Electron beam generated plasmas

Ultra cold sources for atomic layer processing

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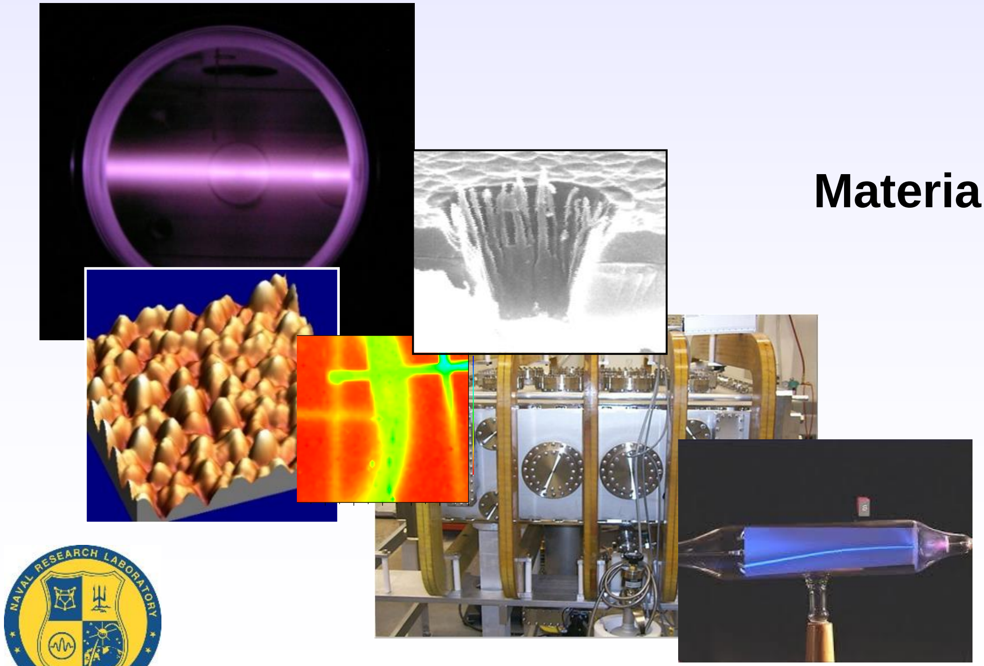
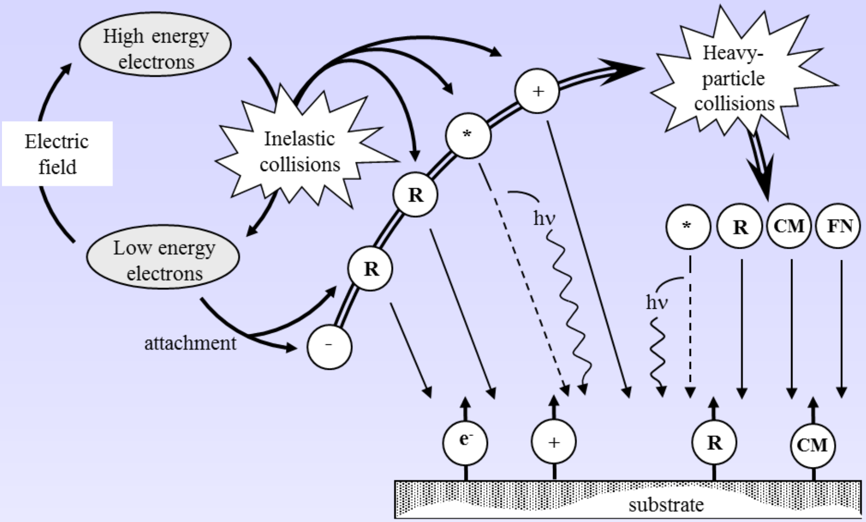
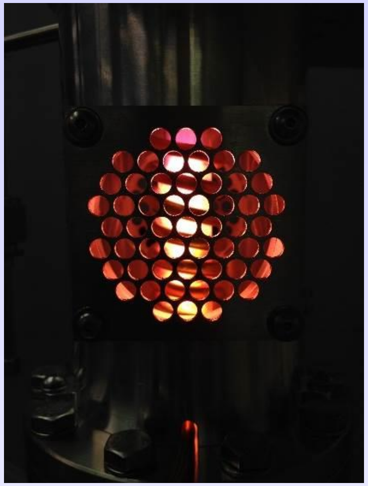
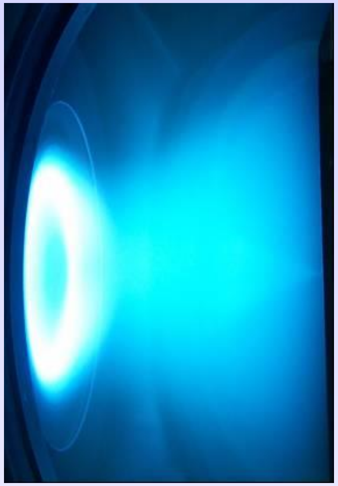


2017 NASA Contamination, Coatings, Materials, and Planetary Protection Workshop
July 18-20, 2017
NASA Goddard Space Flight Center
Greenbelt, MD

Low Temperature Plasmas for Processing







- A weekly ionized but collectively neutral gas comprised of
    - Electrons and ions (positive and sometimes negative)
    - Excited neutrals (some of which relax via photon emission)
    - Reactive radicals (or molecular fragments)
- The non-equilibrium nature of low temperature plasmas provides a very unique environment capable driving physical and chemical changes in exposed materials
    - Etching
    - Deposition
    - Chemical modification

Adapted 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).

The unique environment of plasmas

- Non-equilibrium: $T_e > T_{gas} \approx T_{ion}$
- $T_e \approx$ 1-10 eV
- Cold gas: T_g ~ 300 ºK (Room Temp)
- 1 eV ≈ 10,000 ºK

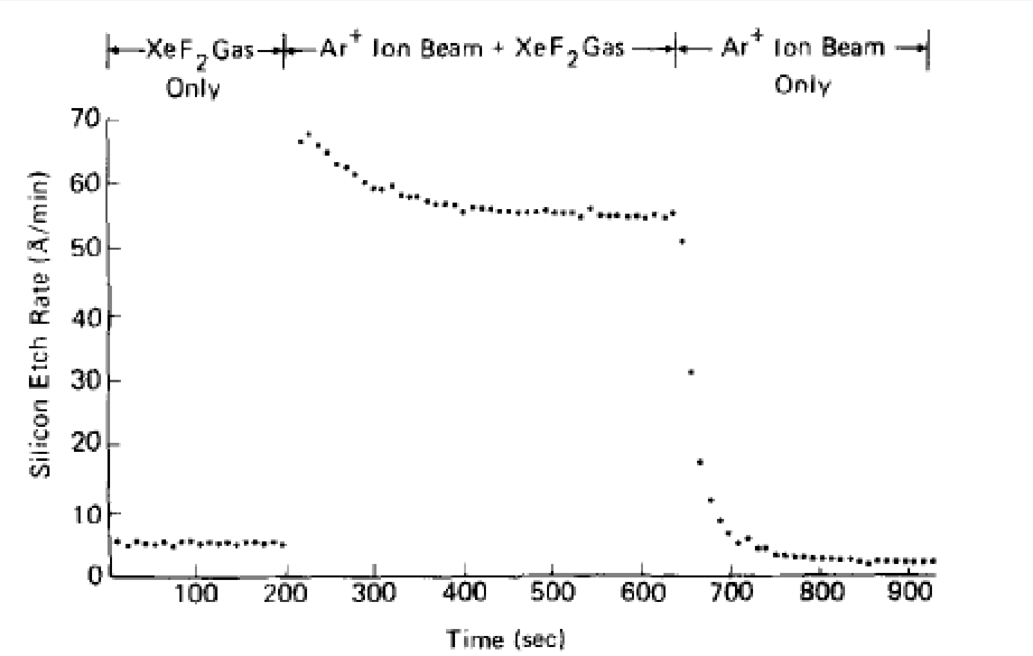
Gas-phase generation of chemically active species

