

# Electron beam generated plasmas:

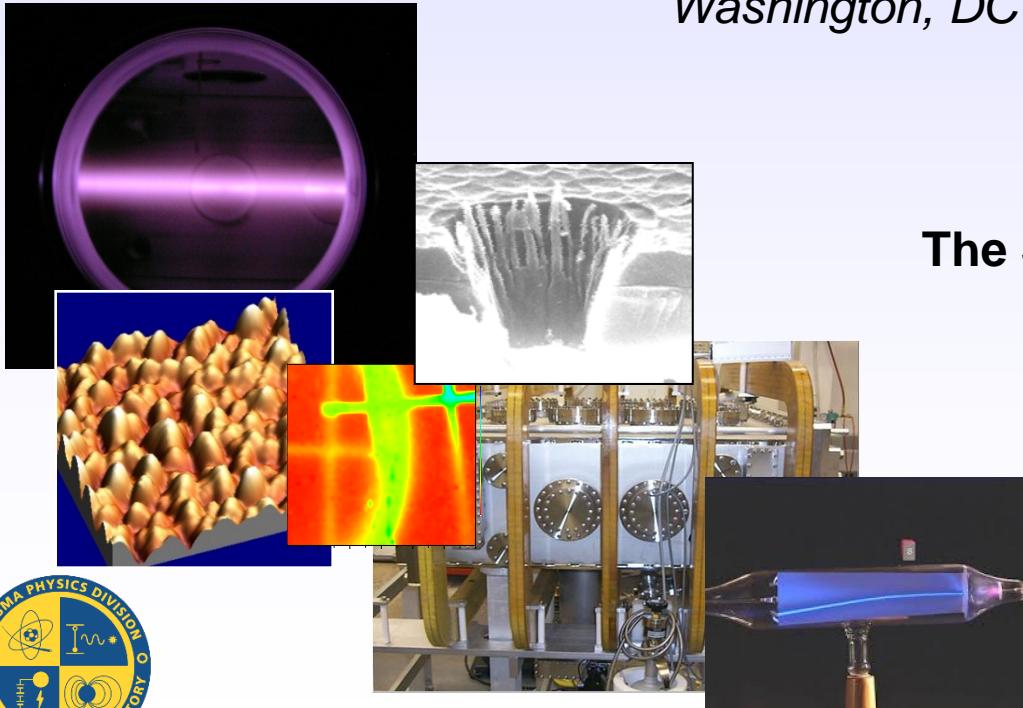
Ultra cold sources for low damage, atomic layer processing

---

Scott G. Walton

Plasma Physics Division, Naval Research Laboratory

*Washington, DC 20375*



The Surface Preparation and Cleaning  
Conference (SPCC)

April 19-20, 2016

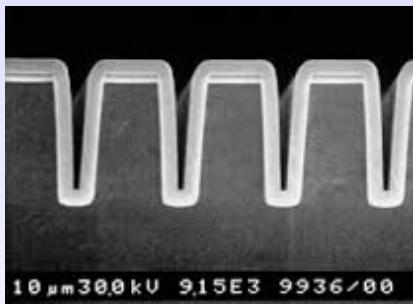
Santa Clara, CA



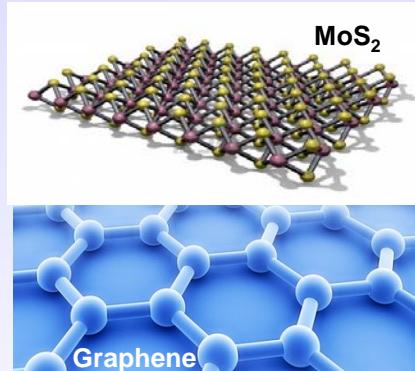
# Motivation

As material demands evolve toward the single nanometer-scale dimensions, one would like to systematically modify *one and only one monolayer* at a time, without "damaging" other layers

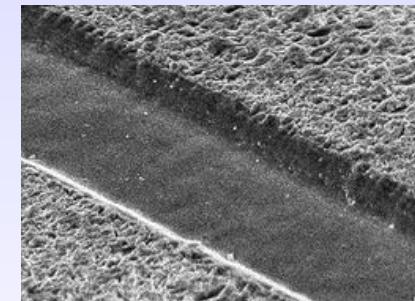
Atomic layer  
etching/deposition



2-D material processing



Polymer processing



## Plasma Requirements

- Precise control over the *flux of species* and the *ion energy* at surfaces during processing
- For very thin materials (e.g. 2-D materials), the energy of incident ions should be low as possible to minimize damage while processing



A. Agarwal and M.J. Kushner, J. Vac. Sci. Tech. - A, 27, 37 (2009)

K.J. Kanarik, G. Kamath, R.A. Gottsch, Solid State Technology, Volume 55, Issue 3, (2012)

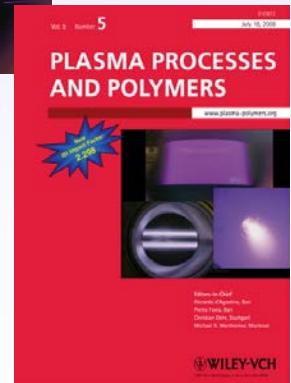
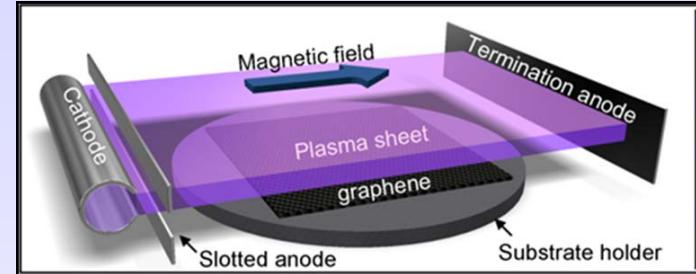
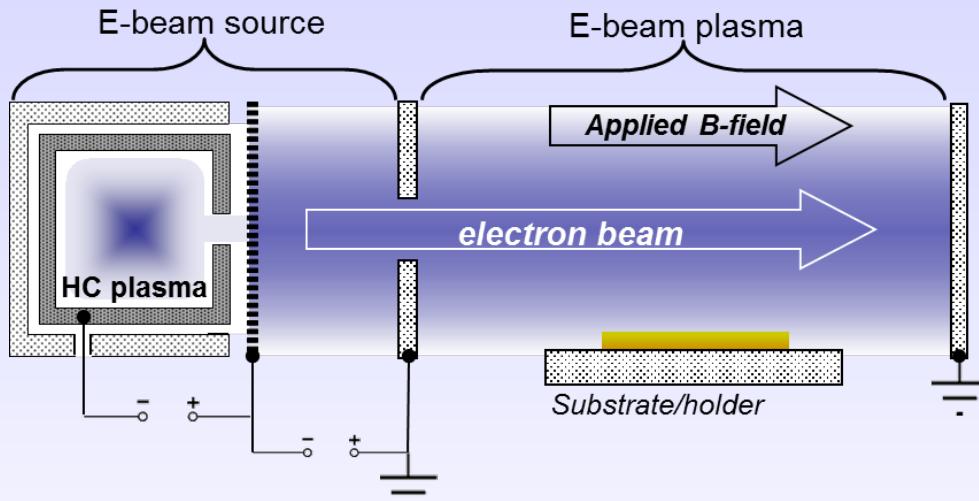
G. S. Oehrlein, D. Metzler, and C. Lia, ECS J. Solid State Sci. Technol. 4(6), N5041-N5053 (2015)

# **Electron Beam Generated Plasmas**

- Unique control over species production**
- Inherently low electron temperature and thus, uniquely low ion energies**

# Electron beam generated plasma processing system

## Large Area Plasma Processing System (LAPPS)\*



### Basic Operation

- High energy beam injected into background
- Creates Plasma
  - Ionizes: Charged Particles (ions and electrons)
  - Excites: Species emit photons
  - Dissociates: Reactive Radicals



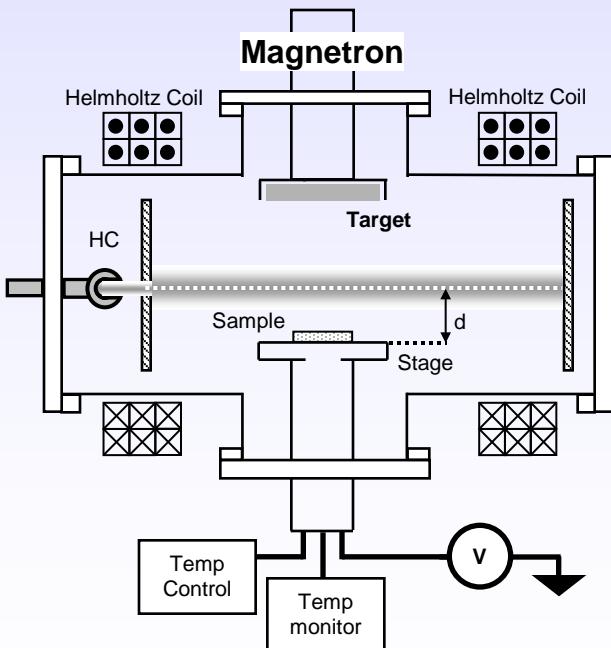
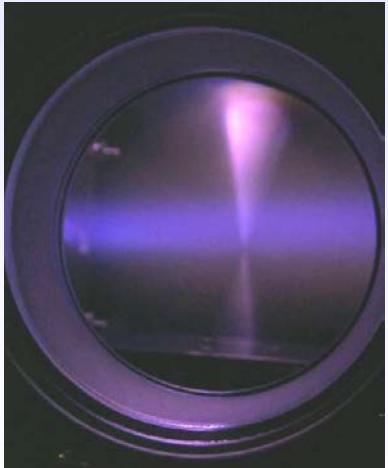
\*Meger et al., US patent no. 5,874,807 (Feb. 1999)

# Platforms for processing

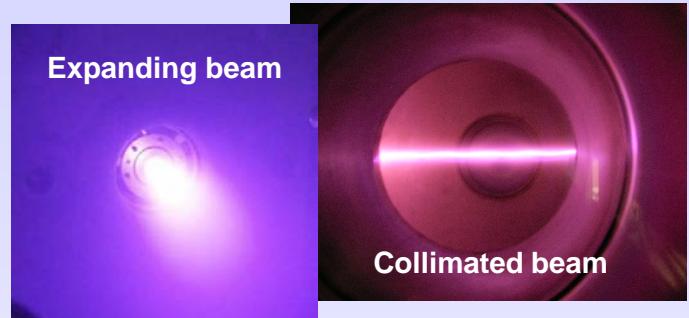
Source is decoupled from reactor geometry

