APPLICATIONS OF LOW TEMPERATURE PLASMAS: STATUS, SCIENTIFIC ISSUES AND OPPORTUNITIES*

Mark J. Kushner University of Illinois Dept. of Electrical and Computer Engineering Urbana, IL 61801 mjk@uiuc.edu http://uigelz.ece.uiuc.edu

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Contributing Group Members

- Rajesh Dorai
- Ananth Bhoj
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AGENDA

- Applications of Low Temperature Plasmas
- What challenges and opportunities lie ahead for plasma technologies?
 - Materials Processing
 - Lighting
 - Atmospheric Pressure Plasmas
 - Bioscience
 - Nanoscience
- Concluding remarks

DEFINITION OF TECHNOLOGICAL PLASMAS

- Technological plasmas are a power transfer media.
- Electrons transfer power from the "wall plug" to internal modes of atoms / molecules to make "benign" species into "reactive" species.



• Once activated, their physical or chemical potential may be used to make products (add or remove materials, photons...)

COLLISIONAL LOW TEMPERATURE PLASMAS





Materials
 Processing





Spray Coatings



PLASMA MATERIALS PROCESSING FOR MICROELECTRONICS

PLASMA MATERIALS PROCESSING FOR MICROELECTRONICS

- The fabrication of conventional microelectronics has met and bested extreme challenges as the nm scale is approached and exceeded.
- Plasma science has played a critical role in virtually all aspects of meeting these challenges
 - Physical Vapor Deposition
 - Plasma Enhanced Chemical Vapor Deposition
 - Etching
 - Cleaning
 - Passivation
 - Plasma sources of UV radiation for lithography (Hg lamps to EUV)

PLASMA ETCHING-TRANSISTORS, INTERCONNECT

- Plasma etching is at the heart of microelectronics fabrication. Advance techniques have produced feature sizes below lithography limits.
- Challenges for etching novel low-k (dielectric) materials for interconnect have been met.



• Ref: F. Huang, P. Ventzek





SOPHISTICATED PLASMA TOOLS





AMAT Ionized Metal PVD



- AMAT-Komatsu PECVD for flat panel displays
- Ref: Ashok Das

PLASMA PROPERTIES: ICPs IN Ar/c-C₄F₈/CO/O₂



- Complex multi-component gas mixtures are used to optimize the flux of reactants to the substrate.
- Dozens of radicals and ions may be generated by dissociation and ionization of the feedstock gases.

 Ar/c-C₄F₈/CO/O₂ = 60/5/25/10, 10 mTorr, 600 W ICP, 13.56 MHz, 20 sccm.



IEADs TO SUBSTRATE: MERIES IN Ar/C₄F₈ /O₂

- Acceleration of ions into the wafer by applied bias generates fluxes of a wide variety of ions.
- These Ion Energy and Angular Distributions (IEADs) activate etching processes.
- 40 mTorr, 2000 W MERIE, 215 sccm, Ar/C₄F₈ /O₂ = 200/10/5, 100 G

SELECTIVITY IN MICROELECTRONICS FABRICATION

• Fabricating complex microelectronic structures made of different materials requires extreme *selectivity* in, for example, etching Si with respect to SiO₂.





• AMD 90 nm Athlon 64

• Complex features are fabricated by selectively removing one material but not another with near monolayer resolution.

FLUOROCARBON PLASMA ETCHING: SELECTIVITY

• Selectivity in fluorocarbon etching relies on polymer deposition from dissociation of feedstock gases.



- Compound dielectrics contain oxidants which consume the polymer, producing thinner polymer layers.
- Thicker polymer on non-dielectrics restrict delivery of ion energy (lower etching rates).

ICPP04_14

• G. Oerhlein, et al., JVSTA 17, 26 (1999)

CHALLENGES IN TAILORING PLASMAS FOR SELECTIVE ACTIVATION

- Advanced applications will require extreme selectively by producing desired plasma chemical reactions and preventing undesirable.
- The ability to tailor the energy distributions of plasma particles is key to this selectivity.
 - Tailored electron energy distributions: Control formation of radicals and ions; best if also spatially segregated.
 - *Tailored Ion energy distributions:* Should be narrow to differentiate thresholds.
 - *Tailored synergy between ions and neutrals:* Necessary for monolayer control of selectivity, deposition, end-point.
- Robust diagnostics to monitor, develop and control processes.



