S. Naval Research Laboratory, "Precise flux control of ions and radicals using electron beam generated plasmas
10:20-10:40 am	Ken Hara, Texas A&M University, "Multispecies plasma fluid modeling of carbon arc discharge"

10:40-11:10 am Coffee break

11:10-12:10 pm Session W2: Multicomponent, multidimensional, multifunctional materials (Chair: Yannick Engleman, University of Antwerp)

- 11:10-11:30 amAna Borras, Consejo Superior de Investigaciones Científicas, "Advances in the
development of functional 1D and 3D nanostructures"
- 11:30-11:50 am Mohamed Chaker, Institut national de la recherche scientifique-Énergie, Matériaux et Télécommunications, "Metal-insulator transition materials synthesized by pulsed laser deposition"
- 11:50-12:10 pm Elijah Thimsen, Washington University in St. Louis, "Materials with nonequilibrium atomic configuration produced by low temperature plasma"
- 12:10-12:30 pm Concluding remarks and departure

ABSTRACTS

Sunday August 26th

5:20-7:20 pm	Session S1: Plasmas and liquids for environmental, biomedical, and agricultural applications (Chair: David Go, University of Notre Dame)
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6:40-7:00 pm	Michael Keidar, George Washington University, "Adaptive plasma for cancer therapy: physics, mechanism, and applications"
7:00-7:20 pm	Michael Kong, Old Dominion University "Broad-spectrum inhibition of cancer metabolism with cold atmospheric plasma"

Plasma Self Organization in Atmospheric Pressure DC Glows and its role in the modification of metal and liquid anode properties

John E. Foster¹ and Yao Kovach¹

¹ Department of Nuclear Engineering, The University of Michigan, USA

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Self organization is ubiquitous in nature including naturally occurring plasma structures in space. Such phenomena are prevalent in human-made plasmas such as atmospheric pressure plasmas as well. In particular, self-organization is observed in atmospheric pressure DC glows on both metal and liquid anodes.[1] Both types of DC glows are currently being investigated for technological applications such as surface modification, water treatment, and nanoparticle production. Because self-organization occurs concurrently with surface modification and nanoparticle production, these phenomena may play a key role in nanoparticle formation kinetics, effecting not only ion formation in solution, but also ion mass transport via the induction of flow.[2] Indeed, as the surface of the metal or liquid is modified as a consequence of plasma contact, the plasma and resulting patterns can also be expected to be modified as a form of feedback. Here, we review self-organization on liquid and metal anodes. We also discuss the relationship between surface changes, induced liquid chemical changes, and discharge morphology. Additionally, the role of ionic strength and activity upon pattern formation on liquid water surfaces is discussed.

[1] Trelles, J., 2016, Journal of Physics: Applied Physics, 49, 393002.

[2] Naok, S., Satoshi, U., and Fumiyoshi, T., 2014, Japanese Journal of Applied Physics, 53, 046202.

Understanding the Chemistry of the Plasma-liquid Interface through Experiment and Theory

Paul Rumbach¹, Hernan E. Delgado², David M. Bartels³, R. M. Sankaran⁴, and David B. Go^{1,2}

¹ Department of Aerospace and Mechanical Engineering, University of Notre Dame, USA

² Department of Chemical and Biomolecular Engineering, University of Notre Dame, USA

³ Department of Chemistry and Biochemistry, Notre Dame Radiation Laboratory, University of Notre Dame, USA

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It has been shown that a wide variety of metallic nanoparticles can be synthesized by placing a low-temperature plasma in direct contact with an aqueous solution. The prevailing hypothesis is that free radicals produced in the plasma phase solvate and reduce metallic cation precursors to form the nanoparticles. Our work has shown that solvated electrons produced by the plasma are an important reducing agent in many plasma-liquid systems. This talk will describe our experimental method for directly measuring solvated electrons *in situ* at a plasma-liquid interface. A series of analytic models describing the fundamental chemistry, transport, and electrostatics of the interface will also be presented. Various factors that influence the efficiency of nanoparticles synthesis, such as gas composition and solution conductivity, will be discussed and explained.

A plasma-based process for treatment of perfluoroalkyl substances (PFASs) in ion exchange brine regenerant solution: reactor design challenges and physicochemical processes at the plasma-liquid interface

Selma Mededovic Thagard, Mikhail Vasilev, Chase Nau-Hix

Department of Chemical and Biomolecular Engineering, Clarkson University, USA * presenting author email: smededov@clarkson.edu

Plasma-based water treatment (PWT) utilizes electrical discharge plasmas formed in contact with or in the vicinity of water to degrade chemicals within contaminated water. Plasma in these conditions is capable of producing a diverse range of highly reactive species with relatively low energy input and without chemical additives, which makes PWT a promising alternative treatment technology and has inspired decades of investigation and development.

We have recently developed a bench-scale process based on electrical discharge plasma that is capable of treating perfluoroalkyl substances (PFASs) in groundwater from a naval site with high enough efficiency to rival leading treatment technologies. Following extensive experiments with the bench-scale plasma reactor, a scaled-up continuous-flow prototype unit was constructed wherein the PFASs degradation rates far exceed those attainable in the bench scale version of the reactor.

While the pilot scale plasma reactor system will soon be demonstrated for the treatment of PFAS-contaminated groundwater at an Air Force Base, a more practical solution to using plasma to degrade high flowrates of PFAS-containing water is to combine it with an ion exchange (IX) treatment system wherein the plasma is used to treat the IX regeneration brine, a complex chemical mixture of high concentration PFASs, methanol, and sodium chloride. To treat brine, we have adapted the plasma reactor originally developed for low concentration, low conductivity PFAS-contaminated water and this talk discusses treatment challenges associated with two physicochemical properties of brine solutions that had to be overcome in the reactor adaptation process. These include high electrical solution conductivity which reduces the plasma-liquid contact area and low solution surface tension of concentrated PFAS solutions which increases the production of argon-generated foam, causing it to interfere with the formation of plasma.

To improve existing processes and to broaden the range of applications of plasmas formed within and contacting a liquid we also investigated physical and chemical processes occurring at the plasma-liquid interface of low and high conductivity solutions. The goal was to correlate bulk liquid transport processes with the plasma-liquid interface dynamics by combining analytical (chemical) measurements with fluid dynamics investigations. The approach involved measuring degradation rates of Rhodamine B dye, a model compound and quantifying the plasma-induced velocity field in the reactor as a function of the initial dye concentration and solution conductivity. Relative rates of the dye adsorption and reaction at the interface, diffusion to the interface, and convective transport in the bulk were estimated using a 2-D diffusion-convection transient model.

Atmospheric-Pressure Glow Discharges as Tools for the Detection and Identification of Elemental, Molecular, and Biopolymeric Species

Jacob T. Shelley¹, Courtney L. Walton¹, Andrew J. Schwartz², Garett M. MacLean¹, Michela J. Burnley¹, Judy Wu¹, and Gary M. Hieftje³

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While reduced-pressure glow discharges have been used for decades as sources for analytical optical spectroscopy and mass spectrometry, their atmospheric-pressure counterparts have only recently emerged as useful tools in analytical situations. Yet, operating a glow discharge at atmospheric pressure offers a number of unique advantages for analytical spectroscopy including relaxed sample preparation procedures, easier sample introduction methods, and simplified, compact overall instrument designs. As a result, these atmospheric-pressure glow discharges (APGDs) are well suited for portable (or transportable) optical- or mass-spectrometric Furthermore, powering these APGDs with direct-current (DC) voltages/currents devices. minimizes issues with electronic interference, which is an important consideration in the development of portable instrumentation. From a physical and chemical perspective, these plasmas produce highly energetic species (e.g., ions, metastable neutrals, fast electrons, etc.), which can lead to high-energy physical or chemical processes to fragment and ionize molecules. This fragmentation can be so extensive that molecules are broken down into bare elemental constituents. In addition, low-energy ionization reactions can also occur due to the abundance of collisional cooling that can take place at ambient pressures. All of these advantages combined indicate that APGDs can be useful for variety of analytical spectroscopies as well as for the detection and identification of a broad range of analytes.

This presentation will focus on the broad utility and range of applications of low-power APGDs, specifically the solution-cathode glow discharge (SCGD). Our group has recently shown that the possibilities of these devices extend well beyond conventional atomic spectroscopy. By tuning the chemistry of the discharge, we can alter conventional ionization modes to encompass elemental analysis to biomolecular detection to polymer analysis. It was found that SCGD-MS could be used for the detection of atomic, molecular, and biological species directly from solutions. Furthermore, it was found that molecular species could be tunably fragmented through adjustment of SCGD operating parameters. For instance, peptides were tunably fragmented at atmospheric pressure, which led to 100% sequence coverage for many of the peptides examined. The power of this sequencing approach is further realized through coupling SCGD-MS with ultra-high performance liquid chromatography (UPLC). For the determination of elemental species, SCGD-MS was found to offer detection limits in the sub-ppb range for the analytes examined. The exceptional stability of the SCGD as an ionization source will be demonstrated through the measurement of isotope ratios. In the case of uranium, isotope-ratio precisions with SCGD-MS were found to be on par with or better than the gold-standard approaches of thermal-ionization mass spectrometry (TIMS) or multicollector ICP-MS. Finally, efforts towards making fieldable and portable instruments with these APGDs will also be presented.

Adaptive plasma for cancer therapy: physics, mechanism and applications

Michael Keidar

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One of the most promising applications of cold atmospheric plasma (CAP) is the cancer therapy. The uniqueness of plasma is in its ability to change composition in situ. Plasma self-organization could lead to formation of coherent plasma structures. These coherent structures tend to modulate plasma chemistry and composition, including reactive species, the electric field and charged particles. Formation of coherent plasma structures allows the plasma to adapt to external boundary conditions, such as different cells types and their contextual tissues. In this talk we will explore possibilities and opportunities that the adaptive plasma therapeutic system might offer. We shall define such an adaptive system as a plasma device that is able to adjust the plasma composition to obtain optimal desirable outcomes through its interaction with cells and tissues.

This talk will summarize the state of the art of this emerging field presenting various aspects of CAP application in cancer such as role of reactive species, cell cycle modification and in vivo application. The efficacy of cold plasma in a pre-clinical model of various cancer types such as lung, bladder, breast, head, neck, brain and skin has been demonstrated. Both *in-vitro* and *in-vivo* studies revealed that cold plasmas selectively kill cancer cells. Recently mechanism of plasma selectivity based on aquaporin hypothesis has been proposed. Aquaporins (AQPs) are the confirmed membrane channels of H_2O_2 and other large molecules. We have demonstrated that the anti-cancer capacity of plasma could be inhibited by silencing the expression of AQPs. Additional possible cell feedback mechanism was recently discovered. It is associated with production of reactive species during direct CAP treatment by cancer cells. Selective production of hydrogen peroxide by different cells can lead to adaptation of chemistry at the plasma-cell interface based on the cellular input. In particular we have found that the discharge voltage is an important factor affecting the ratio of reactive oxygen species to reactive nitrogen species in the gas phase and this correlates well with effect of hydrogen peroxide production by cells.

Broad-spectrum inhibition of cancer metabolism with cold atmospheric plasma

Hai-Lan Chen,^{1*} Bo Gao,¹ Francis Li,¹ Sudhir Bhatt,¹ Chen Chen,¹ Tony Pomicter,² Michael W Deinginer,² Michael G Kong¹

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Deregulated metabolism is one of ten essential cancer hallmarks and represents a key therapeutic target. With limited clinical success however, current metabolism-targeting therapies are challenged with metabolism plasticity and this has led to calls for novel strategies that can simultaneously target diverse hallmarks of cancer metabolism. Yet, it is unknown whether different cancer metabolism hallmarks, such as altered bioenergetics, enhanced biosynthesis, redox dysfunction, and growth signaling, share common vulnerabilities that may be exploited with a single agent. We hypothesize that this is possible with cold atmospheric plasma (CAP) through its reactive oxygen and nitrogen species (RONS). This presentation starts with quantitative characterization of reaction chemistry in cell-free culture medium and in cancer and normal cells, both under CAP treatment. We then show that the CAP elicited similar lethality in drug-resistant cells of human leukemia, melanoma, and breast cancer despite their genetic differences. Furthermore, a 1-min CAP treatment led to simultaneous inhibition of multiple metabolic enzymes, the AKT/mTOR/HIF-1α signaling, and cellular antioxidant systems in drug-resistant BCR-ABL1positive cells but not their healthy counterparts. CAP was effective in inducing significant apoptosis in mouse BCR-ABL1-positive cell lines and primary CD34⁺ cells from chronic myeloid leukemia patients, but had only limited toxicity toward normal CD34⁺ cells. Mechanistically, CAPmediated broad-spectrum inhibition of cancer metabolism may be through direct protein oxidation of metabolic enzymes and signaling molecules or HIF-1a inhibition-mediated glycolysis inhibition. Pulsed RONS of the CAP is likely to be important to avoid reactivate inhibited HIF-1a. In conclusion, the CAP cocktail of pulsed and diverse RONS offers a novel tool to interrogate simultaneous regulation of diverse metabolism traits in proliferating cells or to explore its utility as a therapeutic intervention of human malignancies.