- Flexible design
- Unique geometries

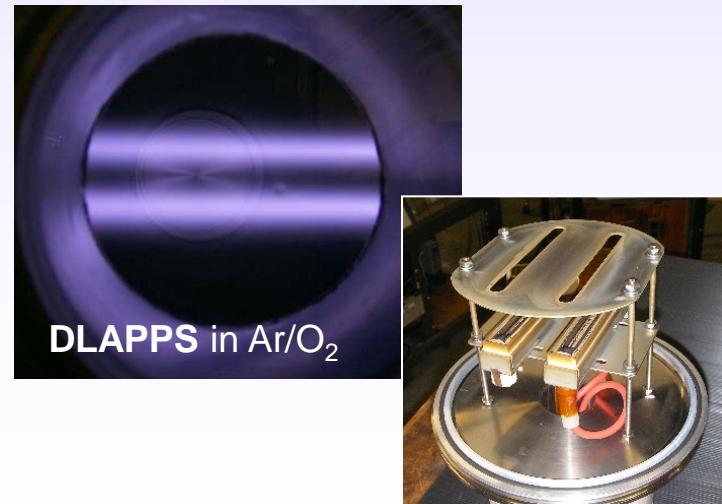
PEPVD\*



Magnetized or not



Roll to Roll\*\*

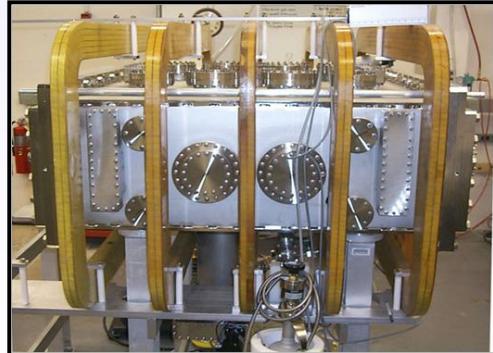
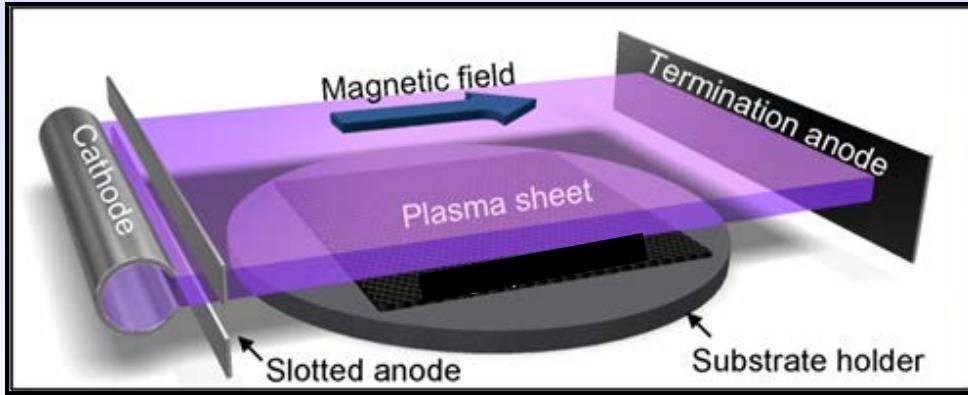


\* C. Muratore, et al., J. Vac. Sci. Technol. A, 24(1), 25 (2006)

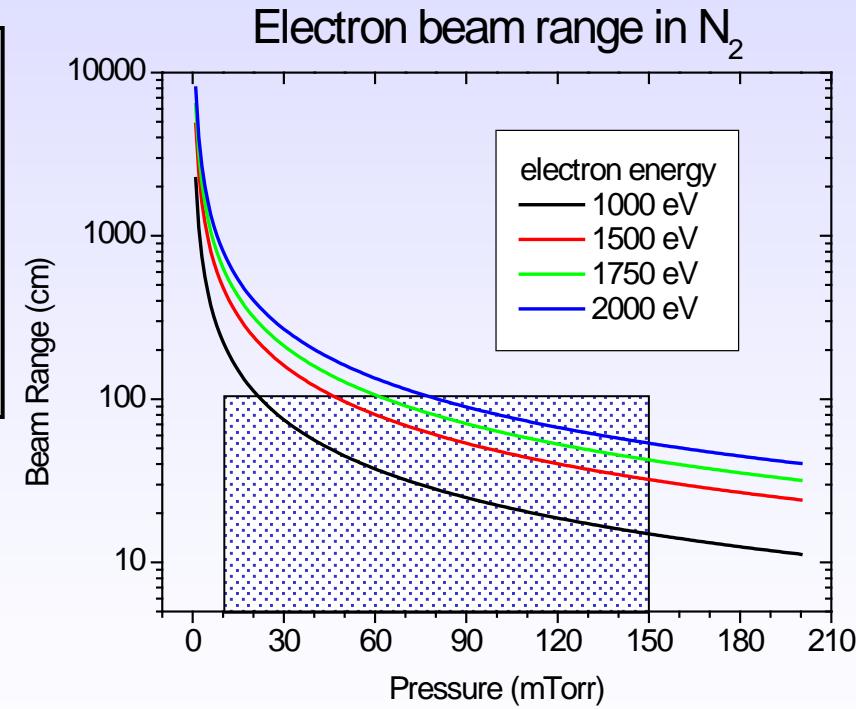
\*\* S.G Walton, et al., Plasma Proc. and Poly. 5, 453 (2008)

# Platforms and processing

- Scaling is straightforward to accommodate large area processing
  - **width** scales with e-beam source width
  - **length** scales with beam energy and pressure



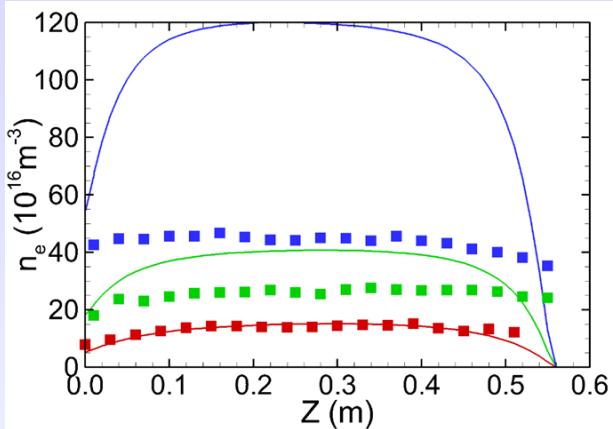
Large area rectangular chamber ( 1 m<sup>2</sup> capability)



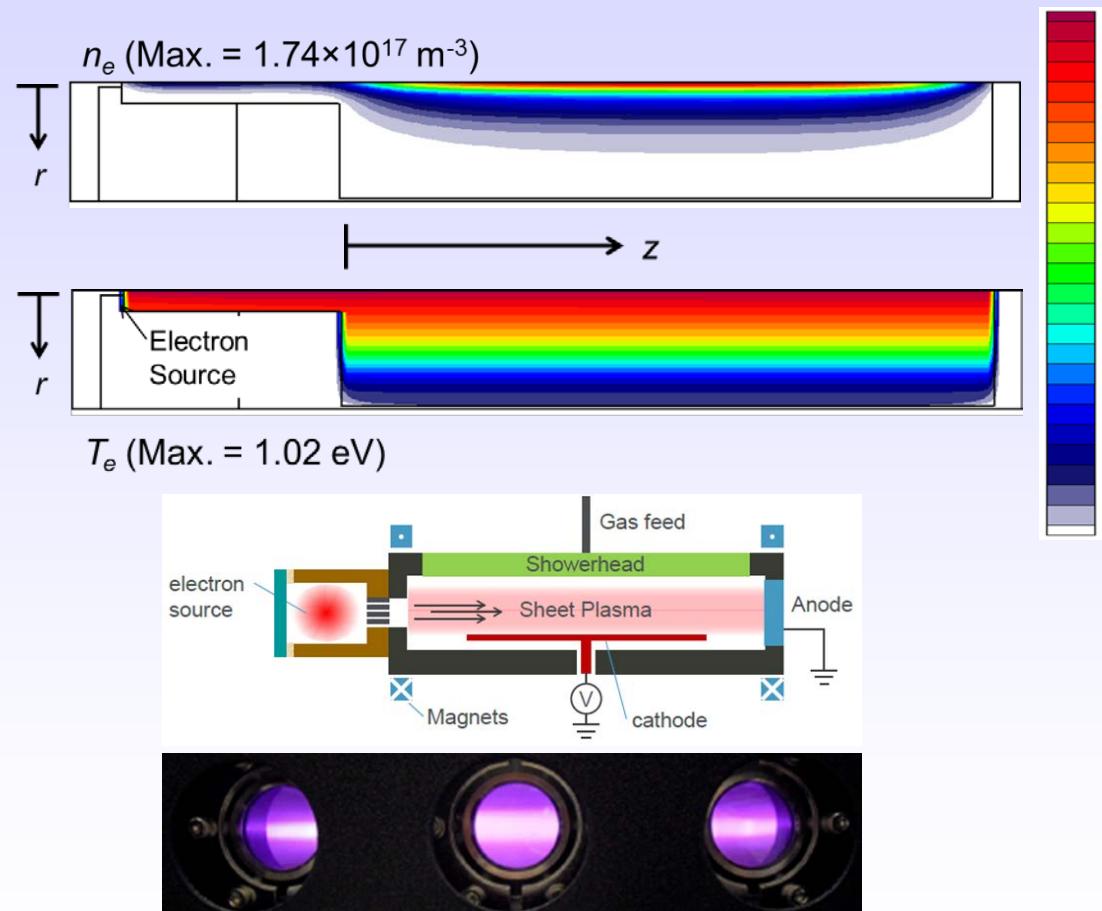
# Platforms and processing

- Source is scalable to large areas without losses in uniformity

Model Validation

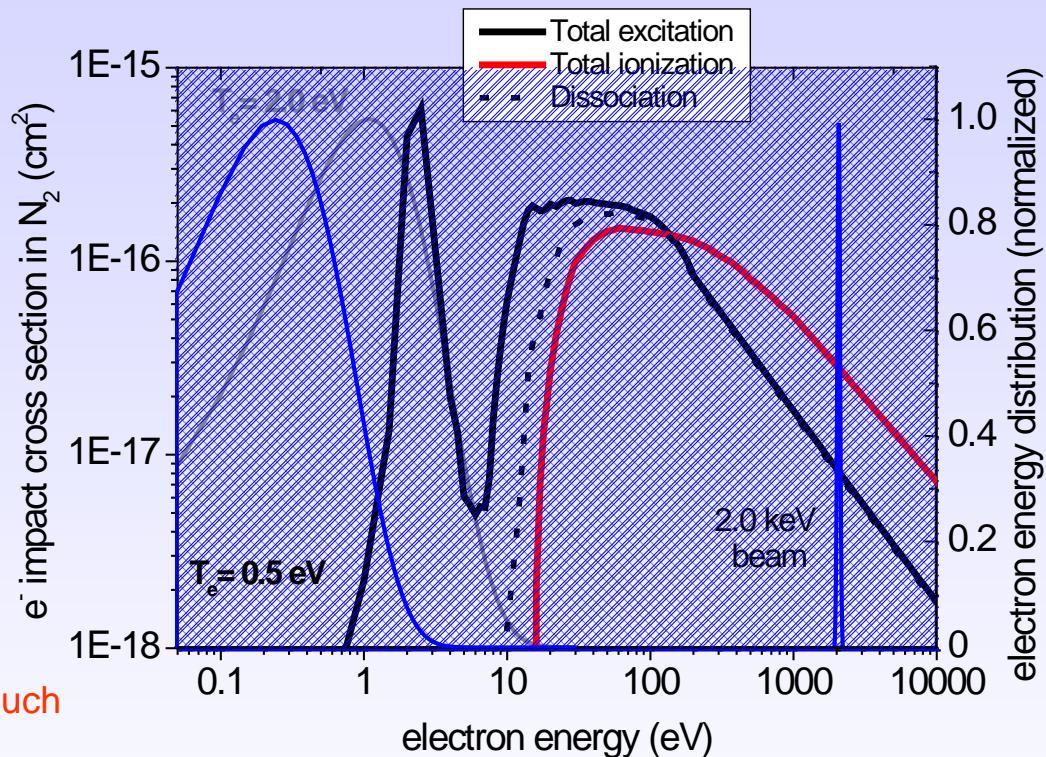


Prototype System



# Plasma generation with high-energy electron beams

- In discharges,
  - electric fields to energize plasma electrons
  - small fraction of electrons ionize gas
  - most energy is used to excite the gas
- The injection of a 2 keV beam into the background gas will directly ionize and dissociate the gas.
  - more *efficiently* ionize
  - no threshold determination
  - ionize all species equally
- The plasma (or secondary) electrons have much a lower energy
  - are not required to sustain the plasma
  - cooled electrostatically and through inelastic collisions

