A PROGRAM IN LOW TEMPERATURE PLASMA SCIENCE AND ENGINEERING:

A Briefing to the NSF Engineering Directorate

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29 January 2015

MEMBERS OF THE BRIEFING TEAM

- Dr. Igor D. Kaganovich, Princeton Plasma Physics Lab
- Prof. Michael Keidar, George Washington University
- Prof. Michael Kong, Old Dominion University
- Prof. Mounir Laroussi, Old Dominion University
- Prof. Mark J. Kushner, University of Michigan
- Prof. Jose L. Lopez, Seton Hall University
- Prof. Sergey Macheret, Purdue University
- Prof. Selma Mededovic Thagard, Clarkson University
- Prof. Gottlieb S. Oehrlein, University of Maryland
- Dr. Daphne Pappas, EP Technologies LLC
- Prof. Mohan Sankaran, Case Western Reserve University

THE LOW TEMPERATURE PLASMA WHITE PAPER

- **The white paper *"A Low Temperature Plasma Science and Engineering Program: Discovery Science for Societal Benefit"* made compelling case that low temperature plasmas (LTPs):**
  - **Represent a vibrant and vital area of science and engineering essential to the quality of life and economic well being.**
  - **Are perhaps unique as a discipline in their intellectual diversity and interdisciplinary breadth.**
  - **Harbor extreme science challenges that quickly result in technologies that provide societal benefit.**
  - **Are vastly under supported in the US compared to investments made by essentially all high-technology based countries.**
- **We proposed a program in Low Temperature Plasma Science and Engineering (LTPSE) in the NSF Engineering Directorate.**
- **The LTPSE white paper is the consensus of 152 Co-Submitters from 69 US institutions and every field of engineering.**

NSF PROGRAM IN LTPSE

- **Request by Dr. Khargonekar**
  - **What are the fundamental research challenges in LTPSE?**
  - **Share a vision of a future enabled by NSF funding by addressing solving these research challenges.**
- **This briefing is our response.**

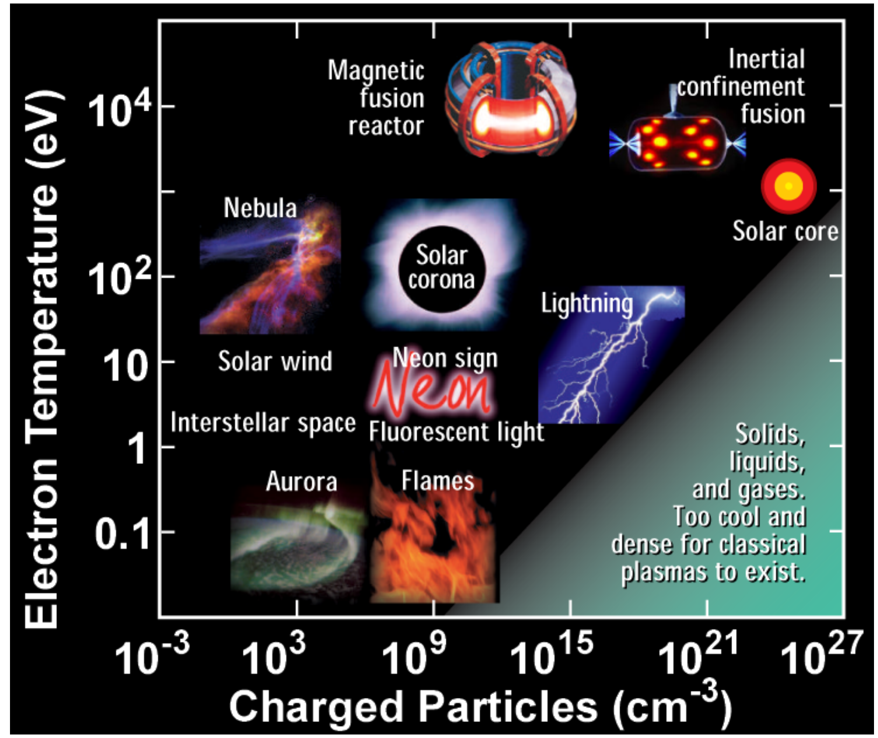
AGENDA

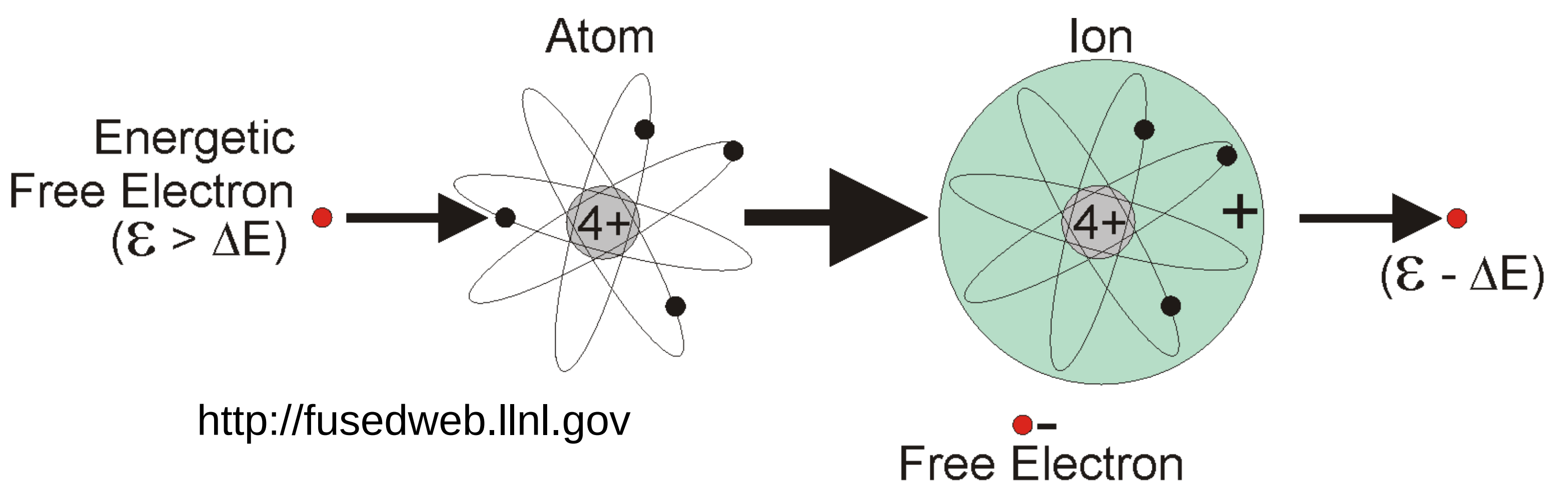
- Overview of Low Temperature Plasmas (LTPs) and their societal benefit.
- National assessments of LTPSE
- The extreme diversity of LTPs and the overarching fundamental research challenge
- Fundamental research challenges across this diversity
- The international perspective
- A vision of the future.

LOW TEMPERATURE PLASMAS AND THEIR SOCIETAL BENEFIT

LOW TEMPERATURE PLASMAS

- **Plasmas (ionized gases), the "fourth state of matter, account for > 99.9% of the mass of the universe (dark matter aside).**
- **An energetic free electron collides with an atom, creating a positive ion and another free electron**

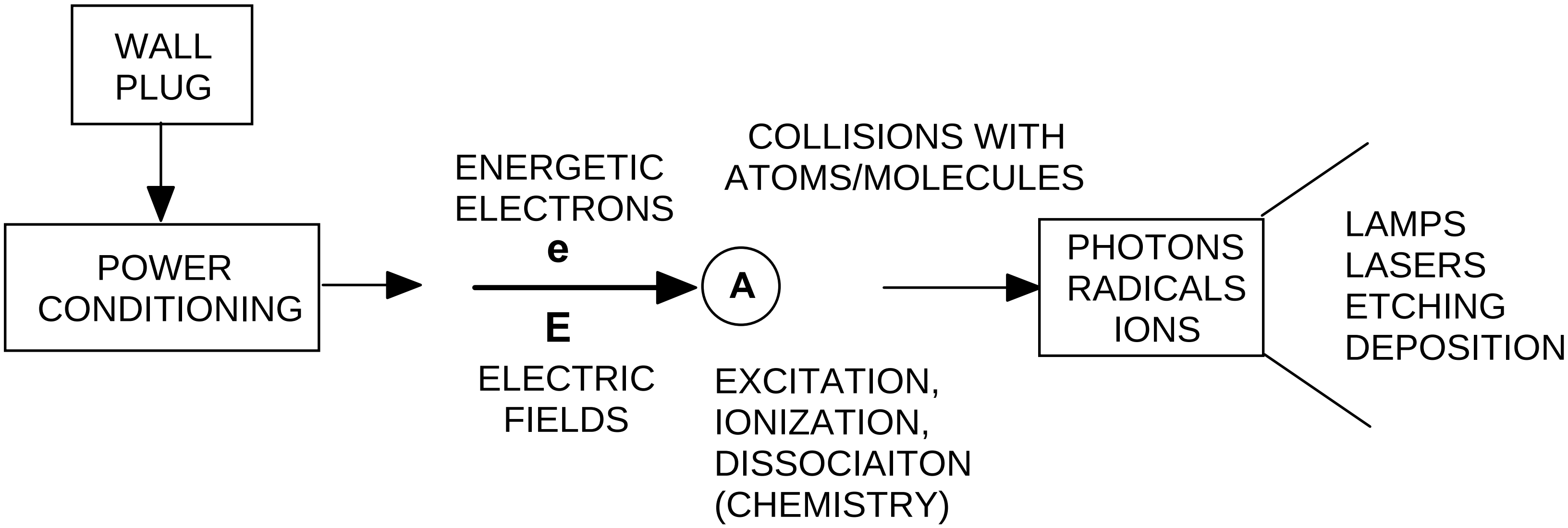




http://fusedweb.llnl.gov

COLLISIONAL LOW TEMPERATURE PLASMAS

- **Low temperature plasmas are a power transfer medium.**



- **Electrons transfer power from the "wall plug" to internal modes of atoms / molecules to "make a product", very much like combustion.**
- **The electrons are "hot" (several eV to 10 eV) while the gas and ions are cool, creating "non-equilibrium" plasmas.**

PLASMAS CREATE REACTIVE SPECIES

$$e + Xe \rightarrow Xe^{*} + e$$

$$Xe^{*} \rightarrow Xe + h\nu$$

$$e + CH_4 \rightarrow CH_3 + H + e$$

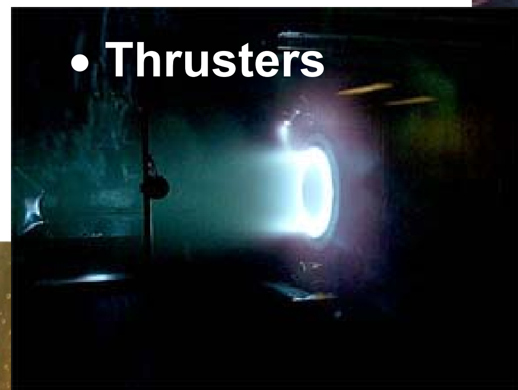
$$CH_3 \rightarrow surface \rightarrow a:CH$$

$$(diamond-like-carbon)$$

- **Electron impact collisions on atoms and molecules produce reactive species.**
- **These species emit photons, modify surfaces, create new materials, provide thrust…**
- **By virtue of creating high quality reactivity at ambient temperatures, LTPs have been leveraged to create a wide range of society benefiting technologies.**

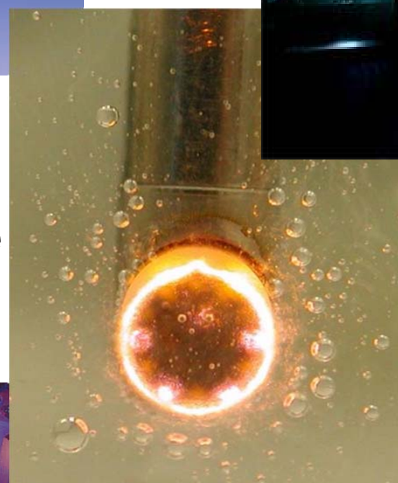
SOCIETAL BENEFIT – SCIENCE BASED TECHNOLOGIES