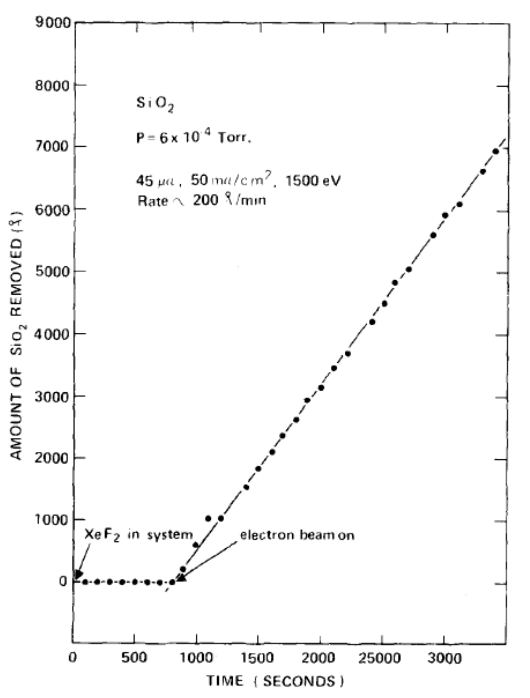
and

Delivery of energy

yields

A synergistic effect at the surface





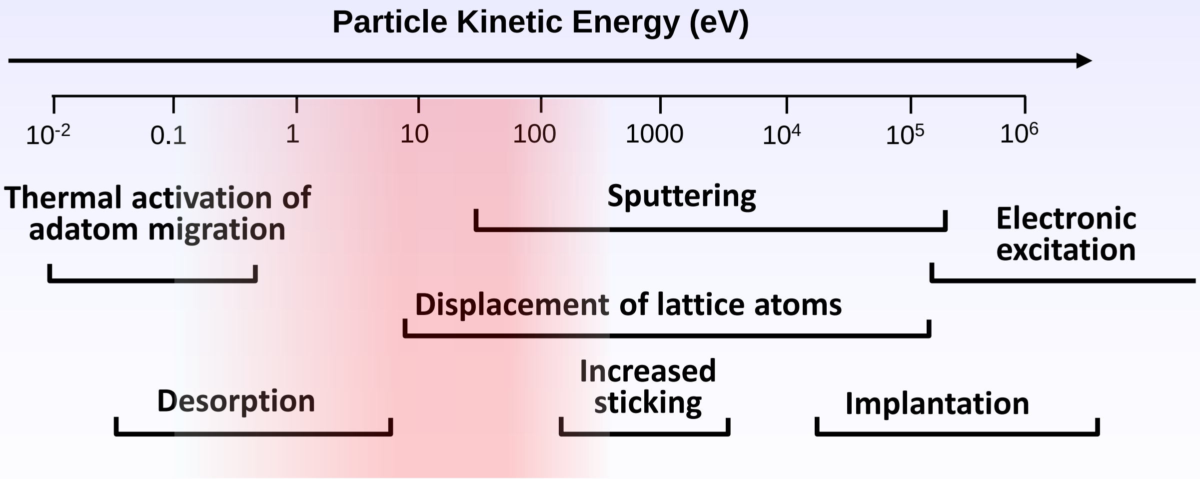
J.W. Coburn and H.F. Winters, Journal of Applied Physics 50, 3189 (1979).

Plasma-Surface Interactions

Particle-driven surface processes and reactions

- Ions, electrons, fast neutrals, and photons transfer energy to the surface
- Energies are set by the intrinsic plasma properties
- Ion energies can be elevated by biasing

Particle-induced surface processes*



Particle Kinetic Energy (eV)

10^{-2} 0.1 1 10 100 1000 10^{4} 10^{5} 10^{6}

Thermal activation of adatom migration

Sputtering

Electronic excitation

Displacement of lattice atoms

Desorption

Increased sticking

Implantation

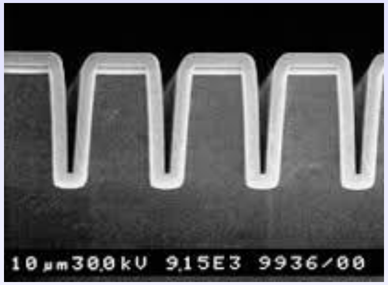
* Adapted From: Grill, A., *Cold plasma in materials fabrication: From fundamentals to applications*, Piscataway: IEEE Press, 1994.

Issues / Motivation

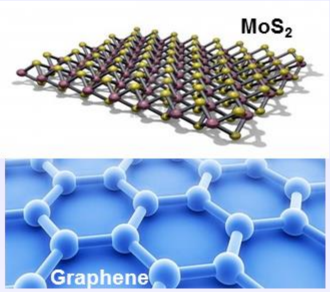
Challenge:

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

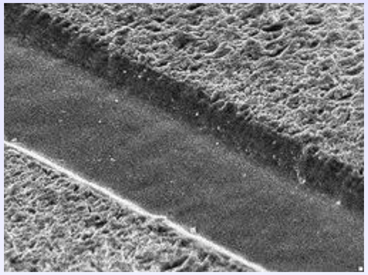
Atomic layer etching/deposition



2-D material processing



Polymer processing



Solutions (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. Kamarthy, R.A. Gottscho, Solid State Technology, Volume 55, Issue 3, (2012)

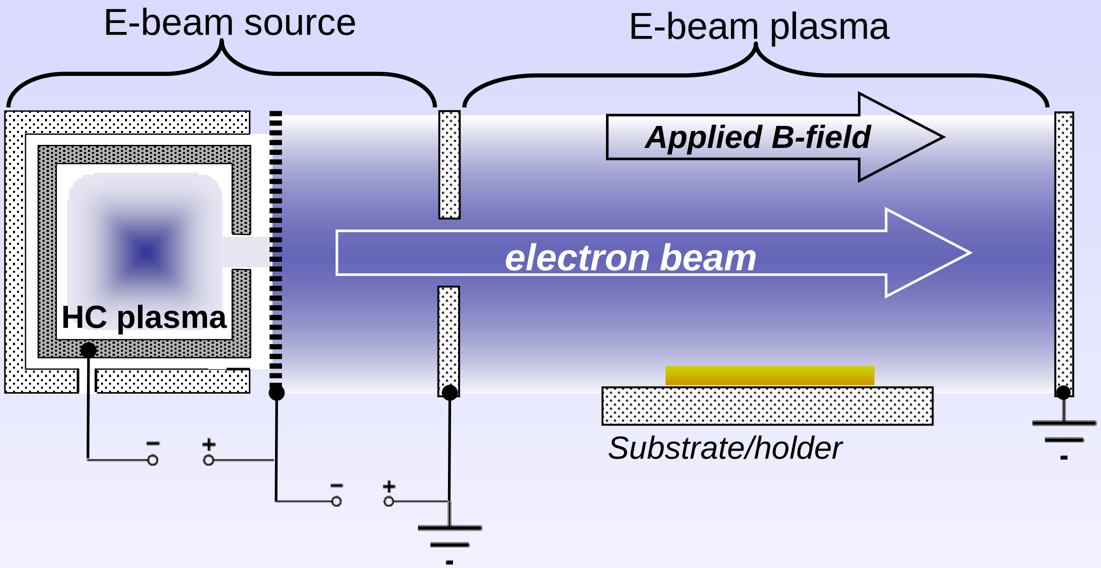
G. S. Oehrlein, D. Metzler, and C. Lia, ECS J. Solid State Sci. Technol. 4(6),) N5041-N5053 (2015)