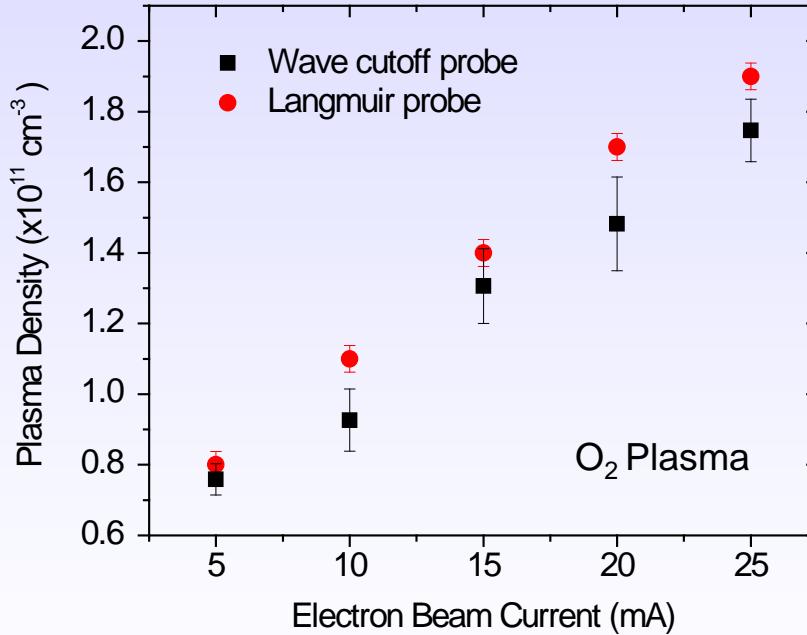
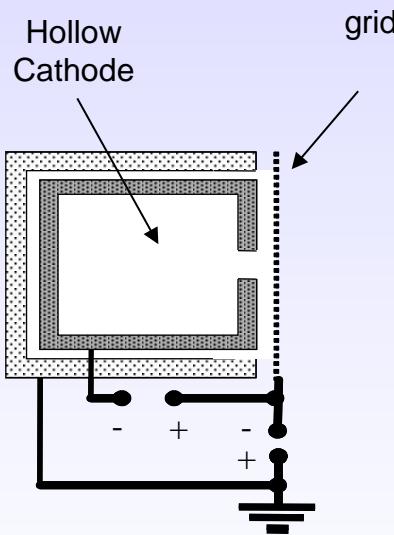


... the resulting plasmas have unique features

# Unique Features of Electron Beam-Generated Plasmas

Simple Control of plasma density and species production

$$\frac{dn_i}{dt} = S_i - L_i = 0 \quad \rightarrow \quad S_i = k I_{beam} P_i \sigma_i$$



Plasma density scales with beam current

E.H. Lock, et al., Plasma Sources Sci. Technol. 17, 025009 (2008)

S.G. Walton, et al. J. Appl. Polym. Sci. 117, 3515 (2010)

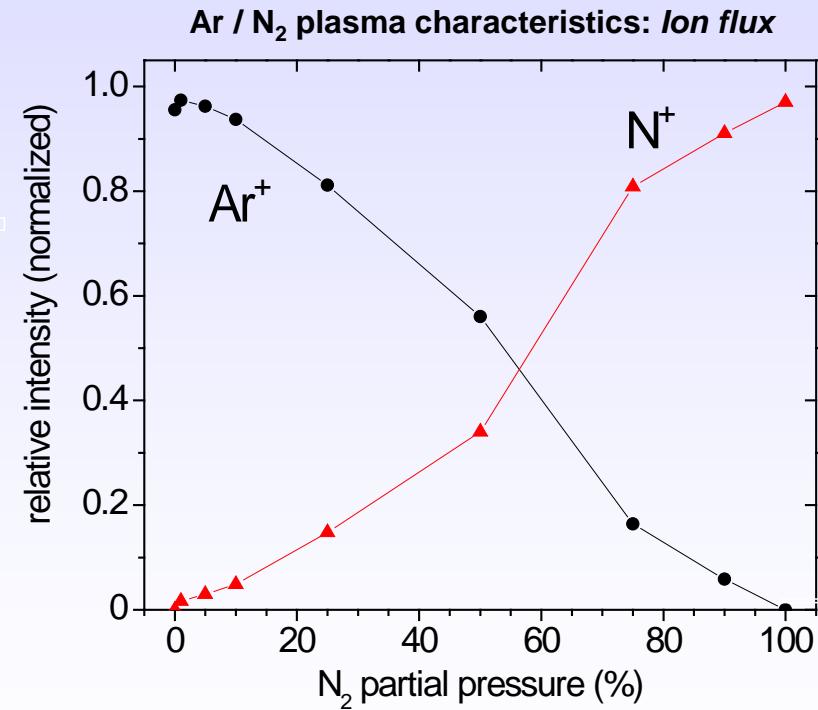
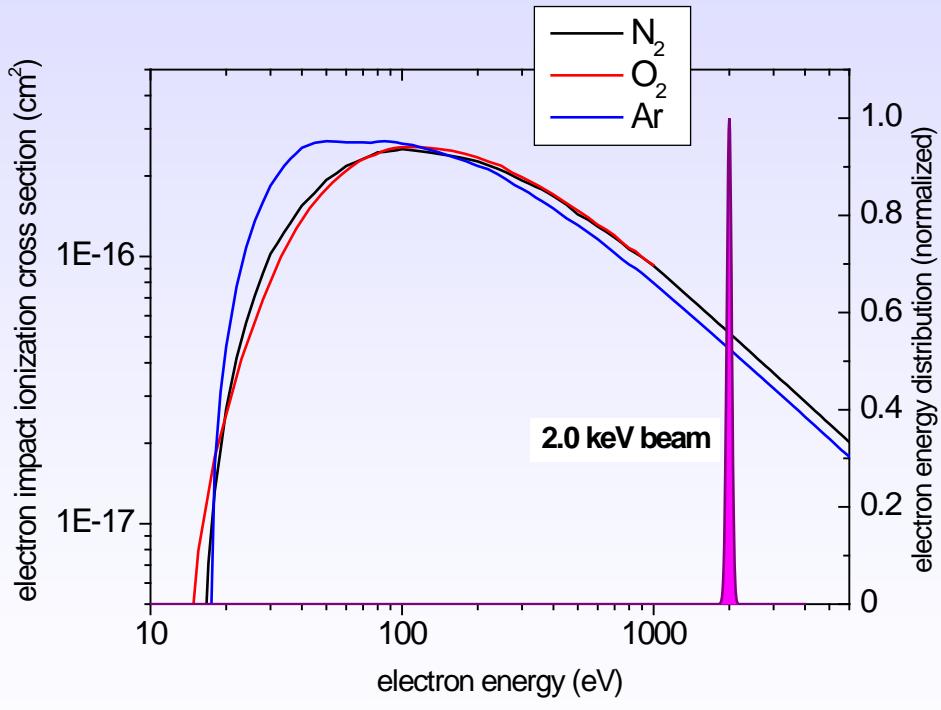
D.R. Boris, et al., Plasma Sources Sci. Technol. 20, 025003-7 (2011)



# Unique Features of Electron Beam-Generated Plasmas

Species generation is proportional to the relative concentrations of the working gases

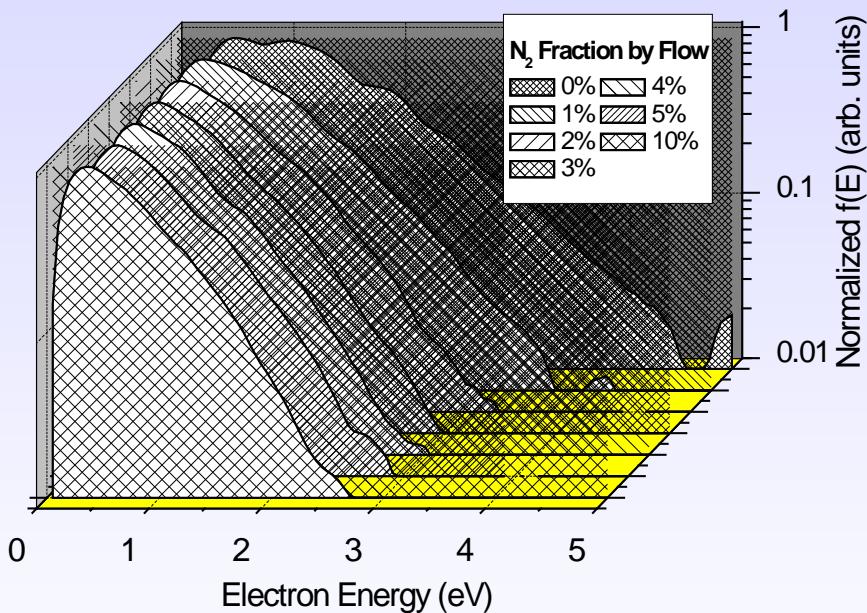
$$S_i = k I_{beam} P_i \sigma_i(E)$$



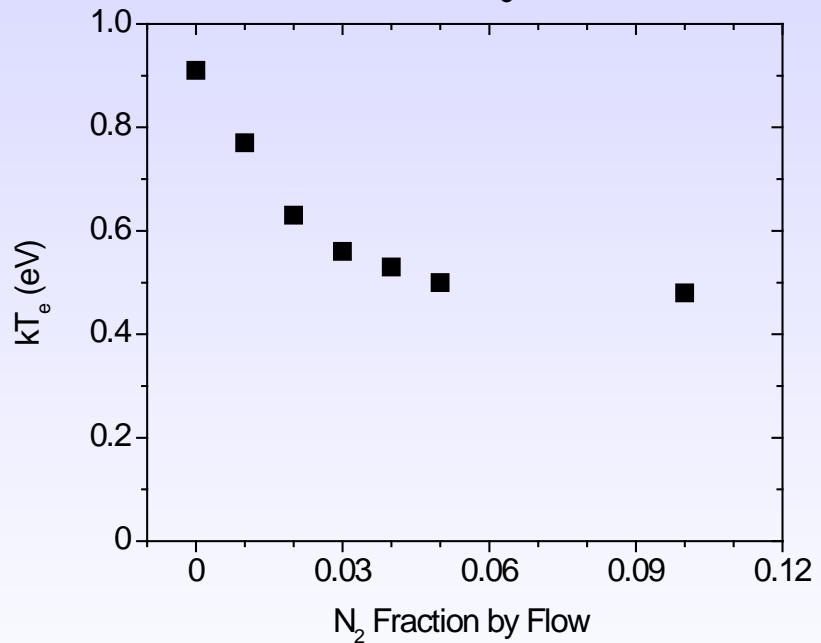
# Unique Features of electron beam generated plasmas

