When Low Temperature Plasmas Meet Surfaces

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Uniqueness of Plasma-Surface Modifications

- Low temperature plasma (LTP) is used in a staggering number of different applications to modify surfaces: why is it so widely used?

- I believe that LTP is a ***uniquely*** powerful tool to modify surfaces

- A few simple calculations illustrate the idea

Ion Impact at Surface

- Ion current density ~ 10 mA cm^{-2} (10^{17} cm^{-2} s^{-1}); time between impacts on area of ~ 1 nm^2 is about 10^{-3} s.

- Energy of single impact dissipates to background heat in ~ 10^{-12} s!

- Conclusion: ion impacts dissipate energy long before another ion hits nearby: *impacts are isolated*

Single ion impact movie

Single Ion Impact at Surface: Peak and Mean Power Deposited

- Ion energy ~ 10^2 eV, deposited in 1 nm^2 and dissipating in ~ 10^{-12} s
- Peak power density dissipated by single ion impact: ~ 10^9 W cm^{-2}!
- But for 10^{17} ions cm^{-2} s^{-1} @ 10^2 eV: average power density ~ 1 W/cm^2

Peak power **is huge: chemical bonds broken easily at surfaces**
Average power **is modest: easily removed, e.g., from wafer backside**

Gradients in time and space near surface enormous

Single Ion Impact at Surface: Processing Implications

- Ions don’t penetrate surface far - ~ several nm typically, so energy is deposited close to surface, in a small area
- A lot of energy is dissipated locally in this small area, but for a very short period of time. This causes chemical bonds to break and then reform in different ways (or sputter/desorb)
- But surface does NOT heat much since ion impacts are isolated and energy shared with entire structure (e.g. wafer) and this can be readily removed

Dramatic surface chemistry at low temperature: First key to LTP uniqueness

Ion Impacts at Normal Incidence

- **Sheaths form** near surface naturally due to mass differences between electrons and ions
- These high field regions conveniently **accelerate ions, often with no collisions**, to allow (nearly) normal incidence impacts at surfaces, converting the potential energy in sheath into kinetic energy at the surface
- Collisionless at fairly **high pressure** if sheath thickness $< l_{mfp}$

**Energetic ion impact at normal incidence:
Second key to LTP uniqueness**

Ion-Neutral Synergism

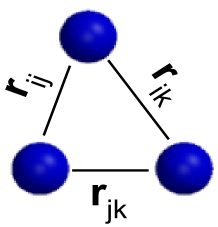
- Neutral, chemically active radicals are of course created in large numbers by electron-impact dissociation in molecular gas plasma
- Surface flux scales with pressure (density) – higher neutral gas pressure allows greater fluxes of radicals, increasing processing rates
- Well known that individual effects of ions and neutrals can be dramatically altered when both impact surfaces:

SYNERGY – *third and perhaps most important key to LTP uniqueness*

Plasma Etch: Nanoscale Feature Control

- Energetic, normal incidence ions coupled with high fluxes of reactive radicals, allowing various ion-neutral synergies (e.g. for etch and for forming protective 'film' to promote selectivity and critical dimension control)
- Plasma can be made (mostly!) uniform over a (fairly!) large area at (relatively!) low cost
- Relatively high pressure operation allows high rates of etch product removal with modest pump (pumping rate scales with pressure; pump capital costs significant)

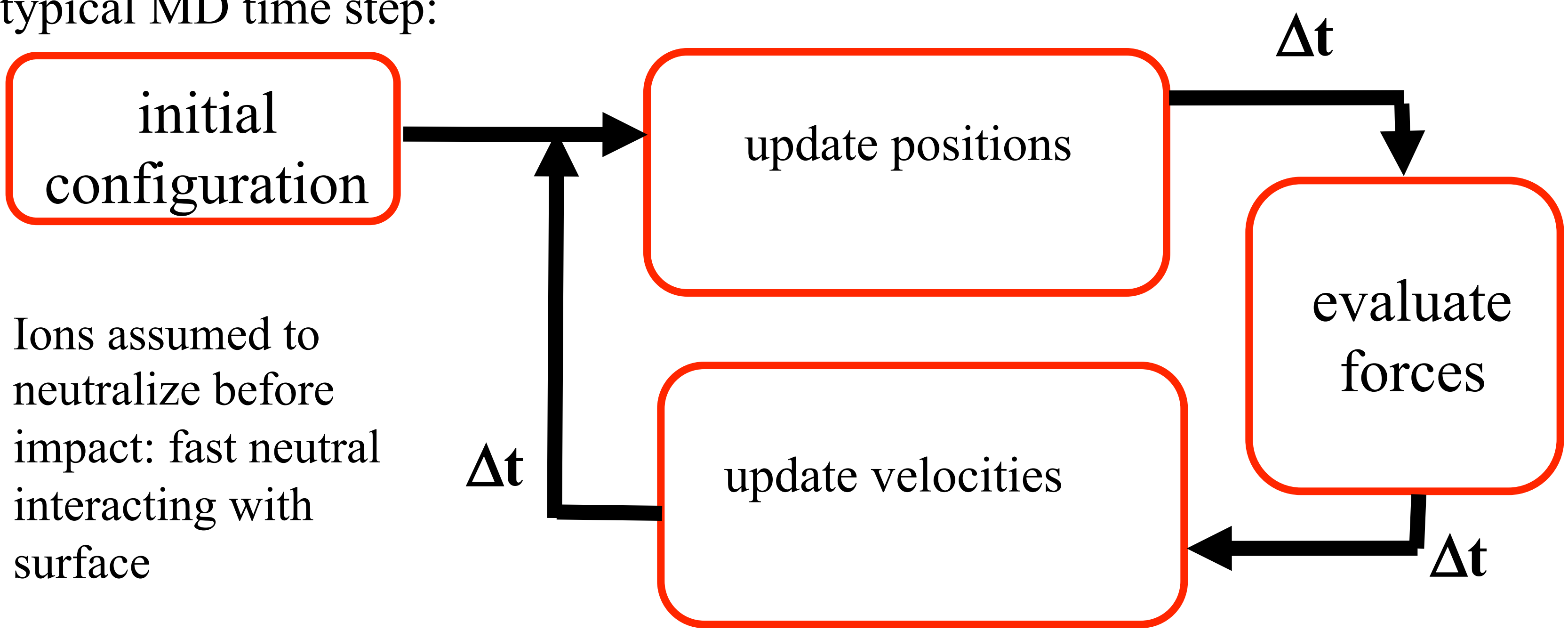
Molecular Dynamics (MD) Simulation



Interatomic Potential → Interatomic Forces

$$\Phi(r) \quad F_i = -\mathrm{grad}(\Phi) = m_i d^2r/dt^2$$

typical MD time step:



Ions assumed to neutralize before impact: fast neutral interacting with surface

$\Phi(r)$ is assumed to model all reactive and non-reactive interactions

Interatomic Potentials

- Tersoff-Brenner style, many body REBO potential for short range covalent bonds like Si-C-F-O-H systems
- Repulsive pair potential (Molière) for Ar 'ion' interactions
- No van der Waals forces

Trajectory vs. 'Snapshot' Movies

- Trajectory movie follows atoms for ~ 1 ps

- 'Snapshot' movie takes images at end of trajectory and combines them to give an impression of time evolution

- ~ 10^3 images of impacts ~10^{-3} seconds apart shows effects on order of seconds of elapsed time

Example 1: Ar^+ on Si

•Ar^+ amorphizes layer, with depth of amorphous layer increasing with ion energy

•Then, lowering ion energy allows layer to partially re-crystallize!

•Complexity due to **varying depth profile of ion energy deposition/bond breaking coupled with kinetics of energy transport vs. atomic ordering/bond re-forming**

Si amorphization snapshot movie

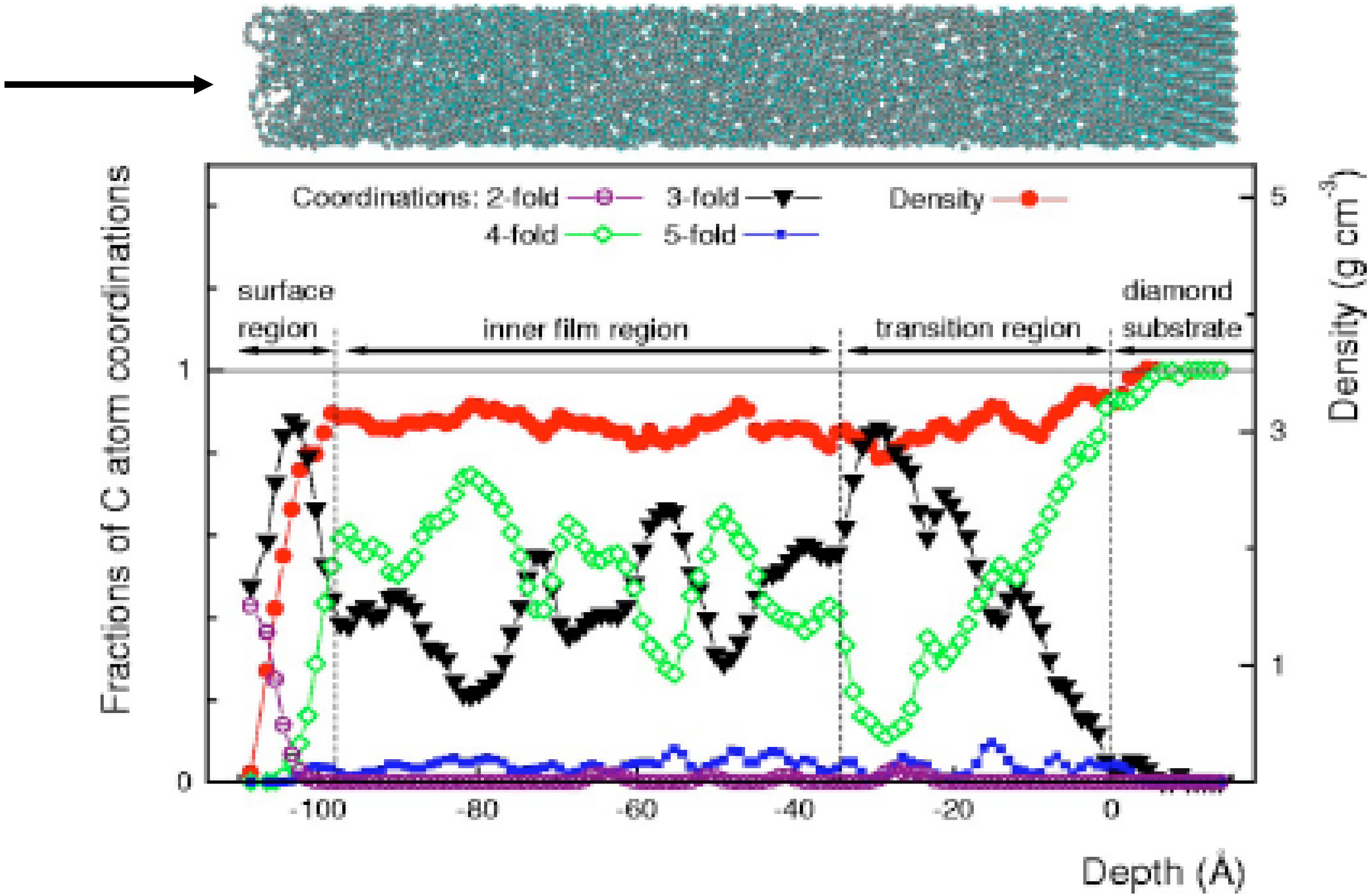
Example 2: ta-C Film Deposition from C^+

•C^+ impacts at ~ 100 eV, growing ta-C film, with depth-dependent sp^3/sp^2 fractions

•Film temperature plays important role in sp^3/sp^2 fraction

•Again, complexity due to varying **depth profile of ion energy deposition coupled with kinetics of energy transport vs. atomic ordering**

MD: ta-C Film Deposition



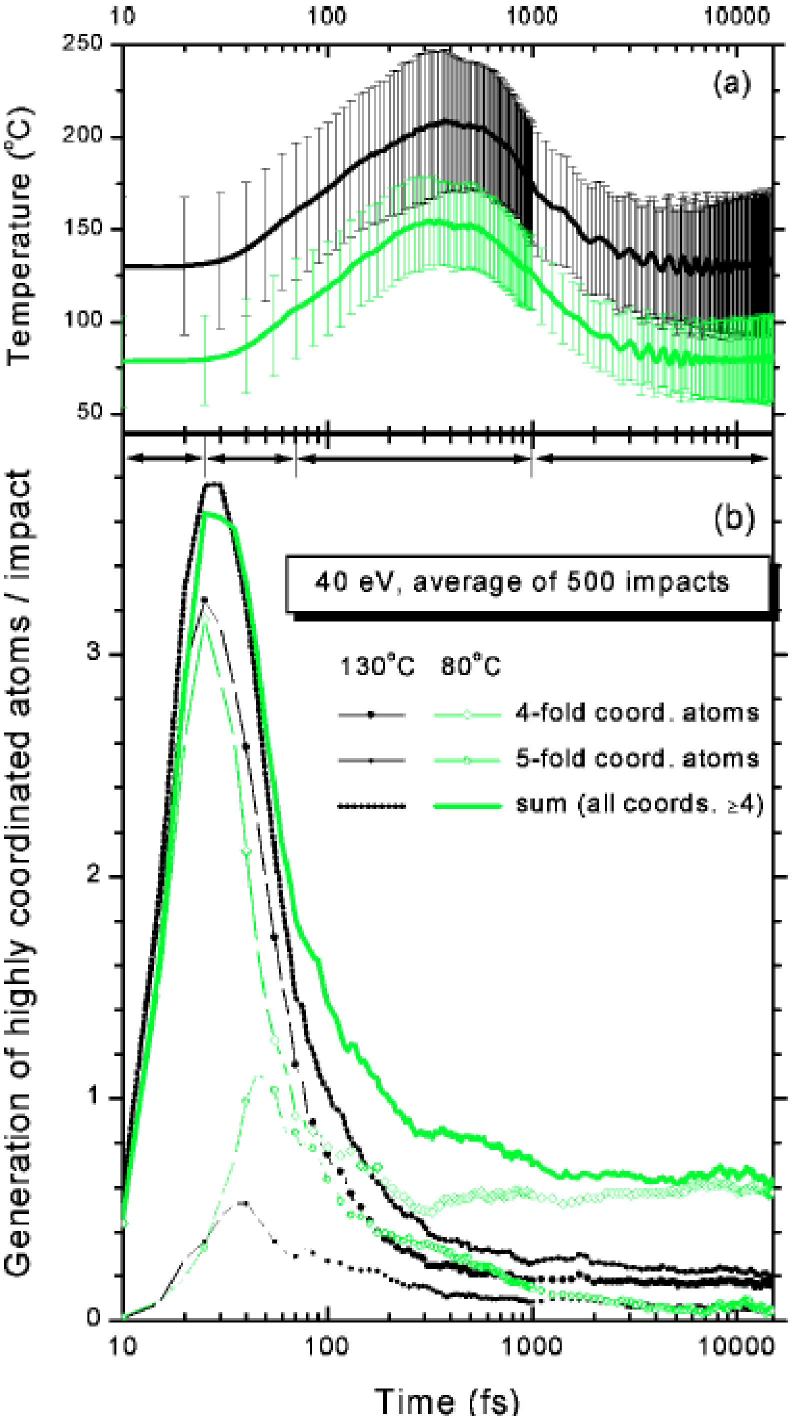
Ion energy: 40 eV; Ion fluence: 1.6×10^{17} cm^{-2}; Jäeger and Belov, 2003

Kinetic Processes Control sp^3/sp^2 fraction

Cell temperature varies with time during trajectories

Highly coordinated atom number varies with time during trajectories

(Jäeger and Belov, 2003)