Monday August 27th

8:40-10:20 am	Session M1: Plasma synthesis of nanoparticles in the gas phase (Chair: Abbas Semnani, Purdue University)
8:40-9:00 am	Lorenzo Mangolini, University of California, Riverside, "Low temperature plasmas for nanoparticle synthesis: fundamentals and applications"
9:00-9:20 am	Jan Benedikt, University of Kiel, "Atmospheric plasmas for generation of nanostructured materials or nanoparticles"
9:20-9:40 am	Rebecca Anthony, Michigan State University, "Plasma-based synthesis and surface modification for photoluminescent nanocrystals"
9:40-10:00 am	Yevgeny Raitses, Princeton Plasma Physics Laboratory, "Arc-based synthesis of carbon nanoparticles and nanostructures
10:00-10:20 am	Souvik Ghosh, University of Minnesota, "Fundamental studies of agglomeration of nanoparticles generated in a dc microplasma"

Low temperature plasmas for nanoparticle synthesis: fundamentals and applications

Lorenzo Mangolini^{1,2}, Devin Coleman², Alejandro Alvarez¹, Austin Woodard², Kamran Shojaei¹, Carla Berrospe¹.

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In this talk we will focus on RF continuous flow plasmas operated in tube reactors and run in a low-to-mid pressure regime (1-10 Torr range). While it is accepted that the interaction between the particles and a plasma produced in such configuration can lead to substantial nanoparticle heating, this has been difficult to probe experimentally. We will discuss our recent progress in monitoring plasma-nanoparticle interaction via in-situ Raman and FTIR. We have taken advantage of the high optical cross section of carbon nanoparticles, and used these techniques to measure the temperature of particles formed in an argon-acetylene plasma. Both techniques provide experimental confirmation that the nanoparticle temperature can exceed 1000K even at moderate input power levels.

We will discuss how to leverage this intense heating to produce nanoparticles of materials that are difficult to process. Beta-silicon carbide nanoparticles can be easily produced by nucleating silicon particles in a first plasma and by exposing them to a methane plasma placed in series with the first discharge. Simple calculations based on the enthalpy of formation of silicon carbide suggest that the nanoparticles temperature can be as high as 2000K during in-flight carbonization, consistent with the observation of high-quality crystalline silicon carbide particles. The use of such particles as inclusion in bulk thermoelectric materials will be described.

We will also discuss the synthesis and processing of titanium nitride nanoparticles using lowtemperature plasmas. Titanium nitride is notoriously difficult to produce in nanoparticle form. We have demonstrated that <10 nm TiN particles with near perfect stoichiometry can be obtained starting using titanium tetrachloride and ammonia as precursor couple. These particles show plasmon resonance in the near infrared, and are of interest for a variety of applications including photocatalysis and photo-thermal conversion. We have found that the optical properties are highly sensitive to the degree of oxidation of the material. A two-steps plasma process will be described in which titanium nitride nanoparticles are coated in-flight with a silicon nitride shell. This approach effectively prevents oxidation of the TiN particles, leading to a large improvement in their plasmonic response in harsh environments.

Atmospheric plasmas for generation of nanostructured materials or nanoparticles

Jan Benedikt¹, Ove Hansen¹, Oleksander Polonskyi², Mohamed Mokhtar Hefny³, David Nečas⁴, Sadegh Askari¹, Judith Golda¹

¹ Institute of Experimental and Applied Physics, Christian-Albrechts-University Kiel, Germany

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Atmospheric non-equilibrium plasmas can generate high densities of reactive species or dissociate effectively precursor gases. Contrary to low-pressure plasmas, the collisions prevent ion bombardment and the diffusion is slow as transport mechanism. On the other hand, energy can be effectively stored in form of excitation energy (metastable atoms, excimers, metastable molecules such as $N_2(A)$) and a convection can be used as an effective transport of reactive species in atmospheric plasma jets. However, the main application of atmospheric plasmas is mainly in surface treatment applications, they are not widely used in applications for thin film generation or etching due to the limited quality of the deposited material, missing ion bombardment and only localized treatment. Their potentials material synthesis are mainly demonstrated in proof of principle experiments [1], where especially interesting is the formation of nanostructured materials [2,3] or nanoparticles [4].

In this contribution, we will discuss the transport of reactive species to the substrate and the effect of recombination reactions on the treatment efficiency. Important effect of highly collisional conditions is that even species with low surface reaction probability contribute very effectively to the surface reactions. Finally, we will report on the use of He/O_2 plasma for the treatment of Cu films at well-defined surface temperature to generate under controlled conditions nanostructured copper oxide layers.

[1] Mariotti D, Belmonte T, Benedikt J, Velusamy T, Jain G and Švrček V 2016 Plasma Process Polym 13 70–90

- [2] Altaweel A, Filipič G, Gries T and Belmonte T 2014 J Cryst Growth 407 17
- [3] Mariotti D and Ostrikov K 2009 J. Phys. D: Appl. Phys. 42 092002
- [4] Askari S, Svrcek V, Maguire P and Mariotti D 2015 Adv. Mater. 27 8011

Plasma-based Synthesis and Surface Modification for Photoluminescent Nanocrystals

<u>Rebecca Anthony</u>², Alborz Izadi, Alexander Ho, and Kyle O'Shea.

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Nonthermal radiofrequency plasma reactors are increasingly popular for nanomaterials synthesis, offering desirable features such as a low-temperature environment, avoidance of liquid-phase reactants, tunable nanocrystal properties via reactor parameters, and scalability. In addition, the nanocrystals can be collected as powders for post-processing, or directly impacted onto substrates in thin-film form, avoiding the need for additional steps such as spin- or drop-casting. Thus, these reactors are versatile and powerful tools for fabricating property-controlled nanoparticles and particle ensembles in the form of colloids or films.

One of the most attractive features of these plasma reactors is the ability to engineer the nanoparticle surfaces both in-flight and after deposition. Silicon nanocrystals (SiNCs) are one material of interest, due to their high natural abundance and relative non-toxicity as compared to many other luminescent nanocrystals such as metal chalcogenide quantum dots. However, one difference between these chalcogenide nanocrystals and SiNCs is the relatively straightforward protocols for shell growth, which can enable bandgap engineering and protection from environmental effects such as oxidation. We present on core-shell Si/SiN_x nanoparticles synthesized using a multi-stage flow-through nonthermal plasma reactor in an effort to protect the SiNC core from oxidative effects and enhance photoluminescence (PL) efficiency. We used silane and argon in the first plasma stage for core SiNC synthesis, followed by a secondary plasma immediately downstream into which we injected nitrogen gas for shell growth. The pressure was 2-4 Torr and both plasmas were operated at 13.56 MHz with 25-35W power. Our multistage approach led to creation of a nitride shell and mitigated some oxidation effects. However, the shell growth is not sufficient to increase the PL yields of these samples.

While unintentional oxidation of SiNCs can create defects, reduce PL yields, and cause shifts in PL peaks, an attractive alternative solution is to create high-quality monodispersed SiNCs with intentionally-grown oxide shells. We also report on our recent efforts to create luminescent core-shell Si/SiO_x nanoparticles synthesized using an atmospheric pressure glow discharge.

Arc-Based Synthesis of Carbon Nanoparticles and Nanostructures

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This work reports on studies of arc-based synthesis of carbon nanomaterials [1]. Applying a set of the developed in situ diagnostics of plasma and nanoparticles, our synthesis experiments revealed that the carbon arc forms a highly inhomogeneous plasma consisting of distinguishable regions with different dominant species, including ions, atoms, molecules and clusters, and nanoparticles [2-5]. Experimental and modeling results demonstrate that different steps of the synthesis process, including generation of a feedstock of atomic and molecular species and ions, formation of larger molecules and clusters, growth of nanotubes, and agglomeration of nanoparticles in large particles and bundles occur in different regions of the arc discharge [2-4,6,7]. In particular, the in situ measurements revealed large clouds of nanoparticles in the arc periphery bordering the region with a high density of diatomic carbon molecules [3,4]. Two-dimensional computational fluid dynamic simulations of the arc combined with thermodynamic modeling show that this is due to the interplay of the condensation of carbon molecular species and the convection flow pattern [2,3]. These results show that the nanoparticles are formed in the colder, peripheral regions of the arc. Plasma effects on the growth of nanotubes will be discussed [6-8].

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Fundamental studies of agglomeration of nanoparticles generated in a DC microplasma

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Atmospheric-pressure microplasmas can controllably synthesize nanoparticles through gas-phase reduction of organometallic precursors. The particles are nucleated and grow in the plasma at near-room temperature conditions. The synthesized particles are often assumed to remain spherical and relatively monodisperse during synthesis because of unipolar particle charging and selective nanoparticle heating. However, in many instances, the nanoparticles collected from such reactors appear as clustered agglomerates, composed of interconnected primary spherical particles. In spite of this observation, particle agglomeration in plasma synthesis is commonly neglected (i.e. unipolar charging is assumed to completely mitigate agglomeration), and few studies have directly examined agglomeration in plasma synthesis systems.

To better understand agglomeration of nanoparticles synthesized in gas phase, our group has implemented ion-mobility mass spectrometry (IM-MS) to analyze as-synthesized carboncoated Ni nanoparticles. We used an atmospheric-pressure DC microplasma with flowing Ar and nickelocene vapor as precursors. In the IM-MS technique, the nanoparticles (in the gasphase) are sampled sequentially in series using a differential mobility analyzer (DMA), aerosol particle mass analyzer (APM) and condensation particle counter (CPC). This instrument combination yields 2-dimensional data containing nanoparticles' particle number concentration as a function of both mobility diameter and mass-to-charge ratio. These raw data can be corrected for the instruments' transmission factors/transfer functions and particle charge distribution on the particles. This two-dimensional size-mass distribution function of the particles directly enables characterization of nanoparticle morphology. The nanoparticles were also analyzed using transmission electron microscopy (TEM).

DMA-APM analyses, as well as TEM with automated image processing, reveal that all examined plasma synthesis conditions yielded highly agglomerated particles that were noticeably polydisperse and highly branched. TEM revealed that they were composed of primary particles smaller than 10 nm in diameter. TEM analysis and IM-MS measurements show that the agglomerate morphologies are well described through a quasi-fractal model, with nearly all examined agglomerates displaying fractal dimensions in the 1.6-2.0 range. The mean masses and mobility diameters of agglomerates increased with increasing precursor concentration and residence time in the plasma. The mass-mobility relationship for the observed agglomerates can further be corroborated with Langevin dynamics simulations of agglomerating, non-interacting particles. From IM-MS based agglomerate structural characterization, we hypothesize that the particle agglomeration may occur in plasma synthesis through one of two mechanisms. First, small neutral species and positively charged particles can get scavenged by larger agglomerates in the plasma volume, leading to agglomerate growth. Second, particle agglomeration can also occur in parallel near the boundaries of the reactor, in regions of low plasma density, which is dominated by ions rather than electrons.