• Jet Engine Spray Coatings

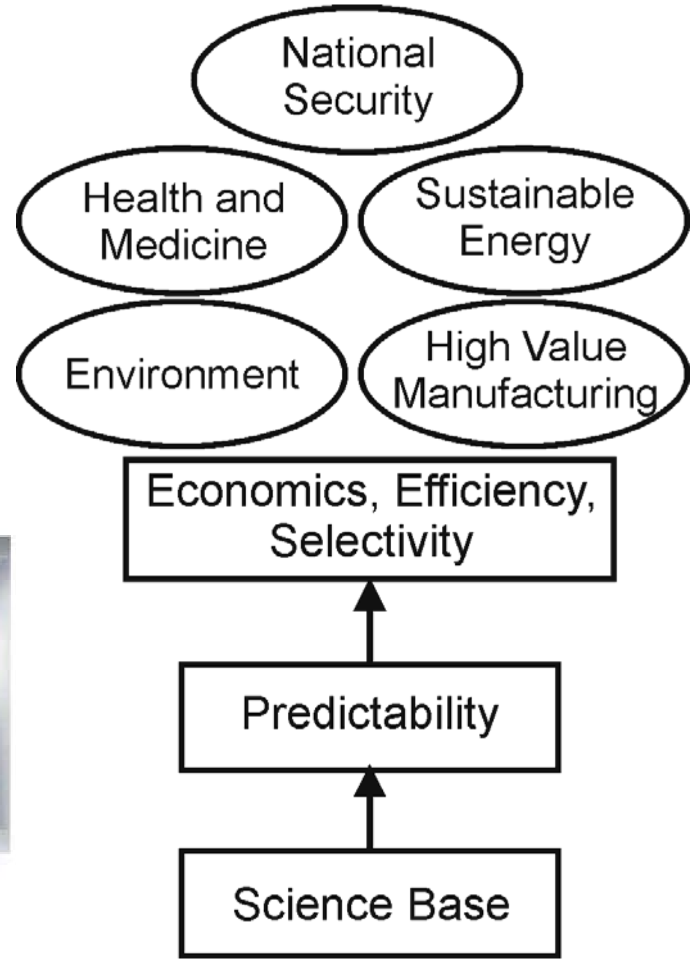


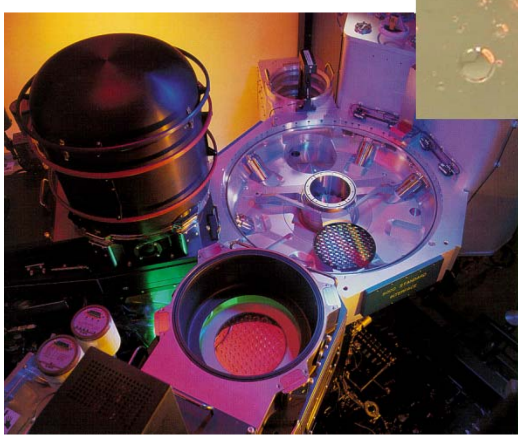
• Thrusters

• Lighting



• Healthcare

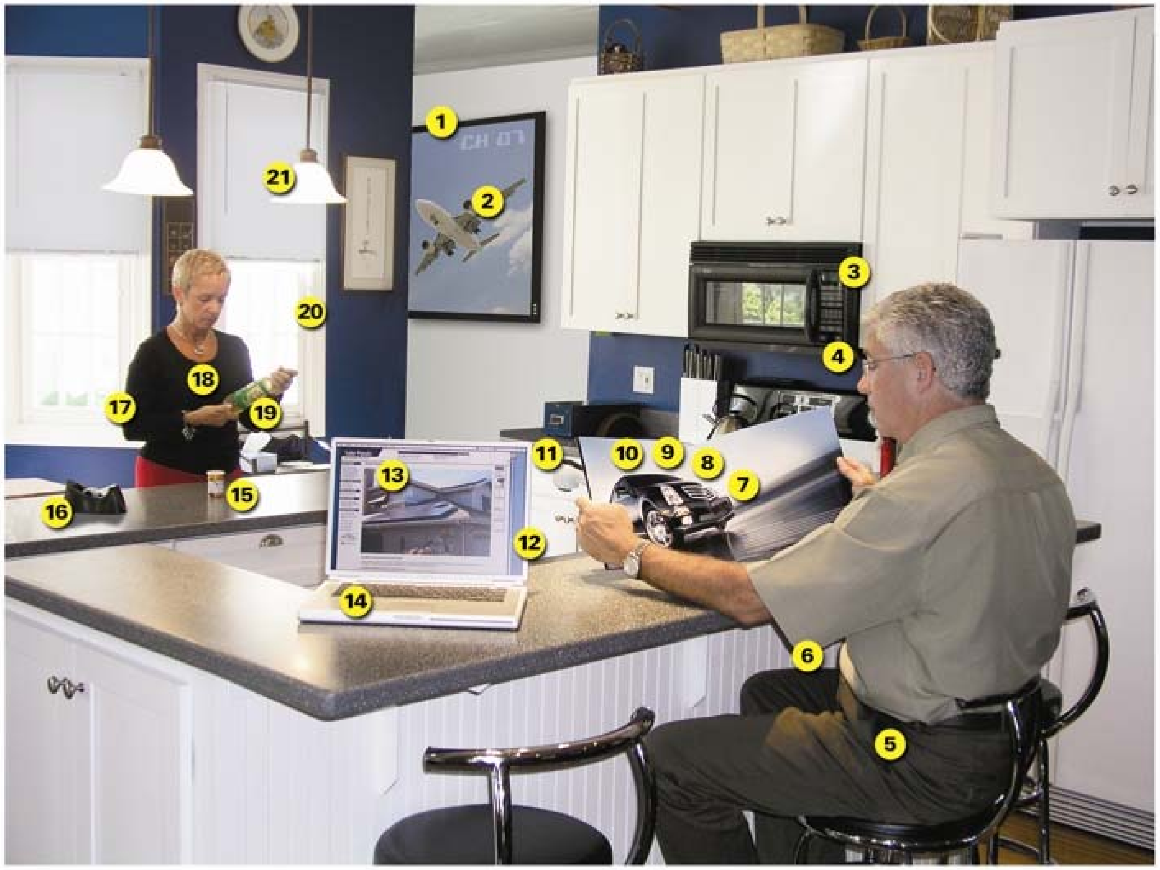




• Microelectronics Processing

• Displays

ROBUST SCIENCE, SOCIETAL BENEFIT



01—Plasma TV
02—Plasma-coated jet turbine blades
03—Plasma-manufactured LEDs in panel
04—Diamondlike plasma CVD eyeglass coating
05—Plasma ion-implanted artificial hip
06—Plasma laser-cut cloth
07—Plasma HID headlamps
08—Plasma-produced H_2 in fuel cell
09—Plasma-aided combustion
10—Plasma muffler
11—Plasma ozone water purification
12—Plasma-deposited LCD screen
13—Plasma-deposited silicon for solar cells
14—Plasma-processed microelectronics
15—Plasma-sterilization in pharmaceutical production
16—Plasma-treated polymers
17—Plasma-treated textiles
18—Plasma-treated heart stent
19—Plasma-deposited diffusion barriers for containers
20—Plasma-sputtered window glazing
21—Compact fluorescent plasma lamp

THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine

- **Low Temperature Plasma Science and Technology has a history and future of robust, interdisciplinary science challenges whose resolution provides immediate and long term societal benefit.**

Ref: Adapted from "Plasma Science: Advancing Knowledge in the National Interest", US National Research Council, 2007.

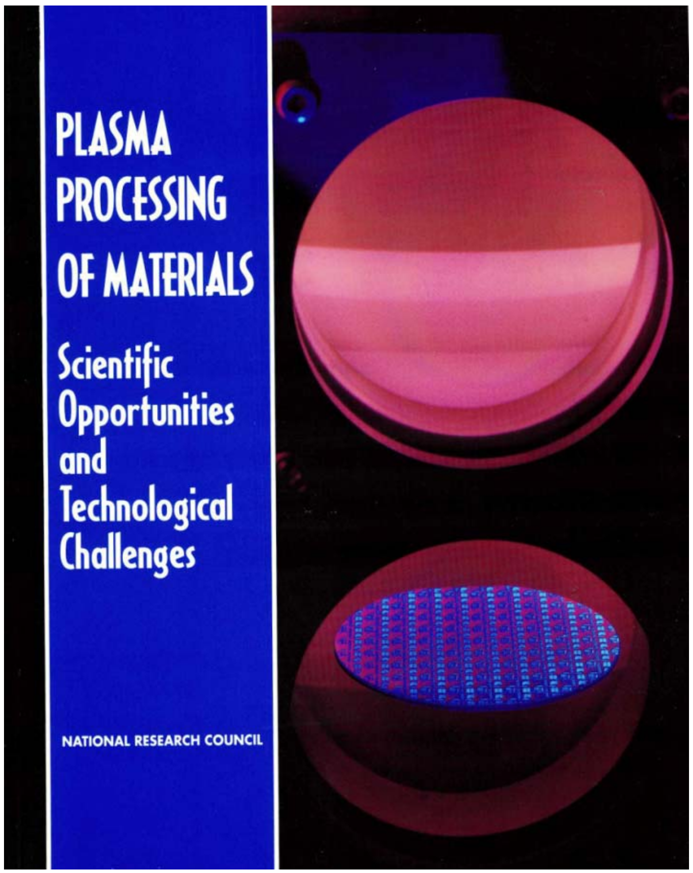
THE WORLD WITH LOW TEMPERATURE PLASMAS

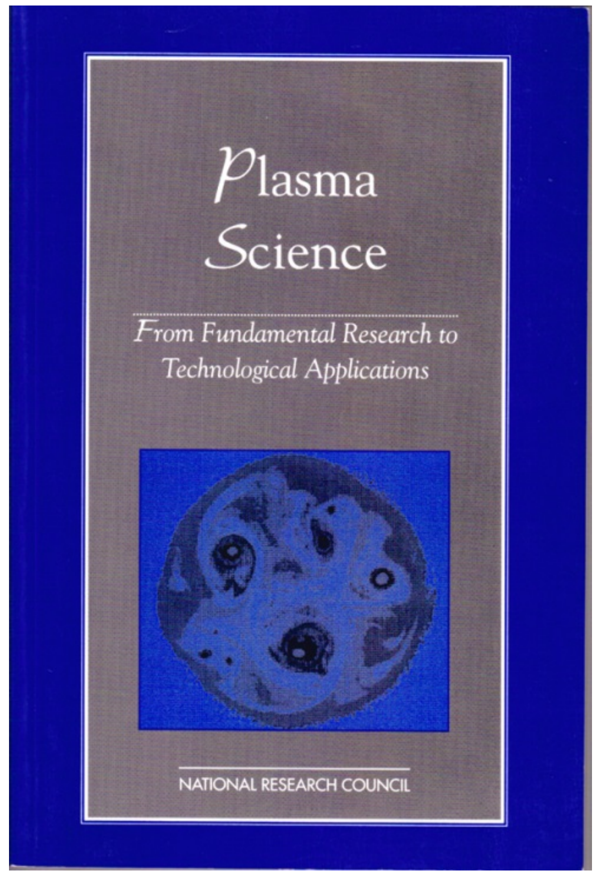
- **Modern society would be a lot less modern in the absence of LTPs. Technologies requiring or enabled by LTPs...**
  - **The internet, laptops, cell phones, massively parallel computing.**
  - **High performance jet engines (modern aviation industry)**
  - **High efficiency lighting, lasers, LEDs, LCDs, flat panel displays**
  - **Long-lived artificial joints, heart stents, biocompatible implants**
  - **High performance optics, coated eyeglasses, CCDs (no LTPs means no Hubble Telescope)**
  - **Solar-cell farms**
  - **Glass enclosed skyscrapers (enabled by heat reflecting coatings)**
  - **Particulate, metal, SO_x/NO_x removal in smokestacks**
  - **Municipal scale AOP and ozone water purification**
  - **Saran wrap (!) and nearly all hydrophilic plastics.**
  - **Nanotechnology**
  - **Inexpensive (and flexible coatings of) artificial diamonds for industry and optics.**
  - **Environmental diagnostics (e.g., ICP-MS)**

NATIONAL ASSESSMENTS OF LTPSE

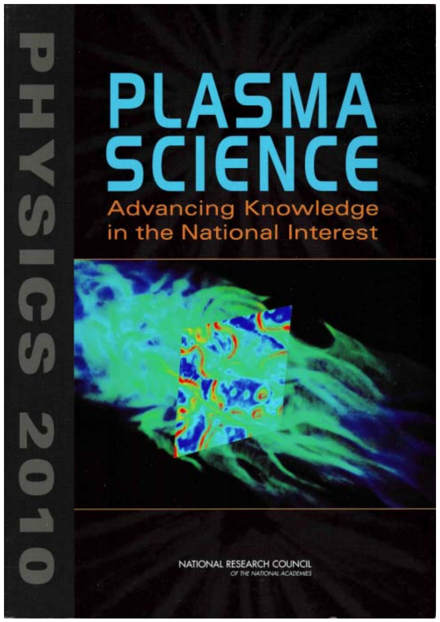
1991 NRC REPORT: “PLASMA PROCESSING OF MATERIALS”

1995 NRC REPORT: "PLASMA SCIENCE: FROM FUNDAMENTAL RESEARCH TO TECHNOLOGICAL APPLICATIONS"





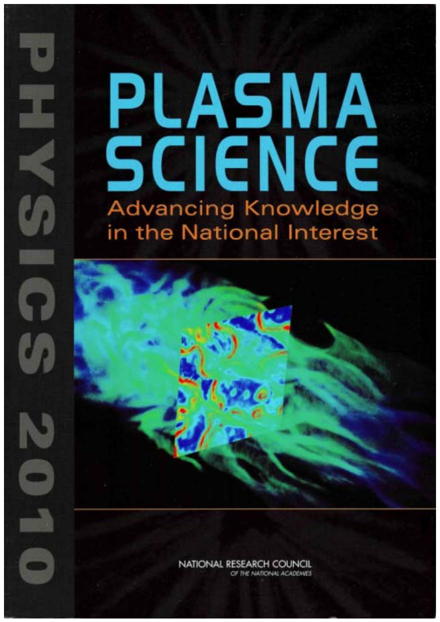
2007 NRC REPORT: PLASMA SCIENCE: ADVANCING KNOWLEDGE IN THE NATIONAL INTEREST



- **Conclusion: [LTPSE] is an area that makes indispensable contributions to the nation's economic strength, is vital to national security, and is very much a part of everyday life. It is a highly interdisciplinary, intellectually diverse area with a rich set of scientific challenges.**
- **Conclusion: The science and technology benefits from [LTPSE], and the health of the field itself, depend on strong connections both with the applications—biology, environment, microelectronics, medicine, etc.—and with several closely allied sciences, notably atomic and molecular physics, chemistry, and materials science.**

Ref: Adapted from "Plasma Science: Advancing Knowledge in the National Interest", NRC, 2007.

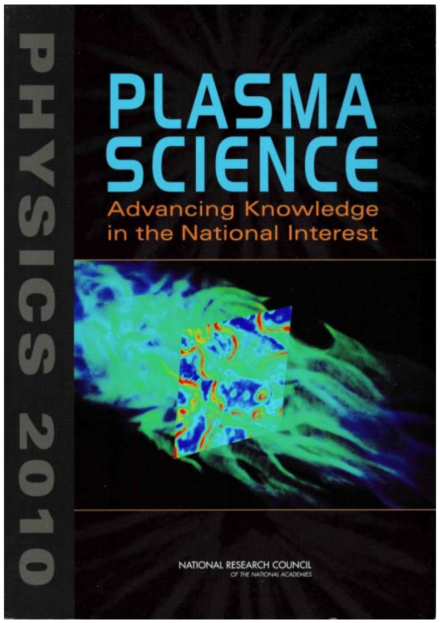
2007 NRC REPORT: PLASMA SCIENCE: ADVANCING KNOWLEDGE IN THE NATIONAL INTEREST



- **Conclusion: There is no dedicated support within the federal government for research in [LTPSE]. The field has no steward because of its interdisciplinary nature and its connection to applications....The basic research, conducted...at U.S. universities, and...potential future applications underpinned by it...are at substantial risk of collapse. The field is in danger of becoming subcritical and disappearing as a research discipline in the United States.**

Ref: Adapted from "Plasma Science: Advancing Knowledge in the National Interest", NRC, 2007.