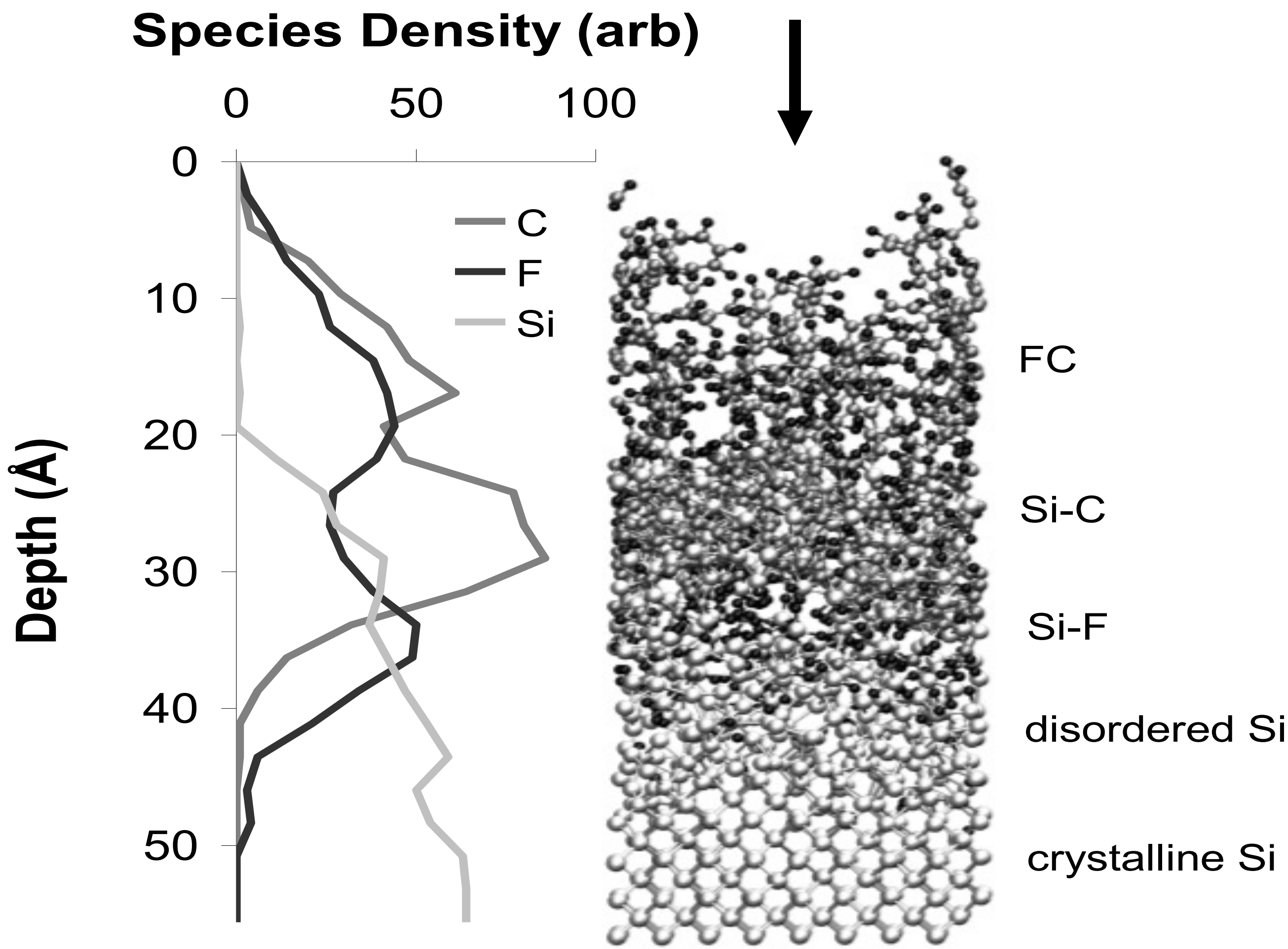
Example 3: Etching Si in Presence of Fluorocarbon Film

•Etching with ‘depositing’ chemistries can result in formation of layered structures near surface

•$Ar^+/F/C_xF_y$ mixtures demonstrate this

•Complex, poorly understood processes induce transport both into and out of surface while promoting various reactions

C_4F_4/ F/ Ar^+ on Si: 'Steady State Layer'



Side view and depth profile of a cell from 5:5:1 C_4F_4/ F/ 200 eV Ar^+ (Si=white, C=grey, F= black).

Snapshot movie

What About ORGANIC Materials (Polymers)?

Well known that polymers are susceptible to scissioning and/or cross-linking by ***electrons*** and ***photons***

- Electron beam and optical lithography are based on this!

Even well known that plasma-generated UV/VUV can strongly alter polymers….

- Earliest paper: may be from Martin Hudis, 1972

Plasma Interactions with Polymers used for Etch Masks

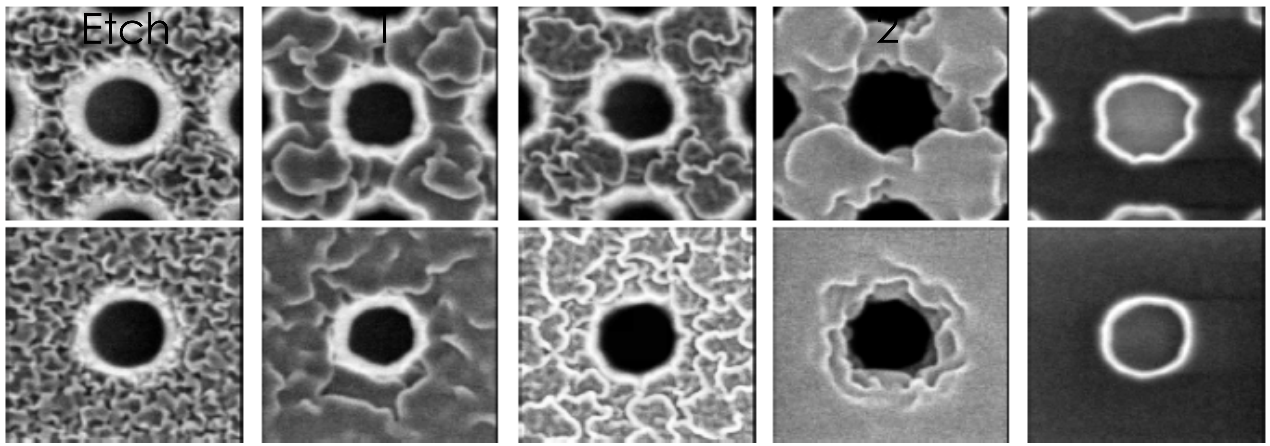
- Masks – *all use plasma etch to remove material!*
  - optically-generated lithography: patterns in photoresist
    - 193 nm immersion
    - phase shift masks
    - optical proximity correction
    - double exposures
  - EUV lithography photoresist
  - block copolymer, self-assembled film masks
  - nanoimprint lithography masks

How Do Plasmas *Roughen* (or Smooth) 193 nm Photoresist ?

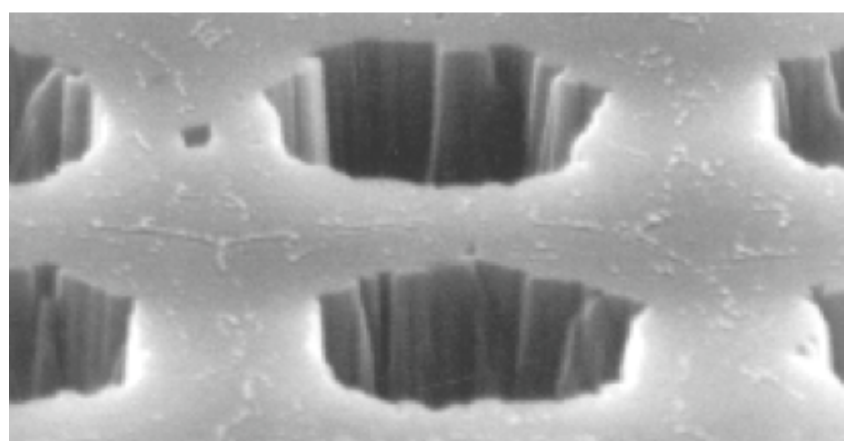
DARC Etch | Oxide Etch 1 | MSL Etch | Oxide Etch 2 | Ash

Dense Features

Isolated Features



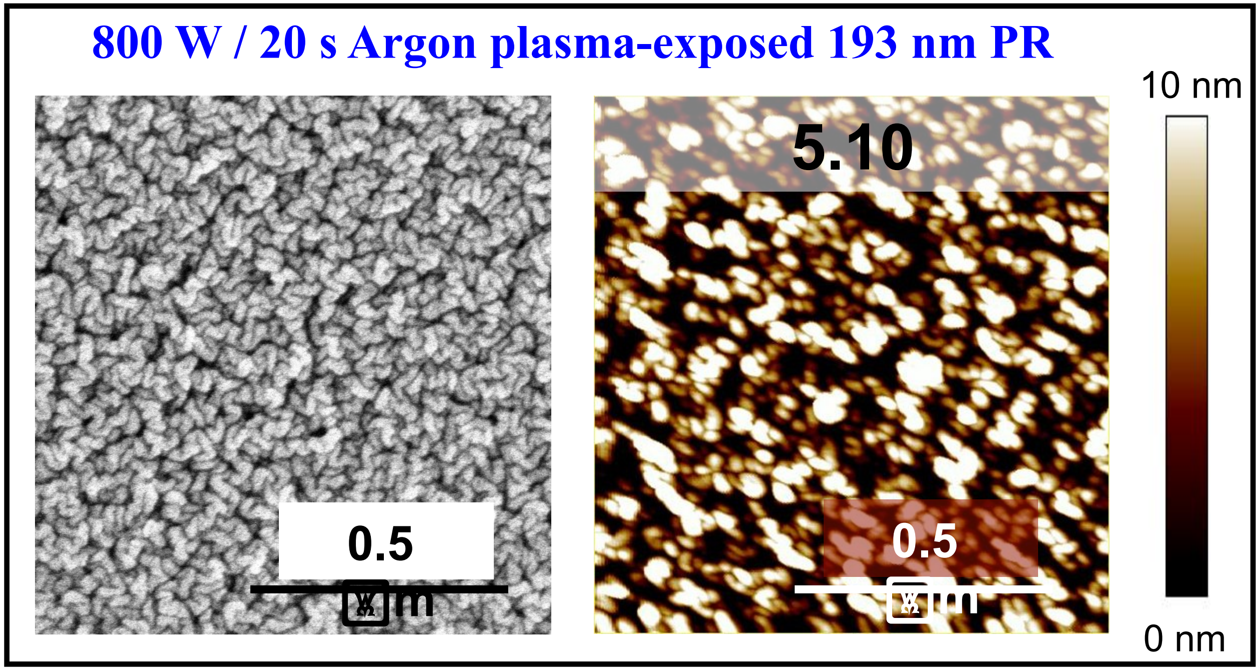
Sidewall striations post-etch



193 nm PR Roughness Observed:
Ar-only plasma

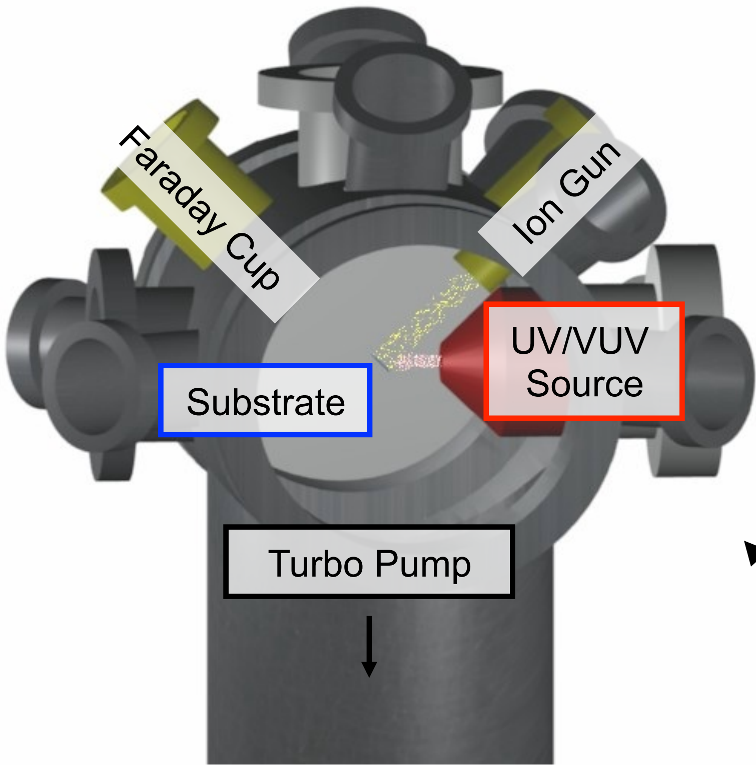
» ICP system: 10 mtorr; V_{dc}~ -150 V; 100% Ar

G.S. Oehrlein et al., UMd

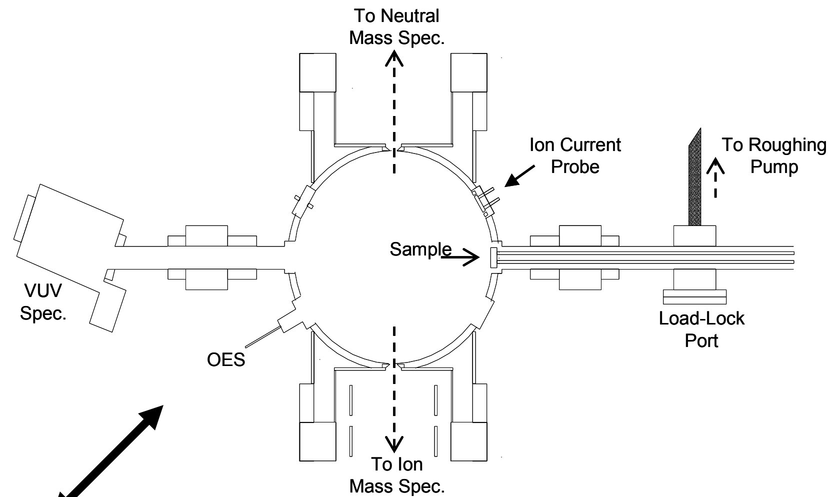


What explains this extreme roughness??

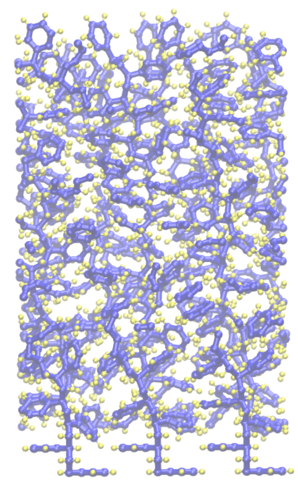
Strategy to Identify Plasma-Surface Alteration *Mechanisms*