Monday August 27th

10:50-11:50 am Session M2: Plasma synthesis of nanoparticles/nanomaterials in the liquid phase (Chair: Ken Hara, Texas A&M University)		
10:50-11:10 am	Angela Capece, The College of New Jersey, "Synthesis of silver nanoparticles in ionic liquids by electron irradiation"	
11:10-11:30 am	Thierry Belmonte, Institut Jean Lamour, "Synthesis of alloy nanoparticles by discharges in liquids: a short review"	
11:30 am-11:50 pm	Daniel Jaramillo, University of Louisville, "Low pressure plasma Interactions with molten metals for materials processing"	

Synthesis of Silver Nanoparticles in Ionic Liquids by Electron Irradiation

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Silver nanoparticles exhibit unique optical, catalytic, and antibacterial properties as a result of their shape and size, making them useful for a variety of applications. Conventional nanoparticle synthesis methods often require high pressures and the use of toxic materials such as organic solvents, reducing agents, and stabilizers [1]. However, plasma synthesis in ionic liquids provides an alternative that circumvents these requirements. Ionic liquids are salts that consist of an organic cation and polyatomic anion and are liquid below 100°C and thermally stable up to 450°C [2]. As a result of their low vapor pressure, ionic liquids can be combined with lowpressure plasmas to produce metal nanoparticles through the reduction of dissolved metal salts by the reactive species produced in the plasma [3]. In this work, we demonstrate the synthesis of silver nanoparticles by irradiating a solution of AgBF₄ powder in the ionic liquid, 1-butyl-3methylimidazolium tetrafluoroborate, using an electron beam with energies ranging from 5 to 20 kV. I will discuss particle seeding and growth and will show images of the liquid droplet during irradiation obtained via field emission scanning electron microscopy (SEM). The silver nanoparticles were characterized using SEM, dispersive X-ray spectroscopy, and X-Ray photoelectron spectroscopy. These results will be presented and the effect of beam energy on particle size and morphology will be discussed.

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Synthesis of alloy nanoparticles by discharges in liquids: A short review

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Since the first syntheses of nanoparticles by discharges in liquids, the conditions required to get alloy nanoparticles with controlled composition are still unclear. There are several ways to produce this kind of materials: discharges created by laser, by high voltage, by acoustic wave, etc. Discharges can be created to erode a surface or to convert nanoparticles already available in a liquid suspension.

Basically, matter emitted from either targets, electrodes or nanoparticles has to melt and cool down at uncontrolled rates to produce alloy with specific distributions of elements. Few models start being available but local conditions are difficult to estimate accurately, especially because all discharges, whichever way they are created, are dominated by huge spatial and temporal gradients.

Conversely, we may imagine using nanoparticles as probes of local plasma conditions. Their size, their composition and even their shape are determined by their residence in areas where they undergo fast changes. This is the reason why discharges in liquids are well-known to lead to broad size distributions of nano-objects.

In this work, we propose a short review to sort among the different media in terms of pressure, temperature and mean lifetime of events to establish a first map where alloy nanoparticles are correlated with prevailing local conditions. This approach aims to better control the synthesis of nanoparticles with chosen compositions for specific applications like catalysis, photovoltaics, photonics, etc.

Low Pressure Plasma Interactions with Molten Metals for Materials Processing

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The enhanced dissolution of gas phase species into exposure with molten metals with plasma excitation is studied for two reasons: (i) to understand the synergistic role of plasma and molten metals for growing silicon nanowires at low temperatures [1]; (ii) bulk growth of Gallium Nitride. Experiments have shown an increment of adsorbed gaseous species into the molten metal in the presence of plasmas at temperatures as low as 100 C. Furthermore, Density Functional Theory (DFT) calculations suggest a strong interaction between atomic hydrogen and molten gallium that is described as a high absorption on the surface, rapid diffusion, and a steady state concentration of the gas inside the bulk.[2]

Using RF plasma excitation of hydrogen containing silane and Ga clusters, we developed a process for making silicon nanowire arrays on thin metal foils. The results suggest low temperature, tipled growth of Si NWs with Ga clusters on a variety of metal foils. Similarly, bulk growth of GaN is studied using plasma enhanced dissolution of nitrogen into molten Gallium at sub-atmospheric pressures at 900C. The crystal growth is studied using Ga mixed with alkali metals to understand sizes of crystals.

Acknowledgments

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Carreon, M.L., Jasinski, J. and Sunkara, M.K. 2014 *Mater. Res. Express* 1 045006
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Monday August 27th

1:30-3:30 pm	Session M3: Plasma physics (Chair: Carles Corbella, Ruhr University, Bochum)
1:30-1:50 pm	Venkatt Ayyaswamy, University of California, Merced, "A general-purpose computational framework for plasma physics and chemistry"
1:50-2:10 pm	Yangyan Fu, Michigan State University, "Gas breakdown in microgaps with electrode surface protrusions: Paschen's curve, non-uniformity of electric field, and breakdown mode transitions"
2:10-2:30 pm	Allen Garner, Purdue University, "Gas breakdown at microscale and smaller gaps: Theoretical unification of mechanisms and experimental assessment of surface roughness"
2:30-2:50 pm	Matthew Goeckner, North Carolina State University, "The physics of pulsed and level-to- level discharges used for material processing"
2:50-3:10 pm	Sergey Baryshev, Michigan State University, "Field emission to glow discharge transition in nanodiamond vacuum diode"
3:10-3:30 pm	Sung-Jin Park, University of Illinois, "Microplasma Technology in Nanoscale Processes and Environmental Science: Future for the Social Impact,"

A general-purpose computational framework for plasma physics and chemistry

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The role of computations in understanding the fundamental physical and chemical processes that are of relevance to various low-temperature plasma applications cannot be overstated. In this context, a general-purpose, user-friendly computational framework capable of performing efficient two-dimensional and three-dimensional simulations could be extremely attractive to the plasma community. The main goal of this talk is to discuss the development of an in-house plasma solver - plasmaFoam - developed in the OpenFOAM framework. The plasmaFoam code is capable of dealing with an arbitrary chemistry model and solves the continuity equation and momentum equation for all species involved apart from an electron energy equation and the heat equation to determine heavy species temperature. The governing equations are solved using standard finite volume schemes that are at least second-order accurate. The plasmaFoam framework can also include an arbitrary number of dielectric regions that are exposed to the plasma region with suitable surface-charge-based interaction between the two regions. Being a part of OpenFOAM ensures that the plasmaFoam code is massively parallel and can demonstrate good scalability. The application of the solver to representative low-temperature problems are presented and the results discussed in detail. One-dimensional simulations of microwave microplasmas at various pressures and excitation frequency are first presented with the results compared with particle-in-cell with Monte Carlo collision simulations and experimental data available from the Hopwood group[1]. The one-dimensional results will extend the results presented by Verma et al. [2-3] for frequencies up to 4 GHz. Two-dimensional simulations are then presented for an argon microwave microplasma device with coplanar electrodes. The influence of pressure and frequency on the electron dynamics and plasma properties is outlined. The electrical characteristics and operating modes of the microplasma along with their frequency response are also highlighted. While the talk will primarily focus on argon plasmas with a relatively simple chemistry model, the plasmaFoam code can handle more complex plasmas involving hundreds of reactions. It can also be coupled with other external codes performing simulations such as molecular dynamics enabling suitable exchange of information.

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Gas Breakdown in Microgaps with Electrode Surface Protrusions: Paschen's curve, Nonuniformity of Electric Field, and Breakdown Mode Transitions

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Gas breakdown in microplasmas and microdischarges with characteristic lengths less than 1mm is key in many applications, including micro-electro-mechanical systems (MEMS), micro-switches, and microchip devices[1,2]. With greatly reduced dimensions, discharge characteristics are strongly influenced by geometric features, such as electrode surface protrusions [3].

In this work, gas breakdown in microgaps with an electrode surface protrusion are characterized in various discharge regimes. First, using a two-dimensional fluid model, the breakdown voltages in microdischarges dominated by secondary electron emission are quantified when the discharge current enters the subnormal regime from the Townsend regime. The breakdown voltage as a function of gas pressure in a microgap with a cathode hemi-ellipsoidal protrusion is compared to the non-protrusion gap. The cathode surface protrusion results in a combined Paschen's curve, which transits from the wide gap behavior (gap distance between the two parallel electrodes) at low pressure to the narrow gap behavior (gap distance between protrusion apex to the anode) at high pressure, resulting in relatively low breakdown voltage in a significantly wider pressure range. It is observed that the discharge automatically optimizes its discharge path to obtain the lowest breakdown voltage. Second, the effects of the protrusion size and the aspect ratio on the breakdown voltage are examined. It is found that the breakdown voltage is more sensitive to the protrusion size than to its aspect ratio. Increasing the protrusion's aspect ratio shows a non-monotonic impact on the breakdown voltage. The effects of the discharge polarity and the microgap's aspect ratio on the breakdown voltages are also investigated. The key parameters for the Paschen's curve are the shortest and the longest discharge paths, the electric field enhancement between protrusion tip and the opposite electrode, and the effective cathode emission area. Third, using a semi-analytical mathematical model by Go et al [4] and also considering non-uniformity of the first Townsend avalanche coefficient, the breakdown transiting from the secondary electron emission dominant regime to the field emission dominant regime is identified with the perturbation of the surface protrusion.

The surface protrusions in microdischarges have a profound impact on breakdown voltage, whether resulting from surface roughness, damage, or by design. This work provides insights into the design of microgaps with controlled breakdown voltage across many orders in pressure via the shaping of protrusions [5].

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Gas Breakdown at Microscale and Smaller Gaps: Theoretical Unification of Mechanisms and Experimental Assessment of Surface Roughness

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Traditional gas breakdown arises due to Townsend avalanche and is predicted theoretically by Paschen's law (PL). While PL predicts a minimum breakdown voltage as a function of the product of gas pressure and gap distance, experiments often show an absence of the minimum or an extended plateau for microscale gaps [1]. Hypothesized to be driven by field emission, many models have attempted to predict breakdown in this regime by unifying PL with the Fowler-Nordheim equation [1]. Applying a matched asymptotic analysis yields universal (true for any gas), closed form solutions for breakdown from the field emission regime to the conventional PL that match experiment [2]. These models suffer from common challenges that they are limited to gap distances above the mean free path and they require fitting the field enhancement factor, which limits their application for a priori prediction of gas breakdown.

This talk summarizes the background of this theoretical analysis and extends it to nanoscale gaps while also introducing experimental assessments of the impact of electrode surface roughness on gas breakdown for microscale gaps. We first modify the universal breakdown model [2] to obtain the empirical linear fit for vacuum breakdown from first principles while also predicting the transition in breakdown mechanism observed experimentally using a novel, in-situ optical imaging technique. Further reducing gap size below the mean free path of an electron means that the involved mechanisms should resemble vacuum, motivating our efforts in unifying the universal breakdown model from [2] with the Child-Langmuir law [3] and the Schrödinger equation [4] to predict gas breakdown from quantum scales to the PL. Finally, we assess microscale gas breakdown as a function of surface roughness by polishing the surfaces at various grits and measuring the resulting breakdown voltage [5]. Breakdown voltage decreases for increased surface roughness and following repeated voltage applications, suggesting that the noticeable electrode surface changes in measured breakdown voltages. The implications of these results on understanding the relevant physics and practical device design will be discussed.

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The physics of pulsed and level-to-level discharges used for material processing

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As the critical dimension of devices have shrunk, the processing technology has changed. In the 1970's much of the processing was "wet chemistry." Now most of the critical processing steps employ "dry processing," e.g. plasmas of one form or another. Plasmas are not the "perfect" processing technology, particularly as critical dimension of devices have continued to shrink. As long as two decades ago, it was understood that there were a number of mechanisms via which plasmas might induce damage on a device. [1,2] For a multitude of reasons, pulsed and level-tolevel plasmas have often been considered the most viable processing technology for overcoming the limitations of continuous wave processing. However, the combination of pulse rate, duty factor, power levels, gas species, flow rate and pressure, provides one with an almost endless free parameter space. This makes finding a set of "ideal" parameters difficult at best. For example, the plasma will 'extinguish' under some fully pulsed conditions while under other very similar conditions it will not 'extinguish'. This leads to very different restart during the plasma on portion of the pulse, 're-ignition' vs 're-energization'. In 're-energization', plasma sheaths will exist prior to the reapplication of power – while in 're-ignition' the sheaths need to be reestablished. This subtle, yet significant, difference changes how power is initially deposited into the system. Such knowledge is critical in helping the general low-temperature plasma community establish guidelines for optimizing the use of pulsed and level-to-level discharges in industrially relevant processing conditions. In this talk, we will examine what is known about such systems and how that might impact the use of pulsed and level-to-level discharges.

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pp 65-81, https://doi.org/10.1016/S0167-9317(99)00430-X.

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Field Emission to Glow Discharge Transition in Nanodiamond Vacuum Diode

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Nitrogen-incorporated ultrananocrystalline diamond, (N)UNCD, is an unconventional field emitter (FE) that performs simply in planar thin film configuration and has turn-on fields as low as 10 V/ μ m. Its synthesis is scalable while growth can be done on various metal substrates. Thus, the thin film (N)UNCD is a flexible FE platform, which was employed to build and prototype a cathode technology for electron linacs [1, 2].