$T_e$  is low and dependent on background gas

EEDF in beam channel



$T_e$  in beam channel



EEDF cools with increasing nitrogen concentration

Leading to a corresponding drop in  $T_e$



D. R. Boris, et al., Plasma Sources Sci. Tech. 22, 065004-6 (2013)

G. M. Petrov, et al., Plasma Sources Sci. Tech. 22, 065005 -8 (2013)

# Unique Features of electron beam generated plasmas

Very low  $T_e$  provides very low ion energy

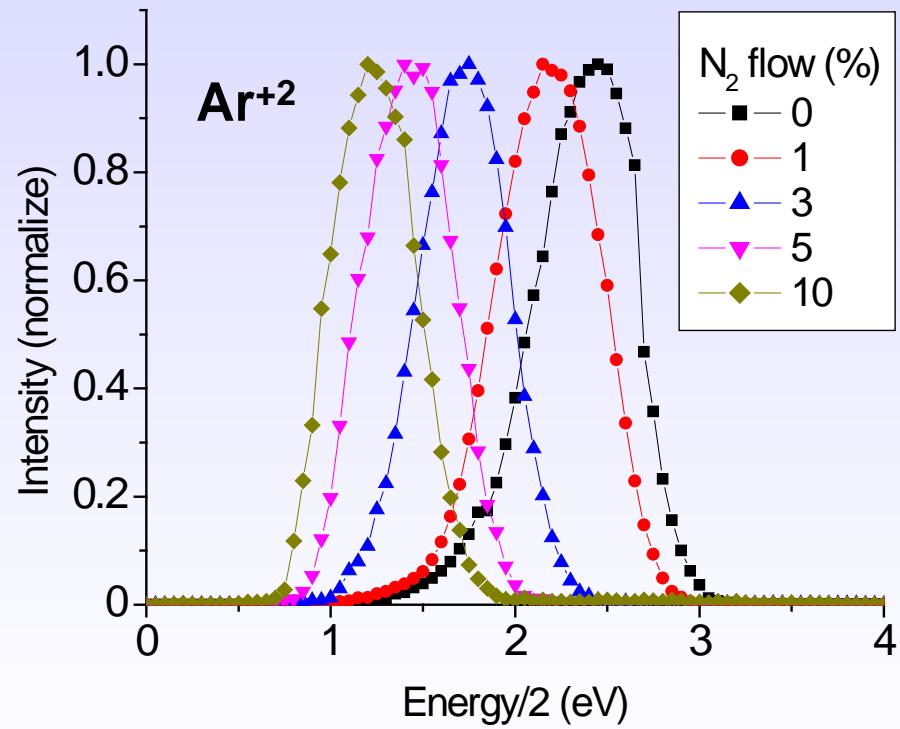
## IED at Electrode surface

Plasma Potential:

$$V_p = T_e \ln(M/2\pi m_e)^{1/2}$$

Ion Energy:

$$E_{ion} = V_p - V_{sb}$$

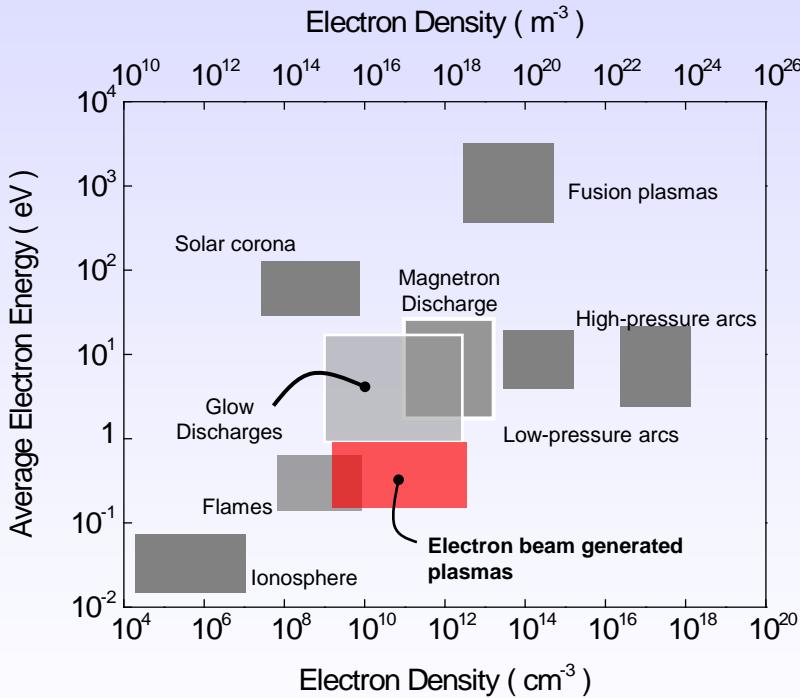


D. R. Boris, et al., Plasma Sources Sci. Tech. 22, 065004-6 (2013)

G. M. Petrov, et al., Plasma Sources Sci. Tech. 22, 065005-8 (2013)

# Unique Features of electron beam generated plasmas

**Electron Beam Generated Plasmas** have a fundamentally low  $T_e$  (even at high plasma densities) and thus provide a large flux of low energy ions



Plasma sources (discharges) used in materials processing

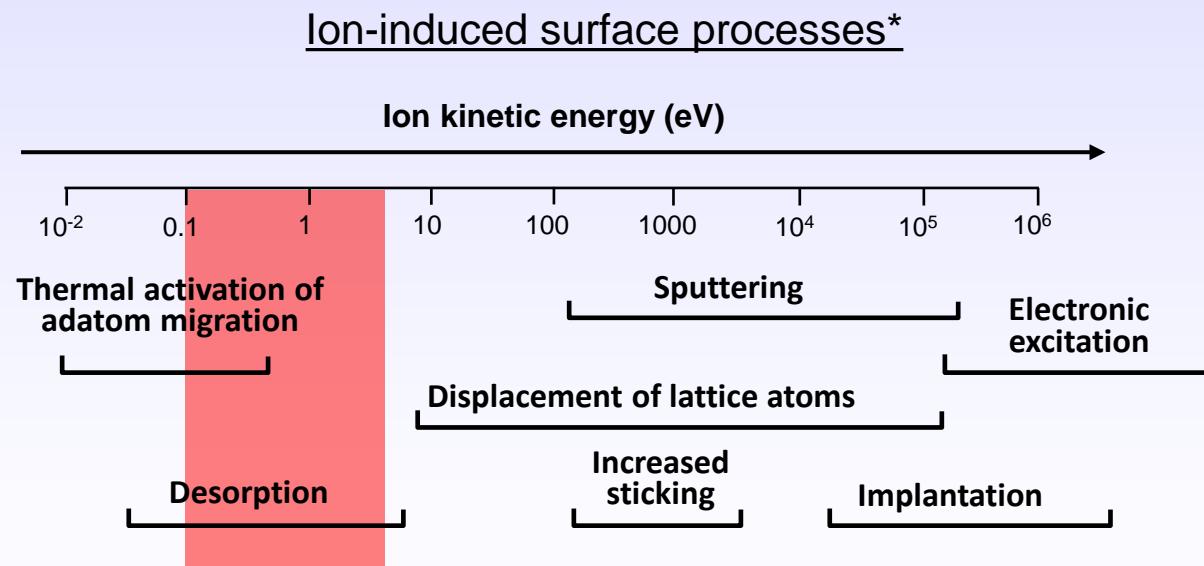
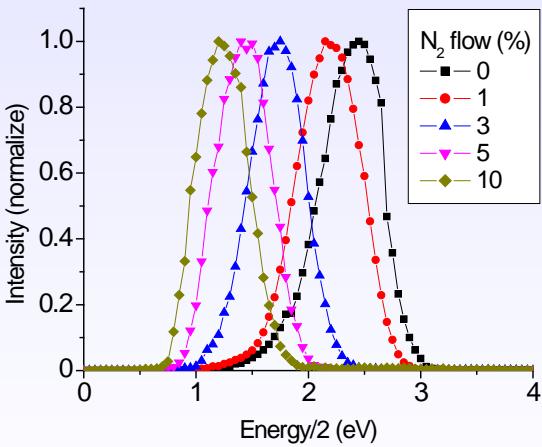
Type	$T_e$ (eV)	$n_e$ ( $\text{cm}^{-3}$ )	$\text{KE}_{\text{ion}}$ (eV)
ICP	4	$10^{11}$	20
ECR	4	$10^{11}$	20
DBD	2 - 10	$10^{13}$	10 - 100
RIE	8	$10^{10}$	40
DC Diode	2 - 10	$10^{10}$	10 - 100
CCP	1 - 5	$10^9$ - $10^{10}$	5 - 25
<b>Electron Beam</b>	<b>0.3 - 1</b>	<b><math>10^9</math> - <math>10^{12}</math></b>	<b>1.5 - 5</b>

From: S.G. Walton and J.E. Green, "Plasmas in Deposition Processes," In *Handbook of Thin Film Deposition Technology: 3rd Edition*, ed. Peter Martin, Holland: Elsevier (2009).

# Processing implications

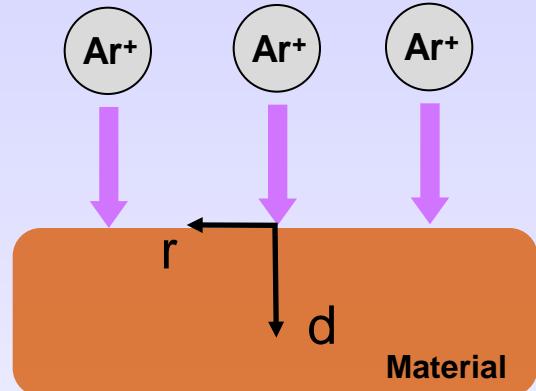
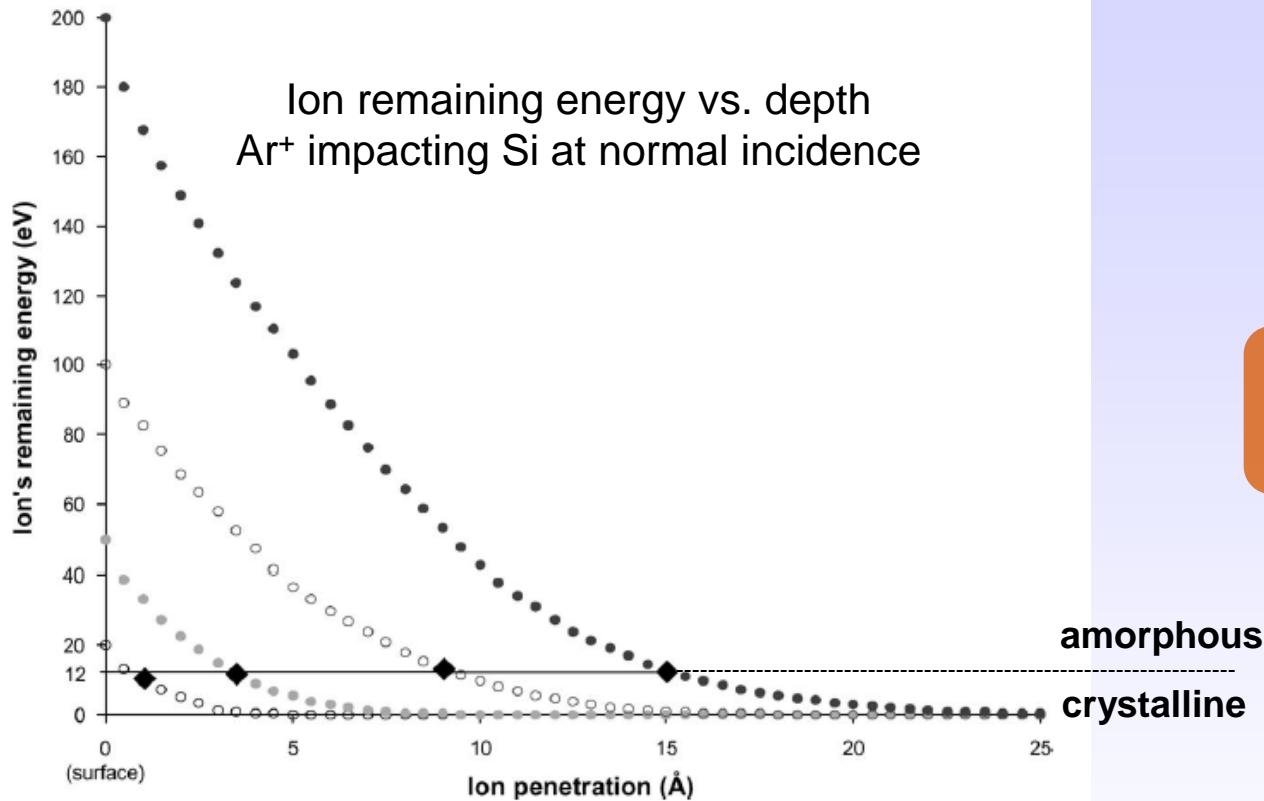
## Electron beam generated plasmas provide:

- Unique control over the production of species and their transport to surface
- $n_e$  is high ( $10^{10}$ -  $10^{11} \text{ cm}^{-3}$ );  $T_e$  is very low ( $\approx 0.5 \text{ eV}$ )
- In the absence of any biasing, a mix of reactive species in concert with a large flux of very low energy (0 - 5 eV) ions



\* Adapted From: Grill, A., *Cold plasma in materials fabrication: From fundamentals to applications*, Piscataway: IEEE Press, 1994.