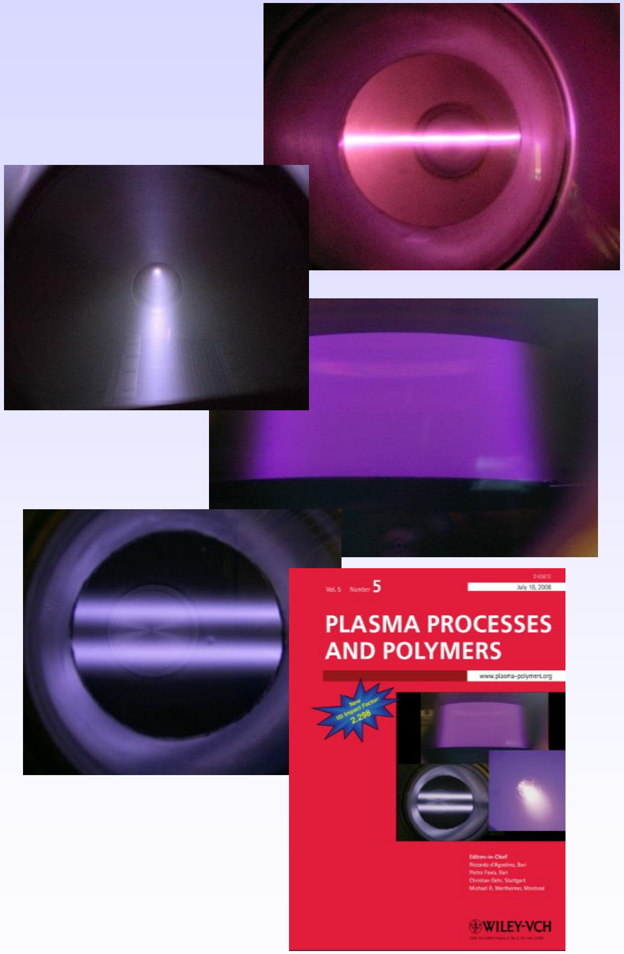
Electron Beam Generated Plasmas

(Ultra low T_e Plasmas to address the ion energy challenge)

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)

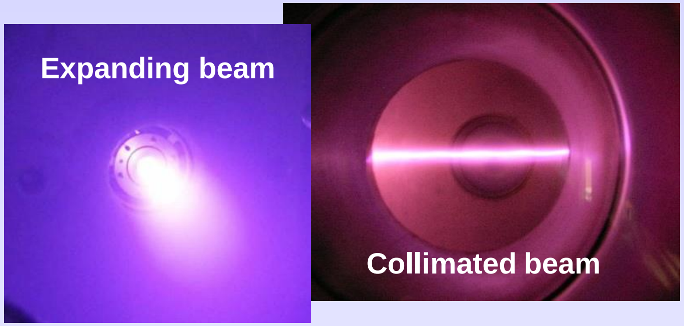
S. G. Walton, et al., ECS Journal of Solid State Science and Technology, 4(6) N5033-N5040 (2015)

Platforms for processing

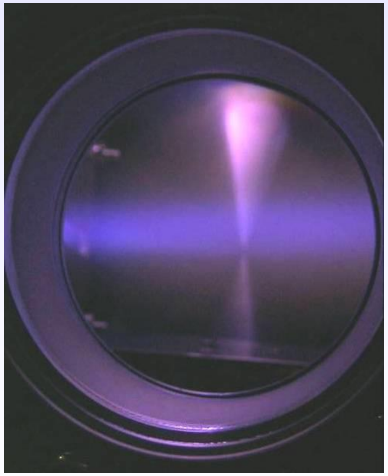
Source is decoupled from reactor geometry