2007 NRC REPORT: PLASMA SCIENCE: ADVANCING KNOWLEDGE IN THE NATIONAL INTEREST

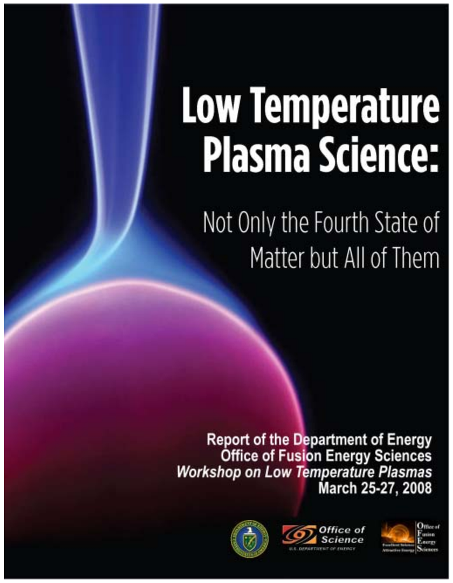


- **Recommendation: To fully address the scientific opportunities and the intellectual challenges within [LTPSE] and to optimally meet economic and national security goals, one federal agency should assume lead responsibility for the health and vitality of this subfield by coordinating an explicitly funded, interagency effort. This coordinating office could appropriately reside within the Department of Energy's Office of Science.**

Ref: Adapted from "Plasma Science: Advancing Knowledge in the National Interest", NRC, 2007.

DOE LOW TEMPERATURE PLASMA WORKSHOP

- **To implement recommendations of the Decadal Study Plasma 2010, a workshop was held in March 2008 to identify scientific challenges in LTPS for next decade.**
- **Charge for Workshop**
  - **Summarize research status.**
  - **Outstanding major scientific questions and potential applications.**
  - **Basic research needed to address questions - prioritized roadmap for an initiative in LTPs.**
- **http://www.science.doe.gov/ofes/ programdocuments.shtml**

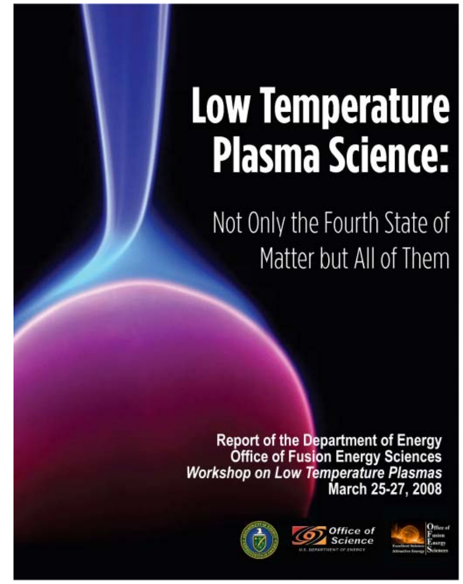


- ***"Low Temperature Plasma Science: Not only the Fourth State of Matter but All of Them"* (September 2008)**

PRIORITIZED RESEARCH OPPORTUNITIES

- ***1: Predictive Control of Plasma Kinetics :*** **Predictably controlling *f(v,r,t)* through fundamental understanding of energy coupling into LTPs underlies our ability to advance the field and utilize LTPs for societal benefit.**

- ***2: Collective Behavior and Non-linear Transport:*** **LTPs produce unique collective behavior and nonlinear transport in part due to broad array of positive and negative ions (and electrons).**

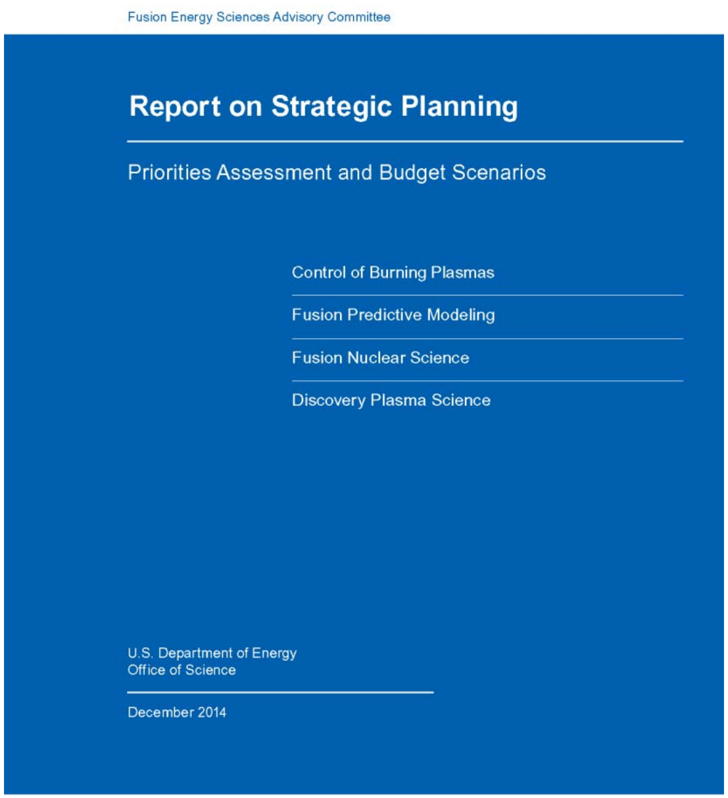


- ***"Low Temperature Plasma Science: Not only the Fourth State of Matter but All of Them"* (Sept 2008)**

- ***3: Interfaces and Multiple Phases in Plasmas:*** **LTPs uniquely interact with multiple phases: solid, liquid and gas. Generating and optimizing plasmas in contact with multiple phases based on fundamental science is now beyond our abilities.**

- ***Cross-cutting Priority: Diagnostics, Modeling, Fundamental Data*** **Advances in all areas require a state-of-the-art foundation in diagnostics and modeling supported by robust knowledge bases of fundamental data.**

CURRENT STATUS OF DOE-OFES LTP PROGRAM


Fusion Energy Sciences Advisory Committee

Report on Strategic Planning

Priorities Assessment and Budget Scenarios

Control of Burning Plasmas
Fusion Predictive Modeling
Fusion Nuclear Science
Discovery Plasma Science

U.S. Department of Energy
Office of Science

December 2014

- **Support for plasmas in DOE comes dominantly from the Office of Fusion Energy Science (OFES).**
- **OFES has supported LTPs through the *Plasma Science Center for Plasma Kinetics* which ends this year.**
- **However, the stated priority of DOE-OFES program is fusion science.**
- **There is no known plan for continuing to support LTPs.**
- **OFES Report on Strategic Planning (December 2014) *essentially has no mention of and makes no recommendation to support LTPs*.**
- **Only support available is through the NSF/DOE Plasma Science Partnership.**

THE DIVERSITY AND DYNAMISM OF LTPs

LTPSE – RAPIDLY EVOLVING

- The LTPSE field is by its nature rapidly evolving. Topics dominating LTPSE conferences now were minor topics 5 years ago.
  - At the 2013 Gaseous Electronics Conference, about 50% of the presentations were on plasmas at high pressure, in contact with liquids or in liquids.
  - At the 2000 GEC, perhaps only 10% were on these topics.
- Although the underlying fundamental science issues are longer lived, the context of investigating fundamentals are driven by applications, which do quickly evolve.
- The applications directly benefit from those science advances.
  - This is intrinsically a good thing… a victory!
  - Quickly transitioning fundamental science advances to society benefiting technologies confirms quality of the science.
  - The often unexpected outcomes of the rapid application of the science feeds back to investigating fundamentals.

LTPSE – EXTREMELY DIVERSE

- <u>Current research in LTPSE spans:</u>
- ***10^9 in pressure*: < 1 mTorr for plasma etching to liquid densities in plasma medicine.**
- ***10^9 in spatial scale*: < 1 nm for plasma penetration into nanoporous materials to meters for flat panel fabrication.**
- ***10^{12} in time*: ps for formation of space charge layers in streamers to seconds (minutes?) for stability of atm pressure arcs.**
- **Hundreds (thousands?) of chemical systems: Rare gases for displays to $Ar/C_4F_8/O_2/CO_2/N_2$ for plasma etching and cytoplasm in cancer treatment.**
- **Bounding surfaces – from silicon to living tissue.**
- **This dynamic range of scientific investigation (and applications) in a single discipline is perhaps unique across the physical sciences.**

PLASMA ROADMAP 2012

REVIEW ARTICLE

J. Phys. D: Appl. Phys. **45** (2012) 253001 (37pp)

The 2012 Plasma Roadmap

Seiji Samukawa, Masaru Hori, Shahid Rauf, Kunihide Tachibana, Peter Bruggeman, Gerrit Kroesen, J Christopher Whitehead, Anthony B Murphy, Alexander F Gutsol, Svetlana Starikovskaia, Uwe Kortshagen, Jean-Pierre Boeuf, Timothy J Sommerer, Mark J Kushner, Uwe Czarnetzki and Nigel Mason

Plasma-etching processes for future nanoscale devices

Plasma deposition processes for ultimate functional devices

Very large area plasma processing

Microplasmas

Plasmas in and in contact with liquids: a retrospective and an outlook

Plasma medicine

Plasma catalysis

Thermal plasma applications, including welding, cutting and spraying

Plasma for environmental applications

Plasma-assisted ignition and combustion

‘Nanodusty’ plasmas: nanoparticle formation in chemically reactive plasmas

Plasma thrusters

Plasma lighting

Plasma modelling at a crossroad

Plasma diagnostics

Atomic and molecular data for plasma physics—challenges and opportunities

- **The JPD Plasma Roadmap 2012 set out highest priority areas in low temperature plasmas.**
- **Exceedingly diverse set of topics, each with fundamental research challenges motivated by applications.**

FUNDAMENTAL RESEARCH CHALLENGES

FUNDAMENTAL RESEARCH AND LTPs

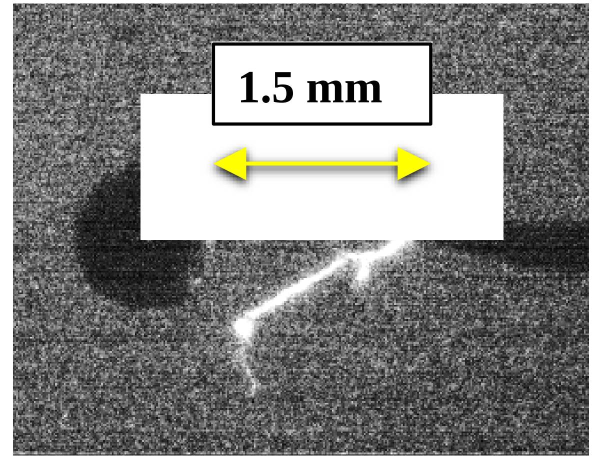
- In many fields of science and technology, a single or small number of research issues dominate the field.
  - Fluid mechanics – turbulence
  - Fusion – reconnection
  - Cell biology – gene expression
  - Computer Science – big data
  - AMO Physics – Bose-Einstein condensates
- Dominating research issues sometimes persist for decades.
- The extremely large parameter space, intellectual diversity, motivating applications and rapidly evolving priorities of LTPs makes it difficult to define a single dominating fundamental research challenge.
- *The compelling strength of LTPs is its intellectual diversity, intrinsic interdisciplinary nature and its many fundamental research issues.*

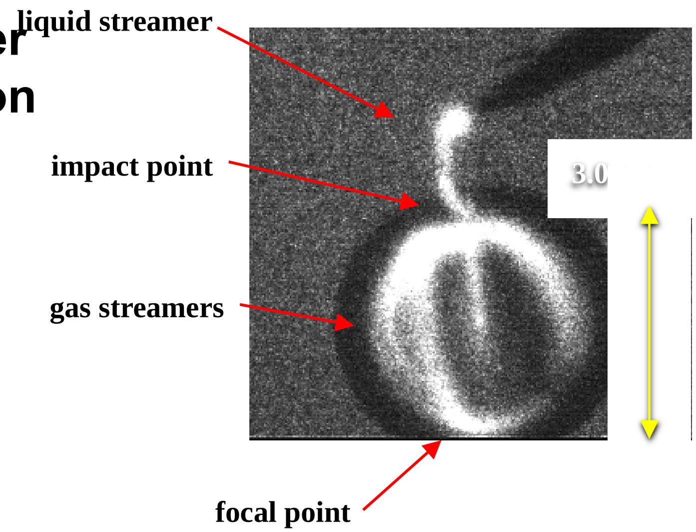
THE CASE FOR A GENERAL LOW TEMPERATURE PLASMA SCIENCE PROGRAM

- **Common Fundamental Research Challenge in LTPs*:***
  - ***Engineering distribution functions of charged particles to control the flow of power to produce desired excited states, chemical reactivity, surface functionality; and innovate technologies using these processes.***
- **Due to the diverse, dynamic and interdisciplinary nature of LTPs, it is difficult to distill this common theme to a narrow enough focus to fit into current NSF programs.**
- **For these reasons, LTPs no longer appear in descriptions of NSF Engineering or DMR programs, and can be a difficult scientific fit for the NSF/DOE Plasma Partnership.**
- **Society is best served by capitalizing on the dynamic and diverse nature of LTPs through a general LTPSE program.**

OVERARCHING FUNDAMENTAL RESEARCH ISSUES

- What are the pathways by which energy derived from an external source is coupled into a gaseous, liquid or solid medium to produce plasma?
  - Low pressure plasmas
  - High pressure plasmas
  - Multiphase plasma formation
- How does the manner in which we couple power into the plasma determine the energy distribution functions?
- How can that power be channeled into produce desired reactive products?
- What is the origin of anomalously high energy particles?