# Processing implications: Low damage

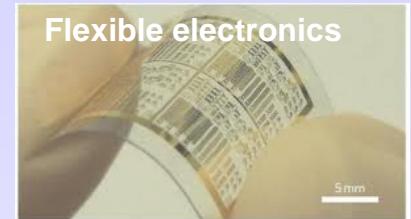


Low ion energy is valuable in maintaining crystallinity

# Target Processing Applications

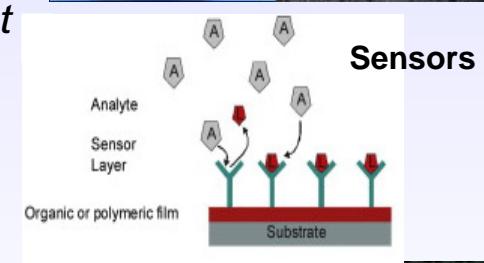
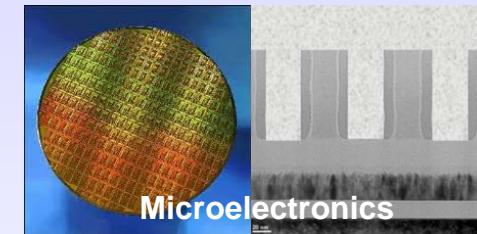
## Chemical Modification of Ion Energy Sensitive Materials

- Chemical modification without physical changes (e.g. surface roughening)
- Polymers or other “soft” materials
- *Sensors and biomaterials applications*



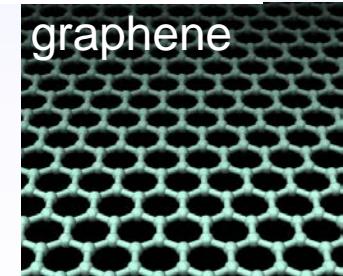
## Atomic Layer Modification

- Graphene Oxide Reduction – *reduction to graphene without damage*
- Graphene (or other 2-D materials) functionalization - *etching is not an option*
- *Sensors and electronic applications*



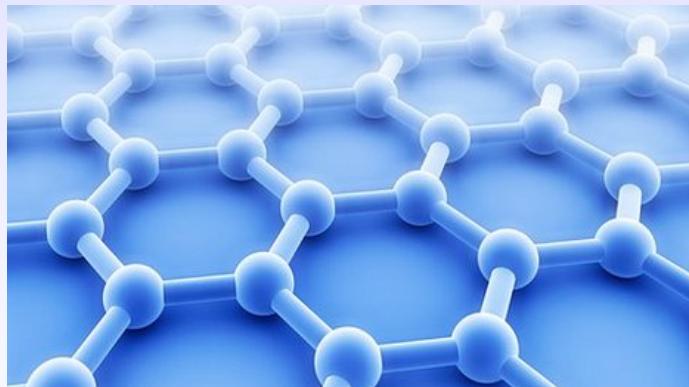
## Atomic Layer Etching

- Selective removal of only one monolayer at a time
- Polymers (e.g. photoresist)
- Silicon
- Metal and/or silicon oxide/nitrides
- *Microelectronics applications*



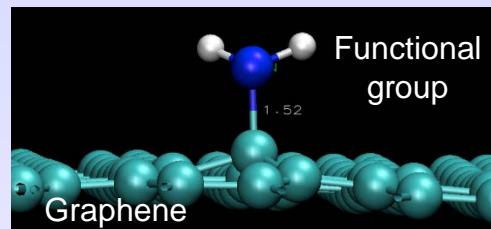
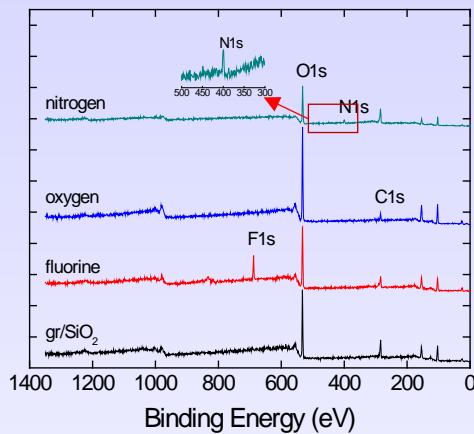
# **Graphene**

## **Processing**

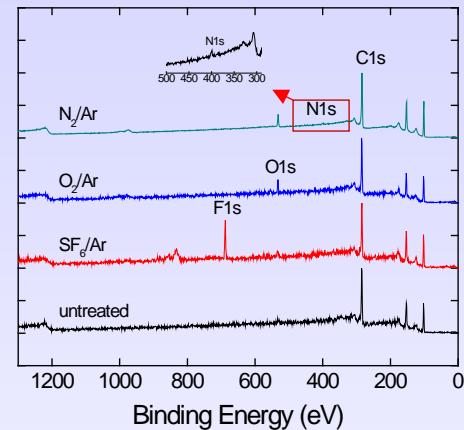


# Functionalized Graphene: Chemical Modification

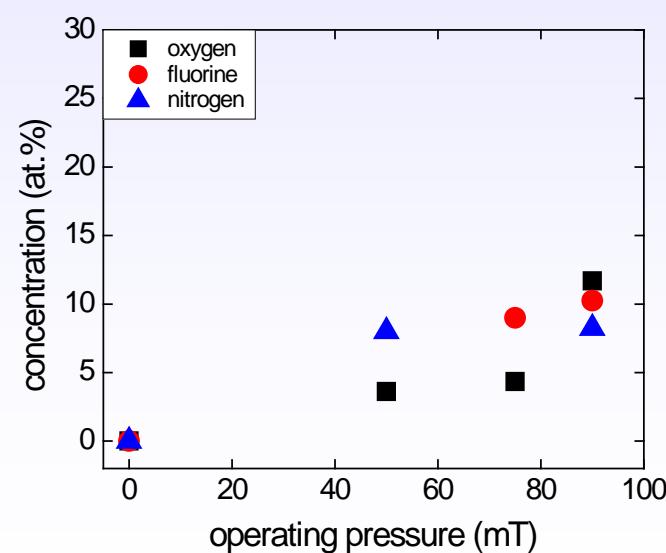
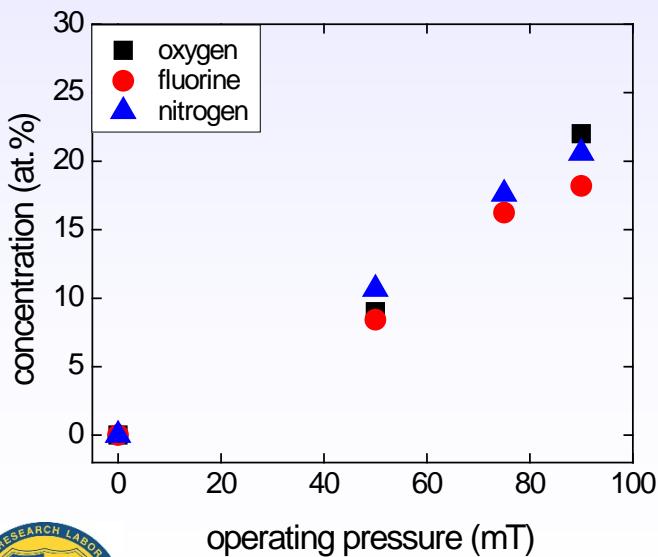
## Graphene on Si/SiO<sub>2</sub> \*



## Epitaxial Graphene on SiC \*\*



Controllably introduce functional groups

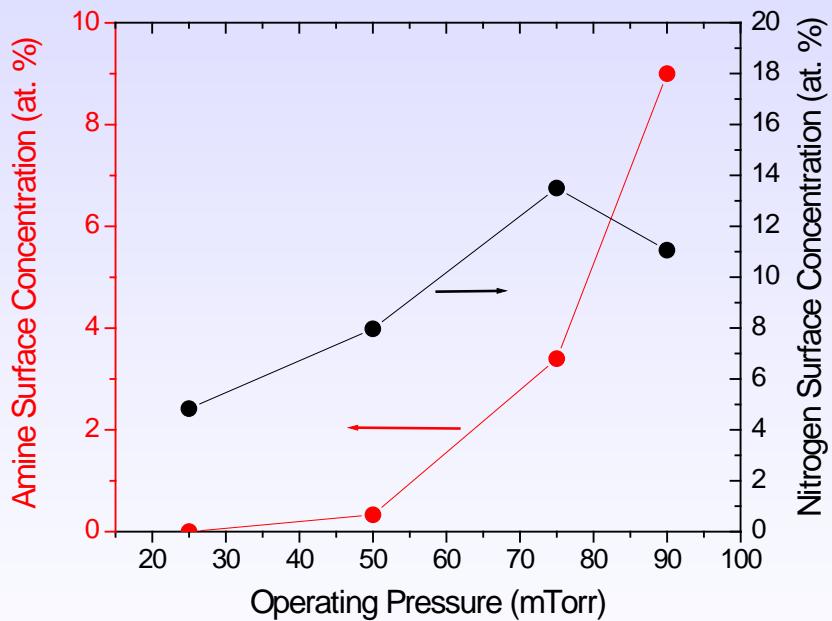


\* M. Baraket, et al., Appl. Phys. Lett. 96 231501 (2010).

\*\* S.G. Walton, et al., Materials Science Forum (2012); 16. S.C. Hernández et al, Surf. Coat. Tech. 241, 8 (2014)

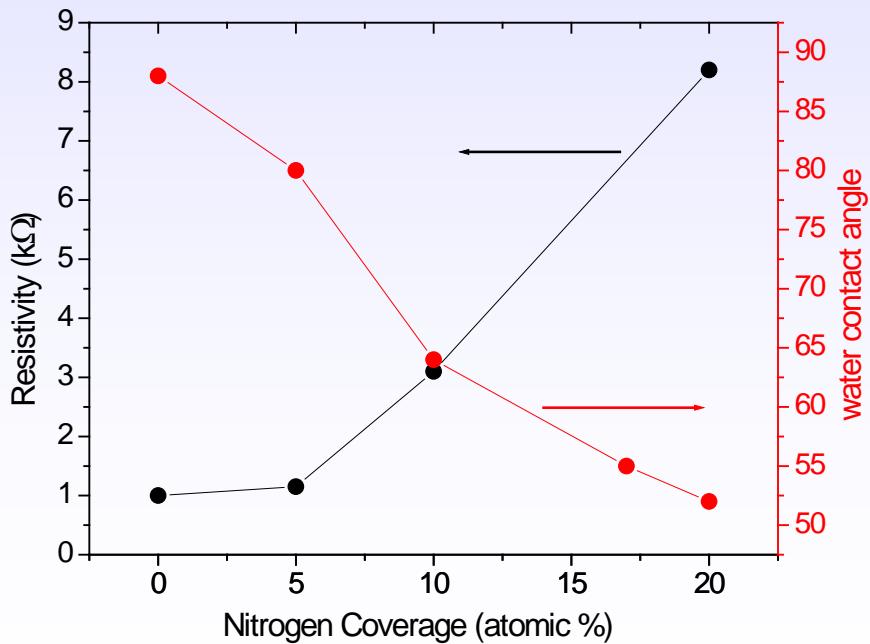
# Functionalized Graphene; Functional Surfaces

- Exposure to ammonia-containing plasmas leads to the incorporation of both primary amines ( $\text{NH}_2$ ) and N
- Surface reactivity increases and sheet resistance remains reasonably low