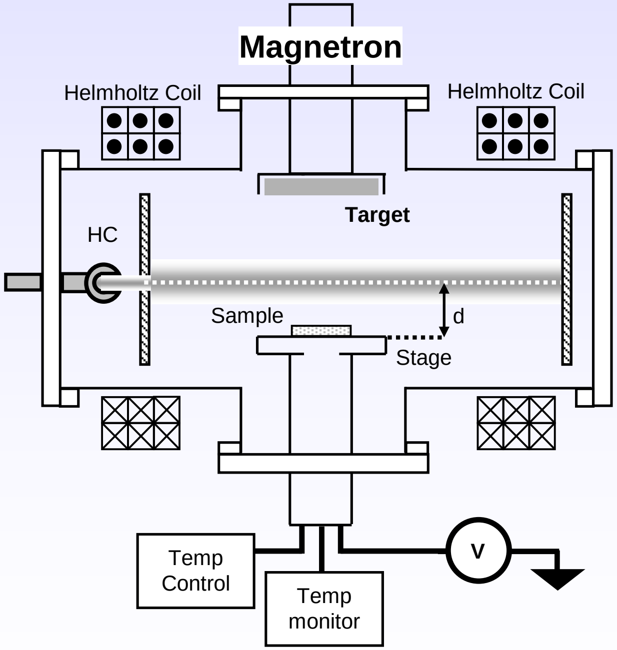
- Flexible design
- Unique geometries

Magnetized or not

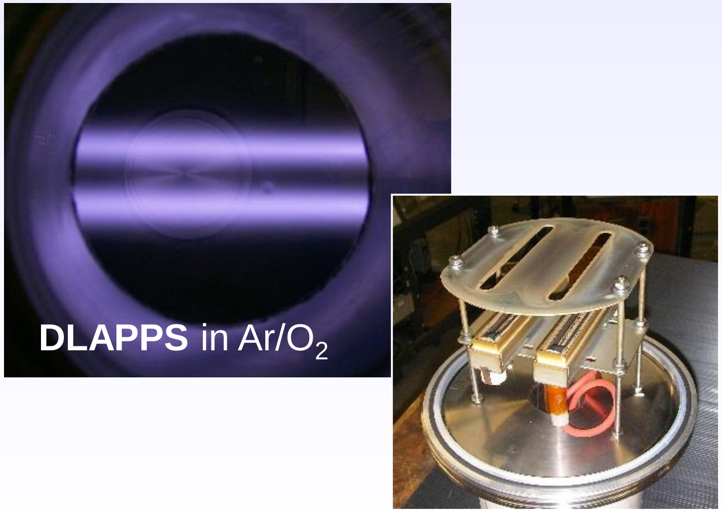


PEPVD*





Roll to Roll**

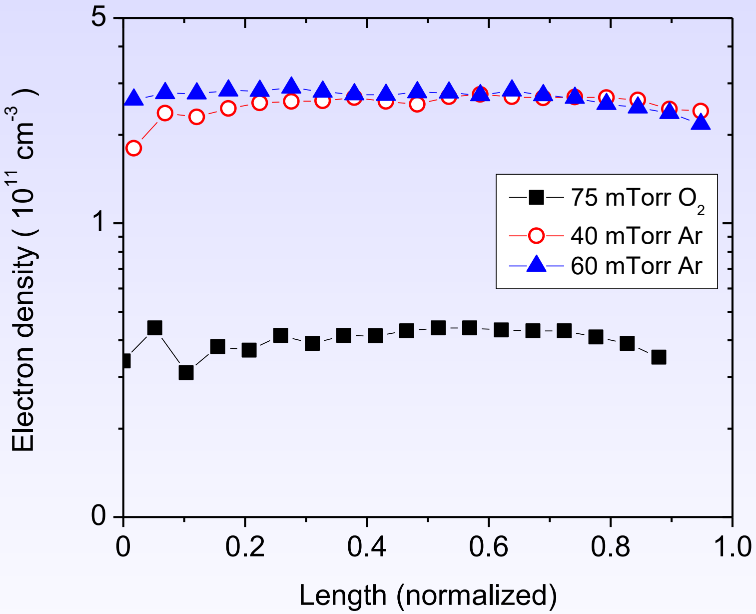


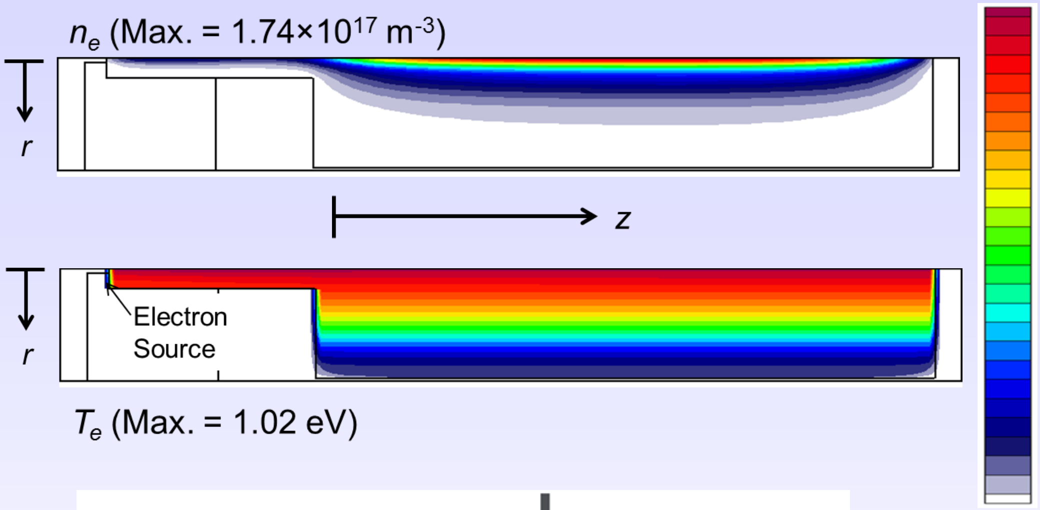
* C. Muratore, et al., J. Vac. Sci. Technol. A, 24(1), 25 (2006)

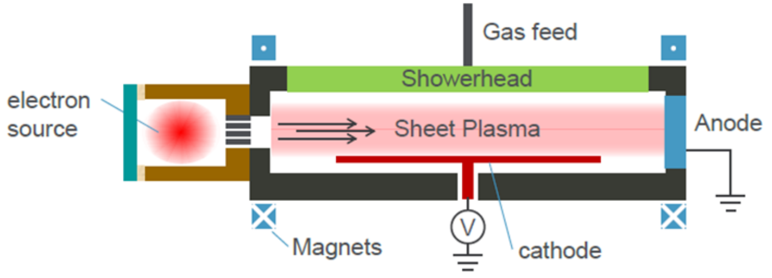
** S.G Walton, et al., Plasma Proc. and Poly. 5, 453 (2008)

Unique Features of electron beam generated plasmas

- Source is scalable to large areas without losses in uniformity



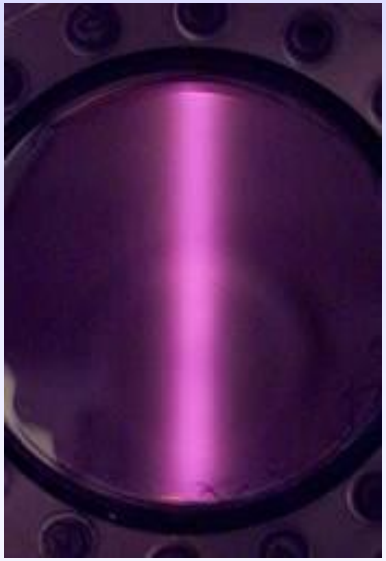


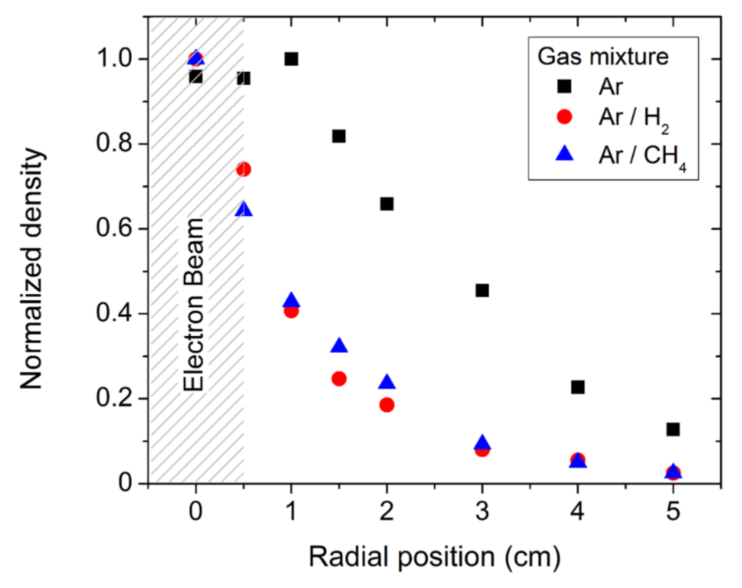


S. Rauf et al., Plasma Source Sci. Technol. 26 065006-12 (2017).

Unique Features of Electron Beam-Generated Plasmas

Plasma *generation* is confined to the electron beam volume





- Noble gas plasmas are diffusion dominated
- Molecular gas plasmas are chemistry dominated (e.g. $e + N_2^+ \rightarrow 2N$)

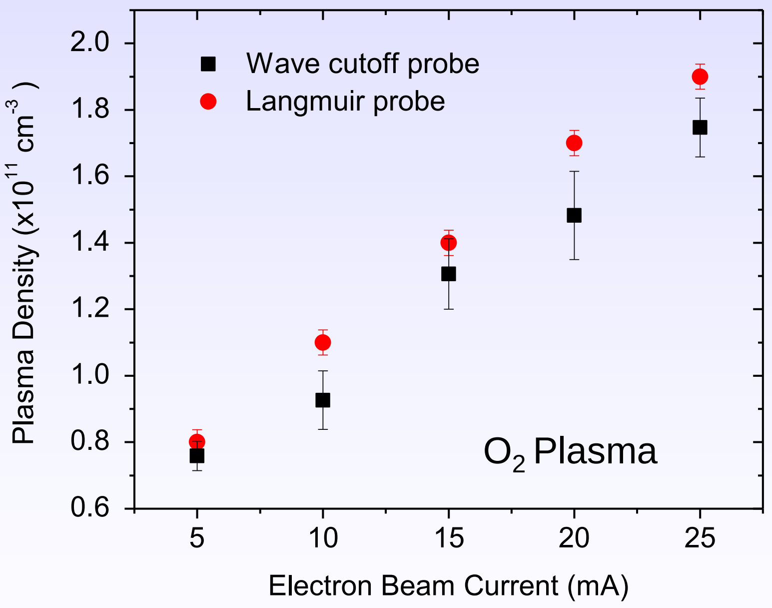
E.H. Lock, et al., Plasma Sources Sci. Technol. 17, 025009 (2008).