Beam Experiments

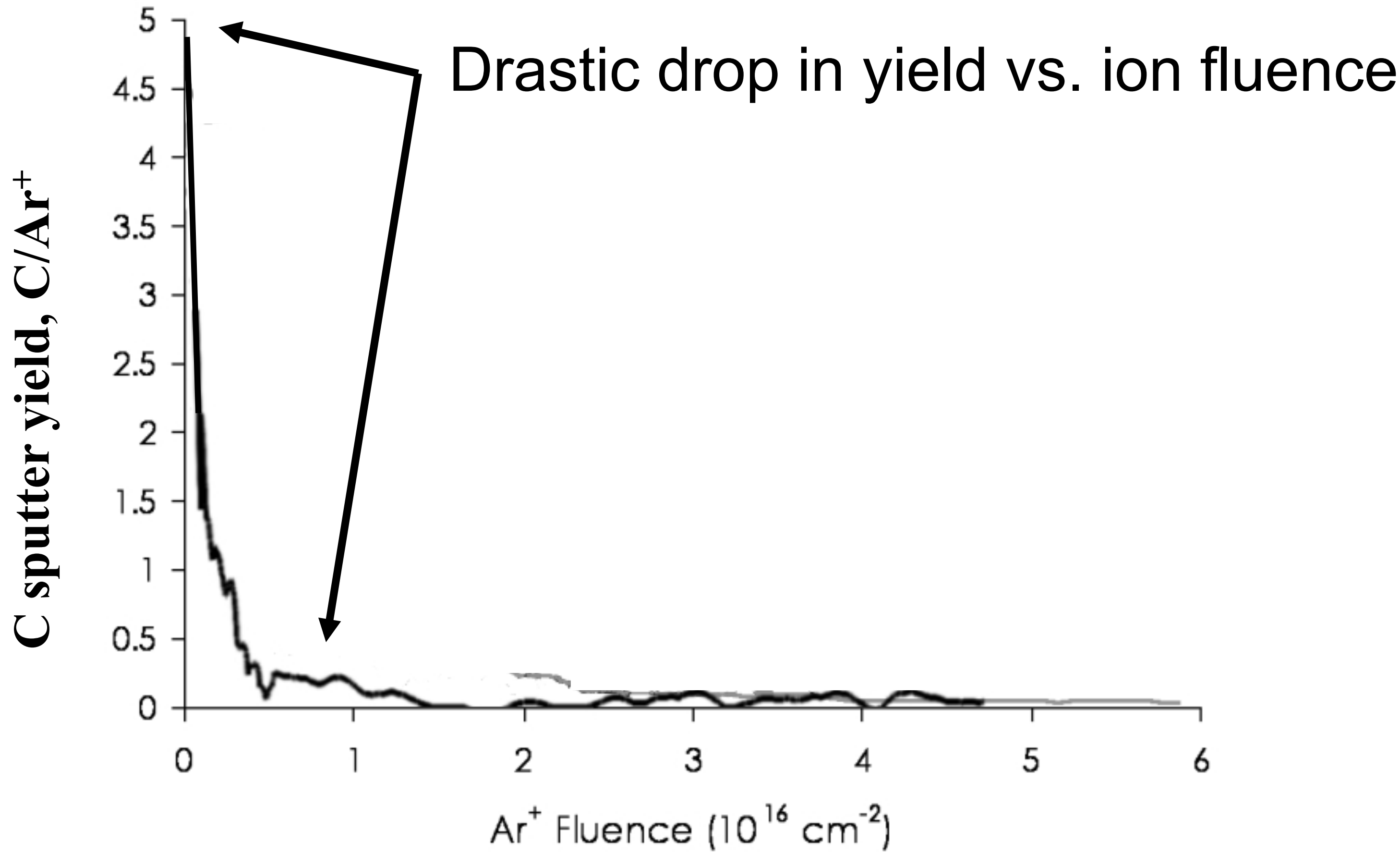


Plasma Experiments



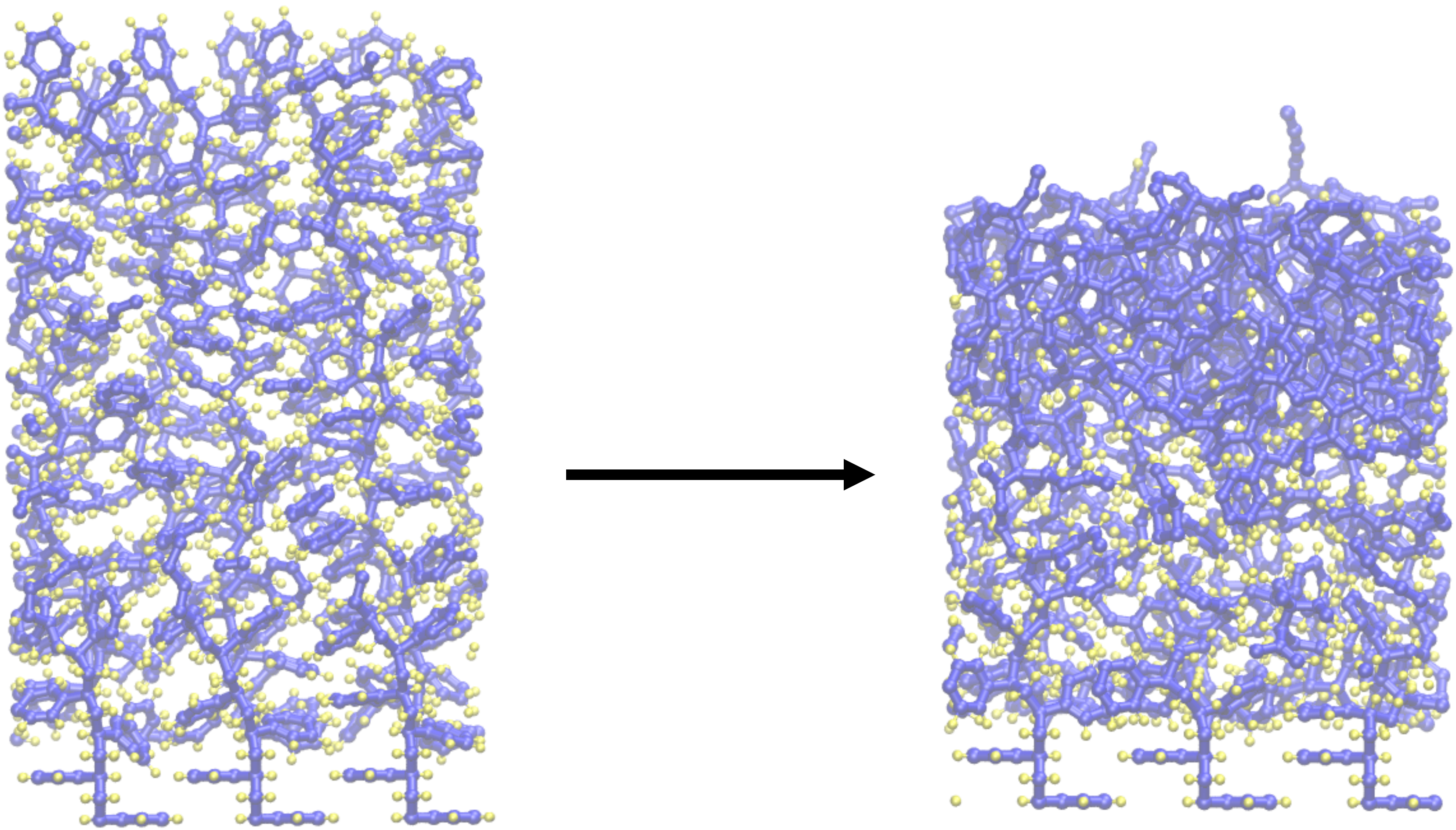
MD Simulations

Measured Ar^+/Polystyrene Sputter Yield (150 eV)



(Similar results reported by J. Zekonyte, V. Zaporojtchenko, and F. Faupel, *Nucl. Instrum. Methods in Phys. Res. B.* 236: 241-248. 2005.)

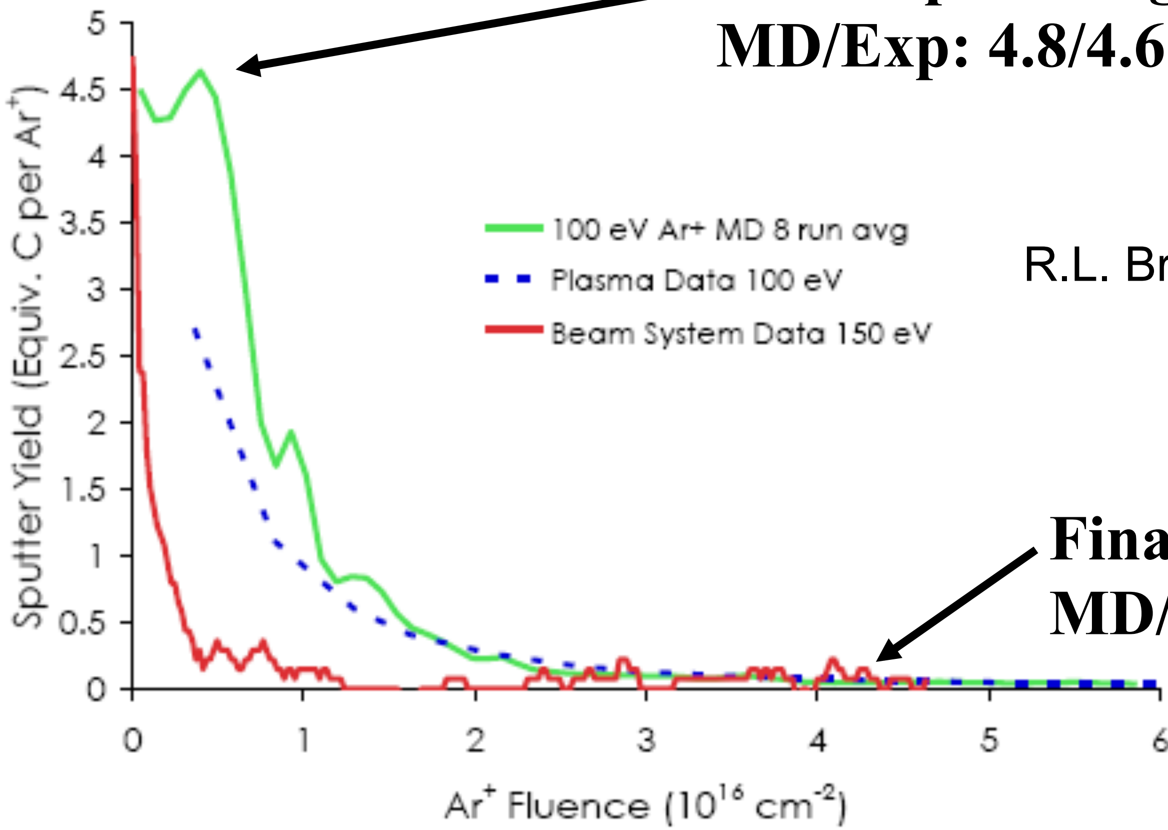
Polystyrene Surface Before and After 10^{17} cm^{-2} Ar^+ Fluence (100 eV)



Near-surface alteractions consistent with separate XPS and ellipsometry measurements of beam-processed samples (G.S. Oehrlein and R. Bruce, UMd)

MD-Experiment Ar^+/PS Yield Comparison (150 eV)

Initial sputtering yield:
MD/Exp: 4.8/4.6



R.L. Bruce, UMd

Final sputtering yield:
MD/Exp: 0.02/0.07

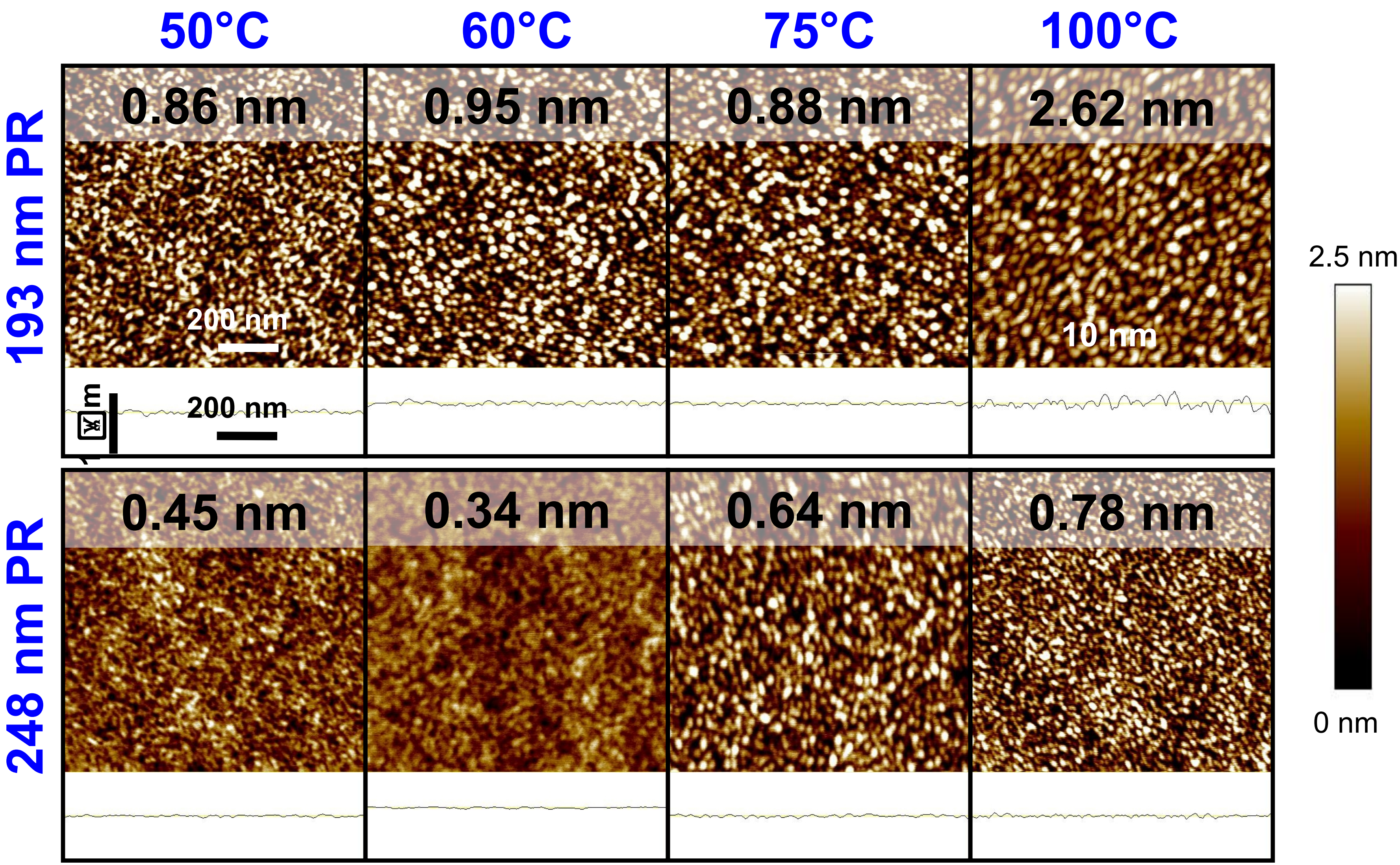
Propose 3 Effects to Generate PR Roughening in Ar Plasma

- Ion bombardment (Ar^+)
- VUV photons
- Substrate temperature (50°C -100°C)

Compare plasma (Ar) and vacuum beam exposures

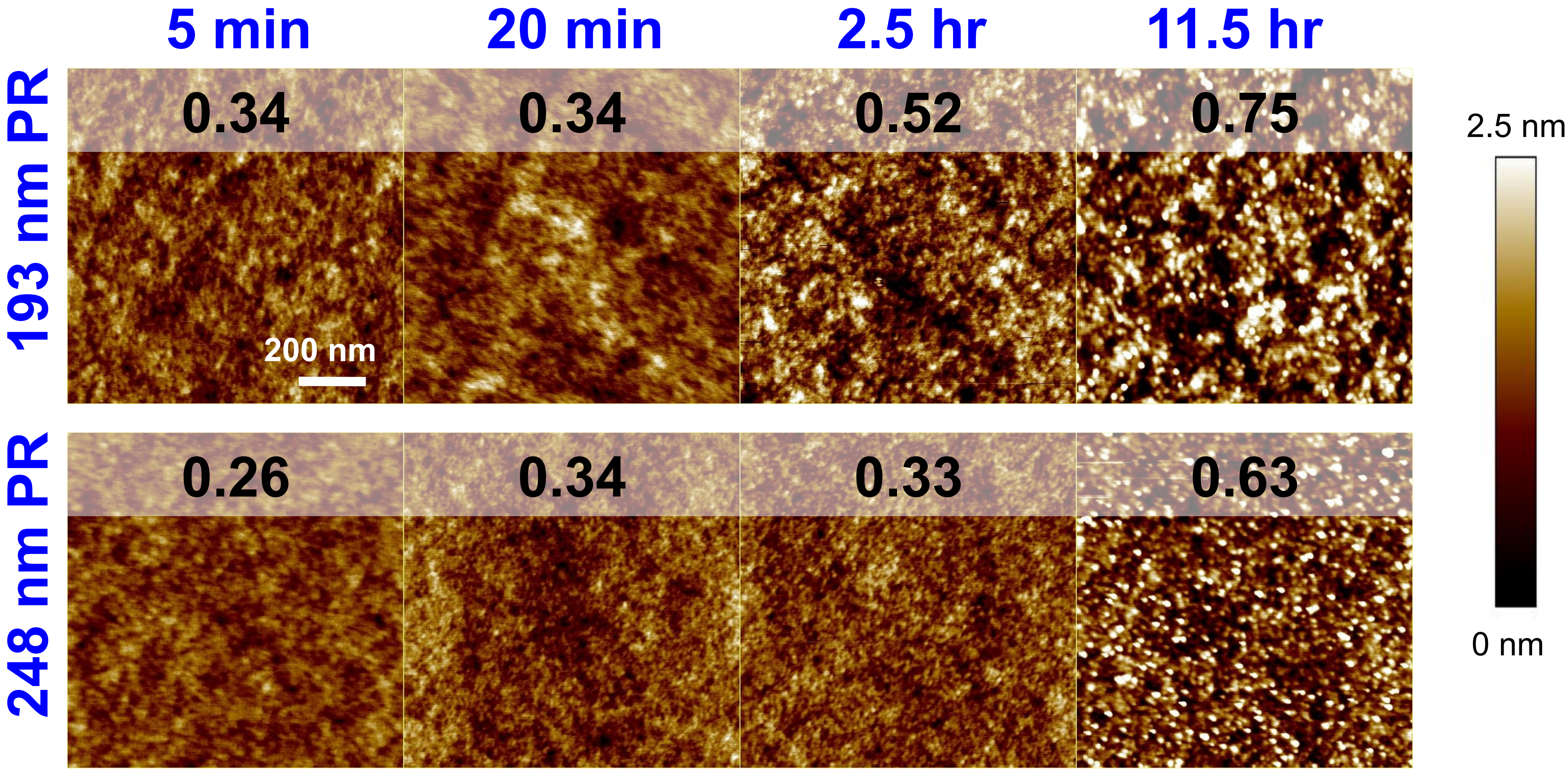
Ion bombardment *only:* Not enough roughening

» 150 eV Ar^+, 4.0 x 10^{17} ions•cm^{-2}



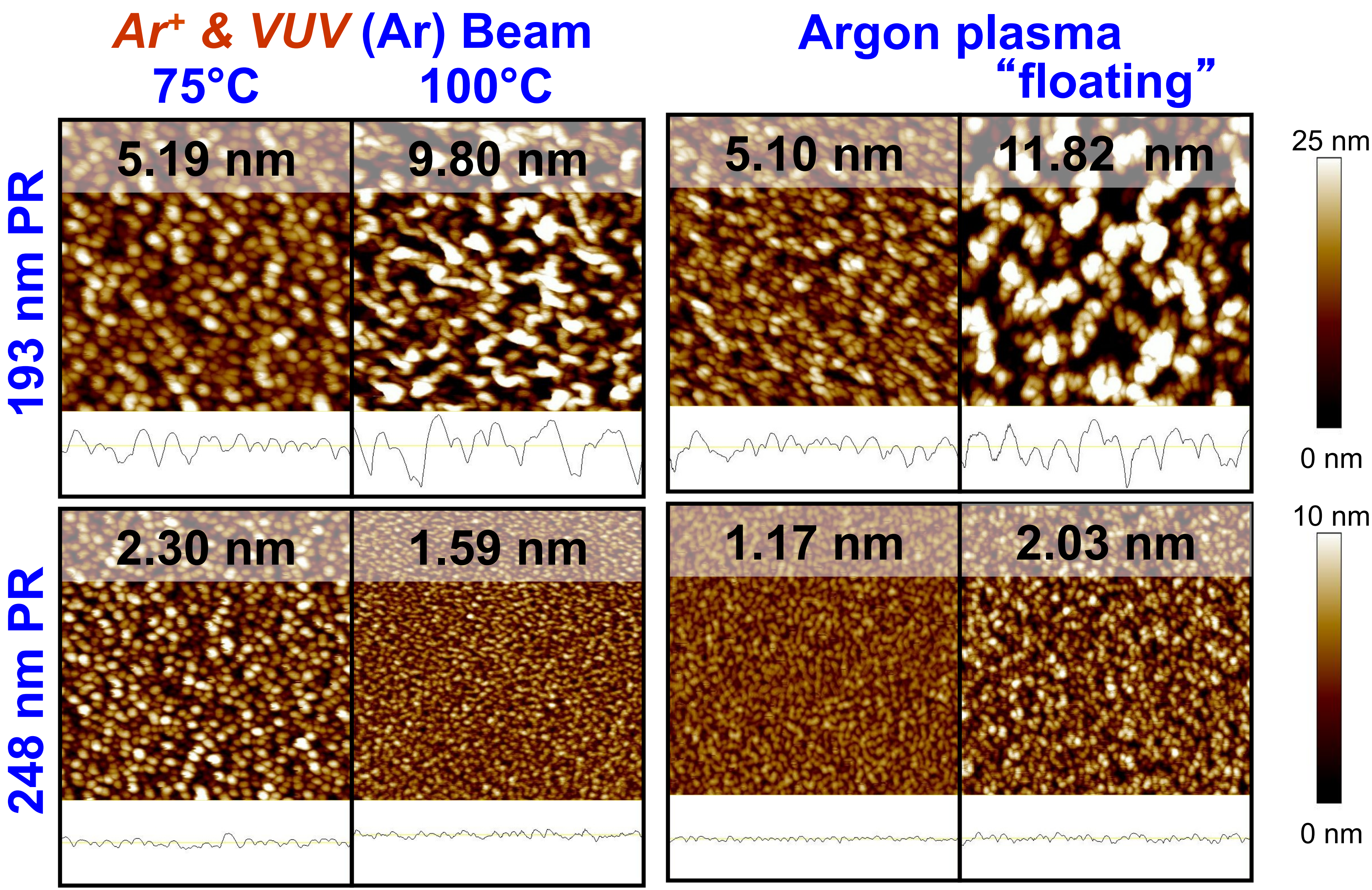
Only VUV: surface observation

» Surface roughness quantified with 1x1 μm^2 AFM images.



