Low Temperature Plasma-Surfaces Interactions: From Computer Chips to Cancer Therapy

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DAMOP
Madison, Wisconsin
June 2-6, 2014
Acknowledgements: Students, Postdocs, Visitors, Research Associates

- Greg Jellum (90) 3M
- M. Surendra (91) IBM
- Lonnie Perrung (92) Pacific Northwest; National Labs
- John Daugherty (94) Lam Research
- Mike Kilgore (94) Novellus Systems
- Tim Nitschke (94) Intel
- Chris Lee (94) Lam Research
- Maria (Gray) Barone (95) Lam Research
- Justin Bukowski (96) Air Products
- Brian Helmer (98) Lam Research
- Gowri (Kamrthy) Kota (98) Lam Research
- S. Mahnovski (99); Rand Corporation
- Mike Vyvoda (99) Start-up Semiconductor company
- Cameron Abrams (00) Professor: Drexel University
- Eric Tonnis (00) Lam Research
- Harmee Singh (00) Lam Research
- Luan Van (2002); US Patent Office
- Frank Greer (02) Novellus Systems/Jet Propulsion Labs
- David Hsu (03) Intel/NREL; Law School
- Mark Kiehlbaugh (03) Lam Research/Micron
- David Humbird (04) Lam Research/NREL
- Mark Nierode (05) Exxon/Mobil
- Yoshi Kimura (05) Lam Research
- Cheng-Che Hsu (06) Professor: National Taiwan Univ.
- Joe Vegh (07) postdoc UCB; Lam Research (09)
- Gopal Choudhary (09); India
- Dustin Nest (09); Lam Research
- Kasi Kiehlbaugh (09); U. Arizona
- Monica Titus (10); Lam Research
- Ting-Ying Chung (12); Lam Research
- Marat Orazov (12); Cal Tech.
- Joe Lee (13); IBM (Albany, NY)
- Matt Pavlovitch (14);

- Han Ming Wu (1996) SMIC, Shanghai, China
- Richard Stewart (1996) Teaching College
- Ales Fiala (1999) Unilever, Netherlands
- H. Date (1998-99) Hokaido University, Japan
- Ming Li (1999) Novellus Systems
- Junichi Tanaka (2000) Hitachi
- Koji Satake (2003) Mitsubishi
- Thierry Czerwiec (2003) Ecole des Mines, Nancy, France
- Erwin Kessels (2005) Eindhoven Univ. of Technology
- Yassine Kabouzi (2006) Lam Research
- Erwine Parg (2006) CNRS, LTM, Grenoble, France
- Insook Lee (2007) Korea
- Yuk Sakiyama (2006-2012) Lam Research
- E. Despiau-Pujo (2008); LTM, Grenoble, France
- Taka-aki Tomai (2008-10) University of Tokyo
- Ning Ning (2009-2011), Ecole Polytechnique, Paliseau, France
- G.Y. Yeom (2009-10) Sungkyunkwan University, Korea
- Emi Kawamura (2009-1012); (with Prof. M. A. Lieberman), Shinji Obama (2011-2012) Hitachi Corporation
- Mierk Anne Schwabe (2012 -) Max Planck Institute
- Hung-wen Chang, (2012-2013) National Taiwan University
- M. Takamasu, (2012-2013) Hitachi Corporation
- Toshi Ono, (2013-14) ; Tokyo Inst. Tech.
- Steve Park, (2013-14); Samsung Corporation
- Zilan Xiong, (2013-); Huazhong Univ., Wuhan, China
- Julie Hubert, (2013); Université Libre de Bruxelles, Belgium
- Jane Dai, (2013); Deakin University, Australia
- Laruent Azarnouche, (2014); LTM, Grenoble, France
- Elmar Slikboer, (2014) ; TUE. Netherlands
- Yeon Ho Im, (2014) ; Chonbuk National University, Korea
- Tomo Watanabe (2013-2014) ; Hitachi Corporation
Lithography/Plasma Etch Pattern Transfer