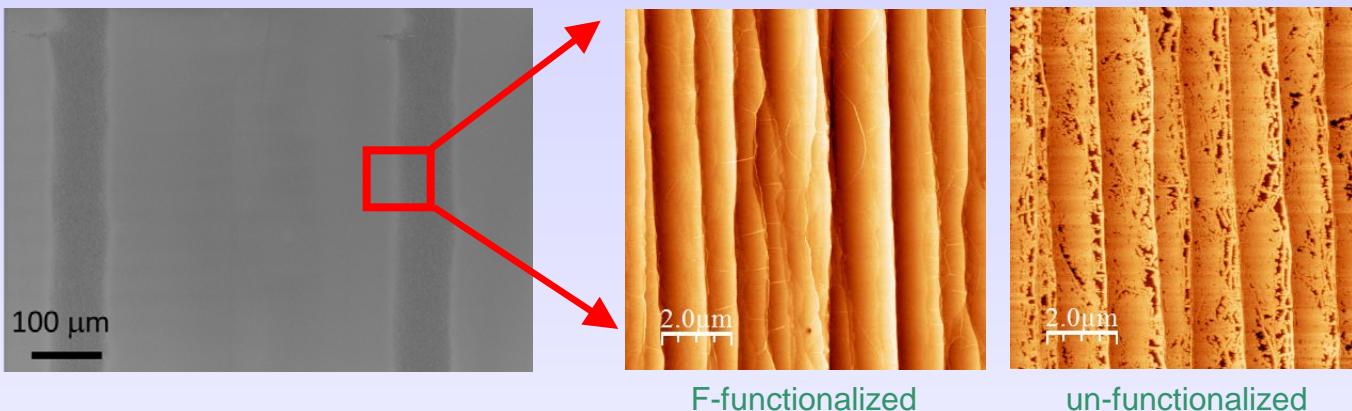
Primary amine coverage

## Sheet resistance and reactivity



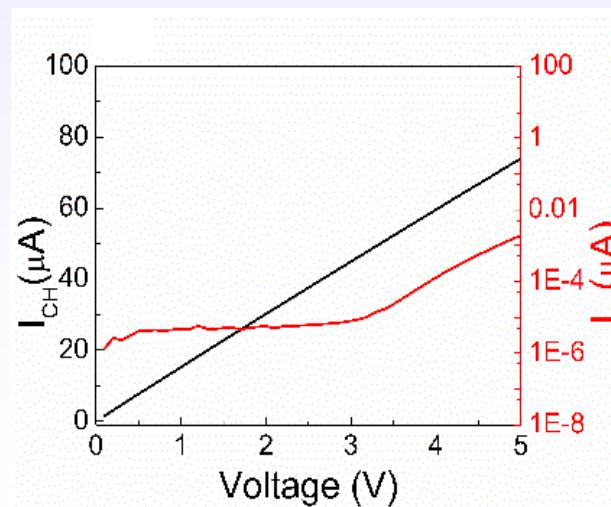
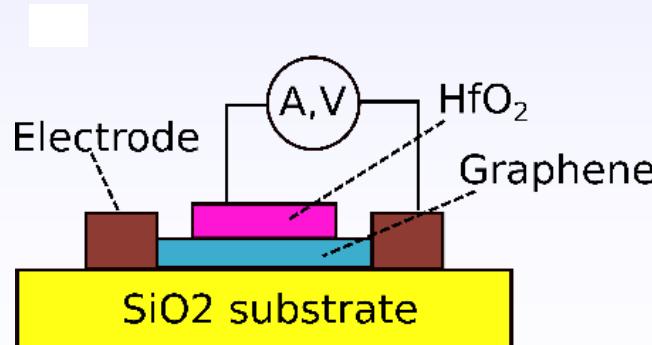
# Functionalized Graphene: Enhanced atomic layer deposition (ALD)

## ALD of $\text{Al}_2\text{O}_3$ on fluorinated epitaxial graphene



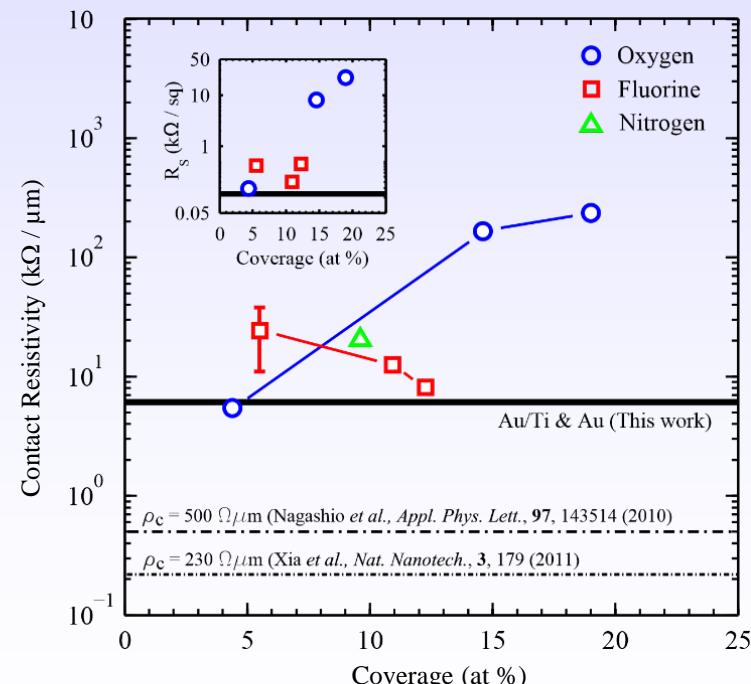
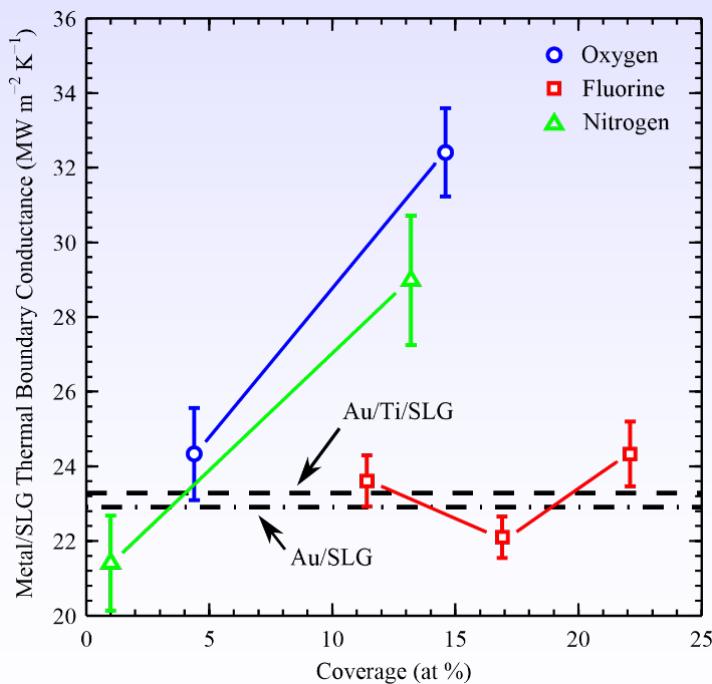
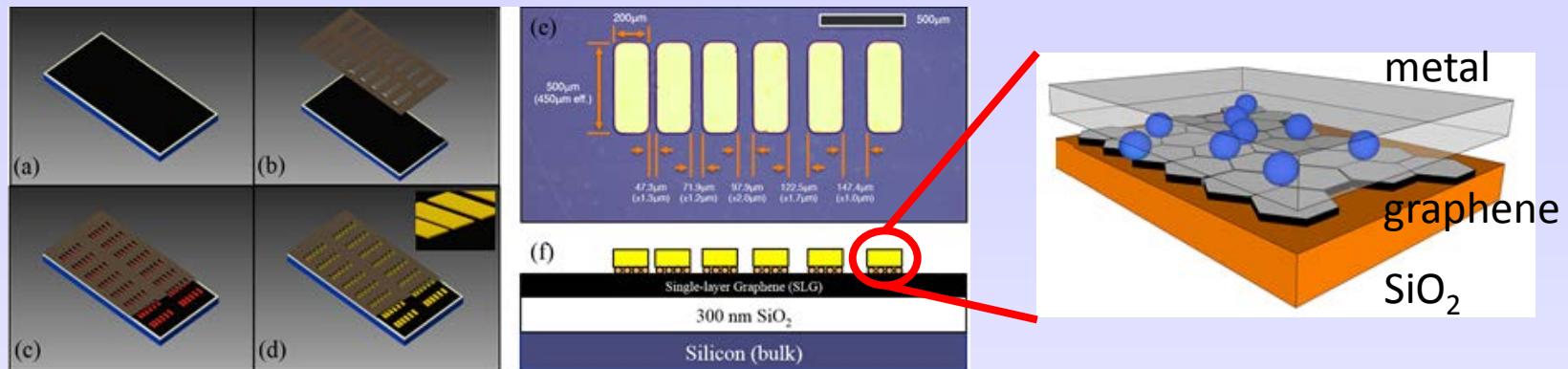
- 20nm of  $\text{Al}_2\text{O}_3$
- Conformal oxide layer only on the functionalized regions

## ALD of $\text{HfO}_2$ on fluorinated CVD graphene\*



Large difference between source-drain current ( $I_{CH}$ ) and source-gate current ( $I_G$ ) indicate successful isolation of graphene

# Functionalized Graphene: Controlling the properties at contacts



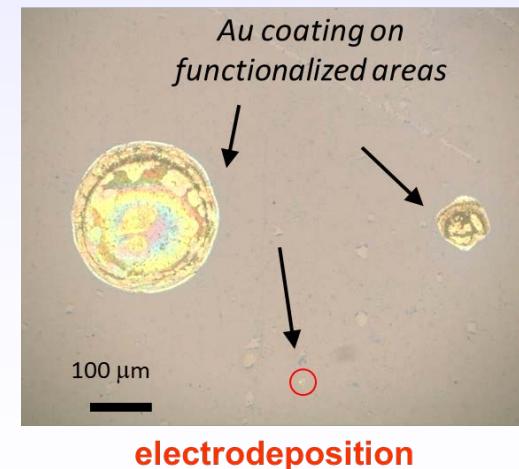
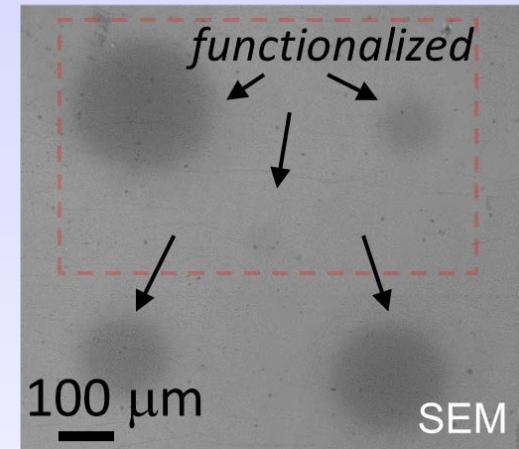
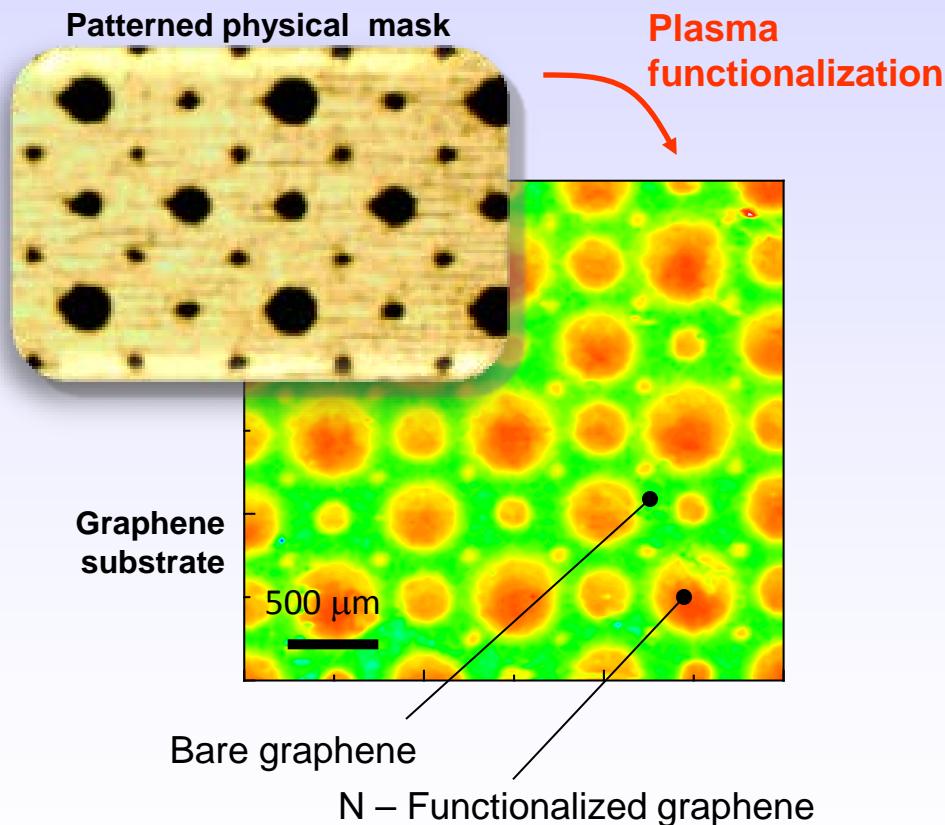
In collaboration with Prof. Patrick Hopkins (UVA)