D. R. Boris, et al., Surf. Coat. Tech. 241, 13 (2014).

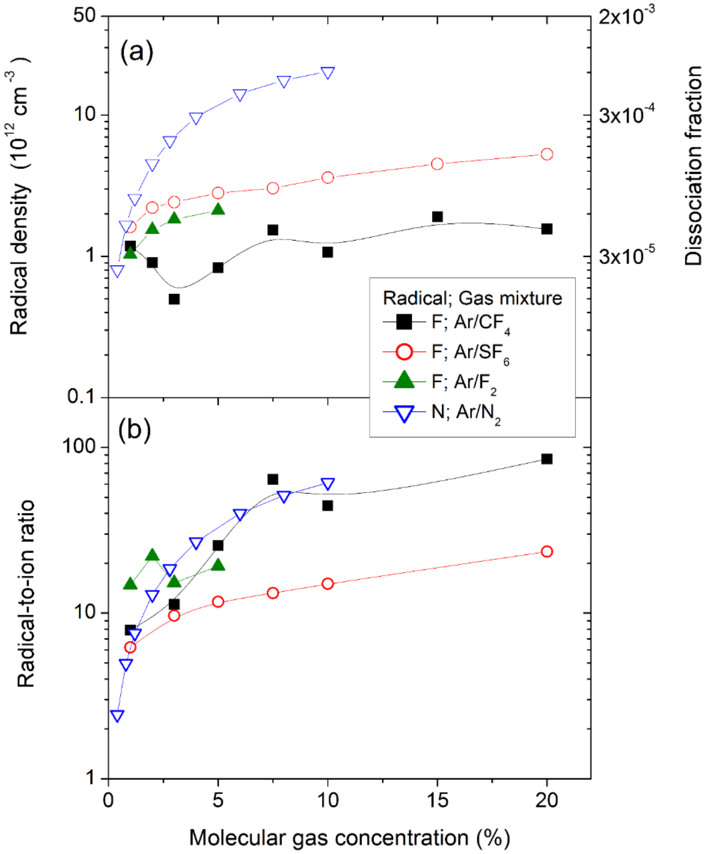
Unique Features of electron beam generated plasmas

Species production is driven primarily by the electron beam and proportional to the relative concentrations of the working gases

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



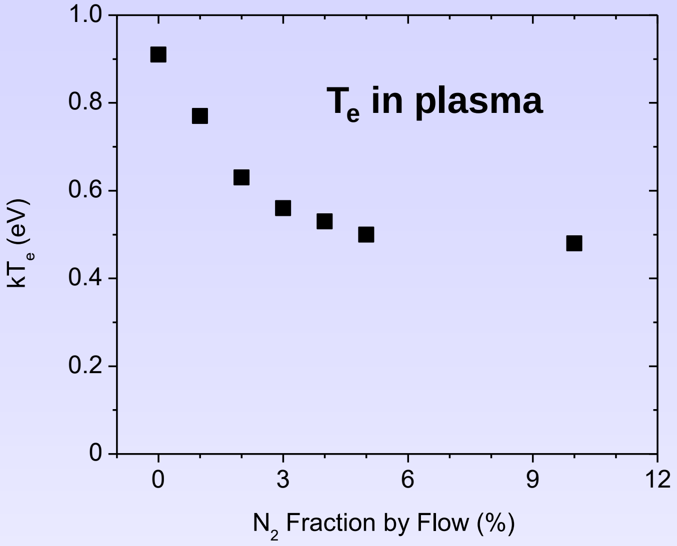
$$S_i = k\, I_{beam}\, P_i\, \sigma_i(E)$$



E.H. Lock, et al., Plasma Sources Sci. Technol. 17, 025009 (2008); D.R. Boris, et al., Plasma Sources Sci. Technol. 20, 025003-7 (2011); D. R. Boris et al., J. Vac. Sci. Technol. J. Vac. Sci. Technol. A 35, 01A104 (2017).

Unique Features of electron beam generated plasmas

Very low T_e provides very low ion energy



Ion Energies at surfaces

Plasma Potential:

$$V_p = T_e \ln(M_i/2\pi m_e)1/2$$

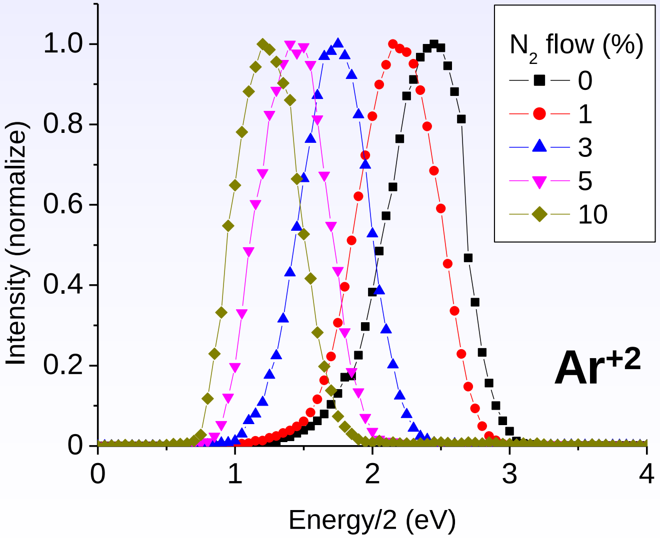
Ion Energy:

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

For a grounded surface, the rule of thumb is:

$E_{ion} \approx (4 - 5) \cdot T_e$

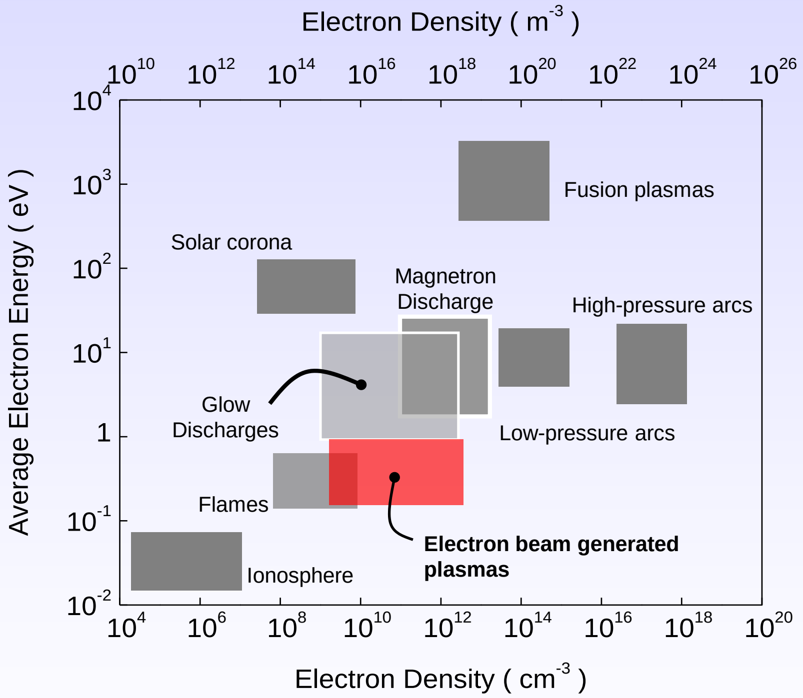
Ion energy at surface



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 vs. beam driven plasmas

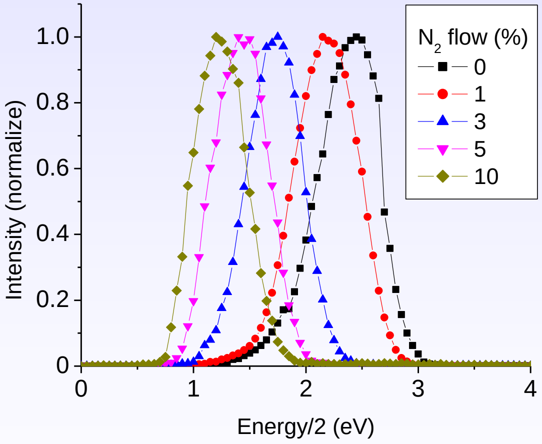
Type	T_e (eV)	n_e (cm^{-3})	KE_{ion} (eV)
ICP	4	10^{11}	20
ECR	4	10^{11}	20
DBD	2 - 10	10^{13}	10 - 100
RIE	8	10^{10}	40
DC Diode	2 - 10	10^{10}	10 - 100
CCP	1 - 5	10^{9} -10^{10}	5 - 25
Electron Beam	**0.3 - 1**	**10^{9} -10^{12}**	**1.5 - 5**

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).