» Minimal surface roughness forms with remote UV/VUV exposure.

Simultaneous Ions and Photons: *agreement!*



PMMA-Based 193 nm PR Roughening Mechanism?

- **Ion bombardment alters near-surface (1-2 nm), creating a heavily cross-linked, C-rich region**
  - **probably *compressively stressed***

- **There is a 1-to-1 correspondence between ion-induced cross-linked surface layer and enhanced roughening**

- **VUV photon penetrate ~ 50-100 nm, breaking C-O bonds; this is known to increase polymer mobility or relaxation dynamics (cf. E. Pargon, LETI)**

- **Heating increases polymer mobility or relaxation dynamics**

PMMA-Based 193 nm PR Roughening Mechanism?

Huang model: wrinkling

Compressively stressed

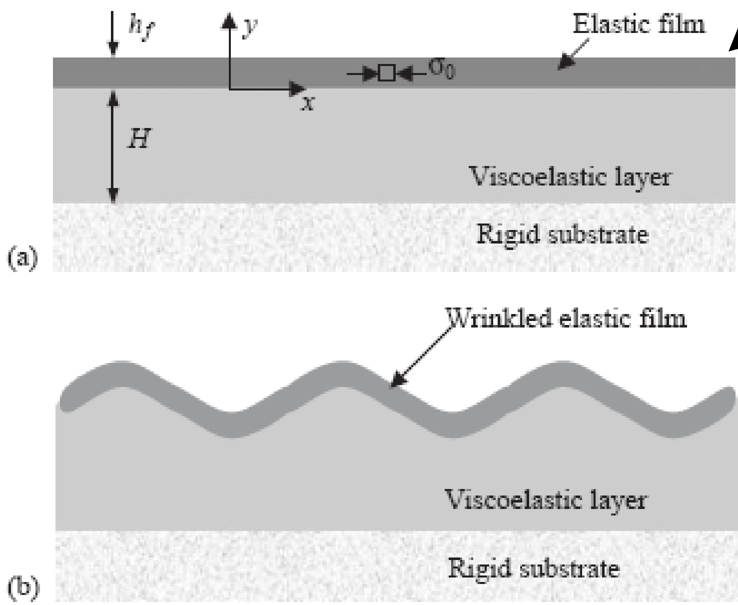
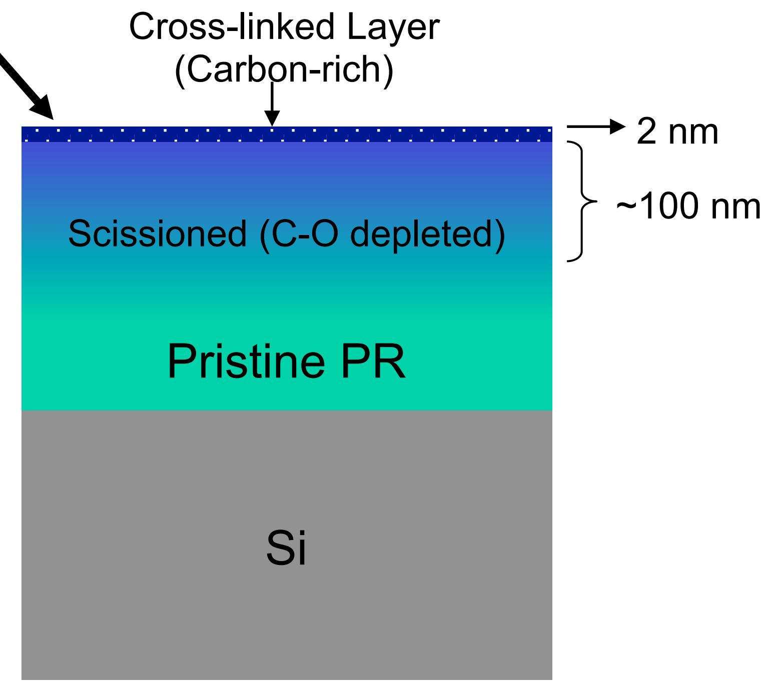


Fig. 1. A schematic of the model structure: (a) reference state; (b) wrinkled state.



Our model of PR in plasma

R. Huang. *Kinetic Wrinkling of an elastic film on a viscoelastic substrate*. J. Mech. Phys. Solids. 53 (2005).

Conclusions: PMMA-Based 193 nm PR Roughening

- **Ion bombardment, VUV photons, (and substrate heating) act *synergistically* to give observed roughening**

- **Comparisons of beam and plasma exposure experiments show similar roughening when ion fluence and energy, VUV fluence and surface temperature are the same – even though fluxes and therefore experiment duration differ by ~ 10^2!**

- **Roughening may be due to wrinkling kinetics driven by compressively stressed near-surface region and accelerated by sub-surface relaxation induced by VUV photolysis (or the corresponding electron-induced bond breakage)**

Plasma medicine: a brief history

1900s~: <u>1st generation (e</u>

• direct contact, massive

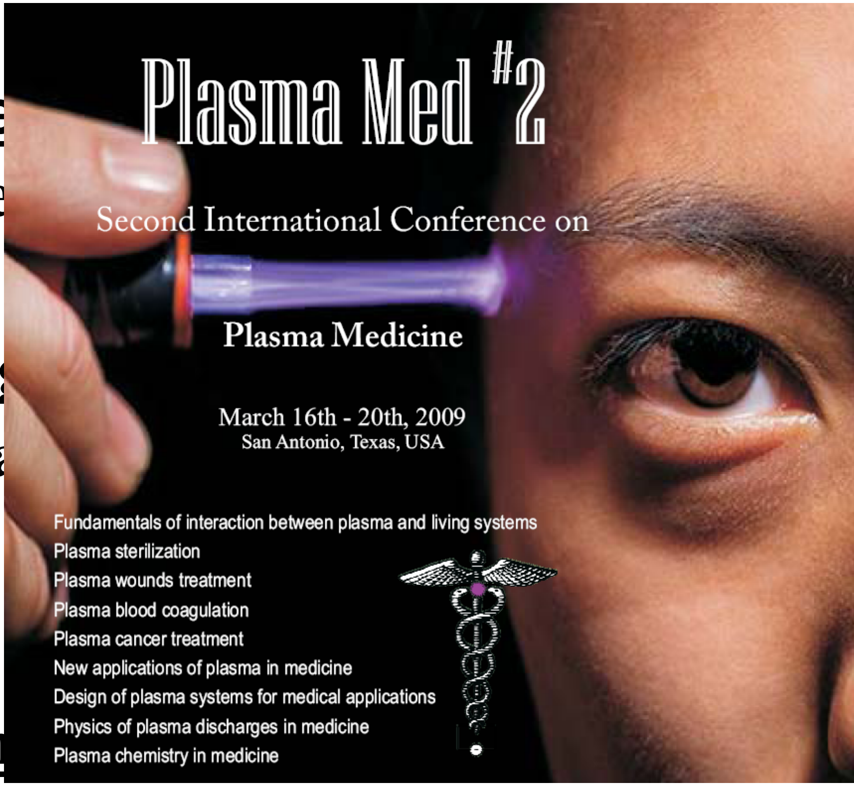
• thermal energy

1970s~: <u>2nd generation (e.g</u>

• low invasive, superficia

• thermal energy

1990s~: <u>3rd generation (an</u>



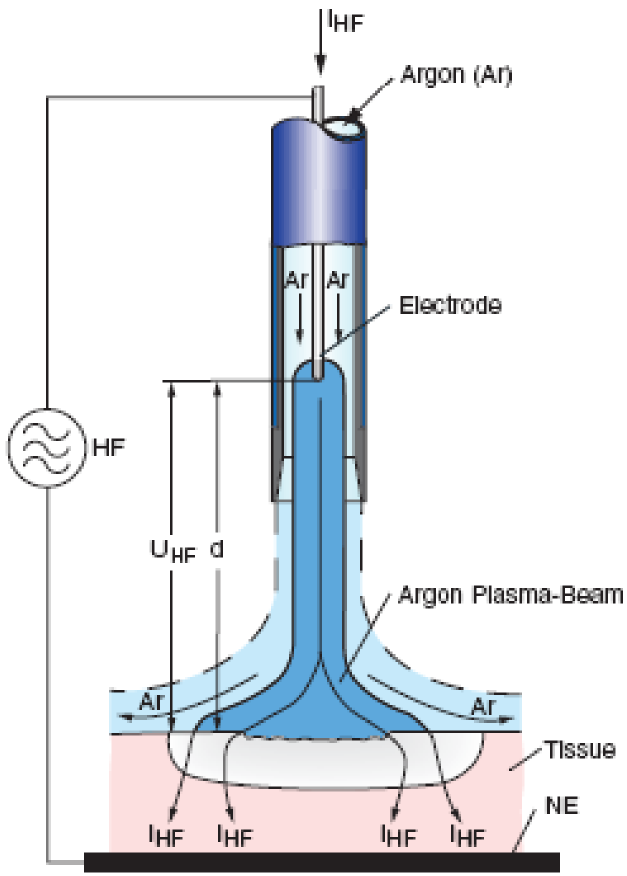
• non-contact, superficial treatment

• UV, reactive neutrals, charged particles, electric field

Plasma-assisted medical device: surgery

- APC (Argon Plasma Coagulator): ERBE, Germany

(http://www.erbe-med.de/)



J. Raiser et al., *J. Phys. D* **39** 3520 (2006)

Tissue ablation and coagulation

APC (Argon Plasma Coagulator)
Example in ***Gastrointestinal Oncology***

Video courtesy of **Dr. Jim Barthel,** Section Head, Endoscopic Oncology Medical Director, Endoscopic Oncology Area, Moffitt Cancer Center & Research Institute, Tampa, Florida

0-15 s: visualization and targeting of area of Barrett's precancerous epithelium in the esophagus (dark pink area).

15 s – 1.5 min: pulsed (16 Hz; 12 W; Ar 1.2 l/m). Surface coagulation from thermal effect is obvious.

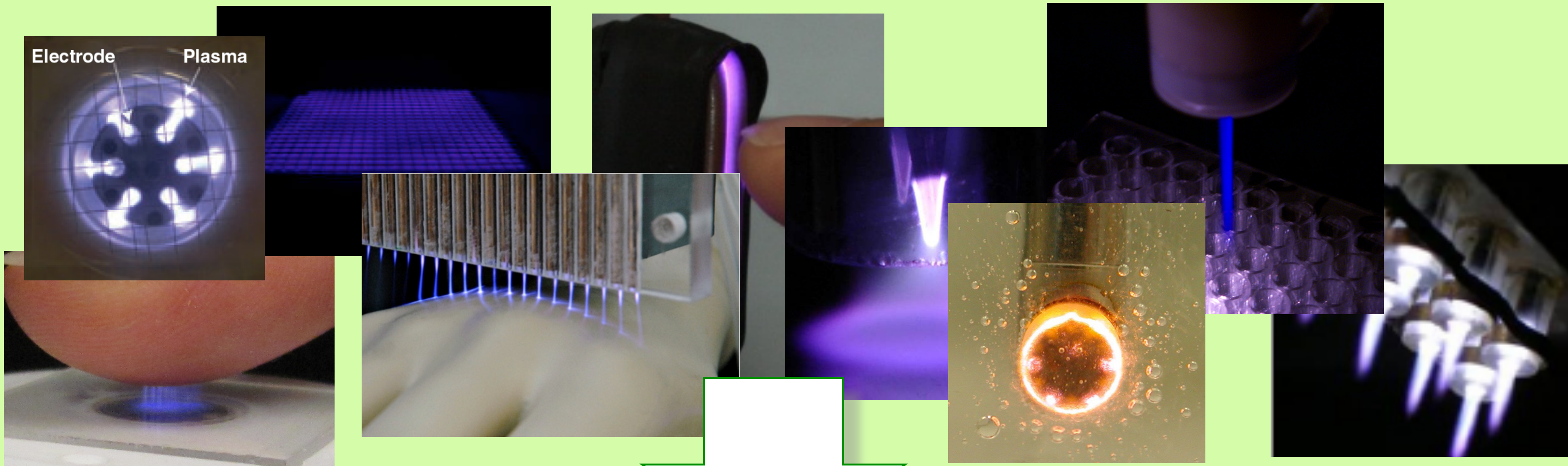
1.5 – 2 min: physical removal of coagulum to expose underlying tissue layer.

2 min – end: pulsed (16 Hz; 6 W; Ar flow at 1.2 l/m) Non-thermal effects may be predominating. Streamer formation to treatment surface is much less frequent.

What atoms and uncharged molecular entities are being delivered to the tissue surface?

APC surgery video

Many different plasma sources – biomaterial interaction



prokaryotes (bacteria)

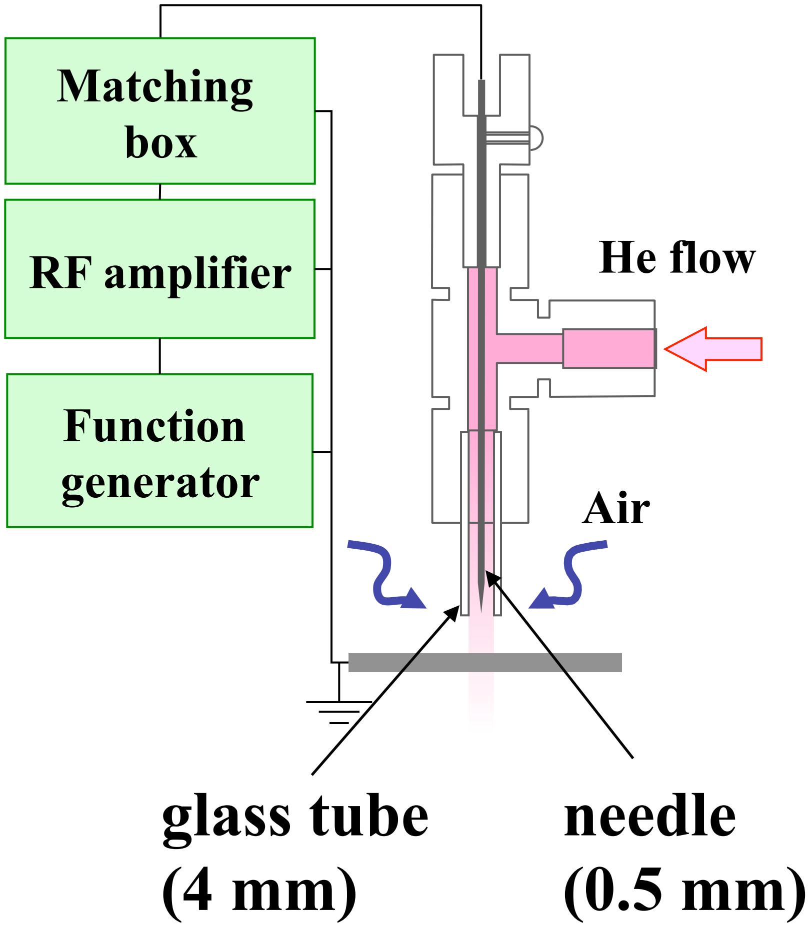
- Gram positive: e.g. *B. subtilis* (vegetative cell or spore)
- Gram negative: e.g. *E. coli*

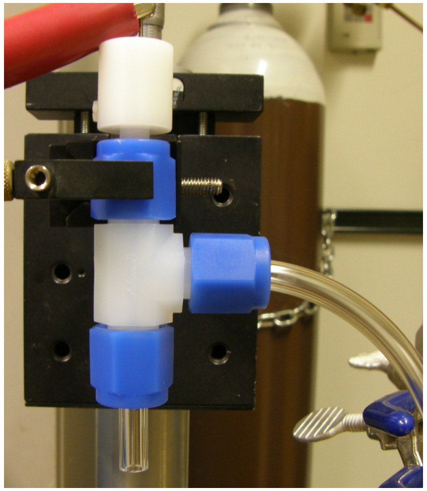
eukaryotes (animal or plant)