**Critical dimension:**

**CD**

193 nm light source
Plasma Essential in Nanoelectronics

We are already in nano feature era

Nano features are no long only for ‘exploratory’ research any more

Floating poly-Si

Si ~10nm Si nano fins

BOX

K. Gopalakrishnan, et. al., IEDM 2005

A MNAB device showing very thin (~10nm) Si nanofins with floating poly-Si regions in between them

Selective epitaxial Si

Gate Offset spacer

Source Drain

L_{gate}=8nm T_{SOI}=4nm

A ‘traditional’ FET device with an ~8nm gate on ultra-thin SOI (~4nm)
**Multi-Scale Plasma Processing**

Example: **Multi-scale Reactive Ion Etching**

Gas Pressure $\sim 10 - 1000$ mTorr; Gas Temperature $\sim 600 - 1000$ K

Electron Temperature $\sim 2 - 8$ eV

$\text{CF}_4/\text{H}_2/\text{Ar}$

Gas Flow in

SiO$_2$ film on Si wafer

SiF$_4$, COF$_2$

Gas Flow Out

$V_{RF} = V_{01}\sin (\omega_1 t) + V_{02}\sin (\omega_2 t)$

plasma sheath $d \sim 1$ mm

atomic scale $d \sim 1$ nm
Ion Impact at Surface

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

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

- Conclusion: ion impacts dissipate energy long before another ion hits nearby: *impacts are isolated*
Molecular dynamics of Ar\(^+\) on Si surface (classical trajectory simulation) shows how impacting energetic species deposit energy into near-surface region.

Impact trajectory lasts \(\sim 0.1-0.2\) ps; lateral boundaries periodic; bottom layer fixed; REBO potentials; ground state/neutral only; kinetic energy color coded.
Single Ion Impact at Surface: Peak and Mean Power Deposited

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

Peak power is high: 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 (~100 eV) 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 $< \lambda_{\text{mfp}}$

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 $\Phi(r)$

Interatomic Forces $F_i = -\text{grad}(\Phi) = m_i \frac{d^2 r}{dt^2}$

typical MD time step:

initial configuration

update positions

evaluate forces

update velocities

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
Etching Si in Presence of Fluorocarbon Film: *Challenge*

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

• $\text{Ar}^+/\text{F}/\text{C}_x\text{F}_y$ mixtures demonstrate this

• Complex, poorly understood processes induce transport both into and out of surface while promoting various reactions
C₄F₄/F/Ar⁺ on Si: ‘Steady State Layer’

Ion/neutral impact 5:5:1 C₄F₄/F/ 200 eV Ar⁺

Side view and depth profile of a cell from 5:5:1 C₄F₄/F/ 200 eV Ar⁺ (Si=white, C=grey, F= black).
Ion/neutral impact 5:5:1
$C_4F_4/ F/ 200 \text{ eV } Ar^+$

Snapshot movie:
series of ‘post-impact’
images connected
together to give
impression of time
evolution.

$\sim 1 \text{ nm x 1 nm}$
periodic lateral boundaries;
fixed lower layer;
Si - blue;
C - gold;
F - white
Challenges of LTP-Surface Interactions

MD simulations can capture many important nanometer-scale phenomena, but huge questions and challenges remain:

What causes and maintains layering?

How to control surface roughness/texture?

What is smallest feature that plasma etch can create?

How to more fully exploit plasma synergies to control surface texture?
Low Temperature Atmospheric Gas Plasma Cancer Therapy: A Brief Introduction

Also: wound healing; infected tissue treatment; dental, dermatological and other applications
Atmospheric Pressure Plasma Sources for Biomedical Applications

(1) Drexel University (USA)  
(2) Cinogy GmbH (GER)  
(3) Old Dominion University (USA)  
(4) IOM Leipzig (GER)  
(5) Eindhoven Univ. of Techn. (NED)  
(6) New York University (USA)  
(7) MPE Garching (GER)  
(8) University of Orléans (FRA)  
(9) McGill University, Montreal (CAN)  
(10) Loughborough University (UK)  
(11) INP Greifswald (GER)

Courtesy: K.D. Weltmann, Greifswald
Plasma Device Creates Radicals/Reactive Chemicals at *Room Temperature*

Helium/O$_2$ mixture; plasma from applied voltage on electrodes

Radicals/reactive chemicals from plasma-air mixture at boundaries of plasma; also E-fields, charges, photons...