P.E. Hopkins et al., Nano Lett. 12, 590 (2012); B. M. Foley et al., Nano Lett. 15, 4876 (2015)

# Chemical Patterning of Graphene

Direct chemical patterning of graphene for greater control over material properties and reactivity

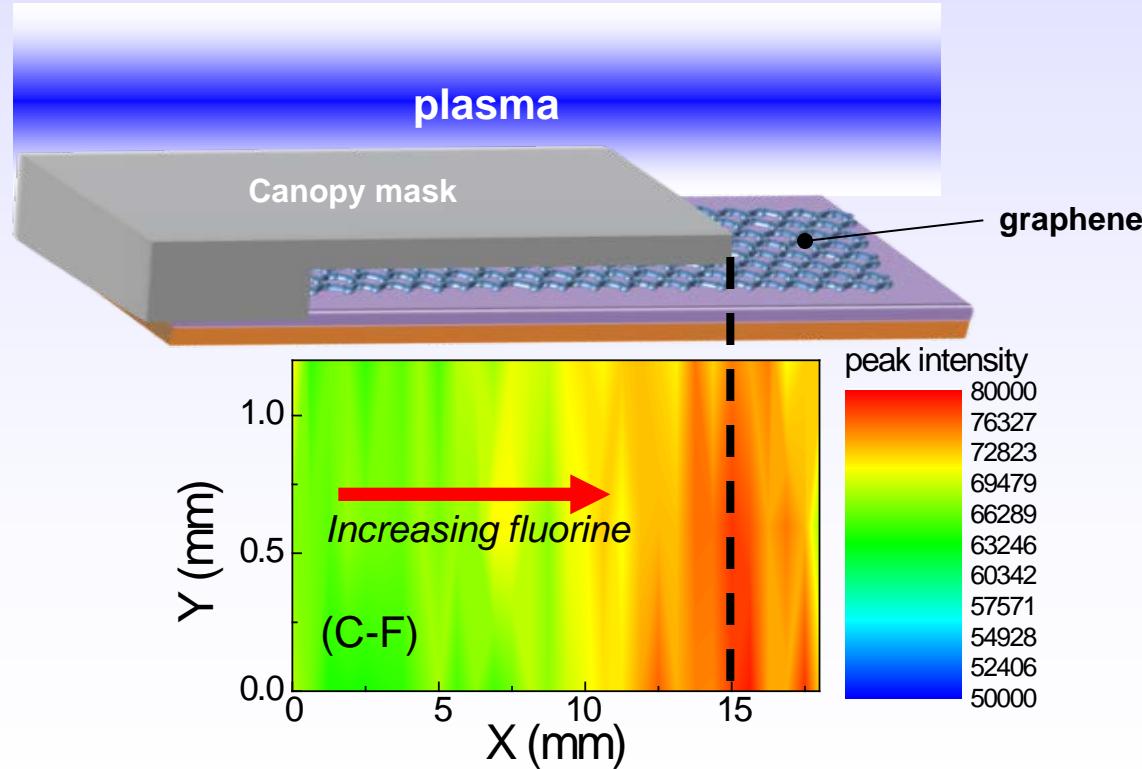
Physical masking technique + plasma functionalization



# Chemical Patterning of Graphene: Gradients

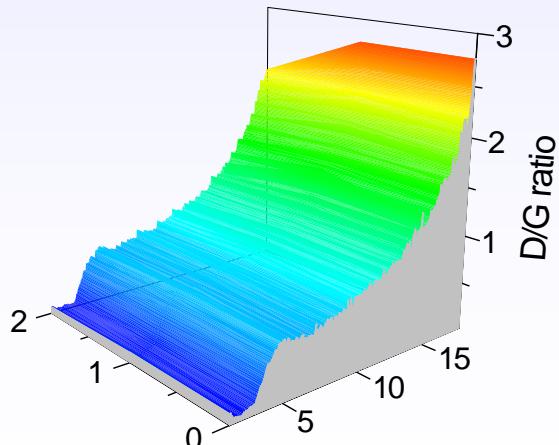
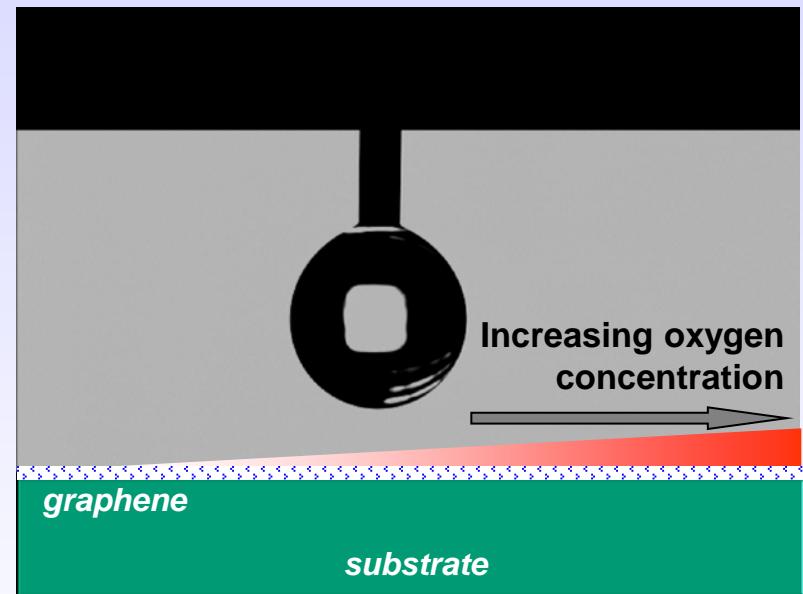
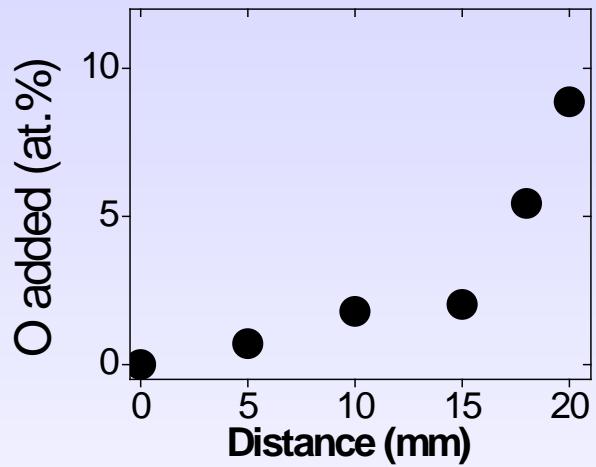
## Producing chemical gradients on graphene

- Canopy mask + plasma functionalization to produce chemical gradients
  - Continuous in gradient direction (x) and uniform laterally (y)
  - Flexibility in chemistry to grade the surface reactivity



# Chemical Patterning of Graphene: Gradients

Oxygen gradient for “pulling”  $H_2O$



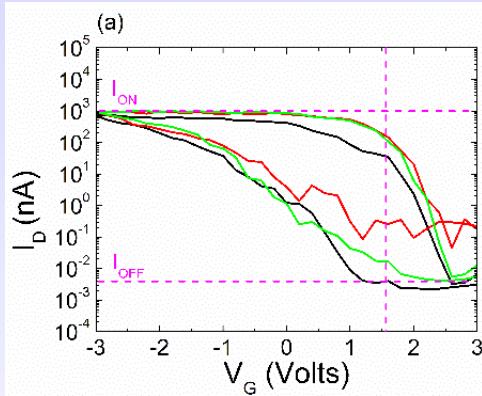
# **Atomic Layer Etch**

# CNT Etching: A comparative study

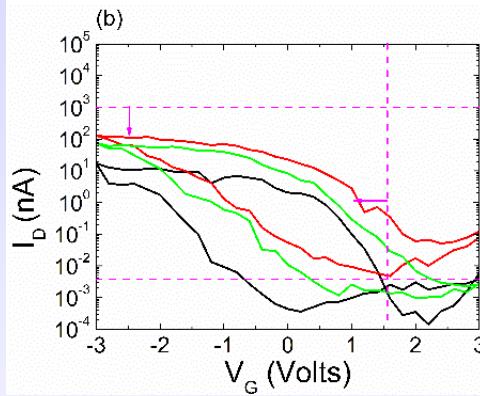
## Compare the response of semiconducting CNT's to CH<sub>4</sub> plasmas

e-beam  
generated  
plasma  
+  
10 V surface bias

Before exposure

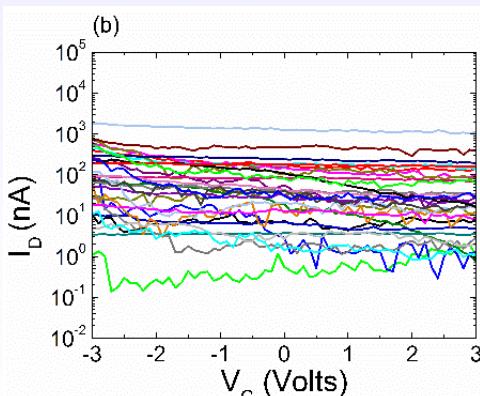
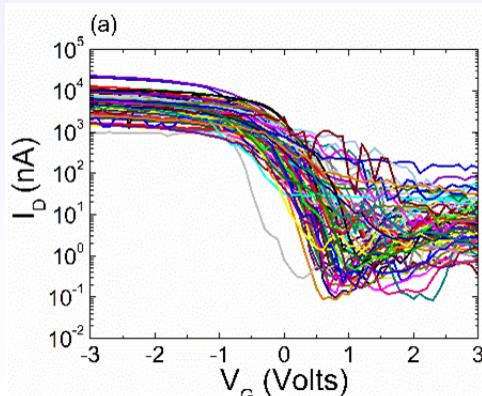


After exposure



- $I_{on}$  decreases
- $I_{off}$  remains similar
- Semiconducting properties generally retained