In a previous study [3], it was established that the total output emission current strongly depends on graphitic sp^2 content inside the diamond sp^3 matrix. Using a field emission microscopy method, it was found that graphite-rich (sp^2 content about 10%) highly conductive and emissive (N)UNCD emitters produced visible light that varied from red, to yellow, to bright blue as emission current and electric field increased. Short after a glow discharge could form – *I*-*V* curve switched from FN to glow discharge behavior, and stable localized microplasma jets formed between the cathode and the anode in the field emission microscope. After analyzing various experimental data, it was concluded that emitting locations on the diamond emitters heated up to at least 3,000 K. This self-induced heating led to emitter material evaporation. The evaporated plume was further ionized and formed microplasma discharges. Another important feature of this process is that the observed dc glow discharge transition was self-stabilized, meaning there was no any external resistor in the circuit. Like many nonmetallic field emitters (N)UNCD features another fundamental diode-to-resistor switching behavior [3] effectively described by the serial resistor model. In (N)UNCD vacuum diode, the diode-to-resistor switching precedes the intense light generation and discharge formation stabilizing the discharge.

In recent years, several reports appeared that discussed field emission driven glow discharge plasma and arc formation in low power CNT/graphene [4] and Si [5] vacuum diodes and high power arc copper device [6]. Our results suggests that glow discharge and arc formation are initiated by cathode activity via intense field emission followed by severe thermal load causing cathode material to evaporate and ionize, and are in agreement with most recent results [6]. Mechanisms inducing the thermal runaway of (N)UNCD cathode material and the nature of the hypothetical serial resistor stabilizing the discharge formation will be discussed. We will also discuss the importance of the gained insight in the context of the breakdown problem in high power MeV electron linacs.

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Microplasma Technology in Nanoscale Processes and Environmental Science: Future for the Social Impact

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Started from the efforts of scientific understanding of confined plasma in the microscopic scale, the overall knowledge of non-equilibrium, low-temperature microplasma technology has been evolved toward to active/passive interaction of surrounding physical and chemical systems, communication between systems, modification and transformation of other materials systems through its unique characteristics. The outperformance of microplasmas as the controllable scale plasma surfaces, photons, electromagnetic sources, nano-/microscale reaction product, and short life active chemical species has provided unique and compelling results not available in physics and chemistry before. At present, the microplasma technology becomes available in many areas of applications and uses, and actively penetrating into the new area.

In this presentation, several examples of new areas of microplasma technology adaptation in the nanoscale processing, semiconductor, chemical reactions, electromagnetic and photophysical processes, and the future evolution of microplasma technology will be introduced. In addition, the contribution of microplasma technology to a social impact through the application for the environmental area in saving human lives will be also discussed.

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Monday August 27th

4:00-5:40 pm	Session M4: Thin film deposition and modification (Chair: Rebecca Anthony, Michigan State University)
4:00-4:20 pm	Erwin Kessels, Eindhoven University, "Ion-surface interaction during plasma-enhanced atomic layer and how it can be used to tailor film properties"
4:20-4:40 pm	Carles Corbella, Ruhr University, "Plasmas and the nanoscale: from surface nanotexturing and plasma-surface interactions towards the synthesis of nanomaterials"
4:40-5:00 pm	J. P. Allain, University of Illinois, "Controlling soft matter nanotopography with directed plasma nanosynthesis resulting in bioinspired antibacterial properties"
5:00-5:20 pm	Holger Vach, Centre National de la Recherche Scientifique, "From aromatic silicon nanoclusters to 2D silicene layers"
5:20-5:40 pm	Eitan Barlaz, University of Illinois, "Micro- and nanotexturing of metal surfaces by femtosecond laser exposure for controllable wettability"

Ion-surface interaction during plasma-enhanced atomic layer deposition and how it can be used to tailor film properties

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Current trends in semiconductor device manufacturing impose extremely stringent requirements on nanoscale processing techniques, both in terms of accurately controlling material properties and in terms of precisely controlling nanometer dimensions. Plasma-based processing remains key in next-generation device manufacturing with plasma-enhanced atomic layer deposition (PEALD) being a method that has obtained a very prominent position in obtaining ultrathin films with atomic scale precision. Although the effects of ion-surface interactions have been investigated for conventional plasma-enhanced chemical and physical vapor deposition in great detail, very little is known about the role of ions during PEALD. In this work, the role of ion-surface interaction during PEALD will be addressed by analyzing the flux and energy of ions arriving at the surface and by linking these results with the material properties obtained. Moreover, it will be demonstrated how the properties of materials (in particular oxides and nitrides of Ti, Hf and Si) can be tailored by controlling the kinetic energy of the ions impinging on the films with RF substrate biasing. This will be shown for planar substrates (up to 200 mm in size) as well as for 3D surface topologies yielding intriguing effects of inducing differing material properties at different surfaces of the nanostructures [1,2,3].

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Plasmas and the nanoscale: from surface nanotexturing and plasma-surface interactions towards the synthesis of nanomaterials

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Plasma nanoprocessing is a very exciting field which comprises synergies between materials science and plasma physics. The discussion is divided in three approaches. (i) The first example consists in the nanopatterning of amorphous carbon films by means of colloidal lithography. Different plasma variables, like gas admixture and input voltage waveform, have been adjusted to tailor the surface properties of the films, such as wettability and friction coefficient. The obtained samples are extremely useful for tribological, nanofluidics and photonic applications [1]. (ii) Investigations of elementary processes on surfaces in contact with plasmas constitute the second example. Controlled beams of ions, neutrals and UV photons are sent to a target in ultrahigh-vacuum to mimic particle bombardment from a glow discharge. The resulting interactions are monitored in situ using different diagnostics [2]. Such experiments have provided benchmarks to model sputtering by reactive plasmas, e.g. secondary electron emission coefficients and modification probabilities of plasma-treated materials (metals, compounds, polymers) [3,4]. (iii) Finally, the third section outlines the first steps to understand the synthesis of nanomaterials by means of atmospheric arc discharges [5]. Special deposition recipes are currently being designed in order to optimize the production of nanoparticles and 2D materials like graphene. Next challenge is the production of advanced nanomaterials with tunable electric and optical properties by arc plasma.

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Controlling soft matter nanotopography with directed plasma nanosynthesis resulting in bioinspired antibacterial properties

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The relationship between material response rate and stimulant rate of plasma irradiation-directed synthesis of soft matter is a topic of interest in many fields of science. Extraction of energetic and excited particles from low-temperature plasmas in a directed approach can yield high-rate stimulants driving soft matter to metastable self-organized states of matter. In particular, nano-patterning of synthetic and natural polymers offer unprecedented control of surface properties that result in novel biomimetic materials of importance to the biomedical space. In this overview we present systematic studies of a variety of soft matter materials where we correlate inherent properties such as visco-elasticity, hardness, surface chemistry and ligand density to irradiation parameters that drive self-organized nano-to-meso scale structure.

We study these structures as unique interfaces with intrinsic anti-bacterial properties that take advantage of surface-mediated antibacterial activity, such as that found for cicada wings [1,2]. Studies in this work elucidate physico-chemical mechanisms resulting in bactericidal properties. A number of polymers are compared and in particular, chitosan, a biodegradable and non-toxic biopolymer with antibacterial properties used in wound treatment, drug delivery and biosensing applications [3], [4]. Mimicking cicada wings, recent studies applied nanopatterned silicon surfaces coated with CS, which resulted in enhanced antibacterial activity, when compared to uncoated Si surfaces [5]. In this work we use low-energy ion and atom particles extracted from a low-temperature plasma source combined uniquely to tailor desired surface nanotopographies. The flux ratios of incident species, their incident angles, fluence and mass are combined and studied. In-vitro tests consist of *E. coli* strains on statistically relevant samples to evaluate antibacterial properties. Electron microscopy imaging evaluates post-mortem features of incubated bacteria induced by the nanostructured surfaces. Relationships between polymer visco-elastic properties and synthesis of desired topographies are compared.

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From Aromatic Silicon Nanoclusters to 2D Silicene Layers

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Our economy consistently pushes for the development of revolutionary materials to meet our ever-increasing technological demands. In this context, we have undertaken in-depth theoretical and experimental studies on the growth of a new allotropic form of silicon and germanium: namely silicene [1] and germanene [2]. In order to rule out any intermixing between Si or Ge atoms and the underneath substrate atoms, as it was the case for some metallic substrates and was confirmed by our molecular dynamics simulations, and to maintain their promising features to be new Dirac materials, we have performed our deposition on chemically inert graphite substrates (HOPG). Several silicene and germanene areas are obtained by the deposition of Si and Ge on HOPG substrates at room temperature and under ultrahigh vacuum conditions. One of our crucial findings is that the silicene and germanene monolayers interact with the graphite substrate *via* van der Waals forces only. Atomic force microscopy and scanning tunneling microscopy images support the formation of quasi-continuous 2D silicon and germanium layers with small buckling, leaving some areas of the HOPG substrate uncovered together with the formation of small 3D Si and Ge clusters.

Our *ab initio* molecular dynamics simulations predict thermal stability of a perfect silicene monolayer on HOPG up to a surface temperature of about 350 °C highlighting the essential role of van der Waals forces bonding silicene or germanene to the surface. The van der Waals interaction is strong enough to stabilize the deposited monolayers even above room temperature, but weak enough to prevent any alloying of Si or Ge atoms with C atoms. Consequently, the outstanding electronic properties of silicene and germanene, such as Dirac cones, are preserved even after their deposition on the graphite surface. The simulation of the growth mechanism of the silicene sheet on HOPG at room temperature shows how silicon hexagons spontaneously form and remain at a vertical distance corresponding to the van der Waals distance above the surface.

The main problem of previously observed high-buckled silicene is its strong oxidation that occurs when exposed to air. In our work, however, we demonstrate that the use of highly oriented graphite substrates leads to air-stable low-buckled silicene nanosheets. This conclusion derives from the excellent agreement between the experimental observation and *ab initio* calculations of the corresponding Raman peak located at 542.5 cm⁻¹ which is completely different from the ones measured for silicene grown on Ag(111) surfaces [3]. We are confident that in the future by using more sophisticated growth methods, larger areas of these ultrathin films can be obtained which can be detached and transferred for device applications.

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Micro- and nanotexturing of metal surfaces by femtosecond laser exposure for controllable wettability

Eitan Barlaz, Chisung Ahn, Joseph Bottini, Tyler Nguyen, David Ruzic

Current limitations to the improvement of heat transfer across liquid metal interfaces stem from the competing need to alter the wettability of the metal while protecting against chemical modification. Conversion coatings are frequently inappropriate for extreme temperatures and may represent an unacceptably high cost of manufacture. A more robust solution would be to alter wettability of metal surfaces by physical as opposed to chemical processes. On metal surfaces patterned with microstructures, the spacing of periodic structures strongly influences wettability. Such changes impact the critical heat flux that a boiling heat transfer system is capable of withstanding. We report on changes in wettability of a variety of metal including copper and stainless steel following exposure to a femtosecond laser. The changes to surface microstructure are tuned using multiple wavelengths of light as well as angle of impact. Microstructure was observed by SEM, wettability was tested via contact angle measurements.

Tuesday August 28th

9:00-10:40 am	Session T1: Plasma sources (Chair: Angela Capece, The College of New Jersey)
9:00-9:20 am	Steve Shannon, University of Texas at Dallas, "Advances in source design to extend process to the atomic scale"
9:20-9:40 am	Abbas Semnani, Purdue University, Microwave microplasma: From destructive power- limiting effects to promising high-power tuning applications
9:40-10:00 am	Gary Eden, University of Illinois, "Microcavity plasmas and their macro-impact"
10:00-10:20 am	Jeffrey Hopwood, Tufts University, "Plasma-reconfigurable metamaterials and photonic crystals"
10:20-10:40 am	Sergey Macharet, Purdue University, "Nanoscale spatial and temporal manipulation of plasmas for RF electronics"

Advances in source design to extend process to the atomic scale

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Processing down to the nano-scale requires a refined control of plasma parameters. Novel power delivery techniques provide improvements in process uniformity, chemistry, ion flux, and energy flux to plasma facing materials for nano fabrication. In this talk, the utilization of frequency mixing, phase lock control, and RF pulsing for extension of process conditions needed for nanofabrication are reviewed. Advances in measurement techniques to characterize these systems are also presented.