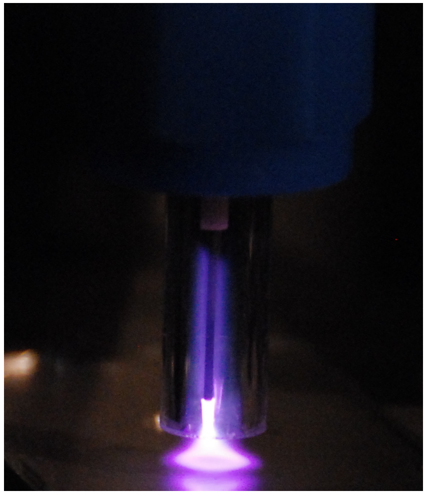
on agar plate
in liquid
biofilm
in vivo

Plasma needle

E. Stoffels, et al., *Plasma Sources Sci. Tehcnol.* 11 (2002) 383.





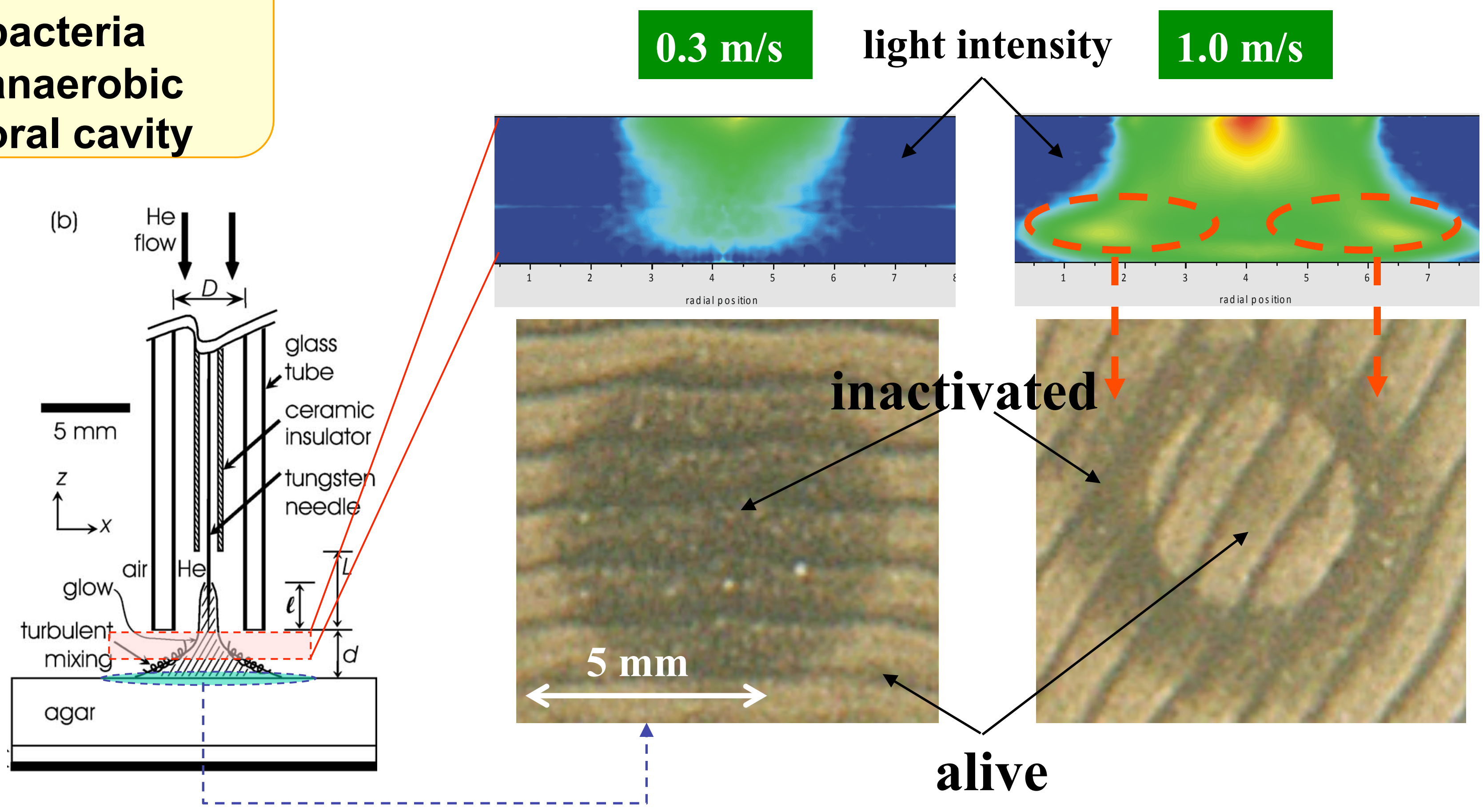


- Frequency: RF (13.56MHz)
- Voltage: 200-400 V_{pkpk}
- He flow rate: ~1 slpm (Re_d < 100)
- Power consumption: ~1 W
- Distance to sample: 1-5 mm

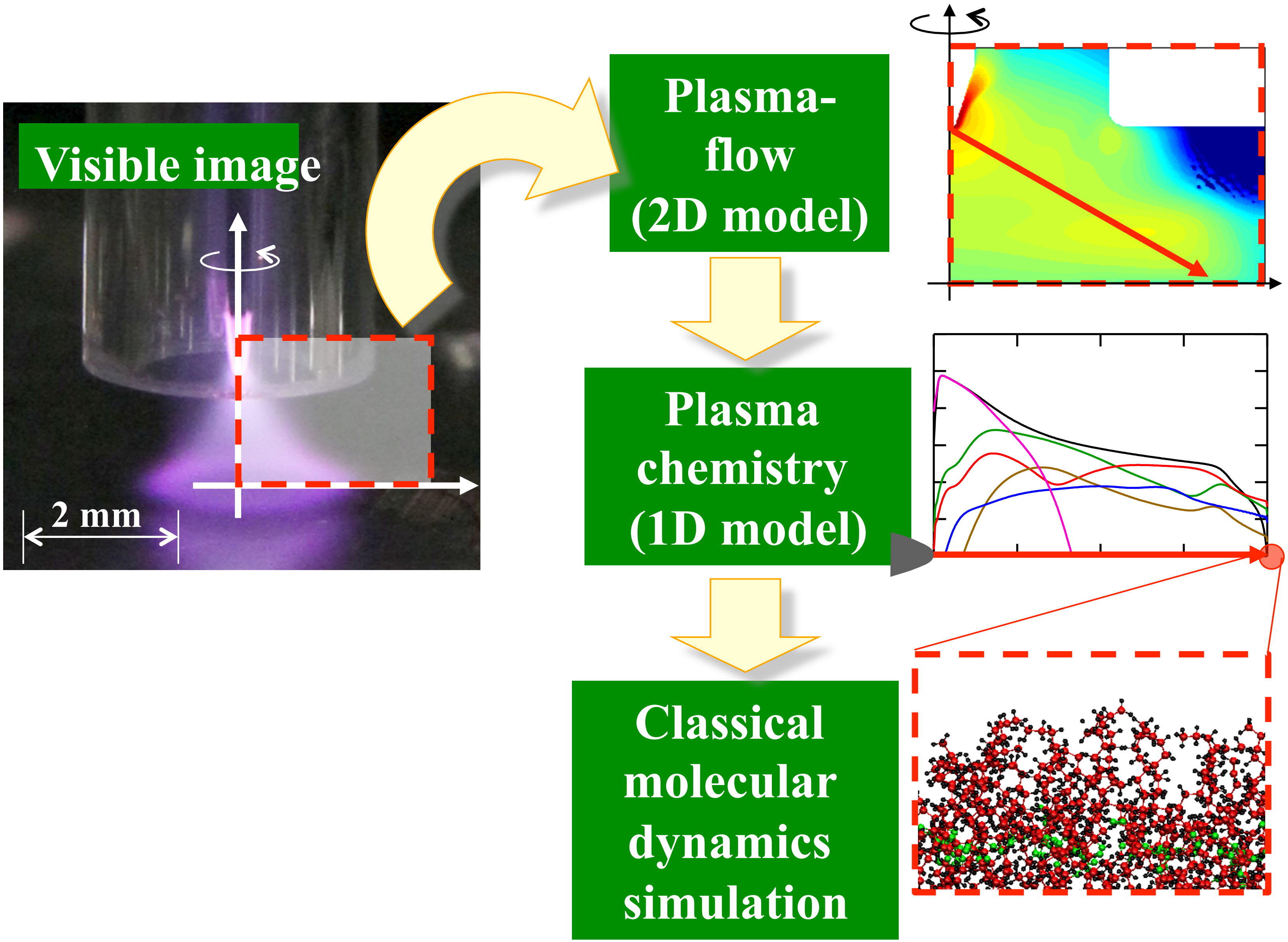
Plasma needle: Bactericidal effects

J.Goree, et al, *J.Phys.D.* 39 3479 (2006) and *IEEE Trans.Plasma Sci.* 34, 1317 (2006)

S. mutans
- **bacteria**
- **anaerobic**
- **oral cavity**

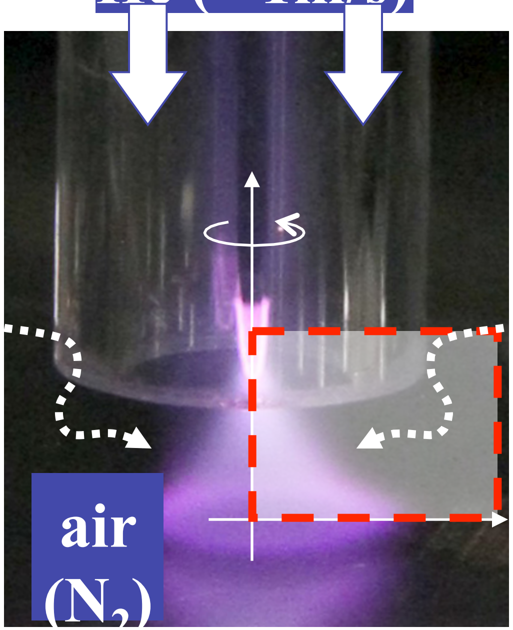


Strategy: hybrid approach



Fluid model: governing equations

He (~ 1m/s)



electron,
He^*, He_2^*,
He^+, He_2^+,N_2+

Neutral Gas flow (He, N_2)

$$\nabla\cdot(\rho\mathbf{u})=0,\nabla\cdot(\rho\omega_{\mathrm{air}}\mathbf{u}-\rho D\nabla\omega_{\mathrm{air}})=0$$ **(mass conservation)**

$$\nabla\cdot(\rho\mathbf{u}u_i)=-\nabla p-\nabla\cdot\overline{\overline{\boldsymbol{\tau}}}+\sum q_i n_i\mathbf{E}$$ **(momentum conservation)**

$$\nabla\cdot\left(-\lambda\nabla T+\mathbf{u}c_{\mathrm{p}}T\right)=\Phi+\sum q_i\mathbf{\Gamma}_i\mathbf{E}+Q_{el}$$ **(energy conservation)**

ion momentum
collisional heating

temperature
velocity
species density

Plasma dynamics

$$\frac{\partial n_i}{\partial t}+\nabla\cdot\mathbf{\Gamma}_i=S_i$$ **(mass conservation)**

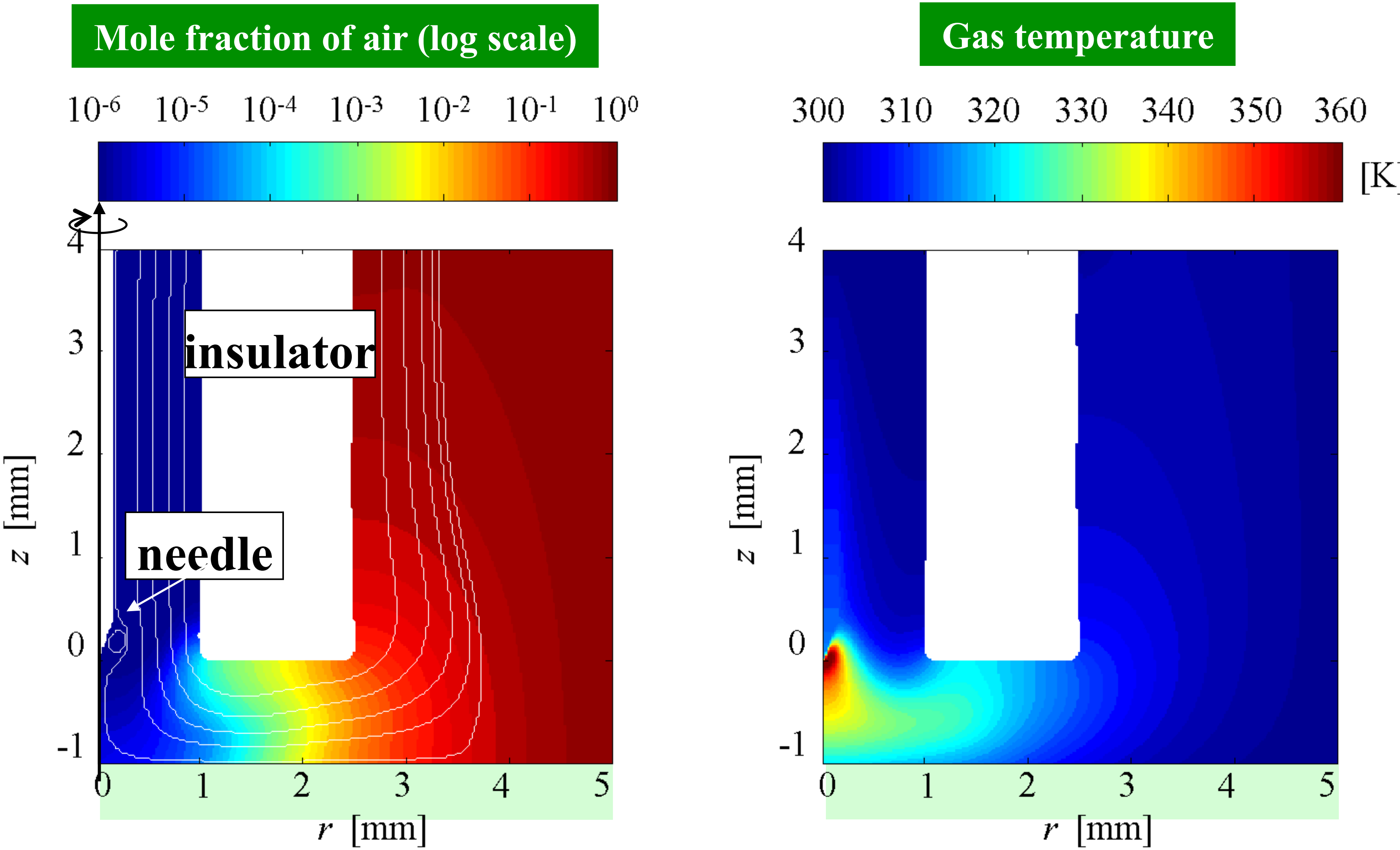
$$\mathbf{\Gamma}_i=\mathrm{sgn}(q_i)n_i\mu_i\mathbf{E}-D_i\nabla n_i+n_i\mathbf{u}$$ **(drift-diffusion)**

$$\frac{\partial(n_e\varepsilon)}{\partial t}+\nabla\cdot\left(\frac{5}{3}\varepsilon\mathbf{\Gamma}_e-\frac{5}{3}n_eD_e\nabla\varepsilon\right)=-\mathbf{\Gamma}_e\cdot\mathbf{E}-Q$$ **(electron energy)**

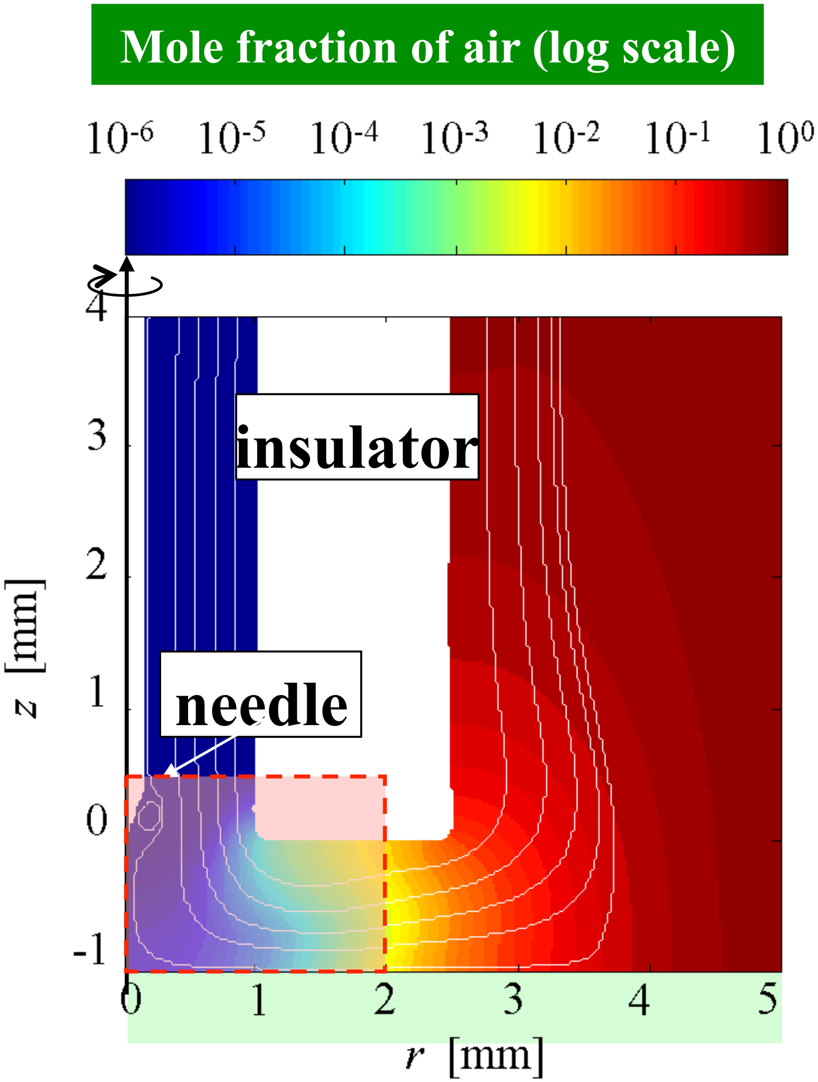
$$\varepsilon_0\nabla\cdot\mathbf{E}=\sum q_i n_i$$ **(Poisson's equation)**