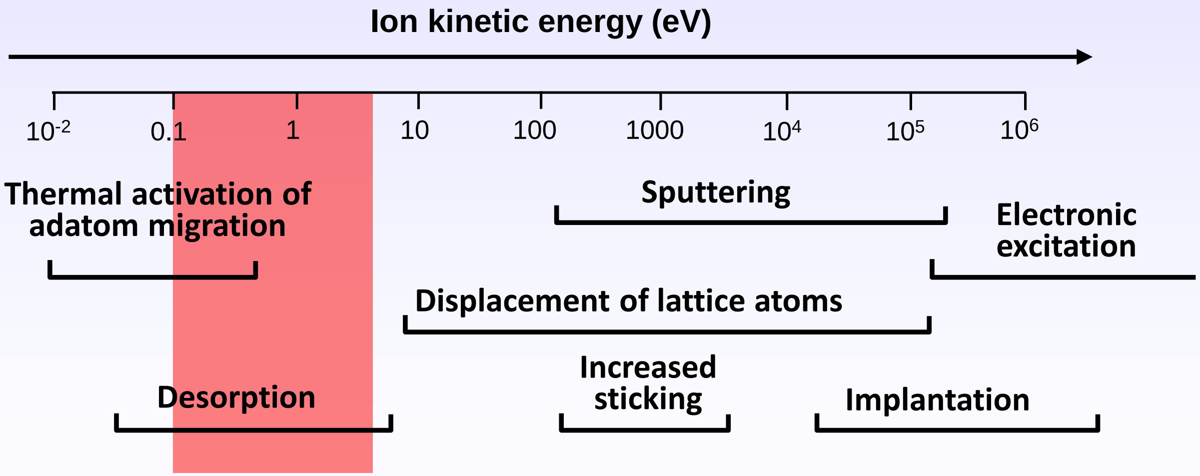
Processing implications

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} cm^{-3}); T_e is very low (≈ 0.5 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



Ion-induced surface processes*



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

Target Processing Applications

Chemical Modification of Ion Energy Sensitive Materials

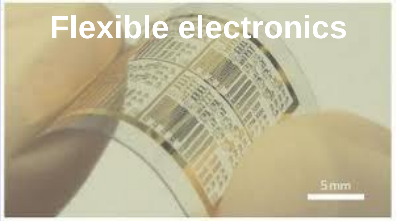
- Chemical modification without physical changes (e.g. surface roughening)
- Polymers or other “soft” materials
- *Sensors and biomaterials applications*

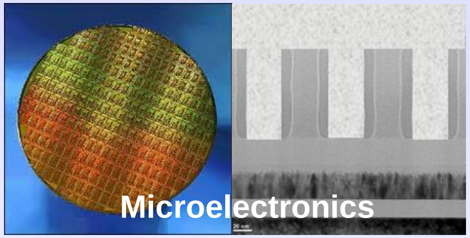
Atomic Layer Modification

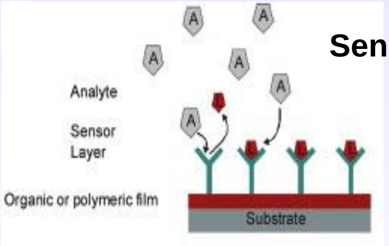
- Graphene Oxide Reduction – *reduction to graphene without damage*
- Graphene (or other 2-D materials) functionalization - *etching is not an option*
- *Sensors and electronic applications*

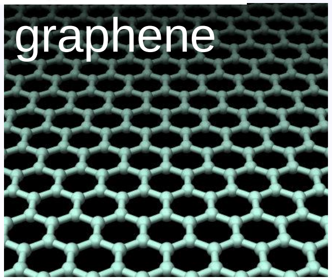
Atomic Layer Etching (and cleaning)

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



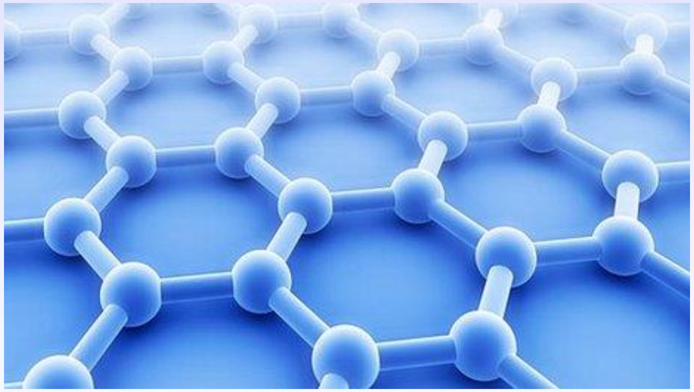






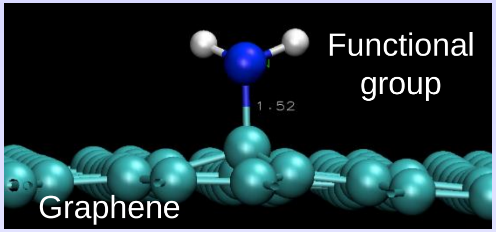
Graphene Processing

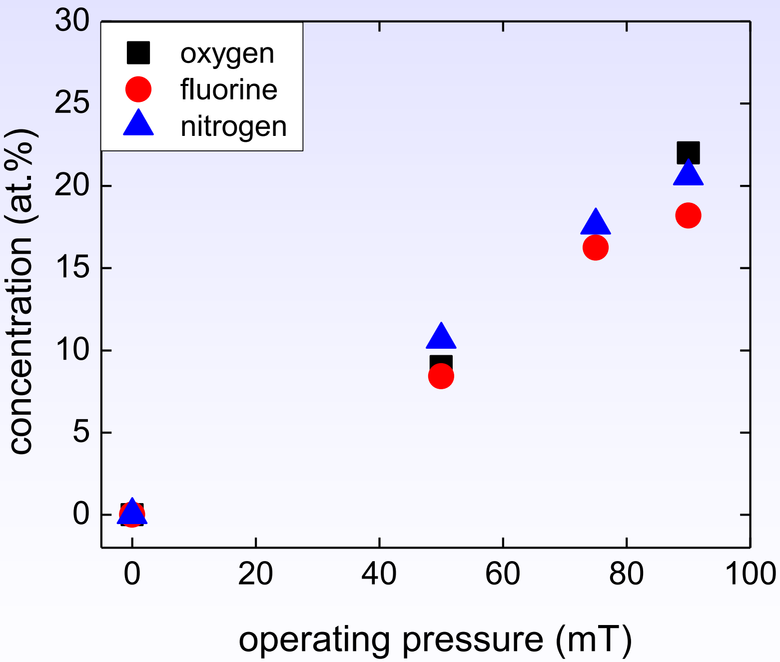
(The advantage of the low ion energies)