TAILORING f(E) BY FREQUENCY

• Plasma tools for multiple processes or recipes (different chemistries) require control of electron energy distribution for optimum generation of precursors.



• [e], ICP, 10 mTorr, Ar/Cl₂ = 70/30.

Model results from HPEM Ref: K. Seaward, S. Samakawa

TAILORING FLUXES USING MULTIPLE FREQUENCIES

- 2 Frequency RIEs are rapidly becoming the tool of choice for dielectric etch.
 - High frequency is more efficient for heating electrons and so controls ionization and the magnitude of ion flux
 - Low frequency produces little electron heating but controls ion energy incident on the wafer.



TAILORING FLUXES USING MULTIPLE FREQUENCIES

 Over a wide parameter space, ion fluxes can be controlled by high frequency power; ion energy distribution controlled by low frequency.



• Plasma density, Ion flux



• Argon, 10 m Torr

- Ion Energy Distributions
- Boyle, Ellingboe, Turner, PSST 13, 493 (2004)

DIFFICULT TO ACHIEVE SELECTIVITY: BROAD IEADS



- Broad ion energy distributions makes it difficult to resolve thresholds for etching; and so selectivity is poor.
- Ar, 40 mTorr, 300 sccm, 500 W 40 MHz (top), 500 W 5 MHz (bottom), 100 G

Ion Energy Control – Tailored Waveform through Frequency and Active Electronics



• From from Hyun-Ho Doh, et al, JVST A 15 664 (1997).





Ref: K. Seaward

Electronics Research Labor atory Plasma Processes Project K. L. Seaward, 9/15/03

NARROW IEDS: CUSTOMIZED BIAS WAVEFORM



 Non-sinusoidal biases enable control of sheath potential, and narrowing of the IED.



 15 mTorr, 500 W, 200 V_{p-p}, Ar/C₄F₈ = 75/25, 100 sccm

SPEED AND SELECTIVITY: CUSTOM WAVEFORMS



 Recipies combining custom waveforms and dynamically adjusted biases optimize speed and selectivity.

ANIMATION SLIDE CLICK ON FIGURES-AVI FILES IN SAME DIRECTORY See icpp_animate.ppt Optical and Discharge Physics

TAILORING FLUXES THROUGH PULSING

• Processing of thin films depends on the synergy between energetic ions and radical fluxes. Pulsed plasmas which control these contributions produce unique films not otherwise attainable.



- Deposition of low-k fluorocarbon film from perfluoroallyl benzene [L. Han, JVSTB 18, 799 (2000)]
 - Model results from GLOBAL_KIN Ref: K. Seaward

University of Illinois Optical and Discharge Physics

• Pulsed ICP Ar/C₄ F_8 =70/30, 15 mTorr

INSTABILITIES: ELECTRONEGATIVE PLASMAS

 Although rf (10's MHz) excited plasmas operate in a quasi-dc basis, instabilities regularly occur. Most plasma processing tools likely have instabilities which make reproducibility difficult.





- Ionization instability in inductively coupled Ar/SF₆ plasma for etching.
- Chabert, Lichtenberg, Lieberman, Marakhtanov PSST 10, 478 (2001)

PLASMA DIAGNOSTICS HAVE PLAYED A CRITICAL ROLE AND ARE MOVING CLOSER TO THE PRODUCT

- Plasma process and equipment design have and will continue to critically rely on advanced plasma diagnostics.
- Real time control strategies, a requirement for sub-90 nm processing, must also rely on robust, cost-effective diagnostics.
- The most mature plasma diagnostics are typically too far removed from critical measurements of activation of surface processes.
- Non-intrusive diagnostics which provide the state of activating species impinging on surfaces are required for a complete picture.



Kim et al., Rev. Sci. Instrum. 73, 3494 (2002)







Sub-micron Retarding Field Energy Analyzer on a Si Substrate

• MEMS fabricated analyzers (0.7~0.8 µm grid holes on 3.75 µm centers) provide inobstrusive measurements of ion energy distributions directly on surfaces of interest.





Ref: M. Blain

MTIR-FTIR Wall Probe

- Drift in Cl results from change in the Cl 2 recombination on the walls due to deposition of Si-O-Cl products.
- Exposure to SF_6/O_2 plasma resets the walls × to a reproducible condition.