- Liquid water steamer interacts with bubble

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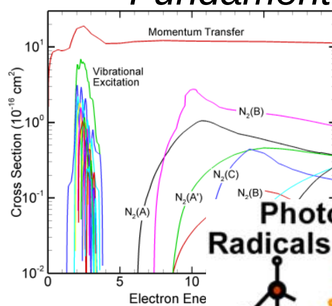
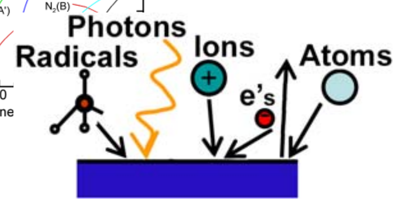
UNIVERSITY OF MICHIGAN

THE FUNDAMENTAL RESEARCH CHALLENGE

- **Crafting and controlling the plasma to channel power into desired modes of atoms, molecules and surface states.**

Fundamental Data

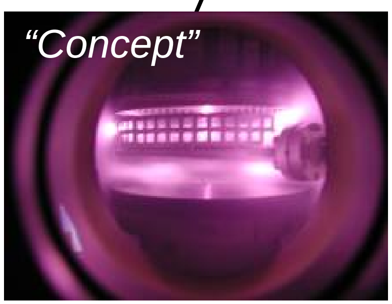




ECR, ICP, CCP, MERIE, DBD, e-BEAM, Pulsed, dc, rf, μwave, mTorr, atm?

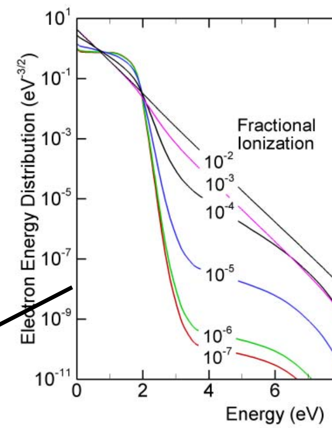
$$\frac{\partial f(\vec{v},\vec{r},t)}{\partial t} = -\vec{v}\cdot\nabla_x f(\vec{v},\vec{r},t) - \vec{a}\cdot\nabla_v f(\vec{v},\vec{r},t) + \left(\frac{\partial f(\vec{v},\vec{r},t)}{\partial t}\right)_{collisions}$$

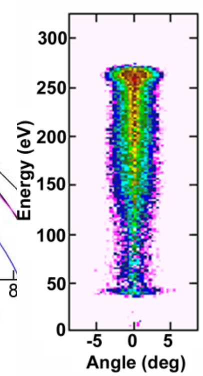
Predict f(v,r,t)

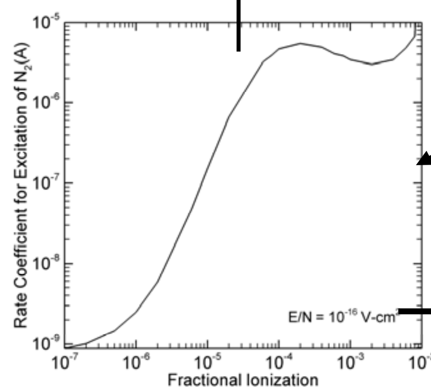


Predict, diagnose Performance

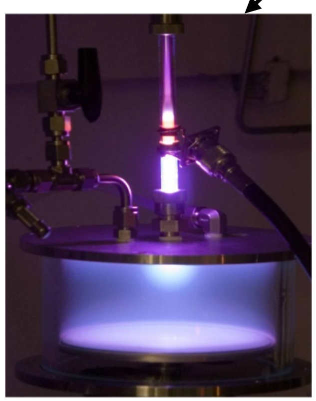
$$\frac{\partial N(\vec{r},t)}{\partial t} = -\sum_{i,j}\int f(\vec{v},\vec{r},t)|\vec{v}|\sigma_{ij}(v)N_j N_i d^3v$$







Implementation

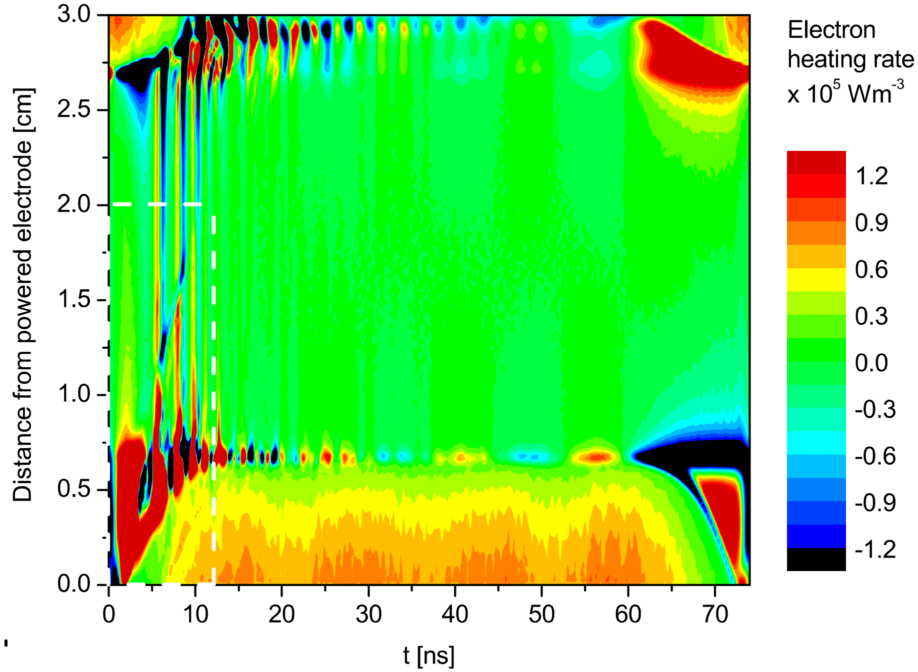


Low Temperature Plasma Science and Engineering

CONTROL OF PLASMAS FOR LOW PRESSURE SURFACE INTERACTIONS

HEATING DYNAMICS AND CONTROL OF PARTICLE DISTRIBUTION FUNCTIONS

- **State of the art plasma materials interactions use plasma sources having multiple frequencies.**
- **The electron heating dynamics in these plasmas rely on resonant and non-local effects as well as plasma-surface interactions (secondary emission).**
- **Fundamental research challenge: Controlling heating dynamics to customize energy distribution functions.**
- **This predictive control of plasma kinetics is the basis for optimizing all plasma surface interactions.**



- **Spatio-temporal dynamics of electron heating rate in a capacitive RF plasma driven at 4 consecutive harmonics of 13.56 MHz at 3 Pa in Argon**

Asst. Prof. Julian Schulze
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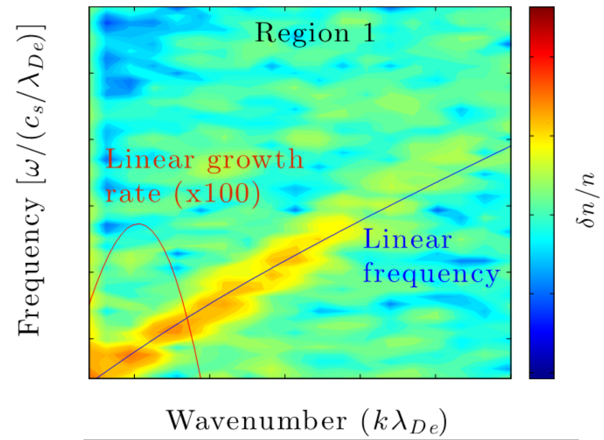
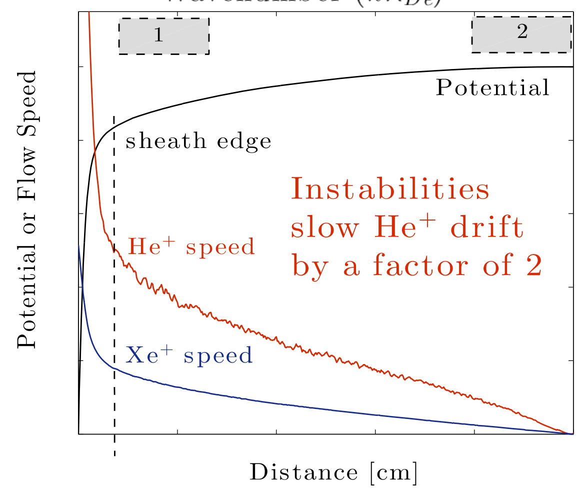
Low Temperature Plasma Science and Engineering

EFFECTS OF PLASMA INSTABILITIES ON PLASMA-MATERIALS INTERACTIONS

- **Most LTPs are bounded – and the interaction of the plasma with surface affects the plasma.**
- **Fundamental research challenges:**
  - **Does the flow of ions out of a plasma excite instabilities?**
  - **Under what conditions? (pressure, density, temperature, etc.)**
  - **How do these influence plasma-boundary interactions?**
- **Societal benefits:**
  - **Controlling instabilities is essential for reproducible plasma materials processing.**





- **Simulations observe that ion flow excites instabilities, influencing ion drift speeds near boundaries**

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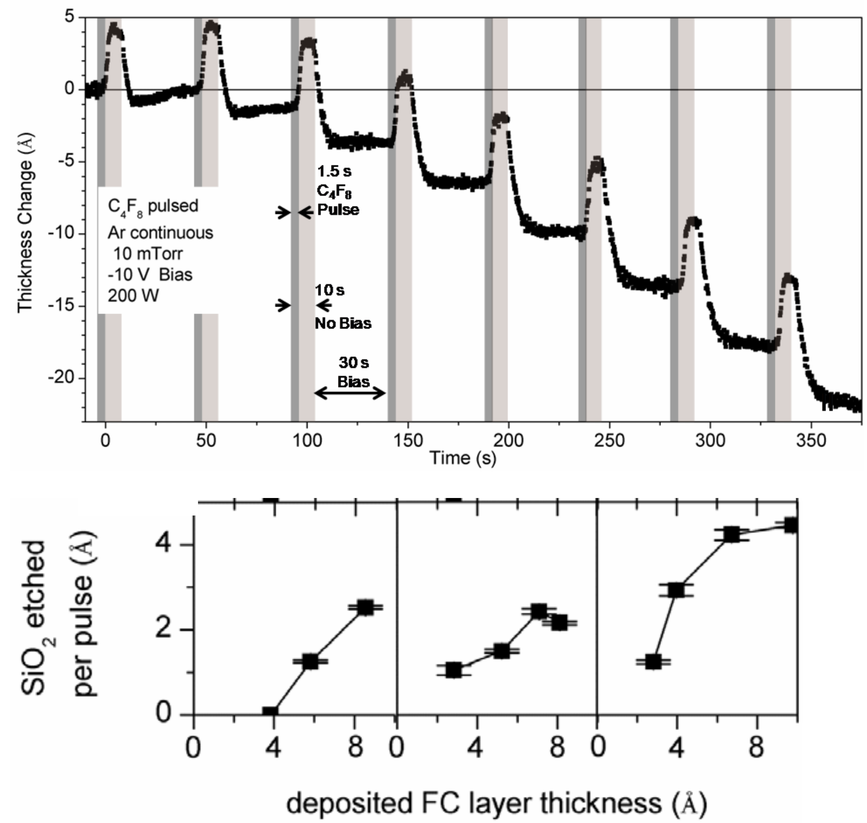
Low Temperature Plasma Science and Engineering

ATOMIC LAYER ETCHING USING PULSED PLASMA

- **Low temperature plasma can provide the non-equilibrium environment to satisfy the technological need for an Angstrom-scale precision etching method as device dimensions approach atomistic scale**
- **Fundamental Research Challenges:**
  - **Establish scientific basis to support rational use of ion-induced chemically enhanced etching chemistries for chemical precursors and substrate materials at the ion energies of interest**
  - **How can we control plasma properties to the extent required?**



Iterative etching of SiO_2 at Angstrom scale (J. Vac. Sci. & Technol. A. 32, 020603 (2014))

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University of Maryland
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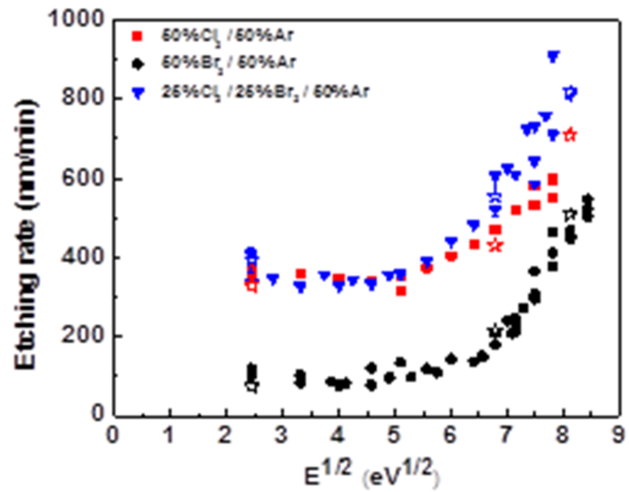
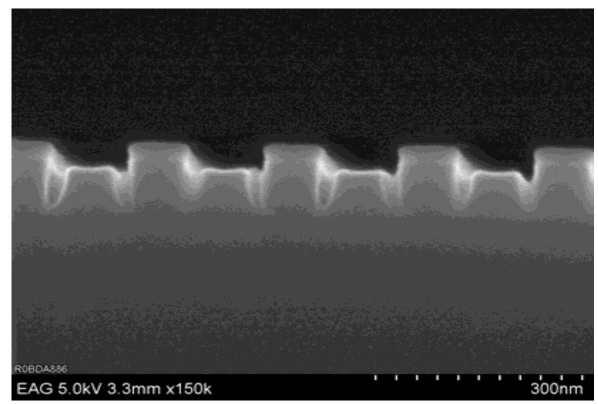
PLASMA PHOTOASSISTED ETCHING (PAE)

- **Etching of p-Si in halogen plasmas persists for sub-threshold ion energies (ε <16 eV).**
- **This *in-plasma* photo-assisted etching (PAE), *unknown 3 years ago*, results in artifacts that may severely impact nano-features.**
- **Fundamental research challenges:**
  - **What is the coupling between gas plasma and solid electronics (electrons, holes, bands, Fermi level, etc.)?**
  - **What are synergistic effects of photons and positive ions, electrons, negative ions, or halogen atoms?**
  - **Do surface plasmons (plasmonics) enable the fast etching observed in subwavelength-size features?**





- **(top) Etch rate of Si vs. $E^{1/2}$ (E=ion energy) in halogen plasmas. (bottom) SEM profile under photo-assisted etching conditions (E<16 eV)**

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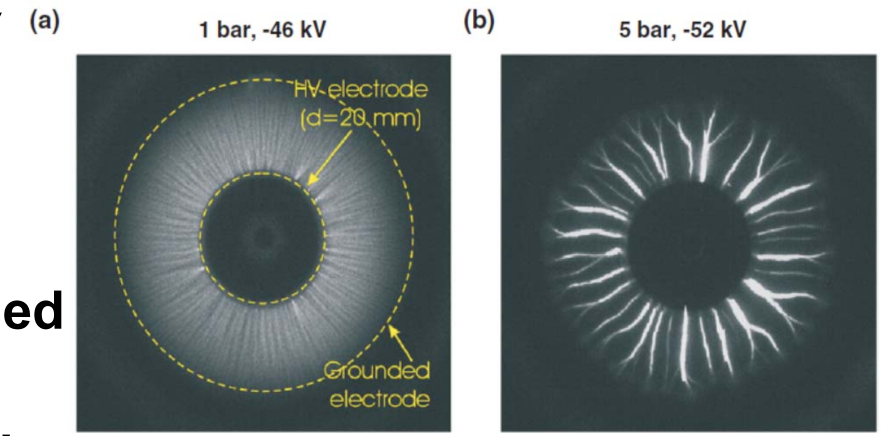
Low Temperature Plasma Science and Engineering

ATMOSPHERIC PRESSURE PLASMAS: THE NEW NORM?