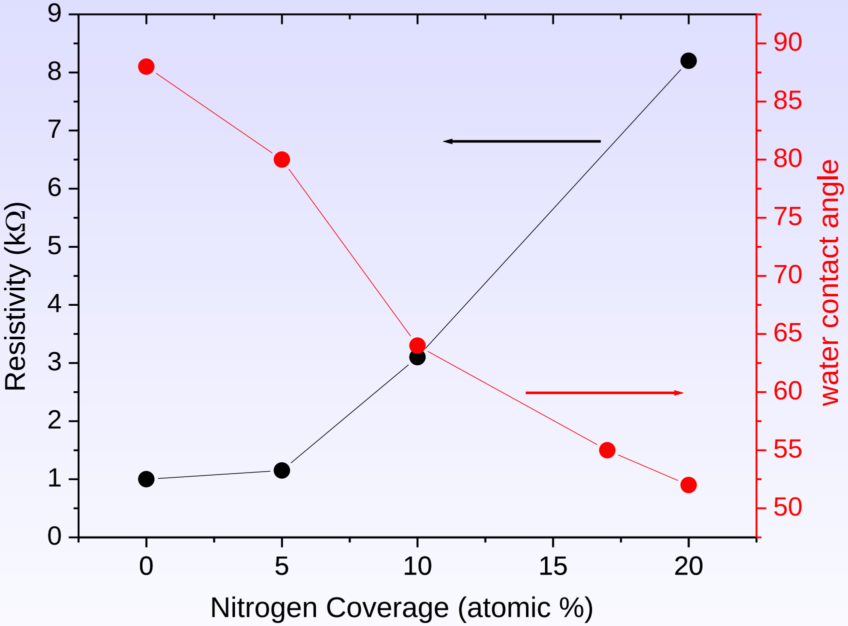
Functionalization of Graphene to Control Material Properties

The addition of functional groups will alter the conductivity and reactivity of graphene





Sheet resistance and reactivity

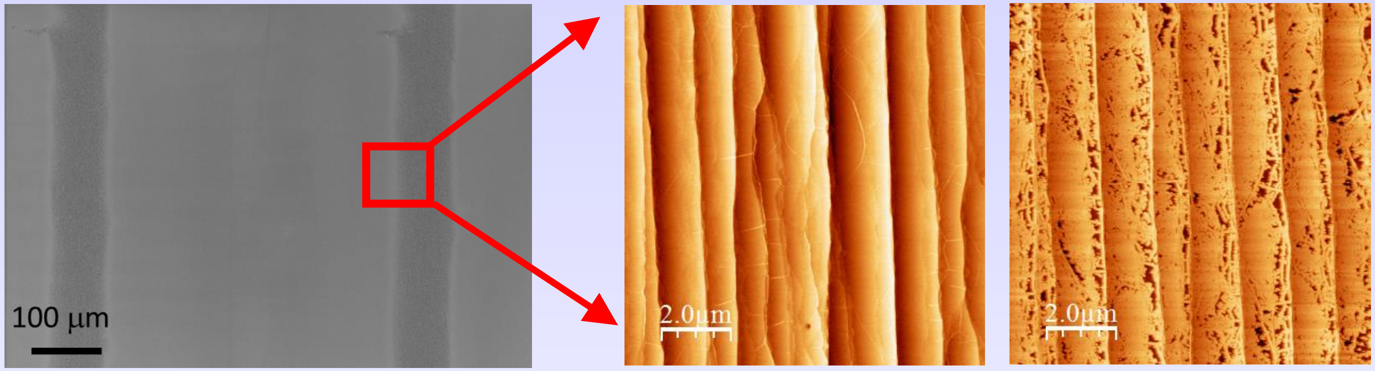


M. Baraket, et al., Appl. Phys. Lett. 96 231501 (2010); S.C. Hernández et al., Surf. Coat. Tech. 241, 8 (2014)

S.G. Walton, et al., J. Phys. D: Appl. Phys. 50 (2017)

Enhanced atomic layer deposition (ALD) on graphene

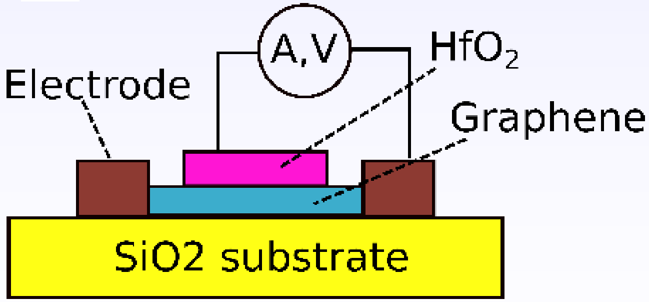
ALD of Al_2O_3 on fluorinated epitaxial graphene

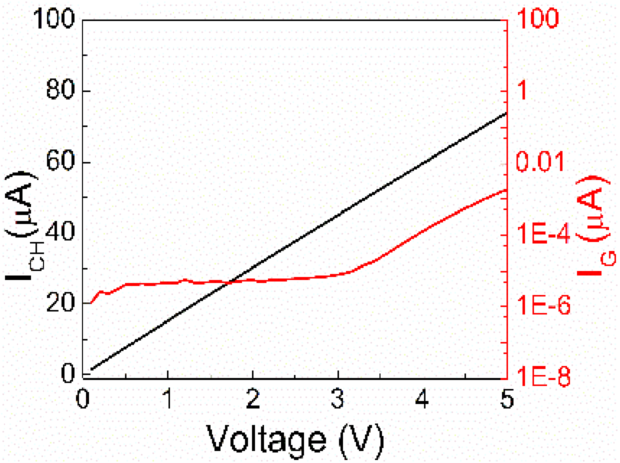


F-functionalized un-functionalized

- 20nm of Al_2O_3
- Conformal oxide layer only on the functionalized regions

ALD of HfO_2 on fluorinated CVD graphene*

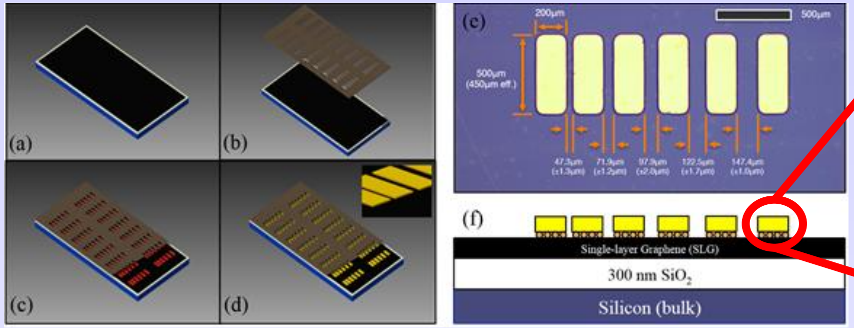


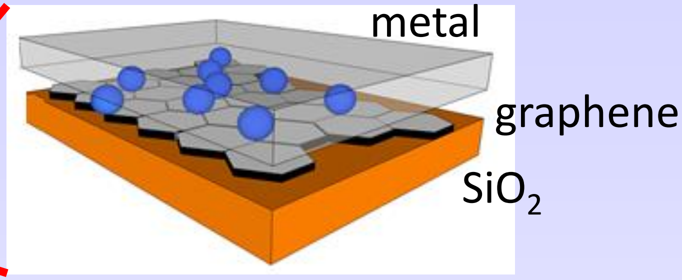


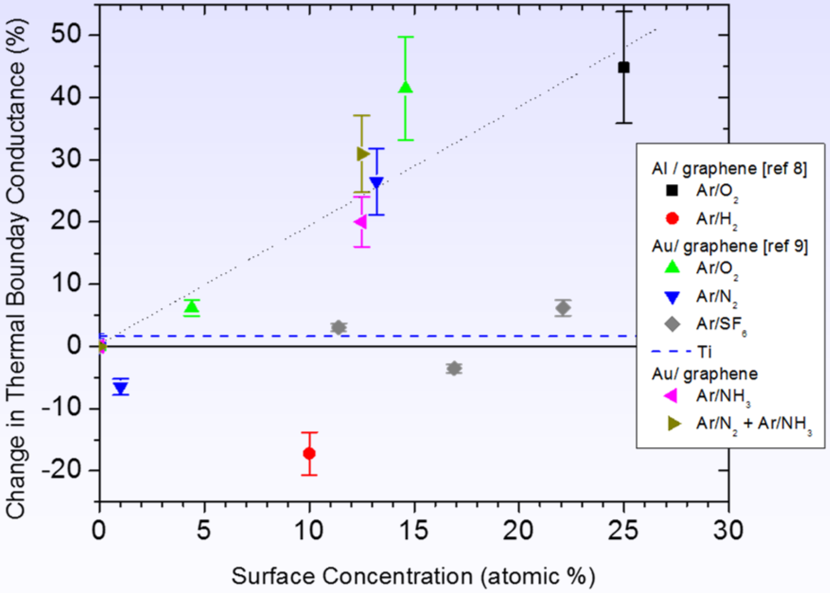
Large difference between source-drain current (I_{CH}) and source-gate current (I_G) indicate successful isolation of graphene