Frequency mixing has previously demonstrated decoupled control of particle and energy fluxes to materials as well as control of the energy width of ion energy distributions for ions incident on the material surface. Expanding on this, results are presented where frequency mixing is combined with phase lock control by utilizing frequencies that are integer harmonics of one another in order to provide a further level of process relevant control. Along with the well documented Electrical Asymmetry Effect, reduction in discharge potentials and control of higher order moments of the ion energy distribution function can be obtained. [1-3] Control of these higher order distribution moments have demonstrated results on critical etch processes, including independent selectivity control between silicon dioxide and silicon nitride removal in etch processes. [4]

Phase lock control of single frequency operating systems running multiple power supplies also presents a compelling pathway for process control, particularly with regard to process uniformity across large substrates. Using a large area dual coil inductive source, spatial control of ion particle flux is demonstrated across an industrial scale 300mm processing substrate. Ion flux, microwave hairpin probe, and B-dot measurements are presented to provide insight into this uniformity control knob.

Finally, pulsed RF power delivery to leverage extended control over time averaged electron temperature and on-surface particle and energy flux is presented. Power delivery strategies for inpulse process control are presented, as are high resolution diagnostics that provide insight into the evolution of plasma parameters during the transient phase of these pulsed systems.

This work has been supported by multiple funding agencies and companies and the author acknowledges the support of the National Science Foundation, Applied Materials Inc., Samsung Electronics, Tokyo Electron Limited, and MKS Instruments. Much of this work was also carried out under the NSF IUCRC for Lasers and Plasmas in Advanced Manufacturing.

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Microwave Microplasma: From Destructive Power-Limiting Effects to Promising High-Power Tuning Applications

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Microwave gas breakdown and plasma formation can be a destructive effect that limits power handling of high-frequency devices and circuits, especially those with tiny gaps which have been enabled using microfabrication [1,2]. When such plasma is formed, the insulated gaps are transformed into relatively conductive regions which may result in performance degradation or even device failure. On the other hand, recent demonstrations have shown that microwave devices based on low-temperature plasma can offer attractive solutions for high-power reconfigurable systems [3-6]. Specifically, electrical conductivity and consequently plasma resistance can be varied by changing the electron number density through controlling the discharge current. Moreover, there would always be a sheath in contact of plasma with a wall. Changing sheath thickness leads to a variable capacitance which is achieved by either controlling discharge current in dc abnormal glow discharge regime [3] or by changing the excitation frequency of the RF plasma [7]. Hence, plasma devices can be used as high-frequency variable resistors/capacitors, depending on the regime, in resonators [3], limiters [4], attenuators [5] and switches [6], especially for high-power applications where other tuning technologies are suboptimal. In microwave-induced plasma, the incoming wave is employed for plasma ignition and hence, there is no concern about plasma power consumption [4,6]. Also, microwave-driven plasma can operate in the α -discharge regime even at atmospheric pressure and thus requires lower operating voltage and power and has much higher stability and much longer lifetime in comparison with dc plasma [4,6]. In this talk, our recent investigations regarding microwavedriven microplasmas and their destructive effects as well as useful applications are discussed.

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MICROCAVITY PLASMAS AND THEIR MACRO-IMPACT: MICROWAVE PHOTONIC CRYSTALS, VUV/UV LAMPS, AND PLASMACHEMICAL PROCESSING

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Several rapidly-evolving developments in the physics, development, and applications of microcavity plasmas will be described. Three-dimensional, plasma photonic crystals, characterized over the past year, serve as narrowband, tunable notch filters, attenuators and reflectors in the 120-170 GHz spectral region (wavelength of approximately 2 mm). Plasma micro-columns arranged in "logpile" structures yield reconfigurable filters offering Q values up to 2000 and dynamic frequency shifts above 300 MHz. Efficient, high power VUV/UV lamps based on interlaced arrays of microplasmas have also been realized. Offering average powers above 30 W and 5W at 172 nm and 222 nm, respectively, peak powers of several hundred watts, and overall efficiencies (electrical-to-optical) as high as 23%, these flat lamps are currently being applied to materials analysis, disinfection, photochemistry, and driving atomic clocks. The plasmachemical generation of ozone from air or oxygen in arrays of parallel microchannels lined with nanoporous alumina has been commercialized, and ozone systems for the disinfection of drinking water and surfaces, cold storage, wastewater treatment, and aquaculture are now in more than 35 countries. Particular emphasis will be placed on the physics of the "chips" developed for plasmachemical processing of air and carbon dioxide.

Plasma-Reconfigurable Metamaterials and Photonic Crystals

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The field of metamaterials seeks to tailor the electromagnetic properties of an artificial structure through the periodic placement of resonators and dielectrics. These miniature objects act as atoms in the metamaterial with the advantage that the placement and resonance of the 'atoms' can be designed with greater flexibility than offered in nature. Of particular interest is the so-called double negative metamaterial for which both the effective permittivity and permeability are negative. This condition gives rise to a reversal of the wave vector and a negative index of refraction.

Conventional metamaterials are designed and fabricated in a fixed configuration. In this talk, however, the introduction of self-initiated microplasmas within the metamaterial is demonstrated to radically change its basic properties. Plasma allows for rapid material reconfiguration due to its power- and pressure-dependent electron density which provides variable conductivity and permittivity. In cases for which $\omega < \omega_{pe}$, the plasma elements may also provide the well-known negative permittivity.

Metamaterials are known to behave as negative permeability volumes when constructed from arrays of split ring resonators (SRRs). The magnetic resonance of the SRR is responsible for $\mu < 0$ for a narrow range of frequency. If the SRR metamaterial is radiated with microwave energy (1-2 GHz), we show that the resonators can breakdown argon gas (1-260 Torr) and create stable steady-state microplasmas within the material. Using an integrated vector network analyzer, one finds that the appearance of plasma can substantially alter the transmission properties of the material. Examples of plasma-enhanced metamaterials include a $3 \times 3 \times 9$ array of split ring resonators excited by 1.5 GHz microwaves radiated from a horn antenna (at 80 W). In addition to metal SRRs, we also demonstrate that cylindrical all-dielectric resonators of CaTiO₃ can also self-initiate microplasmas by radiative power transfer at 1 GHz.

If the periodic array of objects is non-resonant, but the spacing of the artificial lattice is carefully chosen, one obtains a photonic crystal (PhC). The PhC structure may exhibit a bandgap similar to typical semiconductor materials. We demonstrate that a vacancy in the crystal can create a resonant energy state in the bandgap; under EM wave excitation (43 GHz, 1 W) the field within this vacancy is sufficiently high to cause gas breakdown. The vacancy is then 'healed' by the formation of a steady-state plasma and the transmission of energy through the material is suddenly cut-off. This reconfiguration of the PhC acts as a power limiter in which the material transitions from transparent to opaque on the order of the plasma formation time (200-800 *ns*).

Nanoscale Spatial and Temporal Manipulation of Plasmas for RF Electronics

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In this presentation, we discuss how manipulating plasma on nanoscale could help in developing plasma-based reconfigurable radio-frequency RF electronics. First, we discuss generation of microplasmas (d=10-100 µm cavity) at pressures as low as p~10 mTorr, i.e. at pd<0.001 cm·Torr, with voltage lower than 100 V. In a novel concept [1], electrons are generated at the cathode by field emission (FE) from carbon nanotubes (CNTs) or similar nanoemitters, and ions are independently generated in tunneling field ionization (FI) at atomically sharp tips of protrusions from the anode. The electrons and ions then move ballistically in the opposite directions and create a non-neutral plasma without electron-impact ionization. FI generation of ions makes the proposed concept different from field emission controlled discharges. PIC/MCC modeling shows that, for example, electron densities of 10^{11} - 10^{12} cm⁻³ and ion densities of 10^{12} - 10^{13} cm⁻³ can be produced in a 40 µm gap at 7.5 mTorr with only 60 V. One possible application of such device would be an ultrafast (~1 ns down to 20 ps) switch.

The second concept is using high-repetition-rate nanosecond pulses to sustain plasmas for reconfigurable antennas. The application requires high electron density and conductivity, low power budget, and low electromagnetic noise. We discuss theoretical [2] and experimental results showing that applying a very strong electric field over a short (~nanosecond) period of time periodically, with a repetition rate matching or exceeding the rate of recombination, results in most energetically efficient generation of quasi-steady plasma with reasonably high electron density and conductivity. We present and interpret recent experimental results on plasma behavior between the pulses in argon and nitrogen. After the pulse, the relaxation of electron temperature occurs much faster than electron-ion recombination does. Moreover, as the electron temperature in argon plasma drops, the corresponding drop in the collision frequency results in a temporary increase in the electrical conductivity. This, with a proper time-gating, could enable plasma antennas with a good gain and low (due to the low electron temperature) Johnson-Nyquist noise.

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Tuesday August 28th

11:10-12:10 pm Session T2: Energy applications

(Chair: Sergey Baryshev, Michigan State University)

- 11:10-11:30 am Uwe Kortshagen, University of Minnesota, "Nonthermal plasma synthesis of semiconductor nanocrystals for energy applications and electronic materials"
 11:30-11:50 am Zheng Bo, Zhejiang University, "Plasma-enabled growth of vertical graphenes for energy storage"
- 11:50-12:10 pm Michael Gordon, University of California, Santa Barbara, "Microplasma spray deposition of micro-supercapacitors for on-chip energy storage"

Nonthermal plasma synthesis of semiconductor nanocrystals for energy applications and electronic materials

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Nonthermal plasma synthesis of nanocrystals relies on the plasma's pronounced nonequilibrium environment. Molecular precursors are dissociated by electron impact reactions and the resulting molecular fragments and radicals, many of them charged, nucleate to form clusters and nanocrystals. Energetic surface reactions can heat these initial clusters to temperatures that exceed the gas temperature by hundreds of Kelvin. This enables plasmas to form crystalline nanoparticles of strongly covalently bound or ionically bound materials, many of which require high temperatures for crystallization. This presentation briefly discusses the physics of the plasma synthesis process.

Several years ago, our group showed that nonthermal plasmas are capable of producing high quality silicon crystals. With the proper surface functionalization such silicon nanocrystals exhibit high-efficiency photoluminescence, different from bulk silicon material. The high photoluminescense quantum yields are achieved by careful surface functionalization through grafting alkene ligands to the nanocrystal surfaces. Solar luminescent concentration is a potential application for these highly luminescent nanocrystals, which capitalizes on the indirect bandgap nature of the silicon nanocrystals [1].

The ability of plasmas to produce doped nanocrystals has recently enabled new insights into the electronic transport in nanocrystal films, leading to the development of a new theory for the insulator-to-metal transition (IMT) in directly connected nanocrystal networks [2]. Initially demonstrated in phosphorous-doped silicon nanocrystals, we were unable to definitively cross the IMT. This talk will discuss recent progress based on plasma-synthesized zinc oxide nanocrystals. Through a combination of photonic sintering, atomic layer deposition to terminate surface states, and photodoping, we were able to approach [3] and recently unambiguously cross the IMT. The talk will also discuss applications of this methodology to transparent conductive oxide materials [4].

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Plasma-enabled Growth of Vertical Graphenes for Energy Storage

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Graphene nanosheets arranged perpendicularly to the substrate surface, i.e., vertical graphenes (VGs), have many unique morphological and structural features that can lead to exciting properties and a series of applications including energy storage [1]. This talk will cover (i) parameter control of plasma-enabled growth of VGs, (ii) VGs for high performance supercapacitors, and (iii) High-throughput, scalable fabrication of VGs for a wide range of applications.

Plasma-enhanced chemical vapor deposition enables the growth of VGs on various substrates using gas, liquid, or solid precursors on substrates with different morphologies (from planar to cylindrical and foam) and sizes (from bulk to micro- and nano-sized) [2]. This talk will introduce the recent development on the growth mechanism and the influence of a series of important growth parameters on the morphology of VG patterns.

VGs exhibit unique features such as vertical orientation on the substrate, non-agglomerated threedimensional inter-networked morphology, controlled inter-sheet connectivity, as well as exposed ultra-thin and ultra-long edges, and thus are suitable for supercapacitor application [3]. This talk will present two typical examples. First, VGs were grown on carbon microfiber tows as negative electrodes for wire supercapacitors in a wrap-twist architecture, leading to outstanding electrochemical performance and excellent flexibility [4]. Second, VGs can be grown at the interfaces of current collector and active materials, leading to significantly reduced contact resistance and supercapacitors with ultrahigh power density and excellent rate performance [5].

Our recent molecular dynamic simulation work on the insights into the energy storage mechanism of VG based supercapacitors [6, 7], and a customized linear antenna microwave PECVD system for high-throughput, large-scale fabrication of VGs will be also introduced.