PLASMA KINETICS IN HIGH PRESSURE GASES (AND LIQUIDS)

- ***Unexplored regime compared to low pressure plasma kinetics:***
  - **Dominant multi-body processes**
  - **Ionization and charge transport - dense gas approximation often used for liquids (but not correct)**
  - **Extremely fast excitation and heating processes promote instabilities.**
  - **Exceptional spatial gradients and interactions with flow including shockwaves**
- **Fundamental research challenges:**
  - **Ultrafast diagnostics**
  - **Ionization in dense media**
  - **Advanced numerical models**



- **Plasma instabilities leading to constriction of discharges and complex morphology of a pulsed discharge in liquid water.**

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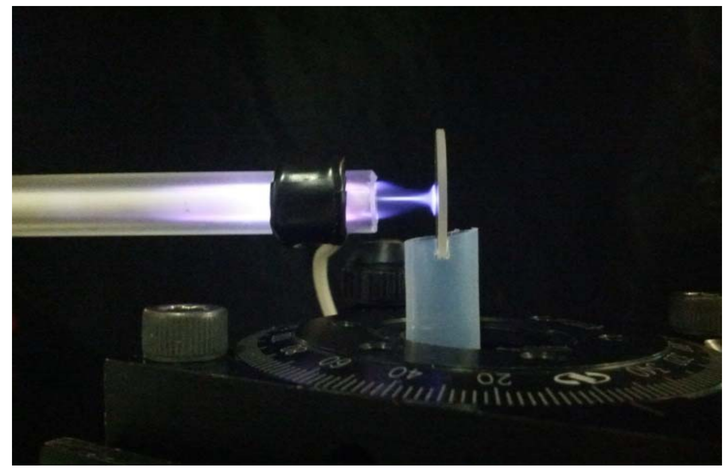
University of Minnesota

Low Temperature Plasma Science and Engineering

ATMOSPHERIC PRESSURE PLASMA (APP): INTERACTION WITH SURFACES

- In APPs the species mean free path is only ~100 nm, the Debye length is ~1 μm, and the power pulse can be ~10-100 ns.
- These conditions present great challenges for diagnostics of APPs near surfaces.
- Fundamental research challenges.
  - What are the surface fluxes of ionic and reactive neutral species, UV and VUV photons?
  - How do species densities and E-field vary in the 100 nm above a surface (≈mean free path) inside surface roughness with Kn ≈1.
  - What are the ion and electron energy distributions under such extreme conditions?



- Atmospheric pressure plasma jet interacting with a solid surface.

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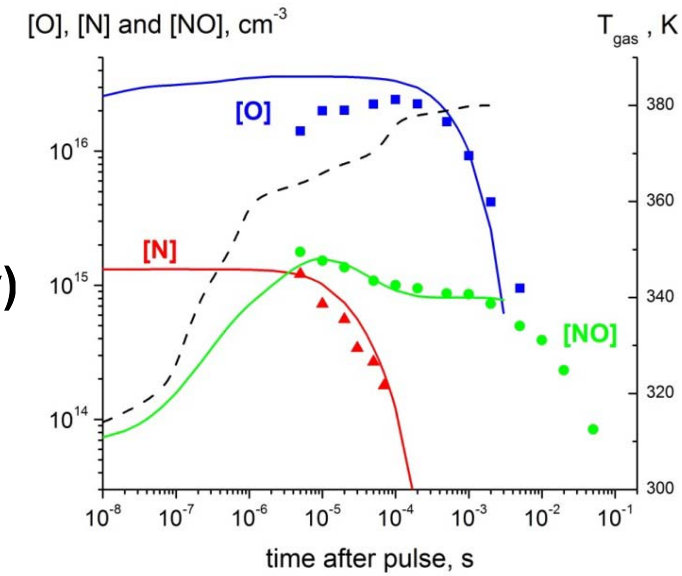
PLASMA KINETICS OF AIR PLASMAS

- Plasma kinetics of air plasmas is at the art of nearly all atmospheric pressure applications.
- Kinetic modeling of "full set of data" in ns pulse air plasmas using LIF / PLIF, TALIF, and ps CARS (T, [$N_2(X^1\Sigma,v)$], [O], [N], and [NO]):
  - [NO] explained by reactive quenching of a manifold of 10 N_2 excited electronic states.
  - NO formation not affected by reactions of $N_2(v)$
  - NO scavenged efficiently by N atoms
- Fundamental research challenge:
  - Expanding conventional reaction mechanisms to electronically excited plasma environment.
  - Combination of spatially- and time-resolved laser diagnostics and kinetic modeling to needed to understand and control (e.g.) NO.



- [O], [N], and [NO] after a ns pulse discharge in air. P = 40 Torr, $T_{peak} \approx 360$ K, $T_v(N_2)_{peak} \approx 1700$ K

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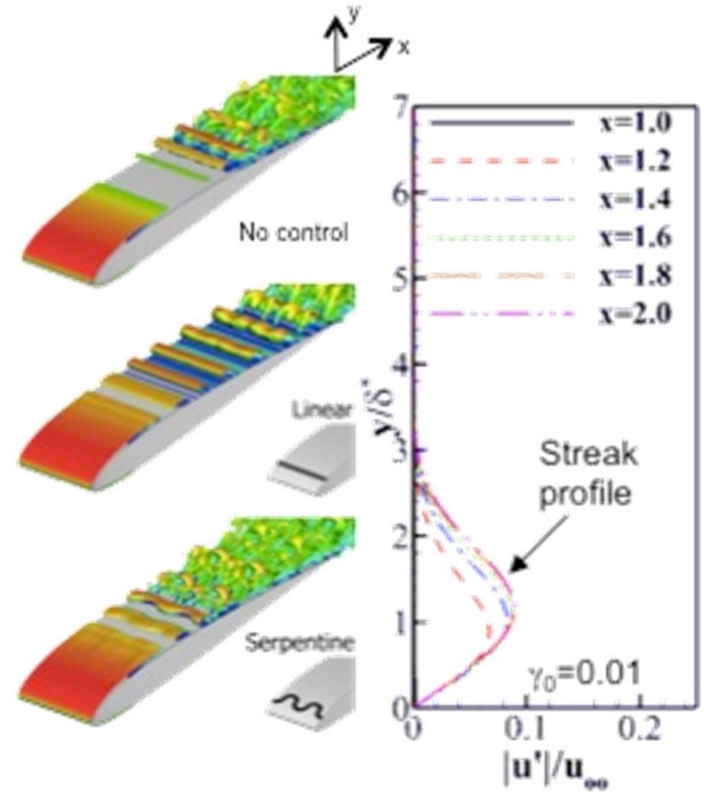
Low Temperature Plasma Science and Engineering

INNOVATIVE COUPLING MECHANISMS OF PLASMA AND FLUID FLOW

- **APPs are rarely uniform glows – have small scale structure 10s to 100s μm.**
- **Structures strongly affect coupling of plasmas with fluid flow impacting laminar to turbulent transition.**
- **Aeronautical boundary layer control critically depends on coupling.**
- **Fundamental research challenge:**
  - **Understanding plasma-flow interactions at micron scales to optimize flow control.**
  - **Dependence of plasma kinetics on micron scale interactions.**
- **Control of interaction may dramatically reduce drag**



- Curved class of plasma actuators show novel possibilities and challenges.

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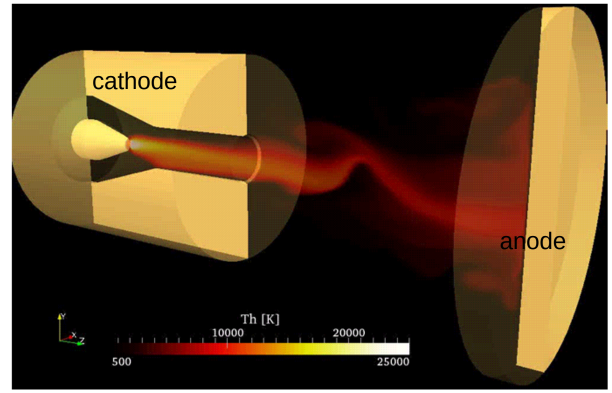
The Foundation for The Gator Nation

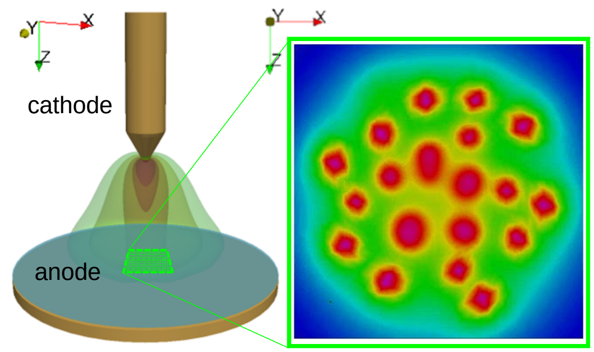
Low Temperature Plasma Science and Engineering

INSTABILITIES IN NON-EQULIBRIUM ATMOSPHERIC PRESSURE PLASMAS

- Atm. pressure LTP flows are constrained to low volume/area ratios that produce pattern formation, instabilities, affect turbulence and limit uniformity/efficiency.
- Fundamental research challenges:
  - Understand range of transport regimes unique to atm-press LTPs
  - Diagnostics and computational models to capture local instabilities & dynamics
- Societal benefits:
  - Materials processing, fuel reforming, environmental remediation, medicine



- Instabilities in nonequilibrium plasma jet



- Spontaneous pattern formation and dynamics

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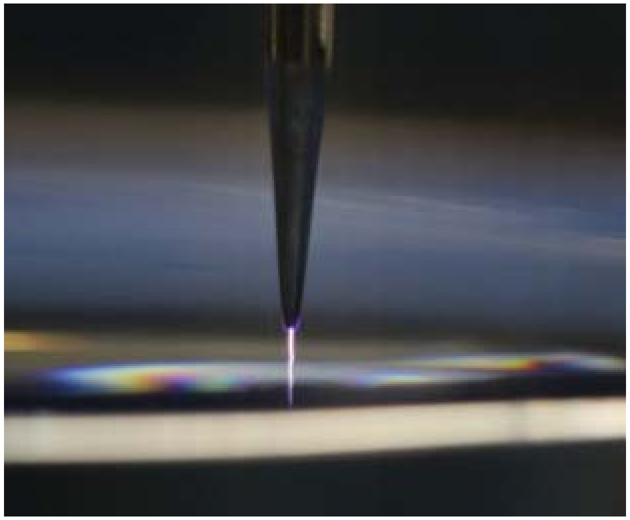
Low Temperature Plasma Science and Engineering

MULTIPHASE PLASMAS AND PLASMAS ON/IN LIQUIDS

PHYSICAL AND CHEMICAL INTERACTIONS AT THE INTERFACES OF PLASMAS AND LIQUIDS

- **Plasmas in contact with liquids are unique interfacial systems that combine dissolution, photolysis, radiolysis, and electrolysis leading to new non-equilibrium chemical and physical interactions.**
- **Broad impact on water purification, healthcare, chemical analysis, and materials discovery.**
- **Fundamental research challenges:**
  - **How do low and moderate energy (~1-10 eV) electrons and ions solvate in solution?**
  - **How do plasma-produced high electric fields restructure the plasma-liquid interface?**
  - **What are the key short lived species and how are they generated and transported across the plasma-liquid interface?**



- **An argon plasma jet formed at the surface of an aqueous solution in atmospheric air, injecting energetic electrons from the plasma into the liquid.**

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Prof. R. Mohan Sankaran
Case Western Reserve University
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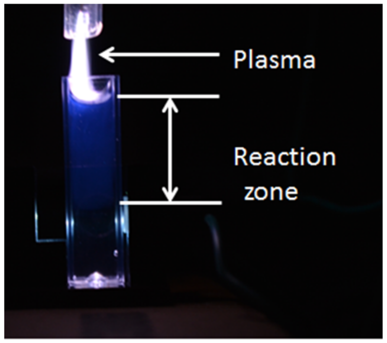
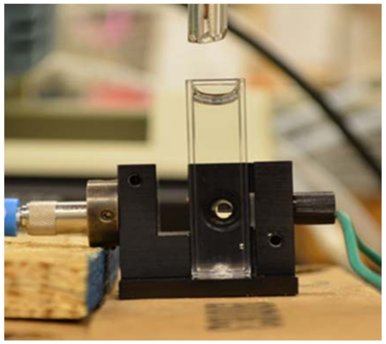
CHEMISTRY OF PLASMAS DIRECTLY IN AND CONTACTING WATER

- Aqueous plasmas (APs) effectively inactivate microorganisms in water and can non-selectively oxidize organic compounds.
- APs are produced by a gas phase plasma on the liquid or in a discharge in the liquid.
- Fundamental research challenges:
  - Determine the oxidative and reductive radicals produced by the plasma, chemical reduction by electrons and H• and oxidation by OH•
  - Role of physicochemical properties of compounds in their degradation
  - Effect of solution electrical conductivity on microbial inactivation.
- Societal benefits: Drinking and wastewater treatment, sterilization, and food processing.





- Fluorescence visualization to estimate the reaction zone between plasma radicals and organic solutes.