Plasma

Ref: E. Aydil

Element





To HgCdTe

Detector

Cl, 10 mTorr, 800 W, 100 sccm



MATERIALS PROCESSING: CHALLENGES

- New materials (metal gates, low-k dielectrics, high-k dielectrics, SiGe/SOI substrates, porous materials).
- Increasing demands on etch selectivity.
- Shorter development cycle (6 months...)
- Lower thermal budgets (lower temperature processes)
- More controllable knobs to provide reliable real time control.
- Use of plasmas as processing tools (e.g., self assembly) as opposed to pattern replication.
- Reduced cost of ownership through plasma tools which are used for multiple processes.
- Improved and more relevant contributions from modeling.
- Ref: J. Cook, T. Mantei, P. Schenborn, P. Ventzek, D. Manos

PLASMAS FOR LIGHTING

IMPACT OF PLASMA LIGHTING TECHNOLOGIES

- Annual US energy use for lighting is 750 TWH (8.2 quads)
 - 8.3 % of total energy consumption
 - 22% of total electrical energy consumption.
- Plasmas are 59% of lighting energy use (13% of total). There are 2.6 billion plasma lighting sources in the US.
- Replacing incandescent lamps with plasma sources will decrease US electrical energy use 5% [20 nuclear power plants or 1.2 Million barrels of oil/day (10% of imports)].
- Greenhouse gas emission commensurately reduced.
- Improving efficiencies and use of plasma lighting will enormously impact the worldwide economy and improve the environment.
 - Ref: U.S. Lighting Market Characterization, Navigant Consulting, 2002
 - DOE Annual Energy Outlook 2003

HID lamps for illumination and Projection

Light Source Technology

CMH white-light metal halide

- precision arc tube made from alumina
- Na, TI and rare earth iodides + Hg
- high efficacy and good colour result from high vapour pressures
- designed to be operated from electronic control gear





Fusion Lighting LCD projector unit



Materials advances - System Design - Models

Ref: David Wharmby

Toulouse COST 2002



Quartz lamps

Ultra-high-pressure mercury

- -quartz arctube
- -mercury + bromine dose
- -200-240 bar operating pressure
- -1.3-1.5 mm arcgap
- -8500 K color temperature
- -excellent lumen maintenance
- -minimal color separation and color shift over life
- -1000-2000 hour life
- -100-150 watts (6000-10000 lumens)

Limitations and shortcomings

- -spectrum is deficient in red
 - color efficiency ~70 percent
- -cannot scale up wattage
 - without shortening life
- -cannot scale down arcgap
 - without reducing efficacy





Ref: T. Sommerer, GE R&D Center



Material transport processes

Quartz metal halide lamp



Light Source Technology

Electrodeless – µwave and RF sources

 Sulphur discharge – Fusion Lighting record 170 lumen/microwave W



• Inductively coupled Rg/Hg lamps



System design

Ref: David Wharmby

LIGHTING: ACCOMPLISHMENTS AND CHALLENGES

- Efficient white sources based on Hg plasmas in fluorescent and arc lamps; and non-white metal vapor lamps.
- Challenges:
 - Highly efficient non-Hg (or Cd, Pb,...) plasma white-light sources or near UV which match phosphors (rare gases, excimers, metal halides, molecular radiators)
 - Thermodynamics of high pressure plasmas.
 - Improving understanding of plasma-surface interactions to extend lifetimes (cathodes); and glow-to-arc transition.
 - Quantum splitting phosphors to improve utilization of UV (2 visible photons from 1 UV reduces US energy use 5-10%).
 - Leverage lighting technologies to other application (e.g., UV sources for water treatment, and vice-versa.
 - Radiation driven non-LTE effects in high pressure lamps.

Light Source Technology

Dielectric barrier discharge (DBD)

- Osram Planon lamp
- Xe discharge with UV radiation from Xe₂* excimer
- 60% efficiency to UV then converted to visible with phosphor



 Osram innovations in electrode structure and pulse power format for uniformity.



Materials advances – System Design - Models

Ref: David Wharmby U. Kogelshatz



ATMOSPHERIC PRESSURE PLASMAS

ATMOSPHERIC PRESSURE PLASMAS

- Atmospheric Pressure Plasmas (APP) have had tremendous technological impact
 - High power lasers (e.g., Excimer lasers)
 - Lighting Sources (e.g., HID lamps)
 - Ozone generators
 - Modification of surfaces
 - Toxic gas abatement



 Atmospheric pressure DBD ozone generator

Ref: U. Kogelshatz

OPPORTUNITIES: ATMOSPHERIC PRESSURE PLASMAS THE CHALLENGE

- APP's provide the potential to selectively generate activated species (radicals, ions and photons) for modification and cleaning of surfaces at low cost.
- Most (many) industrial processes performed with liquid solvents could in principle be performed with APP generated radicals.
- The environmental impact of eliminating liquid solvents for cleaning of parts, removal of paint, functionalizing or sterilizing surfaces would be immense.
- Advanced concepts include improvement of combustion processes, chemical and biological remediation, sterilization, microplasma devices, control of aeronautical flows.
- The potential for APPs to perform "high value" manufacturing is literally untapped.