Mechanisms of plasma-biological effects not understood! (Pretty much at all...)
Murine model: combined effects of plasma + gemcitabine appear approximately additive
NTP: *non thermal plasma*

‘Plasma gun’ device:
thin plastic tube with plasma propagating
~ 1m in He flow
Results from mouse tumor size vs. time
Cold atmospheric plasma for the ablative treatment of neuroblastoma

Ryan M. Walk, Jason A. Snyder, Priya Srinivasan, Jacob Kirsch, Stephanie O. Diaz, Felix C. Blanco, Alexey Shashurin, Michael Keidar, Anthony D. Sandler

Sheikh Zayed Institute for Pediatric Surgical Innovation at Children's National Medical Center, Washington, DC, USA
Walter Reed National Military Medical Medical Center, Bethesda, MD, USA
George Washington University, Washington, DC, USA


Neuro2a cells, a murine neuroblastoma line
What is our **Conceptual Model** for Plasma-Therapy?

**Gas Phase RONS**
- $O$, $OH$, $O_3$, $O_2^-$, $NO$, $NO_2$

**Liquid Phase RONS products**

**Surface Cells**

**Bulk Tissue/Tumor**

**Cell-cell communication:** ‘bystander effect’ leading to tumor apoptosis?

**Immune cell involvement?**

**Plasma-induced increased blood flow/O2?**

**RONS gas species:** transfer into liquid

(Liquid: water, salt, proteins, lipids; RONS react to form products)

**Surface cells:** RONS-macromolecule products induce stress that causes signaling to bulk tissue: *tumor apoptosis*
Speculation: Why is Air Plasma Anti-Tumor?

Air/Water Plasma Chemistry

O, OH, $^1\text{O}_2$, $\text{O}_2^-$, $\text{HO}_2$, $\text{O}_3$
N, $\text{NO}_3$, $\text{NO}_2$, NO, $\text{N}_x\text{O}_y$
$\text{NO}_2^-$, $\text{NO}_3^-$, $\text{ONOO}^-$, H,
$\text{H}_2\text{O}_2$, $\text{HNO}_2$, $\text{HNO}_3$

Innate Immune System Chemistry

Dedon and Tannenbaum, 2004
Radiotherapy radical chemistry:

- **Photons:** ~2/3 therapeutic effect from radicals
We propose to target the antioxidant mechanism of tumor adaptation by an anticancer therapy...by treating cancer cells either with ROS-inducing therapies or with antioxidant inhibiting therapies.
Questions and Thoughts: Plasma Cancer Treatment

1. What are practical issues (access, location, orientation of tumors) for plasma therapy in cancer?

2. What are criteria for going forward? How will we know that plasma is a promising tool? Can we effectively combine plasma and other therapies?

3. There are already multiple papers in literature that address safety (e.g. skin histology, etc.). “Big” efforts in Germany, France, Japan, Korea, Netherlands. Interest growing around world.

4. Recognize that success will depend on proper multidisciplinary team.
Concluding Remarks

1. Scope of plasma-surface applications and underlying science very broad: surface /interfacial materials engineering and plasma biology both promising.

2. ‘Plasma biomedicine’ growing rapidly: but mechanisms still mostly uncertain. RONS/redox biochemistry looks important.

3. Photon-, electron-, ion-, excited state-, radical- biomolecule interactions, often at gas-liquid interfaces, are also key to plasma biomedicine.
TOPICAL REVIEW

The emerging role of reactive oxygen and nitrogen species in redox biology and some implications for plasma applications to medicine and biology

A Final Thought from Will Allis

What is your most significant achievement?

"It's the students I've educated! Whenever I am traveling in some distant, crowded airport, someone inevitably comes up to me and says, 'Professor Allis, I worked with you!' That is my principal contribution, and it's something that's remembered rather than written. That has been the most rewarding aspect of being a teacher."