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Clarkson UNIVERSITY defy convention

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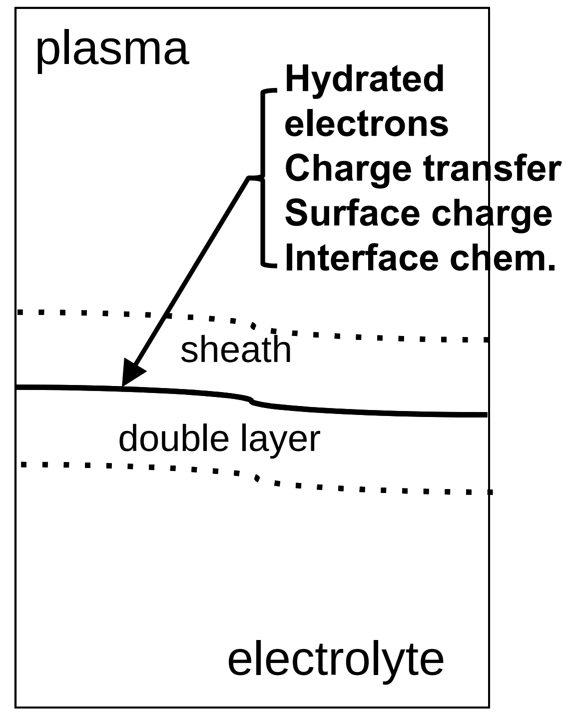
THE INTERFACIAL STRUCTURE OF THE PLASMA-LIQUID INTERFACE

- **The interfacial structure, kinetics and dynamics between the gas phase plasma and liquid is (very!) poorly understood.**
- **No accepted theory for transmission of electrons and ions through surface of liquid.**
- **Fundamental research challenges:**
  - **Understanding, predicting nm sized interface – plasma-sheath on one side, electrochemical double layer on the other(?)**
  - **Consistent description of flow of plasma-generated incident species and emission of liquid species into plasma from interface**
- **Societal benefits: biomedical applications and nanocrystal formation**



- **Elements of plasma-electrolyte interface**

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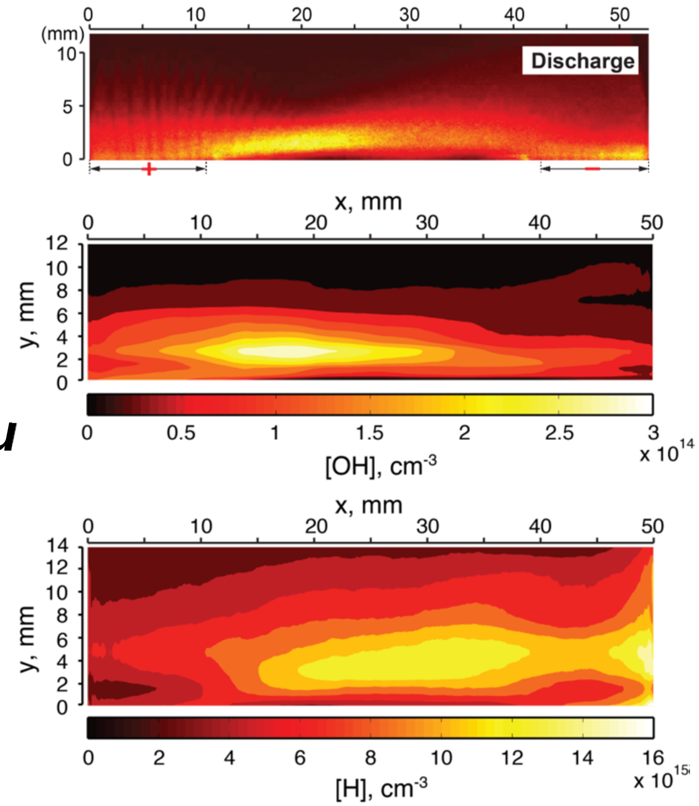
CHEMICAL REACTIONS IN SURFACE IONIZATION WAVES AT LIQUID-VAPOR INTERFACE

- **2-D distributions of absolute [OH] and [H] (LIF / TALIF) measured in ns pulse, surface ionization wave, nonequilibrium plasmas sustained at liquid water / water vapor interface**
- **<u>Major advance:</u> demonstrated capability for absolute, spatially and time- resolved, *in situ* radical measurements (H, OH, O, NO, N) in liquid-vapor interface plasmas (aqueous solutions, alcohols)**
- **Fundamental research challenge: Combine diagnostics and kinetic modeling to <u>understand and control</u> plasma chemical reactions at liquid-vapor interface**



- **[OH] and [H] distributions in a ns pulse discharge in Ar over liquid water surface (at y=0). P=30 Torr, flow left to right**

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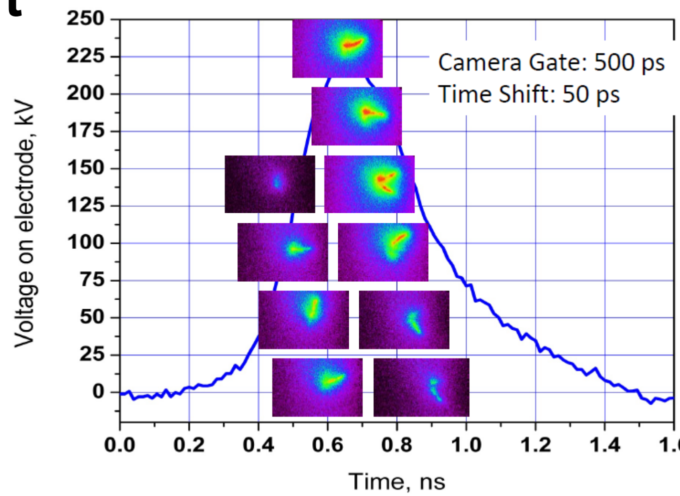
Low Temperature Plasma Science and Engineering

LIQUID AND SOLID-STATE NONEQUILIBRIUM PLASMA GENERATION

- **Liquid or solid media excitation by ultra-short electric discharge without phase change opens the door to new technologies**
  - **Nano-materials synthesis**
  - **Bio-medical technologies**
  - **Direct excitation/picosecond light sources**
- **Fundamental research challenge:**
  - **Electrical fields comparable with intramolecular fields – direct acceleration of free electrons through the atoms**
  - **Electrostriction pressure higher than critical – molecular layers displacement**
  - **Describing kinetics when Boltzmann equation cannot be used.**



- **Picosecond water plasma.**
- **U = 220 kV**
  - **τ = 150 ps rise time**
  - **U/τ = 1.4 MV/ns**
- **Electric field 225 MV/cm (670 Td)**
- **Propagation speed = 5000 km/s ~ 15%c**

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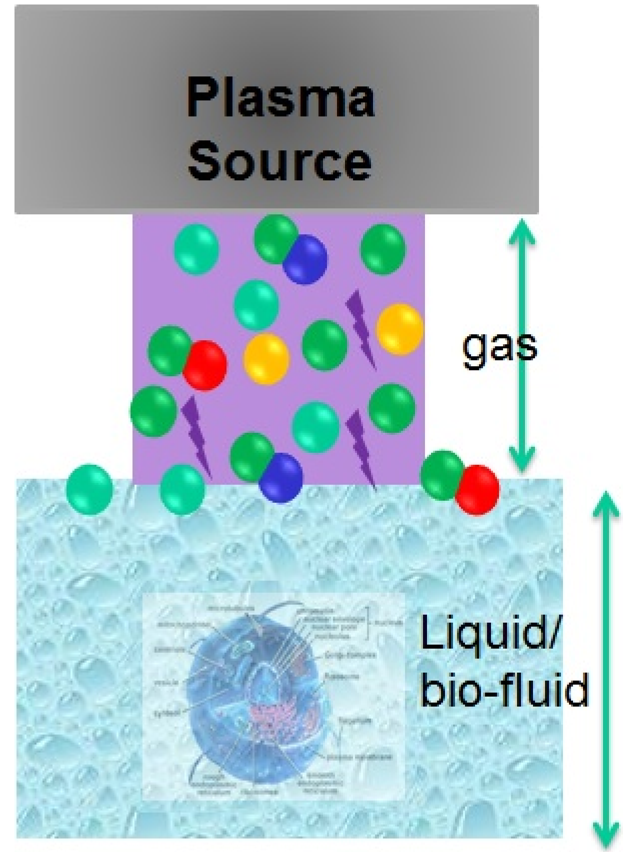
Low Temperature Plasma Science and Engineering

BIOLOGICAL APPLICATIONS OF PLASMAS: FUTURE MEDICAL MODALITIES

LOW TEMPERATURE PLASMA MEDIATED EFFECTS ON BIOLOGICAL SYSTEMS

- **LTPs have been shown to have beneficial biomedical effects:**
  - **Infection control**
  - **Proliferation of healthy cells – wound healing**
- **Fundamental research challenge: Key mechanisms of interaction of LTPs with biological systems are still largely unknown:**
  - **Species generated at the plasma-liquid interface? Concentrations, penetration, and lifetime of solvated species?**
  - **Interaction of relevant species with cells and tissues: effects on lipids, proteins, DNA, cell signaling?**



- **Gas phase/gas-liquid interface/bulk bio-fluid model**

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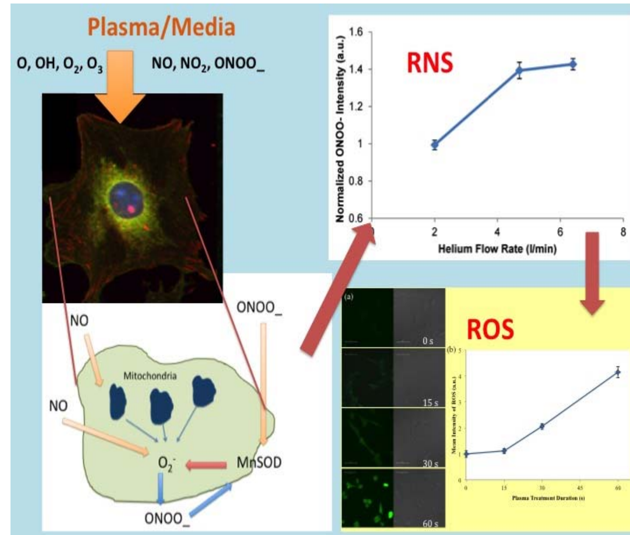
PLASMA INTERACTION WITH LIVING TISSUE: HIV and CANCER THERAPY

- **Plasma interactions with cells lead to activation of various pathways forming solid basis for plasma application in HIV and cancer therapy.**
- **Fundamental research challenges:**
  - **What is the mechanism of low-temperature plasma interaction with soft matter and living tissue on cellular level?**
  - **Accumulated evidence *synergistic* combination of reactive species, electric fields, UV**
- **Knowing where and how reactive species are formed enable control of the plasma interaction with soft matter – living tissue.**



- **Plasma interaction with cell leads to activation of ROS production pathways and deactivation on anti-oxidant system.**

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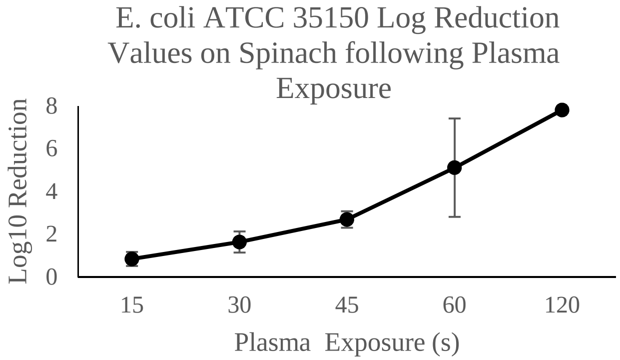
WASHINGTON, DC

PLASMAS FOR FOOD DECONTAMINATION

- **LTPs are effective against pathogens responsible for food borne illnesses.**
- **The electric field, UV, charged particles and antimicrobial compounds originating in the plasma are likely responsible for the biocidal performance.**
- **Fundamental research challenges:**
  - **How do LTPs disrupt the adhesion of bacteria on contaminated organic surfaces?**
  - **Effects of the plasma on the organoleptic properties and nutritional value of treated food are not understood.**
  - **How can LTPs be optimized to deliver the necessary species?**

- **Application of cold plasma on temperature sensitive surfaces**



- **A 99.999% reduction of E.coli on spinach was observed after 60s of exposure to plasma**

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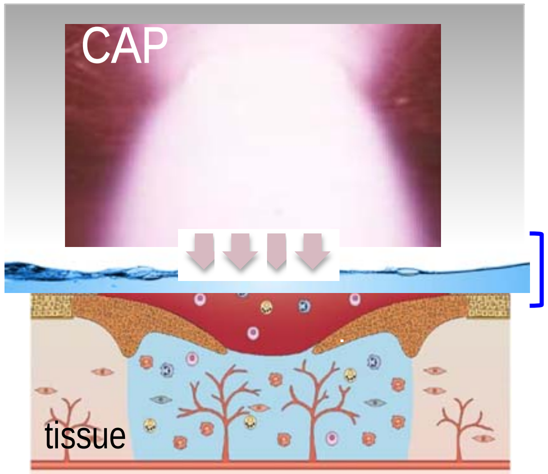
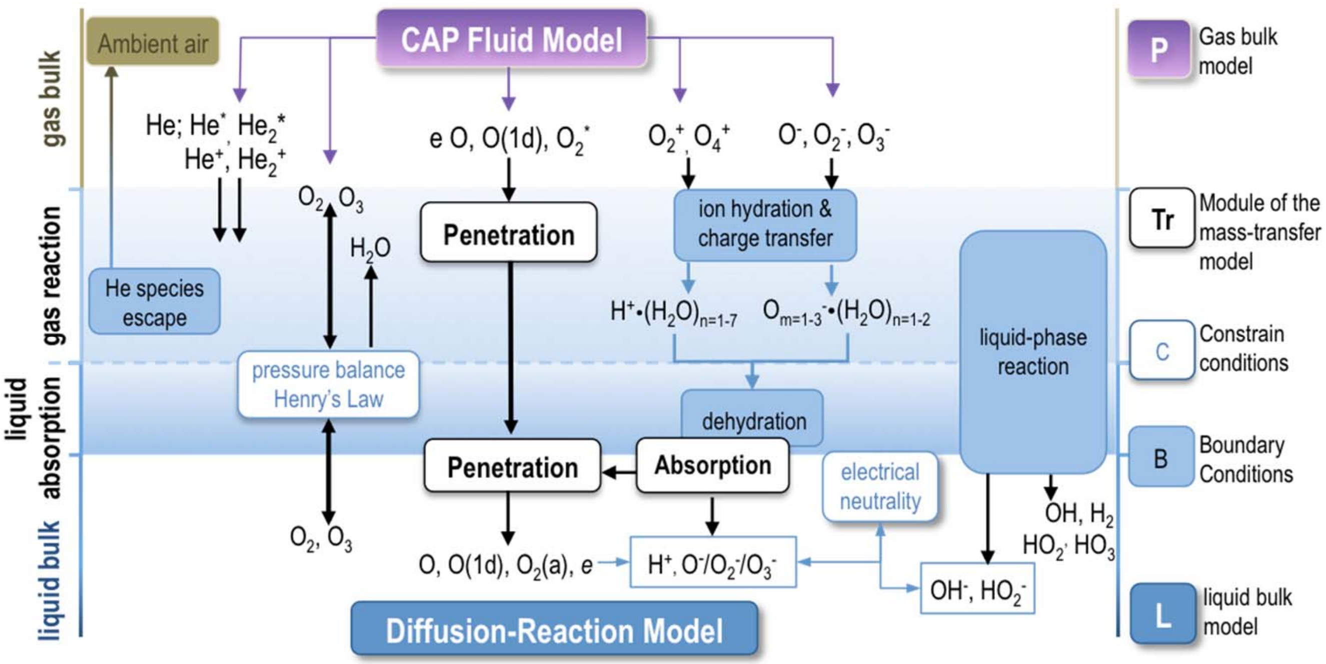
EP TECHNOLOGIES LLC