Low power  
ICP etch tool  
+  
25 W  
surface bias

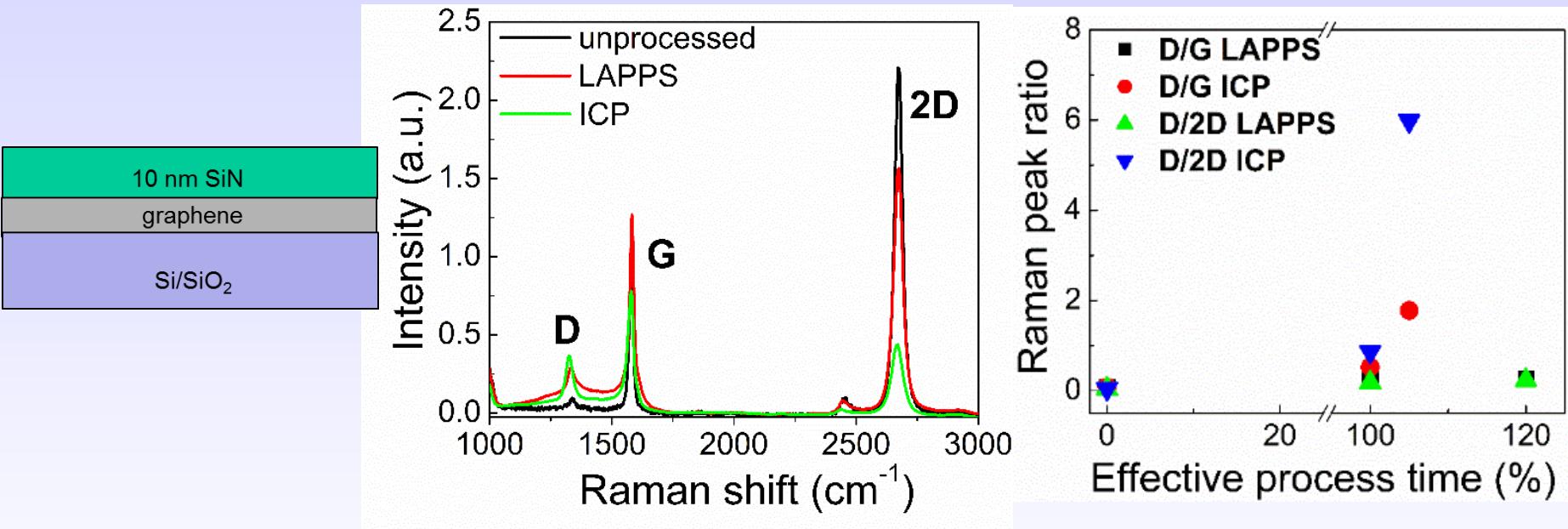


- $I_{on}$  decreases
- $I_{off}$  increases
- Semiconducting properties *not* generally retained



# Etch Stop on Graphene: A comparative study

## Compare the blanket etching of SiN (on graphene) with Ar/SF<sub>6</sub> plasmas



Results show less damage (D/G ratio) to the graphene after e-beam plasma etch compared to ICP etching



## Electron Beam Generated Plasmas

- Unique control over the production of species and their transport to surface
- $n_e$  is high ( $10^{10}$ -  $10^{11} \text{ cm}^{-3}$ );  $T_e$  is very low ( $\approx 0.5 \text{ eV}$ )
- Large flux of very low energy (0 - 5 eV) ions
- Well-suited to advance unique processing applications
  - Ion energy-sensitive materials
  - Atomic Layer Etch (or Deposition)
  - Processing of very thin (~ nm) or atomically thin (2-D) materials



# Thank you

[scott.walton@nrl.navy.mil](mailto:scott.walton@nrl.navy.mil)

This work is supported by the Naval Research Laboratory Base Program



# Select Publication List

- M. S. Osofsky, S. C. Hernández, A. Nath, V. D. Wheeler, S.G. Walton, C. M. Krowne, and D. K. Gaskill, "Functionalized graphene as a model system for the two-dimensional metal-insulator transition," *Sci. Rep.* 6, 19939; doi: 10.1038/srep19939 (2016).
- G.M. Petrov, D.R. Boris, Tz. B. Petrova, and S.G. Walton, "One-dimensional Ar-SF<sub>6</sub> hydromodel at low-pressure in e-beam generated plasmas," *J. Vac. Sci. Technol. A* 34, 021302-12 (2016).
- A. V. Jagtiani, H. Miyazoe, J. Chang, D. B. Farmer, M. Engel, D. Neumayer, S.-J. Han, S. U. Engelmann, D.R. Boris, S.C. Hernández, E.H. Lock, S.G. Walton, E.A. Joseph, "Evaluation of plasma damage to atomic layer carbon materials," *J. Vac. Sci. Technol. A* 34, 01B103 (2016).
- Dominik Metzler, Florian Weilnboeck, Sandra C. Hernández, Scott G. Walton, Robert L. Bruce, Sebastian Engelmann Lourdes Salamanca-Riba, and Gottlieb S. Oehrlein, "Formation of nanometer-thick delaminated amorphous carbon layer by two-step plasma processing of methacrylate-based polymer," *J. Vac. Sci. Technol. B* 33, 051601 (2015).
- B.M. Foley, S.C. Hernández, J.C. Duda, J.T. Robinson, S.G. Walton, and P.E. Hopkins, "Modifying Surface Energy of Graphene via Plasma-Based Chemical Functionalization to Tune Thermal and Electrical Transport at Metal Interfaces," *Nano Lett.* 15, 4876 (2015).
- G. M. Petrov, D. R. Boris, E. H. Lock, Tz. B. Petrova, R. F. Fernsler and S. G. Walton "The influence of magnetic field on electron beam generated plasmas," *J. Phys. D: Appl. Phys.* 48, 275202-8 (2015).
- C.D. Cothran, D.R. Boris, C.S. Compton, E.M. Tejero, R.F. Fernsler, W.E. Amatucci, and S.G.Walton, "Continuous and pulsed electron beam production from an uninterrupted plasma cathode," *Surf. Coat. Technol.* 267, 111–116 (2015).
- D. R. Boris, R. F. Fernsler, and S. G. Walton, "Measuring the Density, Electron Temperature, and Electronegativity in Electron Beam Generated Plasmas Produced in Argon /SF<sub>6</sub> Mixtures," *Plasma Sources Sci. Tech.* 24, 025032 (2015).
- S. G. Walton, D. R. Boris, S. C. Hernández, E. H. Lock, Tz. B. Petrova, G. M. Petrov, and R. F. Fernsler, "Electron Beam Generated Plasmas for Ultra Low T<sub>e</sub> Processing," *ECS J. Solid State Sci. Technol.* 4(6): N5033-N5040 (2015).
- S. U. Engelmann, R. L. Bruce, M. Nakamura, D. Metzler, S.G. Walton, and E. A. Joseph, "Challenges of Tailoring Surface Chemistry and Plasma/Surface Interactions to Advance Atomic Layer Etching," *ECS J. Solid State Sci. Technol.* 4(6), N5054-N5060 (2015).
- Jonathan R. Felts, Andrew J. Oyer, Sandra C. Hernández, Keith E. Whitener Jr, Jeremy T. Robinson, Scott G. Walton and Paul E. Sheehan, "Direct mechanochemical cleavage of functional groups from graphene," *Nature Commun.* 6:6467 DOI: 10.1038/ncomms7467 (2015).
- E.H. Lock, D.M. Delongchamp, S.W. Schmucker, B. Simpkins, M. Laskoski, S.P. Mulvaney, D.R. Hines, M. Baraket, S.C. Hernandez, J.T. Robinson, P.E. Sheehan, C. Jaye, D.A. Fisher, S.G. Walton, "Dry graphene transfer to polystyrene and ultra-high molecular weight polyethylene – Detailed chemical, structural, morphological, and electrical characterization," *Carbon* 86, 288 (2015).
- E.H. Lock, R.F. Fernsler, S. Slinker, I. Singer, S.G. Walton, "Global model for plasmas generated by electron beams in low pressure nitrogen," *J. Phys. D: Appl. Phys.* 47, 425206 (2014).
- S.C. Hernández, V.D. Wheeler, M.S. Osofsky, V. K. Nagareddy, E.H. Lock, L.O. Nyakiti, R.L. Myers-Ward, A.B. Horsfall, C.R. Eddy Jr., D. K. Gaskill, S.G. Walton, "Plasma-Based Chemical Modification of Epitaxial Graphene with Oxygen Functionalities," *Surf. Coat. Tech.* 241, 8 (2014).



# Select Publication List

---

- D. R. Boris, R.F. Fernsler, and S. G. Walton “The spatial profile of density in electron beam generated plasmas,” Surf. Coat. Tech. 241, 13 (2014).
- D. R. Boris, G. M. Petrov, E. H. Lock, Tz. B. Petrova, R.F. Fernsler, and S. G. Walton “Controlling the electron energy distribution function of electron beam generated plasmas with molecular gas concentration: part I. experimental results,” Plasma Sources Sci. Tech. 22, 065004-6 (2013)
- G. M. Petrov, D. R. Boris, E. H. Lock, Tz. B. Petrova, R.F. Fernsler, and S. G. Walton “Controlling the electron energy distribution function of electron beam generated plasmas with molecular gas concentration: part II. Numerical modeling,” Plasma Sources Sci. Tech. 22, 065005 -8 (2013).
- S. C. Hernández, C. J. C. Bennett, C. E. Junkermeier, S. D. Tsoi, F. J. Bezares, R. Stine, J. T. Robinson, E. H. Lock, D. R. Boris, B. D. Pate, J. D. Caldwell, T. L. Reinecke, P. E. Sheehan and S. G. Walton, “Chemical Gradients on Graphene to Drive Droplet Motion,” ACS Nano, 7, 6, 4746-4755 (2013)
- S. C. Hernández, F. J. Bezares, J. T. Robinson, J. D. Caldwell, S. G. Walton, “Controlling the local chemical reactivity of graphene through spatial functionalization,” Carbon 60, 84-93 (2013).
- V. K. Nagareddy, H. K. Chan, Sandra C. Hernández, Virginia D. Wheeler, Luke O. Nyakiti, Rachel L. Myers-Ward, Charles R. Eddy, Jr, Jonathan P. Goss, Nicholas G. Wright, Scott G. Walton, D. Kurt Gaskill, and Alton B. Horsfall “Improved Chemical Detection and Ultra-Fast Recovery Using Oxygen Functionalized Epitaxial Graphene Sensors,” IEEE Sensors Journal 13(8), 2810-2817 (2013).
- Mira Baraket, Rory Stine, Woo K. Lee, Jeremy T. Robinson, Cy R. Tamanaha, Paul E. Sheehan and Scott G. Walton, “Aminated graphene for DNA attachment produced via plasma functionalization,” App. Phys. Lett. 100, 233123 (2012).
- Patrick E. Hopkins, Mira Baraket, Edward V. Barnat, Thomas E. Beechem, Sean P. Kearney, John C. Duda, Jeremy T. Robinson, and Scott G. Walton, “Manipulating Thermal Conductance at Metal–Graphene Contacts via Chemical Functionalization,” Nano Lett. 12, 590 (2012).
- S. G. Walton, C. D. Cothran, and W. E. Amatucci, “Electron Beam Propagation in Magnetic Fields,” IEEE Trans. of Plasma Sci 39(11), 2574 (2011).
- D.R. Boris, S.G. Walton, and R.F. Fernsler, “The LC Resonance Probe for Determining Local Plasma Density,” Plasma Sources Sci. Technol. 20, 025003-7 (2011).
- S.H. North, E.H. Lock, C.J. Cooper, J.B. Franek, C.R. Taitt, and S.G. Walton, “Plasma-based surface modification of polystyrene microtitre plates for covalent immobilization of biomolecules,” ACS Applied Materials & Interfaces, 2(10), 2884 (2010).
- M. Baraket, S.G. Walton, E.H. Lock, J.T. Robinson, F.K. Perkins, “Electron beam generated plasmas for the functionalization of graphene,” Appl. Phys. Lett. 96, 231501 (2010).
- E.H. Lock, D.Y. Petrovykh, P. Mack, T. Carney, R.G. White, S.G. Walton and R. F. Fernsler, “Surface Composition, Chemistry, and Structure of Polystyrene Modified by Electron Beam Generated Plasma,” Langmuir 26(11) 8857 (2010).