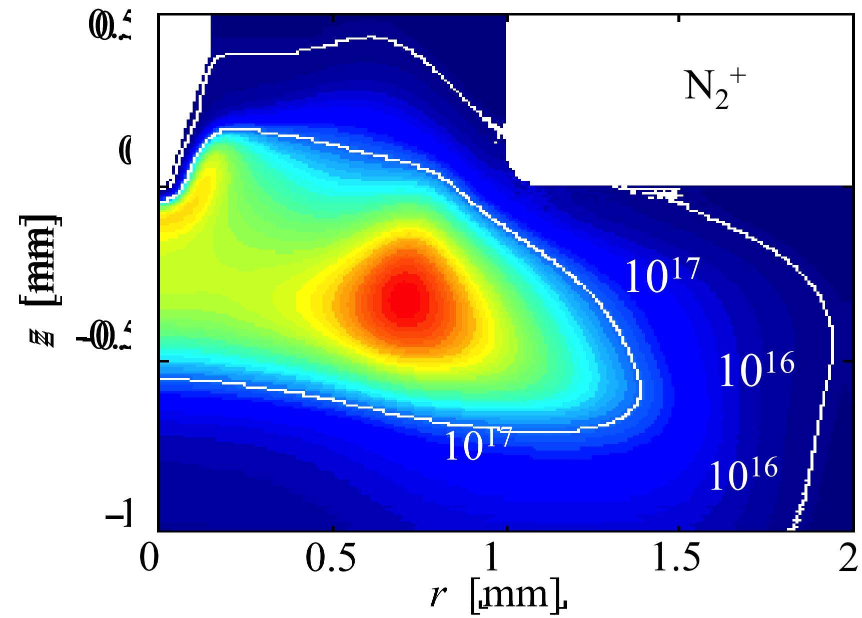
Y. Sakyiama et al, J. Appl. Phys. 101 (2007) 073306 and J. Phys. D 41 (2008) 95204

Fluid model: neutral gas flow

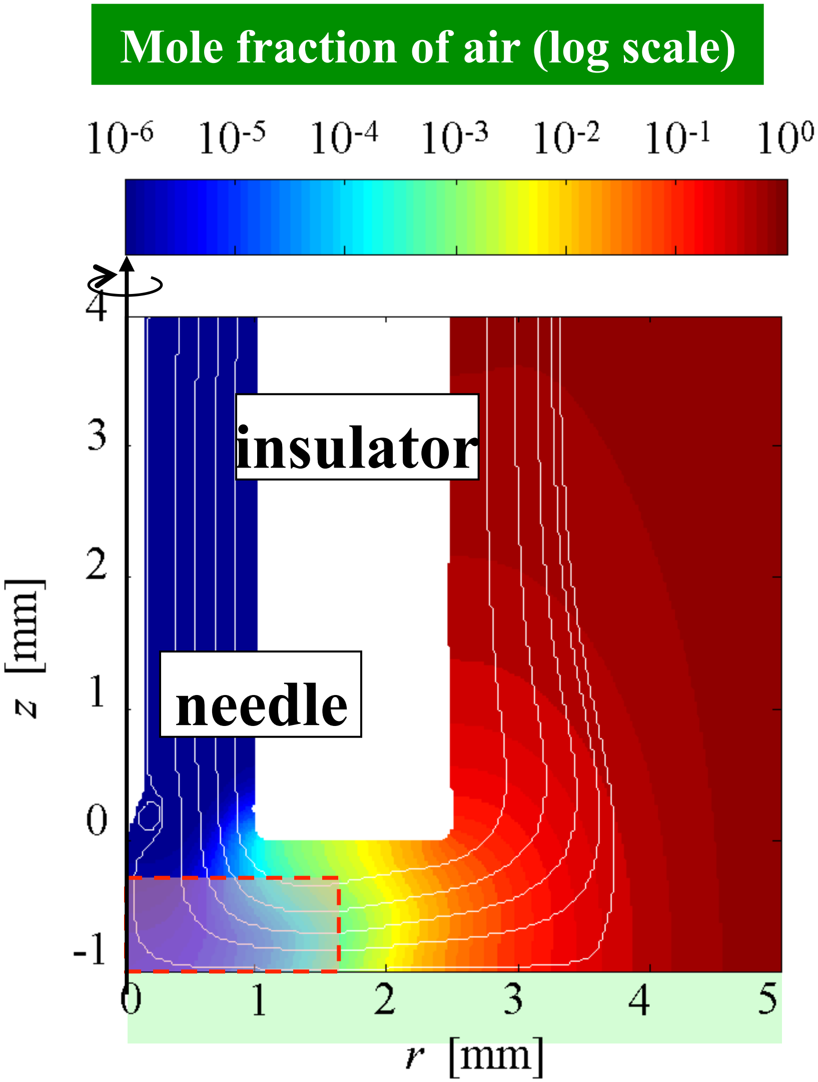


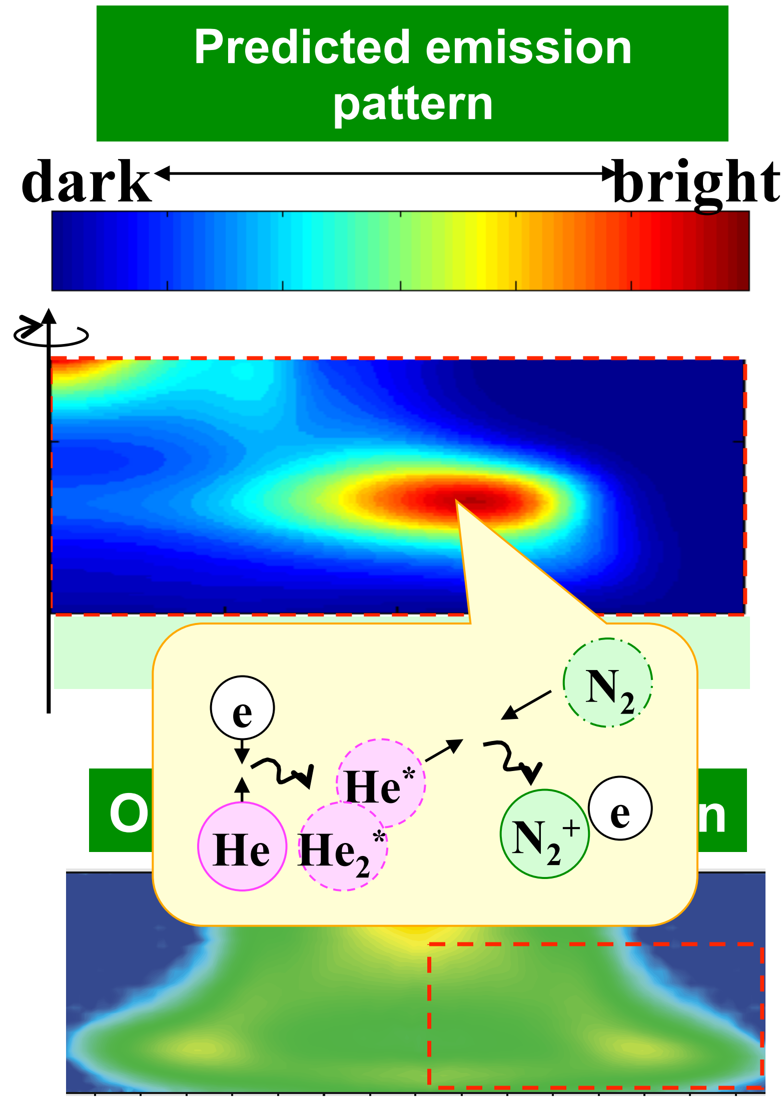
Fluid model: phase-averaged species density





Fluid model: emission intensity

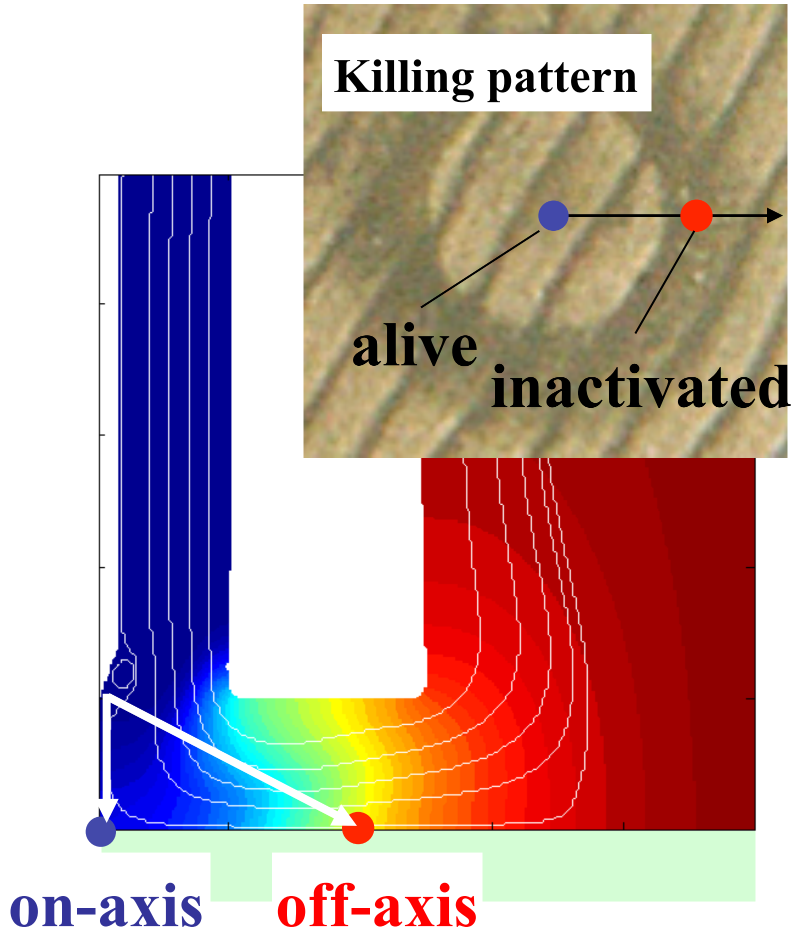




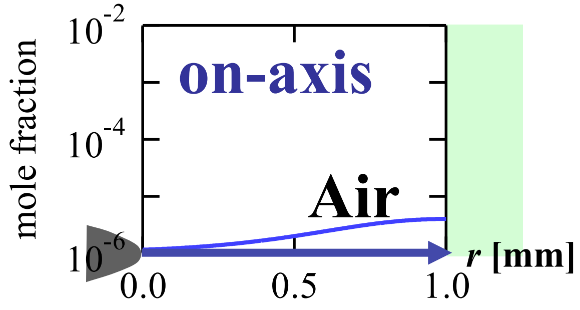
Y. Sakyiama et al, Plasma Sources Sci. Tchnol. 18 (2009) 025022

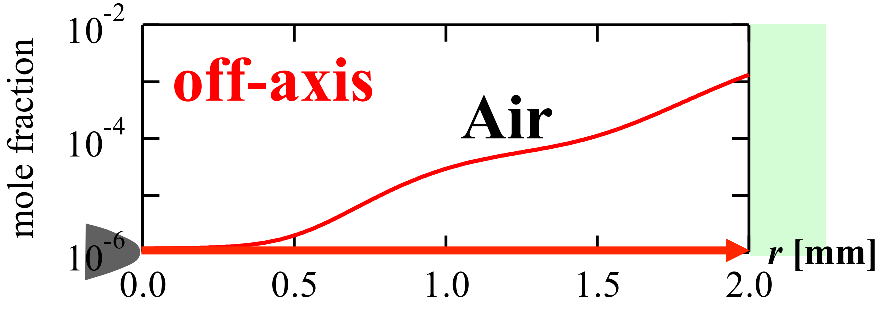
Chemistry model: from 2D to 1D

Mole fraction of air (log scale)



1D plasma model





Chemistry model: chemical reactions

46 species

negative particles: e, O^-, O_2^-, O_3^-, O_4^-, H^-, OH^-

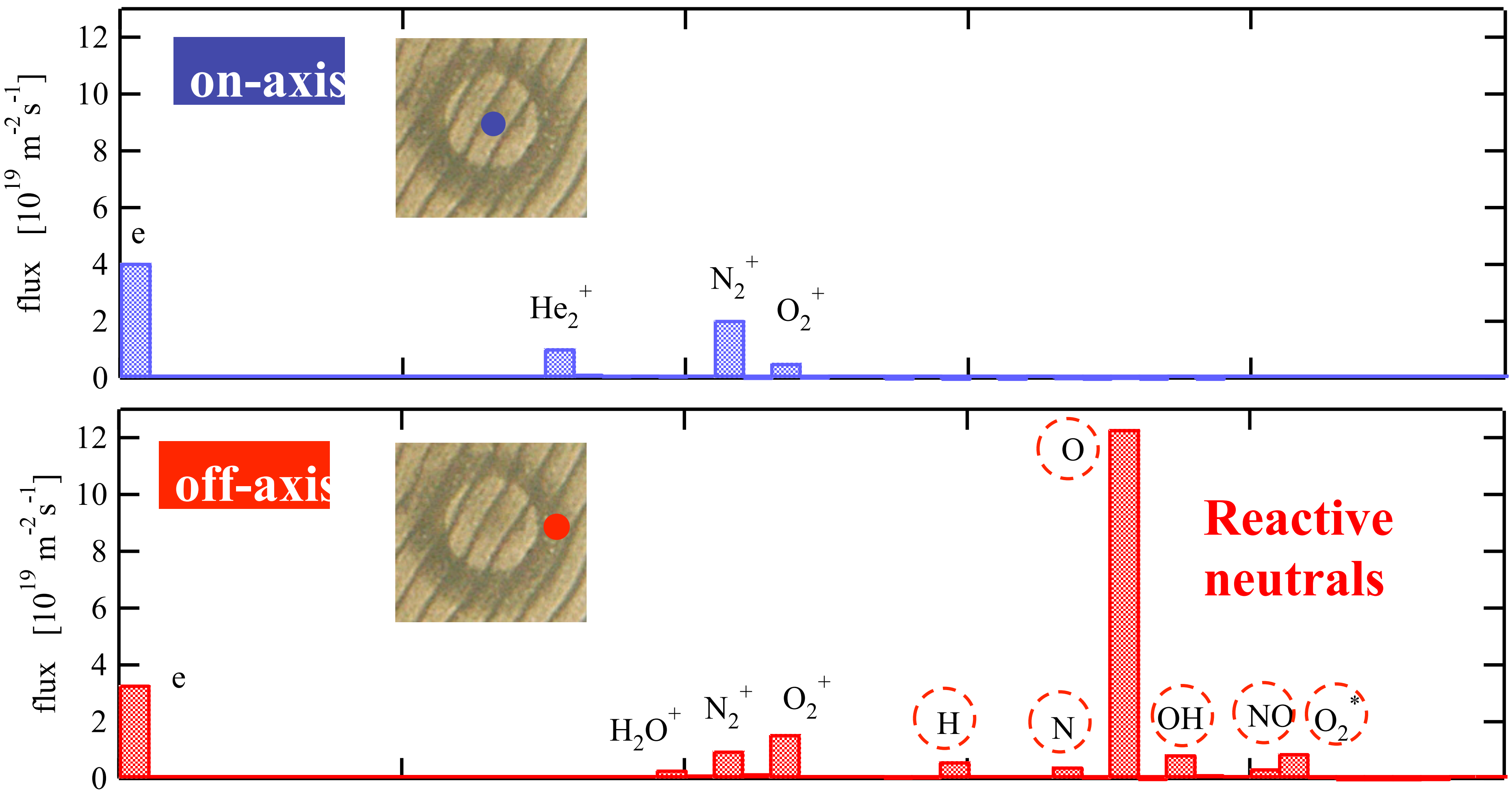
positive particles: He^+, He_2^+, N^+, N_2^+, N_3^+, N_4^+, O^+, O_2^+, O_4^+, NO^+, N_2O^+, NO_2^+, H^+, OH^+, H_2O^+, H_3O^+

neutrals: He, He^*, He_2^*, N, N^*, N_2, N_2^*, N_2^{**}, O, O^*, O_2, O_2^*, O_3, NO, N_2O, NO_2, NO_3, H, H_2, OH, H_2O, HO_2, H_2O_2