ATMOSPHERIC PRESSURE PLASMAS FOR MATERIAL AND SURFACE PROCESSING: COMMODITY TO HIGH VALUE

PLASMA SURFACE MODIFICATION OF POLYMERS



• M. Strobel, 3M

 To improve wetting and adhesion of polymers atmospheric plasmas are used to generate gas-phase radicals to functionalize their surfaces.



- Polyethylene, Humid-air
- Akishev, Plasmas Polym. 7, 261 (2002).

POLYMER TREATMENT PLASMA TOOL

 Web based corona plasmas treated sheet polymers for improved surface functionality.



Tantec Inc.

FUNCTIONALIZATION OF POLYPROPYLENE

- Control of surface energy by plasma treatment results from functionalization with hydrophilic groups.
 - Carbonyl (-C=O) Alcohols (C-OH)
- Peroxy (-C-O-O) Acids ((OH)C=O)
- Functionalization depends on radical fluxes and process parameters [gas mix, energy deposition, relative humidity (RH)].



• Air, corona plasma, 300 K, 1 atm

THE ROLE OF PLASMAS IN BIOSCIENCE

- Plasmas, to date, have played important but limited roles in bioscience.
 - Plasma sterilization
 - Plasma source ion implantation for hardening hip and knee replacements.
 - Modification of surfaces for biocompatibility (in vitro and in vivo)
 - Artificial skin
- The potential for use of "commodity" plasmas for biocompatibility is untapped.



 Low pressure rf H₂O₂ plasma (www.sterrad.com)



Ref: P. Favia





G50P holes= 416μm bar= 84μm

NCTC2544 human keratinocytes onto microstructured PS

PS/PEO-like





N-groups/PEO-like



ATMOSPHERIC PRESSURE PLASMAS: THE CHALLENGE

- Controlling functional groups on polymers through fundamental understanding of plasma-solid interactions will enable engineering large area biocompatible surfaces.
- 10,000 square miles of polymer sheets are treated annually with atmospheric pressure plasmas to achieve specific functionality. Cost: < \$0.05 /m²
- Low pressure plasma processing technologies produce biocompatible polymers having similar functionalities. Cost: up to \$100's /cm² (\$1000's/cm² for artificial skin)
- Can commodity, atmospheric pressure processing technology be leveraged to produce high value biocompatible films at low cost? The impact on health care would be immeasurable.





• M. Strobel, 3M



• Tantec, Inc.

CAN COMMODITY PROCESSES PRODUCE HIGH VALUE MATERIALS?



 Demonstration: corona-rod, 2 mm gap, 15 kV pulse, N₂/O₂/H₂O =79.5 / 19.5 / 1, 1 atm

PLASMA PROPERTIES: PULSED NEGATIVE CORONA Animation Slide

• Development of plasma streamer produces large electric field, electron sources, ionization and radical production.



MIN

ΜΔΧ

 N₂/O₂/H₂O =79.5 / 19.5 / 1, 1 atm, 15 kV, 0-15 ns

SURFACE INTERACTIONS: O RADICALS, IONS





- Positive lons (10⁹ 5x10¹³ cm⁻³)
- Ion penetration is ultimately controlled by surface charging.
- O radicals penetrate deeper into the features.