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Microplasma Spray Deposition of Micro-Supercapacitors for On-Chip Energy Storage

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This talk will highlight some of our recent work on combining microplasma jet spray deposition with low-res photolithography to realize metal and mixed-metal oxide-based supercapacitors for on-chip energy storage. A flow-through, micro-hollow cathode plasma jet with remote anode is used to deliver a highly-directed flux of growth species to the substrate. A diverse range of nanostructured materials (e.g., NiO, MnO₂, RuO₂) can be deposited on any surface, e.g., conductors, insulators, plastics, fibers, and photoresist patterns, in a conformal fashion. In the latter case, high surface area, crystalline NiO and β-MnO₂ nanostructures were directly deposited at room temperature on interdigitated electrodes using photoresist masks, followed by lift-off, to create micro-supercapacitors (MSCs) with sizes ranging from $100 \times 100 \text{ } \mu\text{m}^2$ to $>5 \times 5 \text{ } m\text{m}^2$. Typical deposition rates for MnO_2 were 50-150 nm/min using Ar/O_2 jets seeded with $Mn(hfac)_2$ vapor. The resulting MSCs were tested with different gel electrolytes; CV analysis for MnO₂ with PVA/H₃PO₄ electrolyte gave reasonably square hysteresis loops from 0-0.8V. Volumetric and areal capacitances ranged from 25 F/cm³ at 10 mV/s to ~2 F/cm³ at 50 V/s, corresponding to 600 and ~50 μ F/cm², respectively. The effects of deposition conditions, substrate type, and patterning on film morphology, surface coverage, and MSC electrical behavior will be highlighted. If time permits, we will also discuss Trot, Tvib, and e density measurements on the microplasma deposition source using N₂ and H₂ trace gas OES.

Tuesday August 28th

1:50-3:30 pm	Session T3: Plasma-based manufacturing (Chair: Elijah Thimsen, University of Washington-St. Louis)
1:50-2:10 pm	Luis Velasquez-Garcia, Massachusetts Institute of Technology, "Plasma microsystems for sensing and additive manufacturing"
2:10-2:30 pm	Christian Zorman, Case Western Reserve University, "A novel, low temperature inkjet printing technology based on non-thermal plasma conversion of metal-salt based inks"
2:30-2:50 pm	Sang Han, University of New Mexico, "From materials engineering to device applications: Testing our understanding of nature"
2:50-3:10 pm	Timothy Fisher, University of California, Los Angeles, "Roll-to-roll plasma chemical vapor deposition for scalable graphene production"
3:10-3:30 pm	Remi Dussart, University of Orleans, "Cryogenic etching for advanced processing"

Plasma Microsystems for Sensing and Additive Manufacturing

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Following the success of the semiconductor industry, microelectromechanical systems (MEMS) harness device miniaturization and multiplexing to attain better performance, e.g., respond faster, consume less energy, operate at a lower bias voltage, perform complex tasks. In this talk, two different examples of plasma microsystems developed at the Velásquez Group at MIT will be covered, i.e., a retarding potential analyzer (RPA) [1] and a microsputterer [2]. In both cases, miniaturization enabled device performance better than the state of the art.

An RPA measures the ion energy distribution of a plasma, which is an important parameter that influences processes such as surface ablation and film deposition. Miniaturized RPA designs have been proposed to diagnose cold, dense plasmas [3]; however, these sensors lack adequate signal strength because they have only one sub-millimeter aperture. Using Si microfabrication, smaller dimensions and more stringent tolerances can be attained to improve device performance over the state of the art; in addition, batch fabrication makes feasible per-RPA low-cost production. We recently developed a novel MEMS RPA design intended to measure the ion energy distribution of cold, high-density plasmas [1]. The MEMS RPA has electrodes with scaled-down apertures to be able to measure plasmas with Debye length as small as 50 μ m; in addition, multiplexing the apertures while reducing the aperture pitch, and enforcing active inter-electrode aperture alignment [4,5] results in greater signal-to-noise ratio and resolution compared with a conventional RPA –as much as a 200-fold increase in signal strength and less than half the full width at half maximum.

State-of-the-art microelectronic devices have metal interconnects made via thin-film sputtering and photolithographic patterning –an expensive manufacturing process that can only be carried out by the largest companies and research facilities. Sputtering in the microelectronics industry is done in large high-vacuum chambers; however, the need for vacuum to produce ions can be obviated by reducing the dimensions of the plasma. By constraining plasmas to sub-millimeter lengths in one or more dimensions, it is possible to sustain stable plasmas at higher pressure, e.g. atmospheric pressure [6]. Although there are reports of atmospheric-pressure microplasma sources used to deposit metal [7], they don't address imprint focusing to achieve smaller features or propose a solution compatible with continuous printing. We recently reported a novel, continuously fed microplasma metal sputterer that uses ion-drag focusing to direct-write highly conductive lines narrower than the width of the target [2]. Using a 50 μ m wide gold wire as target and argon or dry air as working gas, the microsputterer produces imprints with minimum feature sizes as narrow as 9 μ m, roughness as small as 55 nm, and electrical resistivity as low as 1.1 μ Ω·m.

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A Novel, Low Temperature Inkjet Printing Technology Based on Non-Thermal Plasma Conversion of Metal-Salt Based Inks

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Inkjet printing is a leading additive manufacturing method to produce patterned metal thin films on flexible substrates. The two leading categories of ink are metal nanoparticle inks and metalloorganic decomposition (MOD) inks. The most commonly-used nanoparticle inks consist of colloidal suspensions that employ organic molecules to stabilize the nanoparticles from agglomeration and precipitation. High temperature (~200°C) treatment is used after printing to remove the insulating organics and sinter the nanoparticles [1-4]. The thermal step can limit printing on polymers such as PDMS, paper, and other temperature-sensitive substrates. Moreover the selection of metals is limited by those available in nanoparticle suspensions, with the most popular being Ag. MOD inks are composed of metallo-organic precursors that have a metal core and supporting ligands bonded by coordinate covalent bonds. The supporting ligands are liberated through a thermally induced reaction (typically >200°C) after printing [5], Recently, MOD inks have been reported that can be reacted at lower temperatures (90°C) [6], but their commercial viability is limited by complicated synthesis schemes and short shelf life.

In this talk, we present the development of an ink-jet printing process that uses a particle-free, stabilizer-free ink and a low-temperature plasma treatment step to produce electrically conductive metallic patterns on temperature-sensitive substrates. The inks are comprised of a metal salt, a solvent, and a viscosity modifier tailored to enable printing using a Dimatix DMP3000 series printer. The as-printed structures are exposed to a low-pressure, non-thermal argon plasma which serves to convert the metal salt-based structures to metal structures with conductivities that approach bulk values. To date, we have demonstrated the process for Sn, Pb, Bi, Cu, Pt, Ag, Pd, and Au-based inks. The plasma-treated structures exhibit varying degrees of porosity that can be as high as 70%, making them particularly well suited for use as active elements in microfabricated sensors. The presentation will include details pertaining to the printing process, material characterization and testing of mechanical, chemical and biological sensors fabricated by this printing process.

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(Invited) From Materials Engineering to Device Applications: Testing Our Understanding of Nature

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My research group has worked on materials science and engineering of semiconductors and metals over the years. As a rigorous test of our scientific understanding, we often demonstrate working devices with improved performance. In this presentation, I will focus on two of our latest projects: (1) stressed-directed compositional patterning of compound semiconductors as a means of creating thermo-mechanically triggered rewritable circuitry[1,2] and, if time permits, (2) metal-matrixcomposite (MMC) gridlines on multijunction solar cells for enhanced electromechanical tolerance to substrate fractures[3] and subsequently prolonged mission lifetime of space vehicles. We have recently shown that a patterned elastic stress field can be used to change the near-surface atomic composition in an epitaxial compound semiconductor film. This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner. For the initial proof of concept, an array of Si pillars is pressed against a relaxed Si_{0.8}Ge_{0.2} substrate in a mechanical press, and the entire assembly is heated to high temperatures. This serves to promote Ge diffusion away from the compressed regions, leaving 100% Si-enriched areas. Careful design of nanopillar array and press assembly allow patterning of Si- or Ge-enriched regions, which can ultimately produce thermo-mechanically triggered quantum dot circuits. We are currently extending this work to InGaAs/GaAs systems. For MMC engineering, multi-walled carbon nanotubes (MW-CNTs) are used to reinforce Ag metal gridlines on commercial triple-junction solar cells. We create a Ag-CNT-Ag, layer-by-layer microstructure, where the top Ag layer intercalates through the CNT network and connects with the bottom Ag layer. Upon successful composite integration, commercial triple-junction solar cells show fill factor and efficiency closely matching standard metallization cells. When the cells are intentionally cracked, the composite-reinforced cells exhibit substantially enhanced crack tolerance against degradation compared to the cells with standard metallization. I will provide details of crack tolerance based on device characterization. The composite metal gridlines show strong potential to improve the lifetime of space photovoltaics against stress-induced cell fracture.

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Roll-to-roll Plasma Chemical Vapor Deposition for Scalable Graphene Production

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ABSTRACT

Recently, roll-to-roll (R2R) chemical vapor deposition (CVD) processes have been implemented to produce graphene with substrate feed rates ranging from 5-100 mm/min. However, this production rate must increase much further to make graphene a feasible product in semiconductor and materials manufacturing industries. Plasma sources can be applied to increase the graphene deposition rate, and additionally, to decrease energy input. This work will describe the implementation of a radio frequency plasma R2R CVD process to deposit graphene on copper and nickel foils, and carbon fibers. The growth process takes advantage of the high-temperature plasma gas that produces active carbon species to accelerate growth kinetics. Thus, supplemental heating of the substrate is unnecessary when using plasma, in contrast to thermal CVD systems that consume high energy to heat the substrate and to decompose the carbon gas source. In situ temperature measurements of the substrate in the plasma region confirm the plasma's ability to heat the substrate to the 1200-1500 K range depending on the plasma power. From these real-time temperature measurements, a heat transfer model is developed and validated to determine the substrate temperature profile during R2R graphene growth. The effects of plasma power and web speed on substrate temperature are explored and correlated to graphene quality. The results indicate that graphene growth on Cu foil is most significantly influenced by the in-plasma substrate temperature, whereas growth on Ni foil is controlled by the substrate cooling rate, which is evaluated from the heat transfer model. Furthermore, the plasma environment is characterized by optical emission spectroscopy (OES) to optimize graphene growth and assess the impact of ion bombardment. The OES results suggest that the quality of graphene deposited on Cu foil is enhanced with increased CH emission and decreased emission from O, H, Ar⁺, C₂, and CN. The process characterization techniques aid in controlling and optimizing graphene growth in a largescale setup, and the talk will conclude with a discussion of applications of the resulting materials in energy and biosensing technologies, as well as plans for a new MHz plasma R2R system supplemented by solar heating.

Cryogenic etching for advanced processing

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The cryogenic etching process offers new perspectives for micro- and nano- technologies. It was first introduced thirty years ago by a Japanese team [1]. In its standard mode for silicon deep etching, it consists in using a low pressure plasma mixture of SF₆ and O₂ interacting with a silicon substrate cooled down to a low temperature of typically -100°C. A SiO_xF_y passivation layer forms on vertical sidewalls and prevents lateral etching for high aspect ratio structures. This passivation layer remains stable at low temperature, but mainly desorbs when the wafer is warmed back to ambient temperature [2]. The passivation mechanisms involved in cryoetching have been studied by different in-situ diagnostics [2-4]. Even if many properties have been evidenced, the mechanism for passivation at low temperature remains not fully understood. SiF₄ and SiF_x molecules seem to play an important role in the passivation layer formation. Molecular simulations have been carried out by Tinck et al. and show that sticking probabilities of F, F₂ and SiF_x species do not depend on temperature between -100°C and 25°C [5]. But the residence time of SiF₄ changes significantly as a function of temperature and seems to play a major role in the growth mechanism. Experiments with SiF_4/O_2 plasmas have been performed in order to study the SiO_xF_y growth at low temperature. Cryogenic processes have also been used for porous SiOCH low-K material etching. A proof of principle was obtained using C_4F_8 and SF_6 plasma mixtures [6] and with a higher boiling point organic reagent [7]. This particular process limits the plasma induced damage of the materials. It consists in filling pores at low temperature by physisorption just before the etching step, preventing diffusion of etching species through the pore channels.

Finally, cryogenic processes could be of interest for Atomic Layer Etching minimizing the reactor contamination.