214 elementary reactions

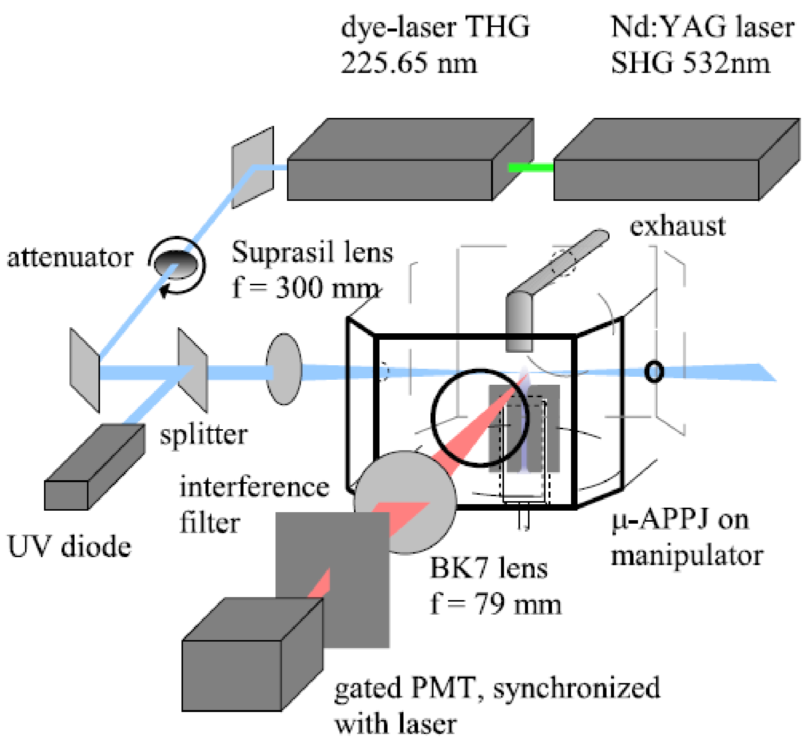
- 21 electron impact excitation/ionization/dissociation reactions
- 20 Penning and associative ionization reactions
- 26 electron recombination/attachment reactions
- 65 charge transfer reactions
- 51 ion recombination reactions
- 31 neutral-neutral reactions

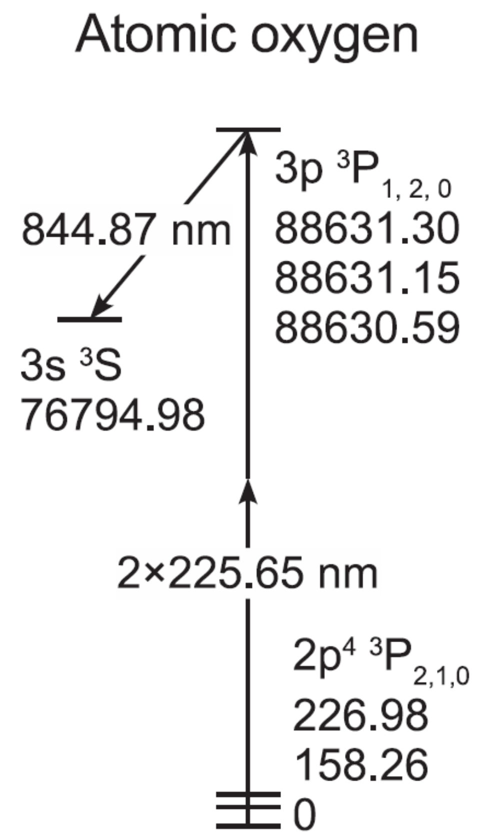
Chemistry model: phase-averaged flux on surface



Model validation: O atom measurement

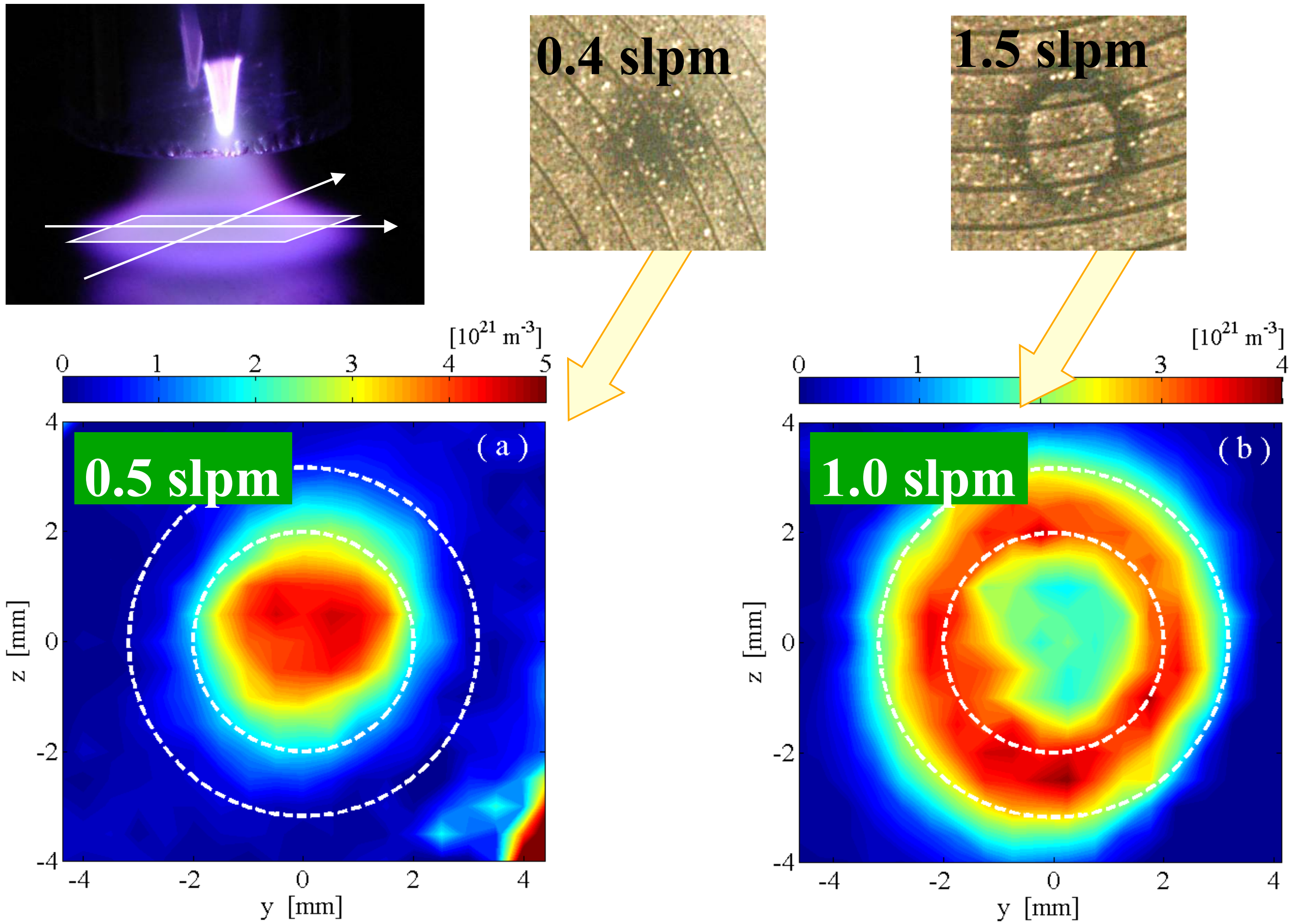
- **TALIF: two photon absorbed laser induced fluorescence**
- **collaboration with Ruhr-Universitat Bochum (Germany)**





N. Knake, et al, *J. Phys. D: Appl. Phys*. 41 (2008) 194006

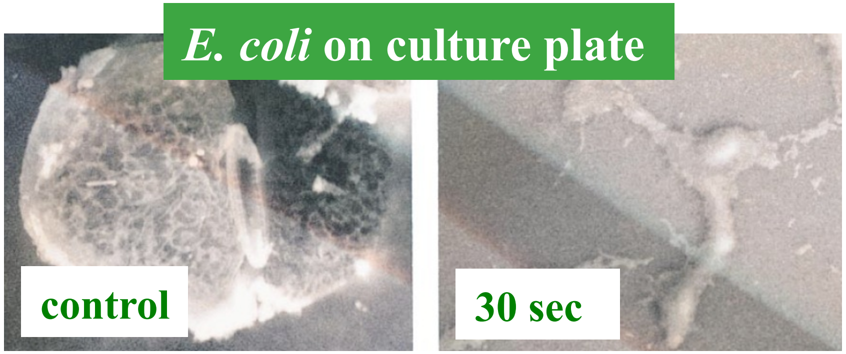
Model validation: measured O atom density



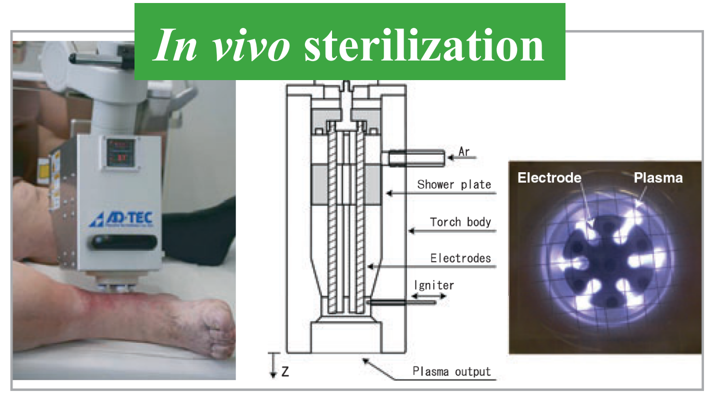
Y. Sakiyama, et al., *Appl. Phys. Lett*. 97 (2010) 151501.

Plasma medicine: where are we heading?

- Decontamination of microorganisms (virus, bacteria, fungi, yeast)

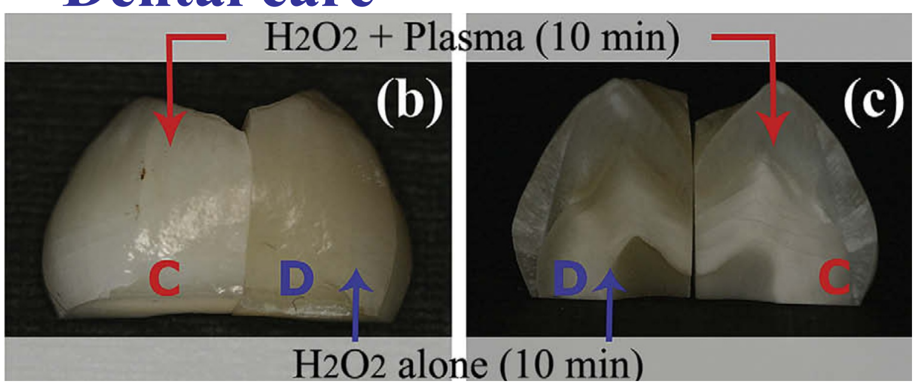


M. Laroussi et al., *IEEE Trans. Plasma Sci.* 27 (1999) 34.



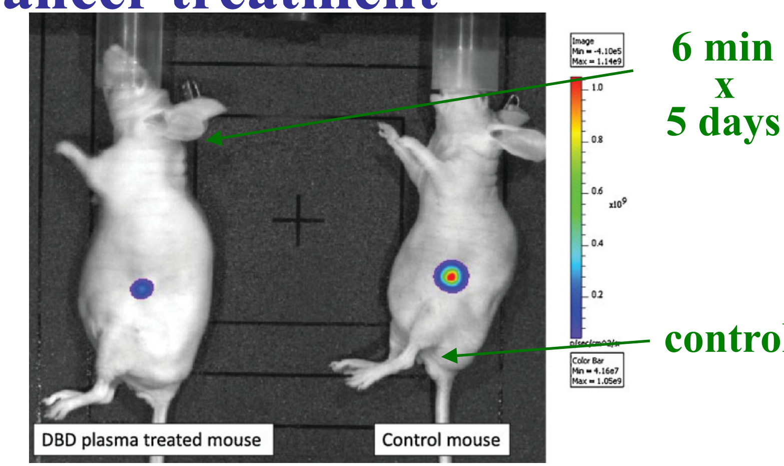
G. Isbary, et al., *Br. J. Dermatol*. 163 (2010) 78.

- Dental care



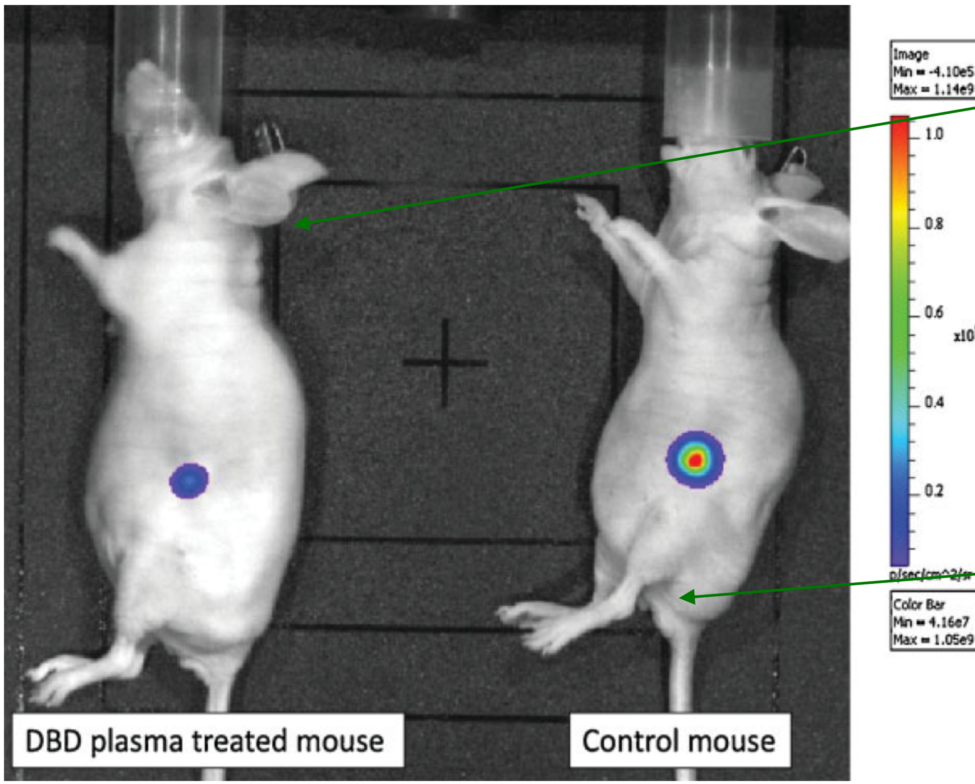
H. W. Lee, et al., *J. Endod* 35 (2009) 587.

- Cancer treatment



M. Vandamme, et al., *Plasma Process. Polym.* 7 (2010) 264.

Recent results show exciting effectiveness of plasma in shrinking tumors *in vivo*….



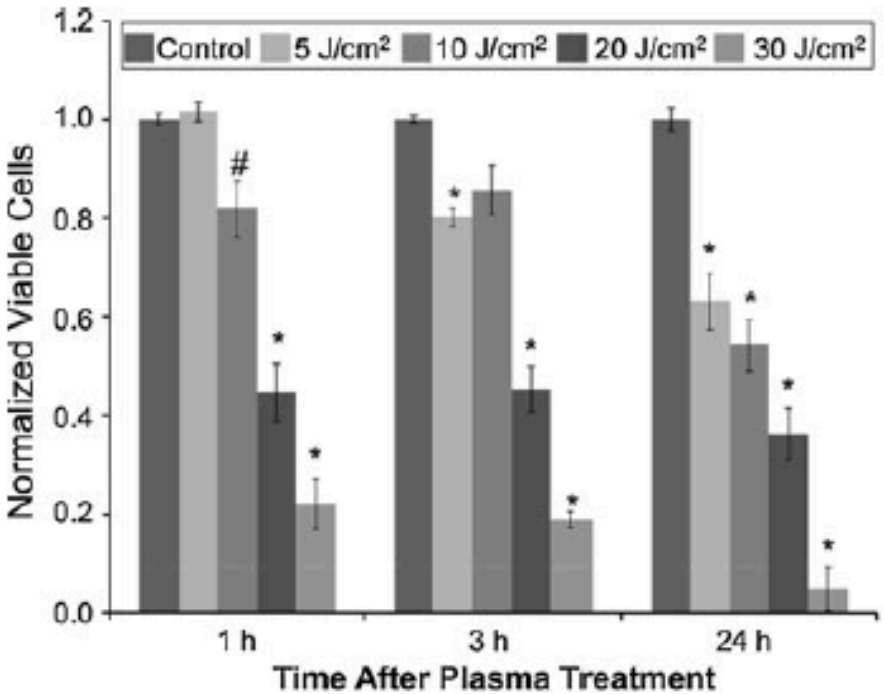
6 min
x
5 days

control

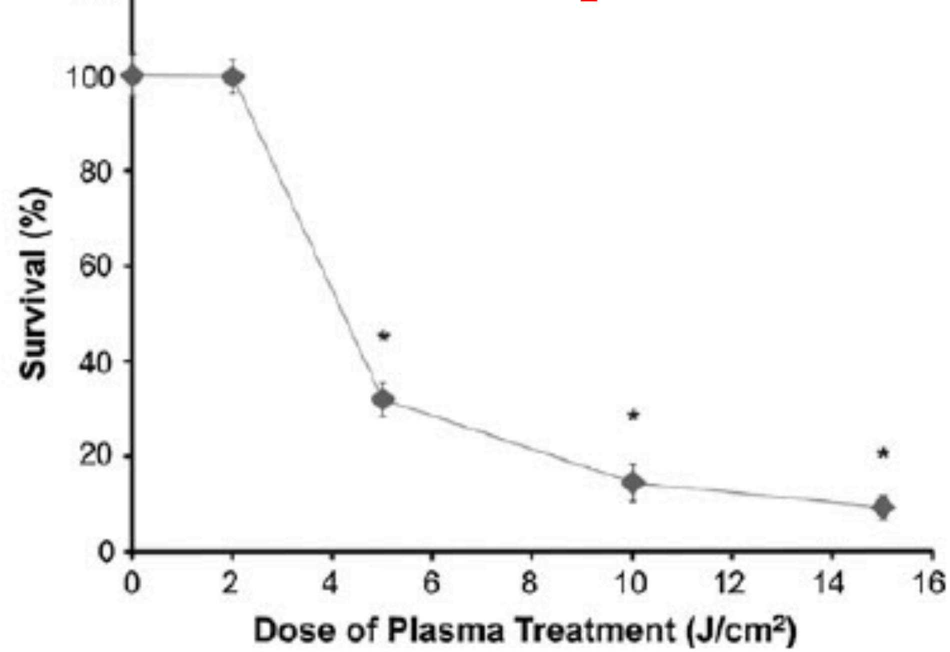
M. Vandamme, et al., *Plasma Process. Polym.* 7 (2010) 264.