FUNCTIONAL GROUP DENSITIES ON POLYPROPYLENE



ICPP04 44

ATMOSPHERIC PRESSURE PLASMAS: SURFACES, PHOTONS, FLOW

APPJ-based Decontamination



Decon Benefits:

- Innocuous feed gases (He, CF_4 , O_2)
- Dry no secondary waste stream

Ref: L. Rosocha

- Actinides potentially recoverable
- Endpoint detection possible
- Decontamination Concept \Rightarrow Volume Reduction
- Energetic plasma electrons dissociate CF₄ forming F atoms
- Oxygen reacts with CF_x molecules to prevent recombination
- Atomic Fluorine etches contamination: Pu(s) + 6F(g) ⇒ PuF₆(g)
- Volatile byproducts (e.g., PuF₆) captured in adsorbent and HEPA filters
- "Rolling Seal" allows motion while eliminating spread of contamination

Los Alamos National Laboratory

Transient Plasma ignition experiments



USC

MICRODISCHARGES: MEMS FABRICATION

• Microdischarges leverage pd scaling to operate at atmospheric pressure with sizes < 10s μ m (pd = 6 Torr-cm, p=1 atm, d = 65 μ m)



 Using MEMS techniques, arrays of addressable MDs can be fabricated for UV generation, displays, "coherent" photonics with "incoherent" sources.

Ref: J. G. Eden, UIUC

In-situ H₂ Generation for Small Scale (i.e. Low Power) Fuel Cells Using a Microhollow Cathode Discharge



ICPP04_47

CONTROL OF AERONAUTICAL FLOWS USING PLASMAS

• Charged particles accelerated in electric fields can produce advective motion of gases through momentum transfer.



 Example of dielectric barrier discharges for flow control

Ref: R. Roth

$$\frac{Force}{Volume} = q \left(\sum_{i} Z_{i} n_{i} - n_{e} \right) E = \rho E = \varepsilon_{o} E \nabla \cdot E$$

- The flight characteristics of airfoils are sensitive functions of the "adherence" of the boundary layer.
- Strategically generated plasmas on wings can beneficially and controllably affect lift and steering.

CONTROL OF AERONAUTICAL FLOWS USING PLASMAS



Ref: R. Roth, Phys. Plasma 10, 2117 (2003)

• A dielectric barrier discharge on the surface of an airfoil prevents separation of the boundary layer.

University of Illinois Optical and Discharge Physics

Ref: T. Corke, AIAA 2004-2127

KEY TO PROGRESS IS LEVERAGING TECHNOLOGIES: MICRODISCHARGE ACTUATORS



- Microdischarges were developed as photon and radial sources.
- Leveraging these technologies enable advances in other areas.
- Arrays of microdischarges may enable control of flow characteristics in "programmable" fashion.
- 600 Torr Ne, 180 V

GAS PUMPING USING MICRODISCHARGS



- Ion pumping is efficient due to ability to produce large cw ion current densities.
- Flexible arrays enable large areas.
- 600 Torr Ne, 180 V

PLASMAS IN NANOSCIENCE

THE ROLE OF PLASMAS IN NANOSCIENCE

- Plasma science has been absolutely critical to the development of conventional microelectronics structures.
- What will the role of plasma science be in facilitating these advances in truly nanoscale science and technology?
 - Atomic layer processing (etch and deposition)
 - Plasma aided lithography (trimming)
 - Selective activation or functionalization of materials on molecular scales (inanimate and living)
 - Self- and directed-assembly
 - Commodity production of nanostructures and nanoparticles.
 - Plasma physics laboratories

SELECTIVE, ALIGNED PLASMA GROWTH OF CARBON NANOTUBES

- Aligned CNT growth can be obtained in a low pressure rf and dc plasmas using different feedstocks.
- Catalyst choice and configuration may dominate.



DC Plasma CVD

Ref: B. Cruden

Cruden et al., J Appl Phys, 12, 363 (2001).



RF Plasma (C₂H₄/NH₃)



DC Plasma (C_2H_2/NH_3)



Ref: U. Kortshagen, U. Minnesota

Atmospheric Pressure Plasmas for Carbon Nanotube Deposition



Microplasmas as Micro-reactors: Nanostructures



MICRODISCHARGES: MINIATURE PLASMA PHYSICS LABS

• Following microdischarges scaling to \geq 10s atm, [e] > 10¹⁹ cm⁻³, d < 0.1 μ m provides a cw source of quantum mechanical plasma(?)



• Ref: Annual Progress Report, "Generation of Micro-Scale Reactive Plasmas and Development of Their New Applications" K. Tachibana, Project Leader, March 2004

CONCLUDING REMARKS

- Low temperature, technological plasmas address an array of high technology and commodity applications.
- The widest use of low temperature plasmas is production of extremely high value materials (e.g., microelectronics) and low values materials (e.g., polymer functionalization).
- The key to advancing the state of the art is improving fundamental understanding while leveraging low cost processes for high value materials. For example,
 - Plasma modified polymers for artificial skin
 - Microplasma produced nanoparticles