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Tuesday August 28th

4:00-5:40 pm	Session T4: Plasma catalysis (Chair: Souvik Ghosh, University of Minnesota)
4:00-4:20 pm	Chris Hadacre, University of Manchester, "In situ investigation of non-thermal plasma driven catalytic reactions"
4:20-4:40 pm	Angel Barranco, Consejo Superior de Investigaciones Cientificas, "Remote plasma deposition and processing of oxide and metal supported nanostructures for multifunctional applications"
4:40-5:00 pm	Richard van de Sanden, Dutch Institute for Fundamental Energy Research (DIFFER), "Plasma dissociation of CO2 using a vortex stabilized microwave plasma flow reactor: new insights in the plasma chemistry"
5:00-5:20 pm	Yannick Engelmann, University of Antwerp, "Plasma catalysis at the nanoscale: A generic Monte Carlo model for the investigation of the diffusion and the chemical reactions of plasma species at porous catalyst surfaces"
5:20-5:40 pm	David Go, University of Notre Dame, "Developing catalysts for plasma systems: Breaking the scaling of conventional catalysis"

In-situ investigation of non-thermal plasma driven catalytic reactions

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Coupling catalysis with non-thermal plasmas (NTP) shows a great potential for enhancing the catalytic activity of kinetically restricted reactions at low temperatures. While the applications cover a wide range of industrially important processes, development of *in situ* investigations is crucial for further development of this field. Generally, three recurring hypotheses in the literature are often proposed to explain the NTP assisted catalysis, namely, modification or heating of the catalyst or the ability of plasma produced species to open up new reaction pathways. Furthermore, to determine the reaction mechanisms there is a need to identify the active sites, reaction intermediates and probe the intrinsic kinetics of the reaction for a working catalyst under realistic conditions.

To investigate which hypotheses are operating under NTP assisted catalysis, we have coupled for the first time a spatially resolved mass spectrometer system (Spaci-FB) with XAFS for NTP assisted catalytic CH_4 oxidation [1]. Gas composition data was correlated with XAFS spectra along the length of bed. No dramatic structural changes to the catalyst were observed and the NTP selectively heats the Pd nanoparticles, injecting sufficient energy to activate the reaction. However, as this temperature is lower than the necessary temperature to activate the thermal reaction, we postulate that the third hypothesis is true, an alternative reaction pathway is in operation.

Information on the surface changes during the NTP activated catalytic reactions in real time and under real reaction conditions are equally important and this was obtained, for the first time, with a newly developed DRIFTS-MS system [2].

The methodologies developed are state-of-the-art and contribute to determining the combined effect of plasma and catalytic reactions.

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Remote Plasma Deposition and Processing of Oxide and Metal Supported Nanostructures for Multifunctional Applications

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In this work, we describe a general procedure for the fabrication at low or mild temperatures of nanostructured oxide and metal films and nanoparticles [1,2]. The procedure is based in the plasma assisted deposition and processing of films from metalorganic solid precursors. The synthetic methodology combines the deposition and plasma processing of hybrid films using inert plasma gases and the direct deposition of inorganic porous structures using oxygen plasma discharges. Experimental parameters such as substrate position, plasma power, treatment duration, and substrate temperature determine the microstructure and properties of the final nanostructures. However, one of the most interesting features of the developed methodology is its straightforward application to different metal elements by using similar experimental parameters.

Examples of functional materials and devices developed by this methodology will be shown. These examples will include the development of tunable optical filters, the fabrication and testing of porous films for photonic sensing and the fabrication of electrodes and counter-electrodes for excitonic solar cells.

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Plasma dissociation of CO₂ using a vortex stabilized microwave plasma flow reactor: new insights in the plasma chemistry

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In a circular CO_2 neutral society, where the use of dense energy carriers based on carbon will still be needed, the re-use of (air captured) carbon dioxide is required. These dense energy carriers can be utilized to mitigate intermittency of renewable energy sources by providing seasonal storage, as feedstock for the chemical industry to replace fossil based feedstock and as green fuels for long haul and air transport. This re-use will require renewable energy, such as from wind and sun, as the input to be fully CO_2 neutral. The paradigm shift which this entails for the (chemical) industry, largely founded on thermal-catalysis based chemistry, opens the possibility to research and develop novel chemical pathways which have a high selectivity and throughput. The use of electrons, from renewable electricity, or photons, directly from the sun, provide scientific and technological opportunities to develop these pathways for chemical conversion.

In this talk I will discuss the use of a vortex stabilized microwave plasma flow reactor at subatmospheric pressure for the conversion of CO_2 . This source partly dissociates the CO_2 gas into CO and O_2 which can be separated downstream of the plasma source by means of membranes. Initial experiments on the integration of the plasma part with solid oxide membranes for oxygen separation provide novel plasma-surface interactions which will be briefly discussed.

Vortex stabilized microwave plasma flow reactors at sub-atmospheric pressure were intensively investigated in the former Soviet Union [1], with impressive results: dissociation degrees in the range of 10-15% at power efficiencies as high as 70-90%. The ruling hypothesis is that the non-equilibrium aspect of the microwave plasma, with its moderate electron temperature of 1-2 eV and a relatively low gas temperature (< 1000 K) leads to relatively high vibrational temperatures which stimulates the "ladder climbing" process of vibrational states towards the dissociative state. In this way, the high energy efficiencies observed can be explained to a large extend by the non-equilibrium character of the plasma. At DIFFER we have obtained results which were as high as 60%, but were so far unable to reproduce the former results by the Soviet Union research groups.

Detailed studies, including measurements of gas temperature by means of Rayleigh and line broadening mechanism, plasma geometry and electron density measurements by microwave interferometry in combination with simple flow modelling, have revealed new insights into complexity and the plasma chemistry of the vortex stabilized microwave plasma flow reactor. The introduction of a hybrid equilibrium-non-equilibrium description, in which key components are a high gas temperature core surrounded by an ideally quenching vortex flow, in combination with a region where "ladder climbing" might be active, provide an alternative explanation for the high energy efficiencies observed. This explanation might also pave the way to plasma reactor designs which surpass electrochemical approaches for CO_2 re-use by means of their selectivity and throughput.

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Plasma catalysis at the nanoscale: A generic Monte Carlo model for the investigation of the diffusion and the chemical reactions of plasma species at porous catalyst surfaces

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We developed a generic Monte Carlo collision model to investigate the behavior of plasma species in the pores of a catalyst. This model specifically aims at gaining more insight in the plasma catalytic mechanisms and to examine the advantages of plasma catalysis over thermal catalysis. As a specific example of the application of this model, we examine the conversion of CO_2 and H_2 to methanol on a porous copper surface. We implemented both the formate and hydrocarboxyl pathways^[1]. The input for this model is based on the plasma compositions of these H_2/CO_2 systems in a DBD reactor, which have been calculated before in our group. We calculated the adsorption isotherms for H_2/H systems and the surface coverage for a H_2/CO_2 plasma on a non-porous Cu(111) surface and compared the results with the coverage inside a catalyst pore. Additionally, our results show the diffusion of the plasma species in and out of the pores, the average spatial distribution of species in the pores as function of the pore dimensions, the catalytic reactions that occur at the catalyst surface and the role of reactive plasma species in the catalytic reaction processes. We examined the dominant pathways that convert CO_2 , studied the methanol yield and compared the selectivity in plasma catalysis with the selectivity in thermal catalysis.

This model can then be combined with a 0D plasmamodel to examine both the effects that the catalytic reactions have on the plasma and the plasma has on the catalytic reactions^[2].

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Developing catalysts for plasma systems: Breaking the scaling of conventional catalysis

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Plasma catalysis has attracted significant attention in the past decade as it has become clear that synergistic effects between the plasma and a catalyst may enhance performance above what either system can achieve alone. However, many efforts have focused on a heuristic approach to developing plasma catalysis systems, typically utilizing catalysts that have been optimized for thermal catalysis. In this work, we present an analysis that shows that the non-equilibrium state of the plasma with a high population of vibrationally-excited states may overcome scaling limitations that are encountered in conventional thermal catalysis. Using the synthesis of ammonia (NH₃) from nitrogen (N₂) and hydrogen (H₂), we develop a microkinetic model that assesses the impact of vibrationally-excited N₂ on the rate limiting step of nitrogen dissociation at the catalyst [1]. Using measured vibrational temperatures from a dielectric barrier discharge (DBD) reactor, we establish a volcano plot that shows that these excited states shift the optimal monometallic catalyst away from ruthenium and toward cobalt and nickel, and experimental measurements of rates in the DBD reactor support this shift. These results show that plasma catalysis systems are inherently different from thermal catalysis systems, and therefore catalyst design and optimization should be considered differently when developing plasma catalysis reactors.

[1] Mehta P, Barboun P, Herrera F A, Kim J, Rumbach P, Go, D B, Hicks J C, Schneider W F 2018 *Nature Catal.* **1** 269-275

Wednesday August 29th

9:00-10:40 am	Session W1: Plasma diagnostics and modeling (Chair: Eitan Barlaz, University of Illinois)
9:00-9:20 am	Chris Hogan, University of Minnesota, "Utilization of aerosol analytical approaches in the examination of non-thermal plasma synthesis reactors"
9:20-9:40 am	Holger Kersten, University of Kiel, "Spatiotemporal diagnostics and extraction of nanoparticles during particle growth cycles in an acetylene plasma"
9:40-10:00 am	David Pai, Centre National de la Recherche Scientifique, "Plasma-fluid-surface diagnostics of nanosecond pulsed plasmas"
10:00-10:20 am	David Boris, U.S. Naval Research Laboratory, "Precise flux control of ions and radicals using electron beam generated plasmas
10:20-10:40 am	Ken Hara, Texas A&M University, "Multispecies plasma fluid modeling of carbon arc discharge"

Utilization of Aerosol Analytical Approaches in the Examination of Non-Thermal Plasma Synthesis Reactors

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Non-thermal plasma synthesis is a proven approach for the production of functional nanoparticles/nanocrystals.[1] Nonetheless, there remain a number of challenges in (1) developing real-time or online techniques to analyze particle production rates and size distribution functions resulting in plasma synthesis [2], and (2) accurately modeling the growth of nanoparticles in non-equilibrium plasma systems [3]. Conversely, in the related field of aerosol synthesis, online measurement techniques and nanoparticle growth modeling approaches have been developed whose implementation in process monitoring and growth rate prediction is somewhat routine. This talk discusses recent efforts in our group to adapt aerosol technology and aerosol modeling approaches to understand particle formation and growth in plasma synthesis reactors. The presentation is divided into two sections. The first section focuses on the application of differential mobility analysis to determine size distribution function of Si nanocrystals produced via silane decomposition in a non-thermal argon plasma flow reactor operated at < 10 Torr. Differential mobility analysis is technique wherein particles are spatially separated from one another via their mobilities (charge to drag ratios); inversion of differential mobility analyzer data yields the particle size distribution function, expressed as the number concentration per unit mobility diameter or per unit collision cross section. While most differential mobility analyzers function at atmospheric pressure, in our study we have employed a novel differential mobility analyzer which can operating stably in the 1-760 Torr range. Mobility measurements reveal that at the outlet of plasma reactor, both positively and negatively charged Si nanocrystals persist at high concentration. Because particles are in such high concentration and are not unipolarly charged, particle-particle aggregation is rapid in the postplasma region, and we develop approaches to minimize aggregation during sampling and measurement. The second part of this study focuses on calculation of nanocluster growth rates (condensation rates) under non-equilibrium conditions via molecular dynamics trajectory calculations.[4] We show that because clusters may have elevated internal energies in nonequilibrium plasmas (brought about by energetic collisions with electrons and ions), the condensation "sticking" coefficient can be reduced significantly in a plasma, as compared to an equilibrated aerosol.

- [1] Kortshagen U R, Sankaran R M, Pereira R N, et al. *Chemical Reviews* 2016 **116** 11061-11127
- [2] Mangolini L Journal of Physics D: Applied Physics 2017 **50** 373003
- [3] Agarwal P and Girshick S L Plasma Sources Science & Technology 2012 21
- [4] Yang H, Goudeli E and Hogan C J Journal of Chemical Physics 2018 148 164304

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Spatiotemporal Diagnostics and Extraction of Nanoparticles during Particle Growth Cycles in an Acetylene Plasma

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Controlled growth and size-selective collection of carbonaceous nanoparticles (C-NPs) seems to be very promising for many applications in nanomaterial processing. One of the most important challenges concerning particle transport and extraction is the description of the force balance which is coupled with the ion and electron currents onto the dust particle surface in electric fields along the plasma presheath and sheath.