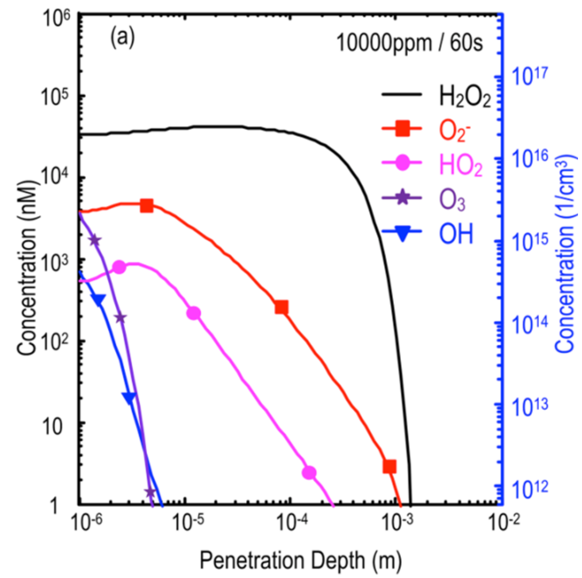
Low Temperature Plasma Science and Engineering



UNDERSTANDING COMPLEXITY IN PLASMA-BIO

- **Even before addressing cellular response to plasmas, the plasma-bioliquid interface is perhaps complex system yet addressed in LTPs.**
- **Fundamental research challenge: *Understand this!***





Chen et al *Plasma Chem. Plasma Process.* 34: 403 (2014)

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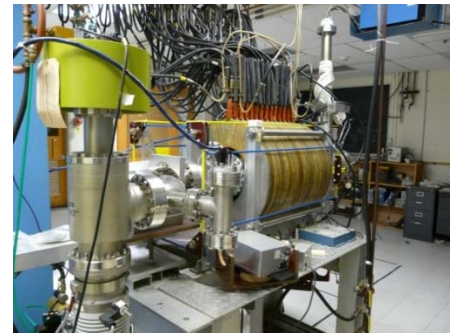
OLD DOMINION UNIVERSITY

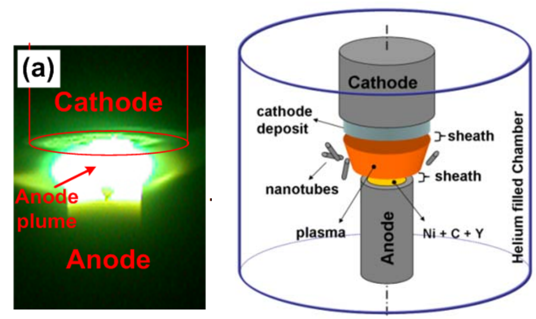
NANOPARTICLES AND NANOTECHNOLOGY

ROLE OF PLASMA-MATERIAL INTERACTIONS IN NANOTECHNOLOGY

- **Nanomaterials have the potential to revolutionize many fields including, electronics, chemical synthesis, energy storage, and environmental and pharmaceutical applications.**
- **Nanomaterial production by low (10^{-3}-10 Torr) and high (1 atm) pressure plasmas to produce various nanomaterials. Growth poorly understood and controlled.**
- **Fundamental research challenges:**
  - **In-situ optical diagnostics of nanomaterials**
  - **Predictive modeling of nanomaterial growth and transport**
  - **Robust control methods of nanomaterial growth**



- **Magnetically Controlled Atmospheric Plasma eXperiment (MAPX) at PPPL**



- **Arc synthesis of carbon nanostructures**

Y. Raitses, I. Kaganovich, R. Car
Princeton University

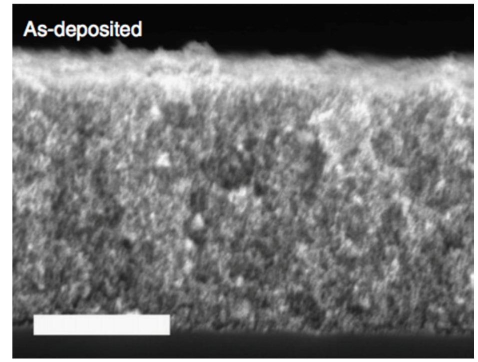
PPPL PRINCETON PLASMA PHYSICS LABORATORY

PRINCETON UNIVERSITY

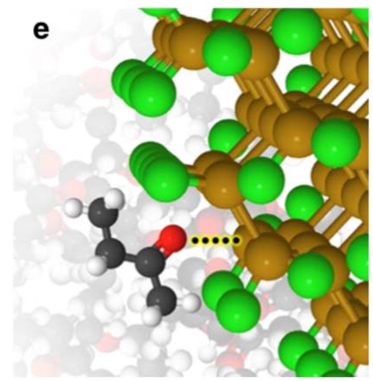
Low Temperature Plasma Science and Engineering

PLASMA-NANOPARTICLE INTERACTIONS AFFECTING PARTICLE STRUCTURE AND SURFACE

- LTPs present a unique *non-equilibrium* environment for nanoparticle synthesis, e.g.:
    - Metastable materials (e.g., materials doped beyond thermodynamic limit)
    - Unique surface properties due to interaction with plasma species
- Fundamental research challenges:
    - How do nanoparticles get heated by surface reactions, electron and ion bombardment?
    - How does bombardment with energetic species affect nanoparticle properties?



Vacancy doped ZnO particles with high mobility (Nat. Comm. 5, 5811 (2014))



Hypervalent interactions at Si-Cl nanoparticle surface (Nat. Comm. 4, 2197 (2013))

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Prof. Steven Girshick
Prof. Uwe Kortshagen
University of Minnesota
Prof. R. Mohan Sankaran
Case Western Reserve University

University of Minnesota

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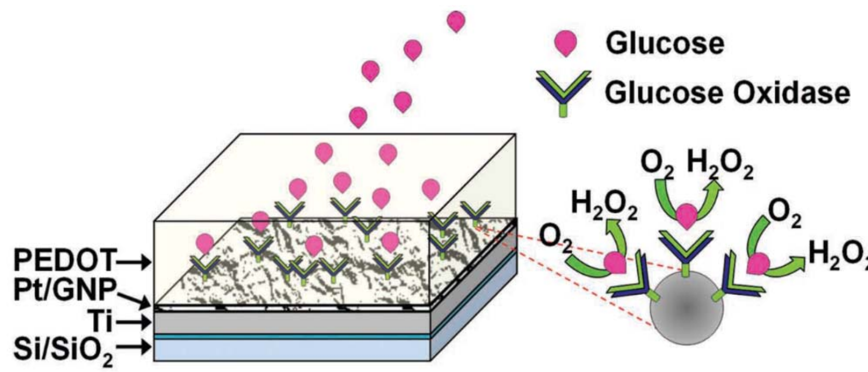
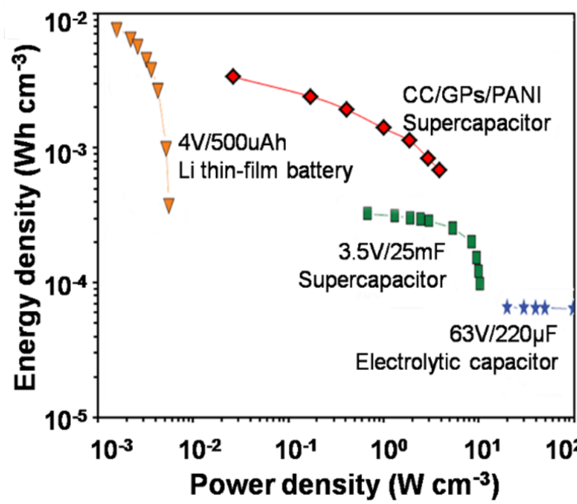
Low Temperature Plasma Science and Engineering

PLASMA ENHANCED CVD OF NANOSTRUCTURES

- PECVD is an efficient process to grow nanomaterials due to lower operation temperatures.
- Nanostructured devices enabled by PECVD:
- Electrochemical Biosensors: Glucose detection limit of 0.3 μm, linear sensing range of 0.01–50 mM.
- Supercapacitors: Higher power density, faster power delivery and better cycle to cycle stability
- Fundamental research challenge:
  - Utilize unique chemistries afforded by PECVD while retaining delicate fine surface structures.



- **Glucose biosensor.** (Ref: Claussen et al. Adv. Funct. Mater. **2012**, 22, 3399–3405).



- **Supercapacitors specific energy and power density compared to Li-ion battery.** (Ref: Xiong et al. Adv. Energy Mater. **2014**,4, 1300515)

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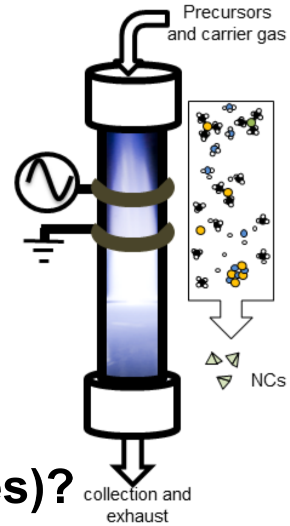
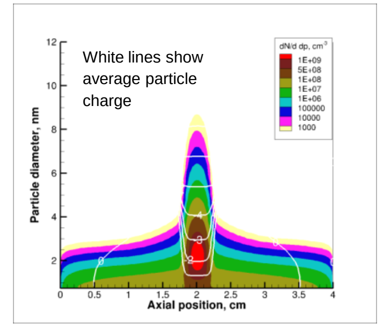
PURDUE UNIVERSITY

Low Temperature Plasma Science and Engineering

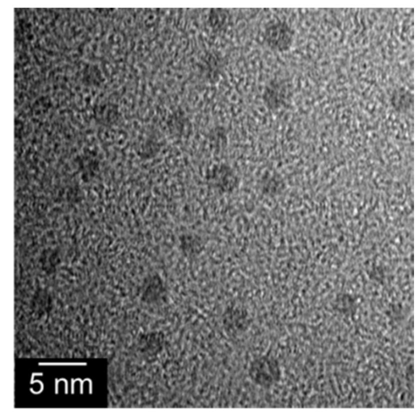
HOMOGENEOUS NUCLEATION OF NANOCRYSTALS IN LTPs

- **Novel nanocrystal (NC) materials can be synthesized (silicon and diamond quantum dots; doped, compound semiconductor quantum dots)**
- **Fundamental research challenges:**
  - **What species and processes govern NC physical and optoelectronic properties?**
  - **How do NC nucleate and grow?**
  - **How can NC with predictable properties be produced?**
  - **Can LTP reactors be used for 2-D confined nanostructure growth (nanorods, nanotubes)?**





Modeling of nanoparticle formation



Nucleation of nanodiamond (Nat. Comm. 4, 1 (2013))

Asst. Prof. Rebecca Anthony
Michigan State University
Profs. E. Aydil, S. Girshick, U. Kortshagen
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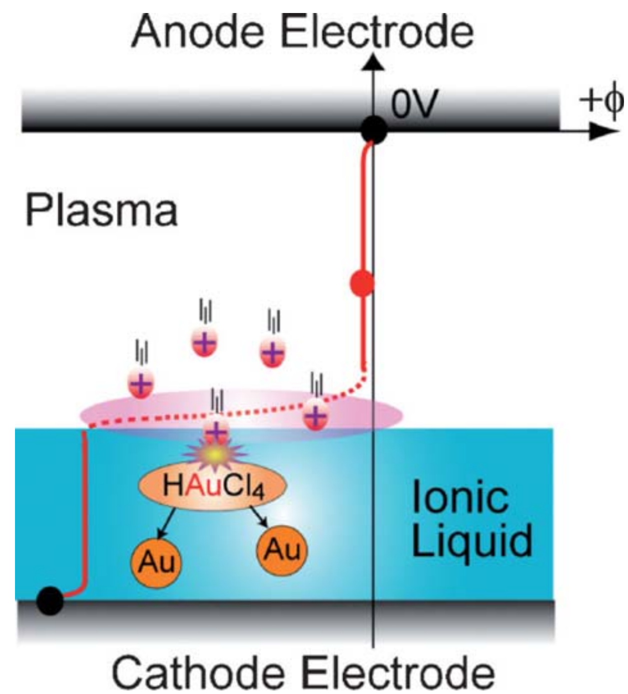
INTERFACIAL PLASMA-LIQUID PROCESSES FOR SYNTHESIS OF METAL NANOPARTICLES

- **Nanoparticle synthesis in chemically reactive atm. pressure, multi-phase plasma interacting with multi-functional surfaces.**
- **Pulsed streamer, arc, pulsed DC glow, and microwave discharges not in/on water, organic solvents and supercritical CO_2 .**
- **Multi-component ionic liquids – alloy nanoparticles.**
- **Fundamental research challenges:**
  - **Mechanisms to maintain spatially and temporally stable plasma-liquid interface.**
  - **Maintaining purity, size distribution of nanoparticles..**