FE-DBD plasma in air

…and *in vitro* (melanoma cells)



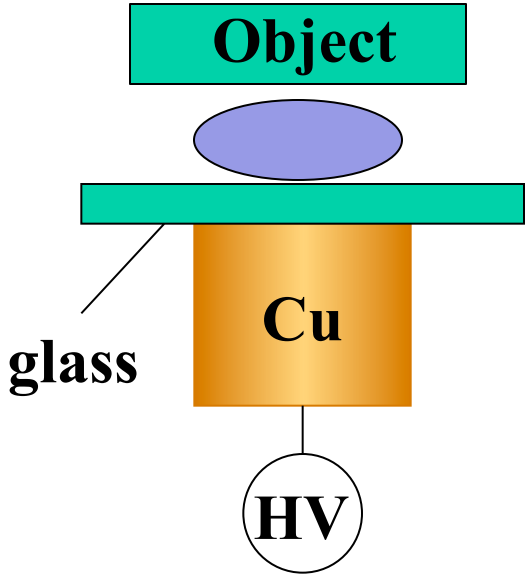
FE-DBD plasma in air



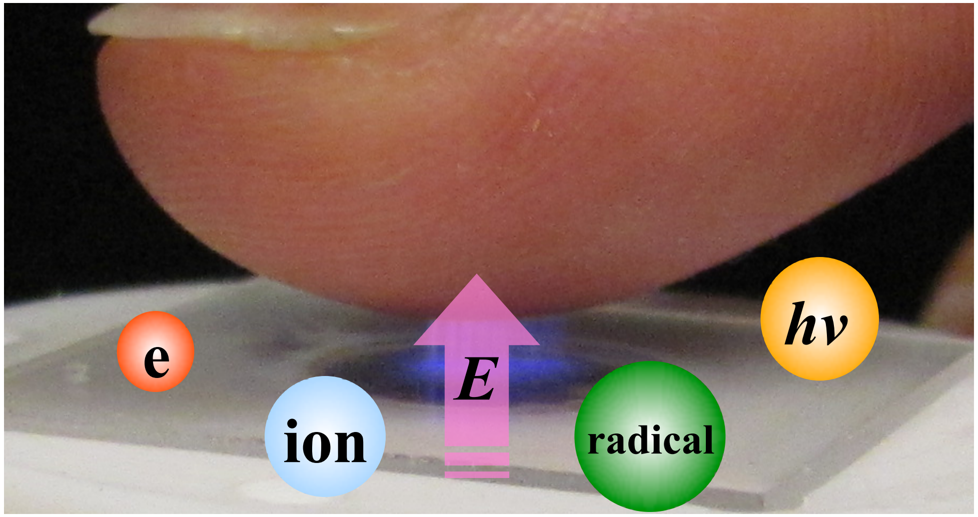
Non-thermal Plasma Induces Apoptosis in Melanoma Cells via Production of Intracellular Reactive Oxygen Species

Sensenig et al., Oct. 29, 2010
Annals Biomed. Eng.

Plasma-biomaterial interactions: surface-active agents?



Plasmas in ambient air at room temperature



• voltage:	10-20 kVpkpk
• frequency:	1-10 kHz
• power:	~ 1W
• distance to finger:	1-3 mm
• gas:	static air in California

Plasma-biomaterial interaction: possible agents

	kinetic energy	chemical reaction	electrostatic
electrons	1-10 eV		negative
ions	~ 1 eV	ROS/RNS	positive/negative
radicals		ROS/RNS	
photons	4-12 eV (UVC)		
electric field			10^6-10^7 V/m
effects	• bond breaking (e.g., DNA) • sputtering	• oxidation (e.g., O, OH) • immune system (e.g., NO)	• membrane disruption (~10^9 V/m) • stimulation

Related to the HUGE biomedical literature…, e.g.

Reactive Species and Antioxidants. Redox Biology Is a Fundamental Theme of Aerobic Life

Barry Halliwell[1]

Plant Physiology, June 2006, Vol. 141, pp. 312–322

The field of antioxidants and free radicals is often perceived as focusing around the use of antioxidant supplements to prevent human disease. In fact, antioxidants/free radicals permeate the whole of life, creating the field of *redox biology*. Free radicals are not all bad, nor antioxidants all good. Life is a balance between the two: antioxidants serve to keep down the levels of free radicals, permitting them to perform useful biological functions without too much damage.

***See also*:**

Halliwell B, Gutteridge JMC (2006) Free Radicals in Biology and Medicine, Ed 4. Clarendon Press, Oxford

Reactive oxygen species: ROS

Radicals	**Nonradicals**
ROS	***ROS***
Superoxide, $O_2^{\bullet -}$	H_2O_2
Hydroxyl, $OH^{\bullet}$	Hypobromous acid, HOBr[a]
Hydroperoxyl, $HO_2^{\bullet}$ (protonated superoxide)	Hypochlorous acid, HOCl[b]
Carbonate, $CO_3^{\bullet -}$	Ozone, O_3[c]
Peroxyl, $RO_2^{\bullet}$	Singlet oxygen ($O_2{}^1\Delta g$)
Alkoxyl, $RO^{\bullet}$	Organic peroxides, ROOH
Carbon dioxide radical, $CO_2^{\bullet -}$	Peroxynitrite, $ONOO^{-}$[d]
Singlet $O_2{}^1\Sigma g^{+}$	Peroxynitrate, O_2NOO^{-}[d]
	Peroxynitrous acid, ONOOH[d]
	Peroxomonocarbonate, $HOOCO_2^{-}$

Halliwell, 2006

Reactive chlorine/bromine species

Radicals	**Nonradicals**
Reactive chlorine	***Reactive chlorine***
Atomic chlorine, $Cl^{\bullet}$	Hypochlorous acid, HOCl[b]
	Nitryl chloride, NO_2Cl[e]
	Chloramines
	Chlorine gas (Cl_2)
	Bromine chloride (BrCl)[a]
	Chlorine dioxide (ClO_2)
Reactive bromine	***Reactive bromine***
Atomic bromine, $Br^{\bullet}$	Hypobromous acid (HOBr)
	Bromine gas (Br_2)
	Bromine chloride (BrCl)[a]

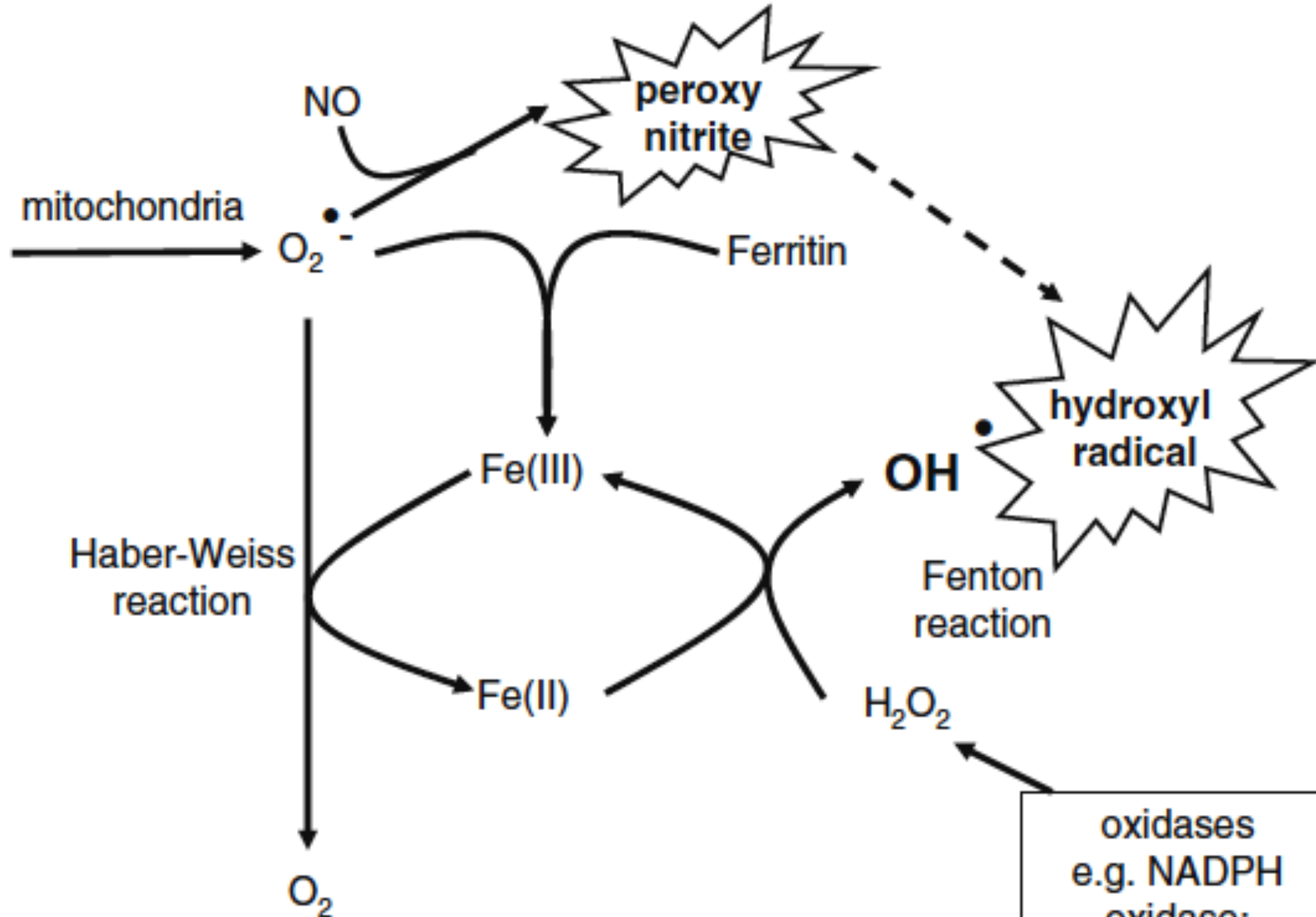
Halliwell, 2006

Reactive nitrogen species: RNS

Radicals	**Nonradicals**
Reactive nitrogen	***Reactive nitrogen***
Nitric oxide, $NO^{\bullet}$	Nitrous acid, HNO_2
Nitrogen dioxide, $NO_2^{\bullet}$ [c]	Nitrosyl cation, NO^+
Nitrate radical, $NO_3^{\bullet}$ [c,f]	Nitroxyl anion, NO^-
	Dinitrogen tetroxide, N_2O_4
	Dinitrogen trioxide, N_2O_3
	Peroxynitrite, $ONOO^-$ [d]
	Peroxynitrate, O_2NOO^- [d]
	Peroxynitrous acid, $ONOOH$ [d]
	Nitronium cation, NO_2^+
	Alkyl peroxynitrites, ROONO
	Alkyl peroxynitrates, RO_2ONO
	Nitryl chloride, NO_2Cl
	Peroxyacetyl nitrate, $CH_3C(O)OONO_2$ [c]

Halliwell, 2006

Towards a unifying, systems biology understanding of large-scale cellular death and destruction caused by poorly liganded iron: Parkinson's, Huntington's, Alzheimer's, prions, bactericides, chemical toxicology and others as examples



Douglas B. Kell

Arch Toxicol (2010) 84:825–889

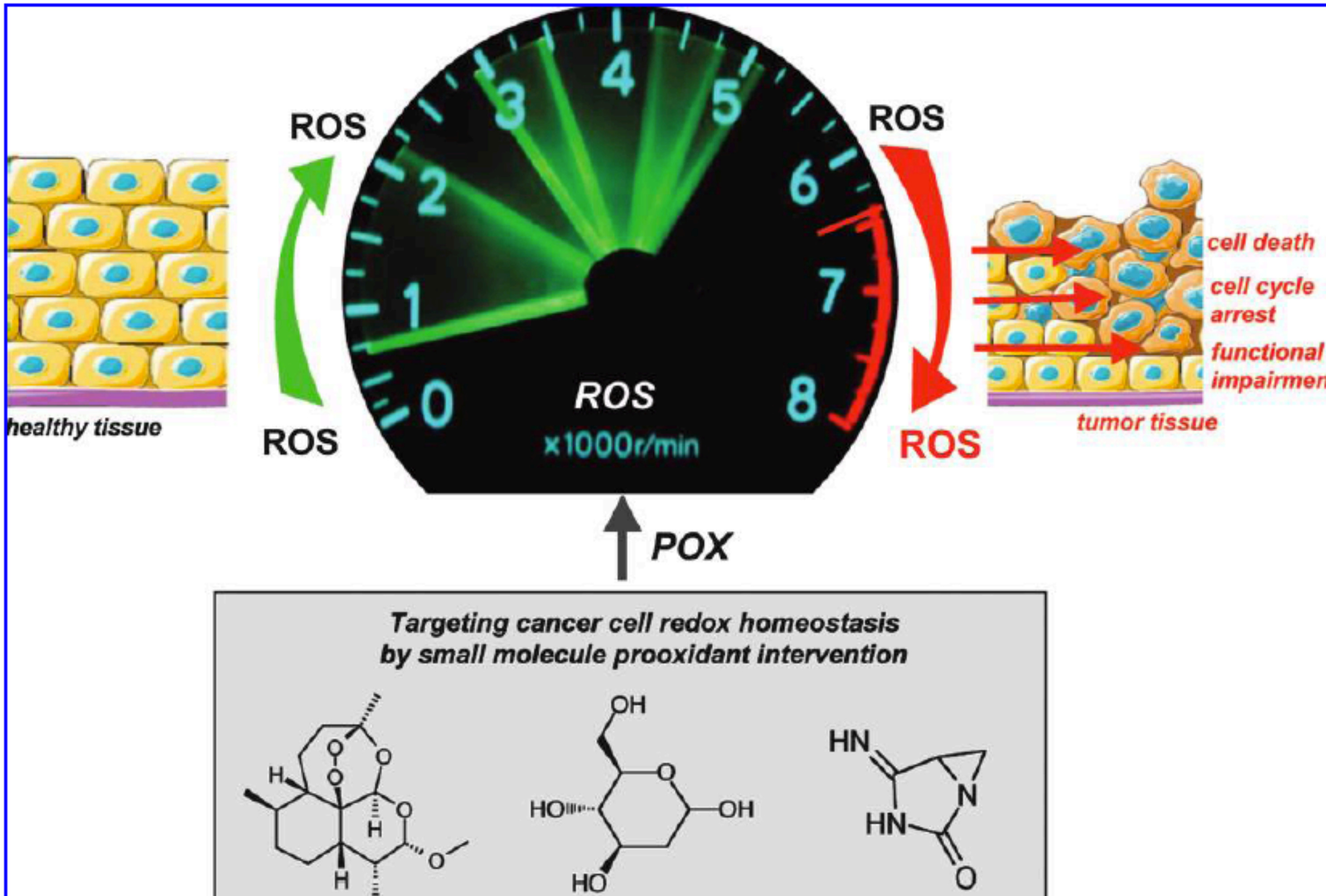
Redox-Directed Cancer Therapeutics: Molecular Mechanisms and Opportunities

ANTIOXIDANTS & REDOX SIGNALING
Volume 11, Number 12, 2009

DOI: 10.1089/ars.2009.2541

COMPREHENSIVE INVITED REVIEW

Georg T. Wondrak



Rationale for plasma-generated reactive oxygen species (ROS) and cancer therapy

- Many cancer therapies are based on the direct or indirect creation of ROS. Radiation therapy, photodynamic therapy (PDT) and many chemotherapies all exploit this effect.

- Low temperature plasmas create ROS in relatively high densities. This offers a compelling rationale for the successful plasma treatment of cancer cells both *in vitro* and *in vivo*. There are also important implications for other applications, such as wound healing.

Concluding Remarks: LTP at Surfaces

- Did not discuss effects of surface processes on plasma

- Combined, synergistic effects of ions, electrons, photons, and reactive neutrals make LTP arguably a ***UNIQUELY*** powerful and versatile surface modification technology

- MD shows ***large, complex temporal and spatial gradients created at surfaces*** by LTP central to understanding plasma-surface interactions

- When the surface is living matter, the biophysical, biochemical and biological complexities are ***IMMENSE***!