Since gravity for nanoparticles is negligible compared to other forces in the gas discharge the particles can be dispersed and confined in the entire plasma volume. Due to the collection of charge carriers (electrons and ions) onto the growing nanoparticles the plasma parameters are affected in a characteristic manner. For example, typical variations of bias voltage, plasma potential, electron density and other discharge parameters are observed during a growth cycle [1,2,3].

In this work, we propose a simple scheme for the collection of C-NPs generated in a capacitively coupled RF plasma (CCRF) in Ar/C2H2 mixtures by the use of differently biased substrates at different positions within the particle cloud. The oscillating dust cloud, in turn, induces spatial variations of the plasma potential. As important parameters we monitored the self-bias voltage at the powered electrode, gas pressure and the shape of the dust particle cloud by laser light scattering and CCD video imaging.

Collection experiments were carried out at different distances from the RF electrode as well as different times during the growth cycles. The collected particles on Si substrates are examined by scanning electron microscopy (SEM). A correlation of the collection time with the self-bias voltage and SEM results are investigated.

By analyzing the temporal behavior of the measured quantities one can obtain information on the nanoparticle growth and, thus, predict the particle size. Furthermore, the spatial distribution of the discharge parameters and the substrate position determine the nanoparticle deposition as well.

In order to fully comprehend the transport and collection of NPs a multi-fluid approach [4] to investigate the charging process, force balance and transport of the NPs through the plasma sheath between the nanodust forming plasma and the silicon substrate has been developed.

[1] Hinz, A., von Wahl, E., Faupel, F., Strunskus, T., Kersten, H., 2015, J. Phys. D: Appl. Phys., 48, 055203.

- [2] Wegner, T., Hinz, A., Faupel, F., Strunskus, T., Kersten, H., Meichsner, J., 2016, Appl. Phys. Lett., 108, 063108.
- [3] Hundt, M., Sadler, P., Levchenko, I., Wolter, M., Kersten, H., Ostrikov, K., 2011, J. App. Phys., 109, 123305.
- [4] Marvi, Z., Foroutan, G., 2014, Thin Solid Films, 550, 381.

Plasma-fluid-surface diagnostics of nanosecond pulsed plasmas

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The physics and chemistry of atmospheric-pressure materials processing environments relevant to the plasma nanoscience community can be studied in detail using time- and space-resolved diagnostics to probe plasmas, surfaces, and fluid flow. Specifically, we combine optical emission microspectroscopy, in-situ Raman microspectroscopy, particle image velocimetry, and/or Schlieren imaging in coordinated studies of plasma-fluid and plasma-surface interactions.

The first example of combined diagnostics concerns nanosecond repetitively pulsed (NRP) microplasmas generated in air at atmospheric pressure. Arc-like levels of ionization can be achieved, and there is also evidence for a similarly high degree of dissociation. Yet, the gas temperature can return nearly to room temperature between pulses, even when the pulse repetition frequency is high. When a conducting substrate biased to high dc voltage is placed at a distance from the microplasma, a plume-like electrohydrodynamic (EHD) flow is induced between the microplasma and the substrate. Time-resolved measurements of the flow field reveal evidence that charged species generated by the microplasma drift rapidly towards the substrate. Moreover, these ions apparently survive over distances of several centimeters in air at atmospheric pressure. The plume can be both thermal and EHD in character, and the relative importance of these properties can be adjusted in a straightforward fashion.

The second example concerns NRP discharges in atmospheric air generated along surfaces consisting of layers of thin and/or thick films deposited on silicon substrates. A surface dielectric barrier discharge geometry is employed, but instead of using bulk dielectric materials, the barrier includes structures involving semiconductors, films, and nanomaterials. This change alone enables the plasma to propagate as a uniform front rather than as streamer-like filaments, which is difficult to achieve when applying voltage pulses with a positive polarity. This form of breakdown is also highly reproducible and stable from pulse to pulse.

Precise Flux Control of Ions and Radicals using Electron Beam Generated Plasmas

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Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. In addition to the need for low damage, the complex device structures proposed for next generation nano-electronics will require control over radical to ion ratio as well. Electron beam-generated plasmas are generally characterized by high charged particle densities (10¹⁰- 10¹² cm⁻³), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. These characteristics provide the ability to precisely control the ion energy at adjacent surfaces and importantly, also the ability to control the ratio of ion to radical fluxes. In this work, we demonstrate this precise level of control using a variety of plasma characterization techniques and demonstrate how the applicability of these features to the processing of select materials systems. Specifically, we will discuss the processing of monolayer material systems such as graphene and MoS₂, where the material properties can be tuned without unwanted erosion or damage. Also SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds is examined with particular attention paid to the etch rates, selectivity (vs. carbon films, Si and SiO₂), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. Lastly, we address the use of electron beam generated plasmas for native oxide removal and subsequent passivation of surfaces. The processing results are compared with plasma diagnostics to gain a better understanding of the process requirements. This work is partially supported by the Naval Research Laboratory base program.

Multispecies plasma fluid modeling of carbon arc discharge

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Arc discharges in atmospheric pressure are used for nanomaterial syntheses. Investigation of the microscopic physics of nanomaterial growth and formation requires a good understanding of the physics of plasma flows in a macroscopic scale [1,2]. Chemical and kinetic processes of nanostructures can be affected by the spatiotemporal evolution of plasma properties, including the electric field, plasma density, gas density, and electron and heavy species temperature. However, it still remains a challenge to fully understand such arc discharge plasma due to its multiscale and multiphysics nature. First, the chemical reactions that occur in the plasma discharge range from atomic scale (e.g., atoms and molecules) to nanoparticles and micrometer-size particles. Second, the plasma physics is complex due to its nonlinear coupling between volumetric reactions, radiation, plasma sheaths, and electrodes (e.g., heat, evaporation, deposition, etc.). Therefore, a plasma model that self-consistently accounts for the complex phenomena is needed to understand the arc discharge plasmas and the processes toward nanomaterial synthesis.

Carbon arc plasma in atmospheric pressure operates as follows. Ablation of the anode material (e.g., graphite) occurs as the anode surface is heated up mainly by the electron current. The carbon species are supplied into the arc discharge and become ionized to conduct current between the electrodes, since the ionization energy of carbon is smaller compared to the inert background gas, such as helium. Carbon ions and neutral atoms approach the cathode, and deposition occurs on the cathode surface. The area of cathode deposition varies as the arc operation changes. The kinetic energy of carbon ions that is dependent on the cathode sheath voltage balances with thermionic electron emission, heat conduction, and other processes such as radiative heat flux.

We developed a one-dimensional (1D) plasma fluid model, in which monatomic carbon, dicarbon, and tricarbon are taken into account. Ground state, electronically excited state, and ions are considered for heavy species. Conservation of mass and momentum are solved for individual species. Conservation of energy is solved for heavy species and electrons. It is shown that the elastic collisions between heavy species and electron-ion Coulomb collisions are large enough so that the bulk velocities of heavy species are in equilibrium except for the near-electrode sheath region. The radial transport is neglected in the model and a quasi-1D approach is used where a plasma core radius is assumed. The smaller the core radius is, the larger the current density becomes. The numerical results predict the enhancement of anode ablation rate when the anode diameter becomes smaller, which is consistent with previous experiments [3].

[1] Iijima S 1991 Nature **354** 56

[2] Vekselman V, Khrabry A, Kaganovich I, Stratton B, Selinsky R and Raitses Y 2018 Plasma Sources Sci. Technol. **27** 025008

[3] Fetterman A, Raitses Y and Keidar M 2008 Carbon 46 1322

Wednesday August 29th

11:10-12:10 pm Session W2: Multicomponent, multidimensional, multifunctional materials (Chair: Yannick Engleman, University of Antwerp)		
11:10-11:30 am	Ana Borras, Consejo Superior de Investigaciones Cientificas, "Advances in the development of functional 1D and 3D nanostructures"	
11:30-11:50 am	Mohamed Chaker, Institut national de la recherche scientifique-Énergie, Matériaux et Télécommunications,"Metal-insulator transition materials synthesized by pulsed laser deposition"	
11:50-12:10 pm	Elijah Thimsen, Washington University in St. Louis, "Materials with nonequilibrium atomic configuration produced by low temperature plasma"	

Advances in the development of functional 1D and 3D nanostructures

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1D nanomaterials like nanowires (NWs), nanotubes (NTs), nanorods (NRs) and nanofibers (NFs) are ubiquitous elements offering outstanding shape-dependent properties of use in many fields and products. These materials can be made in an endless variety and used to create complex and tuneable nanoscale objects with as designed functionalities. A current trend is to use NWs and NTs as building units for hierarchical and 3D architectures owing to their attractive properties such as inherent high surface area and direct charge/light carrier transport pathway in trunks and branches.[1] In this communication we will show the latest advances in the exploitation of plasma assisted fabrication of 1D and 3D nanowires and nanotubes. Among the striking application of these nanomaterials, we will present the development of omniphobic surfaces with capability to repel polar[2] and non-polar liquids and delay the freezing of water up to several hours; the application of the method to the formation of 3D semitransparent nanoelectrodes and one-wire perovskite solar cells and, finally, our preliminary results showing the potential of core@(multi)shell nanotubes in photoelectrocatalysis.

[1] Filippin, A., Sanchez-Valencia, J., Borras, A. et al. 2017 Nanoscale, 9, 8133/8

[2] Macias-Montero, M., Lopez-Santos, M., Borras, A. et al. 2017 Langmuir, 33, 6449/7

Metal-insulator transition materials synthesized by Pulsed Laser Deposition

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This presentation will overview our most recent achievements on the synthesis of metal-insulator transition (IMT) materials using the Pulsed Laser Deposition (PLD) technique that allows an excellent control of material stoichiometry and density as well as of the material nanostructure. We will focus on vanadium dioxide (VO₂) and samarium nickelate (SmNiO₃) that are particularly interesting IMT materials as their electrical resistivity as well as their infrared and terahertz (THz) reflectivity undergo significant changes across the thermo/photo-induced IMT, at transition temperatures $T_{IMT} \approx 68^{\circ}$ C for VO₂ and 110-133°C for SmNiO₃. In a series of investigations, our group has examined the physics governing the IMT of VO₂ and SmNiO₃ thin films and has explored new application opportunities including uncooled bolometers, and smart radiator devices for space applications.

The IMT properties of VO₂, namely the transition temperature, the sharpness of the transition, the amplitude of the properties modification and the related hysteresis width, can efficiently be tailored through doping with an appropriate concentration of donors and/or acceptors and through a proper control of crystallinity, morphology and stoichiometry of the VO₂ films. In order to fully exploit this material for IR and THz applications, we first studied the effect on the IMT characteristics of both W-doping and oxygen pressure (P_{O2}) during the growth of VO₂ thin films synthesized by pulsed laser deposition. In this way, we were able to develop a new type of energy-efficient, light-weight, and high-performance variable-emittance coatings based on VO₂ thin films (smart radiator device) that can passively control the internal temperature of nanosatellites. Second, we propose a $W_x V_{1-x} O_2$ multilayer structure (MLS), with a bottom-up gradient of tungsten content, which displays a combination of excellent electrical characteristics and presents a great potential for the development of highly responsive sensing layers in energy-efficient uncooled microbolometer. Finally, we demonstrate that the control of P_{O2} during the synthesis of VO₂ films is one of the key parameter to tailor their IMT features for specific applications in the THz range, such as sensor-type and memory devices.

We also summarize our recent studies on the synthesis of SmNiO₃ thin films by PLD. We examine the influence of epitaxial strain on the structure, electronic transport and optical properties of epitaxial SmNiO₃ thin films grown on LaAlO₃ (LAO, compressive) and SrTiO₃ (STO, tensile). As the strain changes from tensile to compressive, the transition temperature of the SmNiO₃ samples shifts to lower temperatures. The optical conductivity reveals the strong dependence of the Drude spectral weight on the strain relaxation.

Materials with Nonequilibrium Atomic Configuration Produced by Low Temperature Plasma

Elijah Thimsen

Washington University in Saint Louis

Low temperature plasma (LTP) is allowed by the laws of thermodynamics to increase the free energy of materials that come into contact with the partially ionized gas. That feature is alluring because it grants LTP the ability to generate highly nonequilibrium states of materials. Despite that alluring feature, clear examples are scarce in the published literature of processes that result in products that have a higher specific free energy compared to the feedstock. In this presentation, I will present our recent work focused on promoting endergonic transformations of materials using LTP. Specifically, I will discuss our work focused on transforming the atomic structure of metal nanomaterials and also our work on activating carbon fiber reinforced polymer composites.