- **Positive plasma ions released into ionic liquid initiate physical and chemical reactions at interface of ionic liquid.**

Mark Koepke
West Virginia University
Toshiro Kaneko
Tohoku University

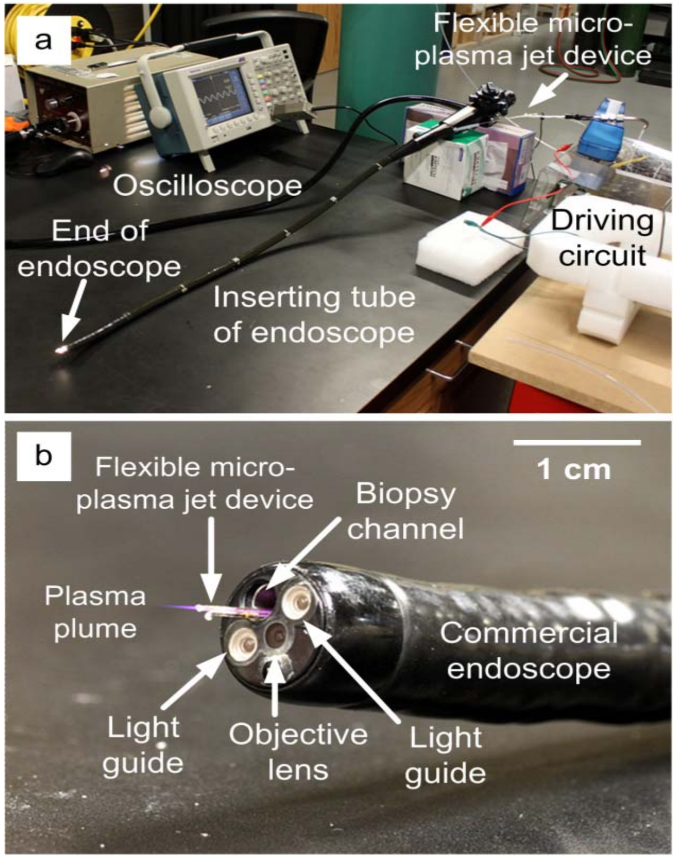
TOHOKU UNIVERSITY

Low Temperature Plasma Science and Engineering

MICROPLASMAS: HEALTHCARE TO CELL-PHONE NETWORKS

MICRO-PLASMA CANCER ENDOSCOPY

- Traditional chemotherapy and radiation therapies cannot target cancers at individual cellular level.
- Microplasmas propagating through flexible tubes enable endoscopic plasma treatment of (pre-) cancerous growths at single cell level. (Now cells are cut out, leaving cancerous cells behind.)
- Fundamental research challenges:
  - Understanding propagation of plasmas in confined geometries.
  - Controlling radical, ion, photon and electric field delivery through capillaries.
- Progress made using hollow-fiber-optic cables.



- A long and highly flexible micro-plasma jet device combined with a commercial endoscope for plasma endoscopy

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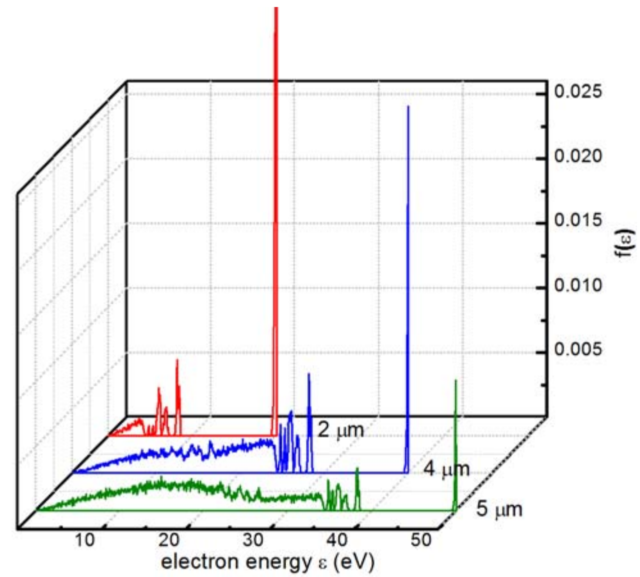
CLEMSON UNIVERSITY

FUNDAMENTAL SCALING OF PLASMAS TO MICRO- AND NANO-SCALES

- **Scaling of plasmas to micro and nanoscales opens new possibilities for plasma science:**
  - **Ultrahigh electron densities (~10^{18} cm^{-3}); large surface-to-volume ratios; massive arrays**
- **Broad societal impact – efficient lighting, chemical sensing, ultrafast computing, gas reforming.**
- ***Merging of gas phase and solid phase plasmas*.**
- **Fundamental research challenges:**
  - **Surface and interfacial processes at micro, nano scales.**
  - **Physical limits of scaling and how can these be achieved.**
  - **How do arrays array interact and couple?**
  - **Diagnostics at extreme dimensions**



- **Kinetic simulations predict electron energy distributions in a 5 µm, 380 torr, Ar microplasma that are vastly different than their macroscale counterparts**

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University of Notre Dame
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UNIVERSITY OF NOTRE DAME

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UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Low Temperature Plasma Science and Engineering

PLASMAS IN MICROCAVITIES WITH NANO-ENGINEERED ELECTRODES

- **Plasmas in microcavities (1-100 μm) at high pressure (100-1000 Torr) with very large surface/volume ratio have very high electron densities, 10^4-10^6 that in "macro" plasmas.**
  - **Surface quality and plasma-surface interactions are clearly critical in microplasmas, but we are just beginning to "scratch the surface".**
  - **Problem: need high voltages and power due to physics of cathode sheath and electron-impact ionization**
- **Fundamental research challenges**
  - **Can surfaces be nano-engineered to enhance electron and ion density by electron field emission (cathode) and field ionization (anode)?**
  - **Would 'shrink' the sheath and enable 10^{13-14} cm^{-3} microplasma at ultralow voltages (~30 V) and low power – new type of plasmas**
- **Microplasma elements incorporated into RF systems (antennas, resonators) to electronically reconfigure them would revolutionize RF electronics, from personal mobile devices to aircraft.**

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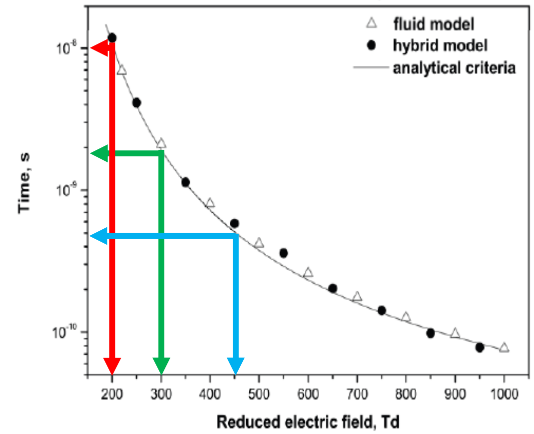
PURDUE ENGINEERING

Low Temperature Plasma Science and Engineering

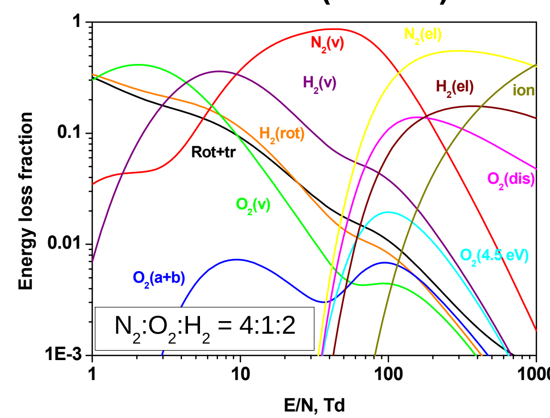
ULTRA-HIGH AND ULTRA-SHORT PULSED ELECTRIC FIELDS

NANO- AND PICOSECOND DISCHARGES AT ULTRAHIGH ELECTRICAL FIELD

- Ultra-short pulsed discharges allow control over electric field in plasma and the direction of energy deposition and media excitation
    - Pulsed gamma and X-rays
    - Ultra-short e-beams
    - Selective molecular excitation/reactions
- Fundamental research issues:
    - Non-local EEDF and formation of run-away electrons. Differential cross-sections
    - Molecular/atomic potential surface modification in external E-field above run-away threshold
    - Dynamics of energy transfer and chemical reactions at non-Boltzmann conditions



- Critical discharge time at P=1 atm. Air. τ(400Td)~1ns



- Discharge energy distribution in H_2-O_2-N_2 mixture vs E/n

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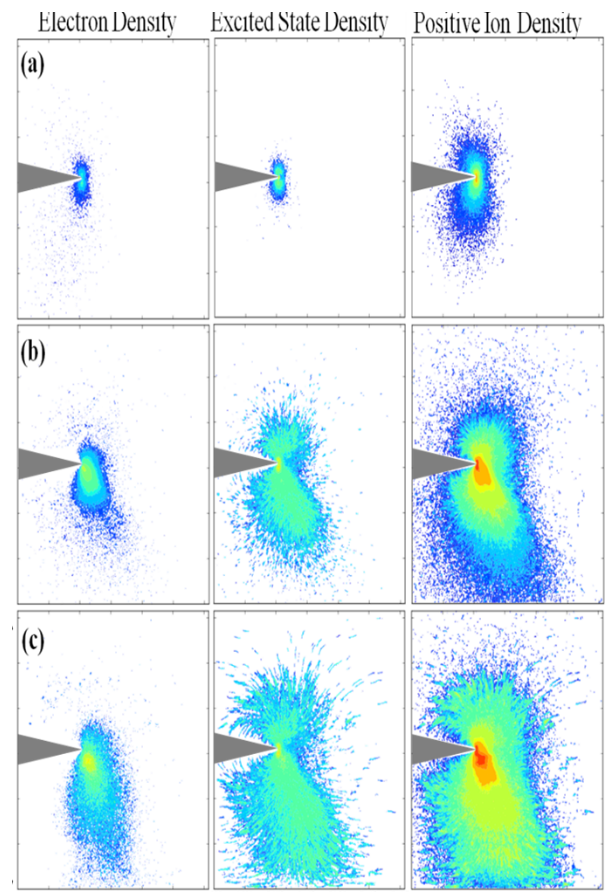
DEI SVB NVMINE VIGET

Low Temperature Plasma Science and Engineering

LTP KINETICS WITH ULTRA-HIGH E-FIELDS

- **Ultra-high E-field pulsed plasmas with provide otherwise unattainable non-equilibrium conditions.**
  - **Capable of increasing process efficiency and open the door to new processes.**
- **Fundamental research issues:**
  - **Understanding increase over more than <u>ten orders of magnitude</u> in a few nanoseconds.**
  - **Vacuum UV drives volume ionization, self-absorption, photoemission from surfaces – none of which is understood.**
- **Societal Impact:**
  - **Efficient lvacuum UV output – biological sterilization, composition analysis.**
  - **Power transmission safety – prediction of transient plasma onset.**



- **Transient plasma, 0 - 25 ns**
- **PIC MCC code, GPGPU**
- **Photon tracking included**

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Low Temperature Plasma Science and Engineering

INTERNATIONAL PERSPECTIVE

INTERNATIONAL INVESTMENTS IN LTPSE

- **Major national and international (EU) programs in the fundamentals and applications of LTPs over several decades with per-capita investment far exceeding the US: Germany, France, The Netherlands, Belgium, Italy, Portugal, Japan, China, Korea, UK**
- **Germany: Multiple LTPSE focused research centers (perhaps 4) with funding levels commensurate with STC/ERC.**
- **Japan: Has had and continues to have multiple national initiatives in LTP topics ranging from materials processing to microplasmas and now plasma medicine. (MITI / METI)**
- **France, Netherlands: National initiatives in plasma medicine.**
- **UK: Engineering and Physical Sciences Research Council (EPSRC), NSF equivalent, invests $6.6M/year in basic research in LTPs. This is a per-capita equivalent of $33M/year in the US, 10-20 times larger than our present investment.**

THE FUTURE VISION ENABLED BY THE NSF LTPSE PROGRAM

THE FUTURE WORLD WITH LTPs

- **With continuing advances in LTPs enabled by the NSF LTPSE program, there will be (or be better)...**
  - **Ever finer resolution and more capable microelectronics using graphene, nanotubes and other nanostructures.**
  - **New modalities in human healthcare – cancer treatment, wound healing, HIV, Alzheimers**
  - **Next generation mobile devices (cell phones) by reconfigurable, plasma based antennae and RF electronics**
  - **Human monitoring sensors (e.g., real time glucose)**
  - **Bacteria and viral control for drug-resistant strains**
  - **Advanced water and air treatment on municipal scales, and point-of-use water purification for 3rd world communities.**
  - **More efficient combustion with tunable reactions – automobiles to jet engines**
  - **Advanced batteries, solar cells, photonics, drug delivery, enabled by plasma produced nanostructures and nanoparticles.**

THE FUTURE WORLD WITH LTPs

- **With continuing advances in LTPs enabled by the NSF LTPSE program, there will be (or be better)...**
  - **Agile UAVs through plasma flow control.**
  - **Micro-thrusters for constellations of nano-satellites.**
  - **Asteroid retrieval and interplanetary missions enabled by plasma propulsion.**
  - **Non-equilibrium materials with unprecedented functionality (e.g., metastable a-Si:H for photovoltaics)**
  - **Roll-to-roll processing of inexpensive, large-scale flexible electronics.**
  - **Radiation sources for vacuum ultraviolet imaging**
  - **Carbon recovery from CO_2.**

CONCLUDING REMARKS: THE LTPSE PROGRAM

- A program in Low Temperature Plasma Science and Engineering (LTPSE) in the NSF Engineering Directorate will
  - Enable addressing fundamental research challenges that rapidly translate to societal benefit.
  - Empower a new generation of scientists and engineers to advance the field into new regimes.
  - Retain (regain?) the US reputation as the LTP innovators in one of the most intellectually diverse fields of science and technology.
  - Enable a vision for the future that links solving fundamental challenges in plasma science to advances in materials science, biotechnology, nanotechnology, environmental stewardship.
  - That's called engineering.

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