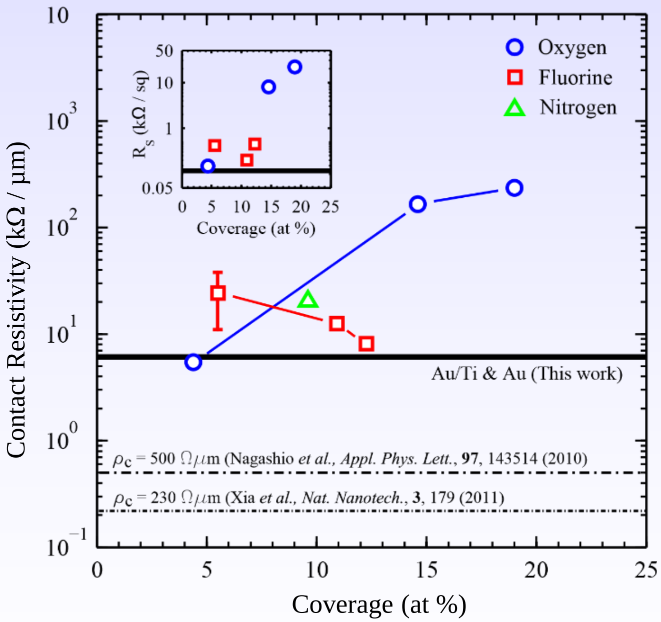
* In collaboration with IBM: A. V. Jagtiani, et al, J. Vac. Sci. Technol. A 34, 01B103 (2016)

Functionalized Graphene: Controlling the properties at contacts









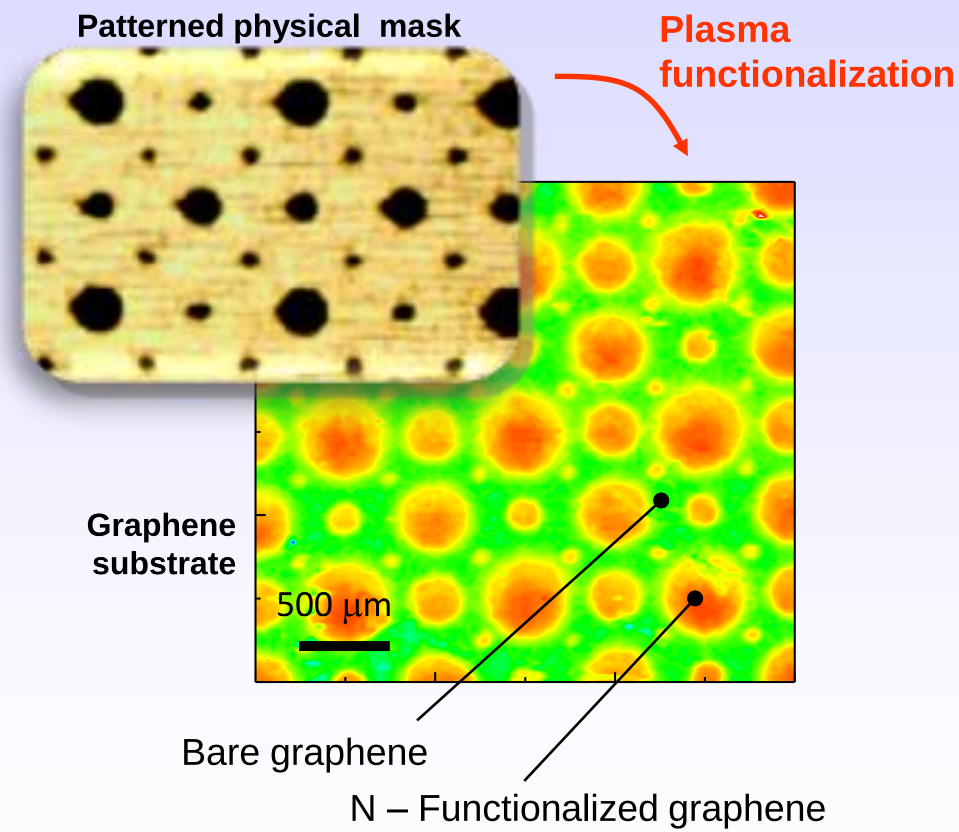
In collaboration with Prof. Patrick Hopkins (UVA)

P.E. Hopkins et al., Nano Lett. 12, 590 (2012); B. M. Foley et al., Nano Lett. 15, 4876 (2015); S.G. Walton et al., Surf. Coat. Technol. 314, 148 (2017).

Chemical Patterning of Graphene

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

physical masking technique + plasma functionalization



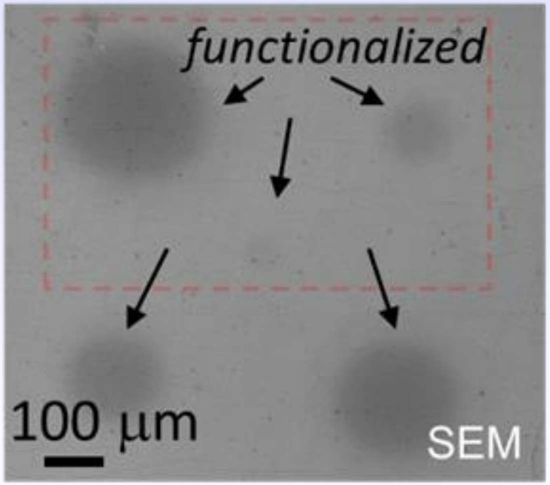
Patterned physical mask

Plasma functionalization

Graphene substrate

Bare graphene

N – Functionalized graphene

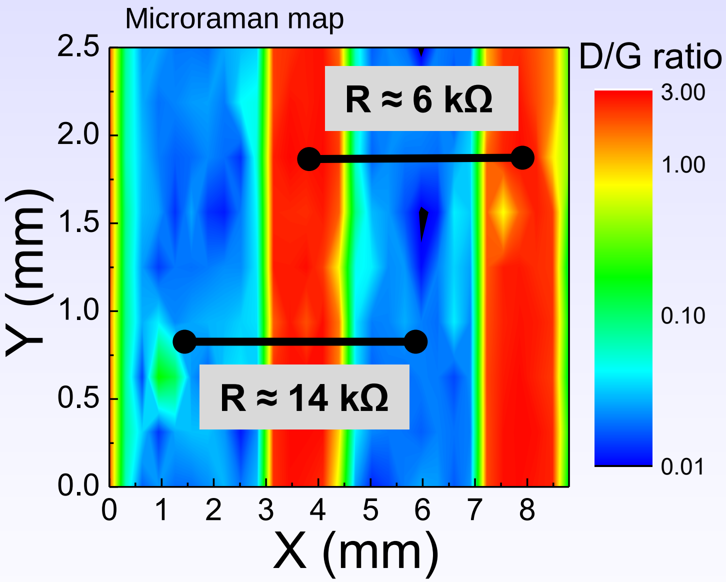


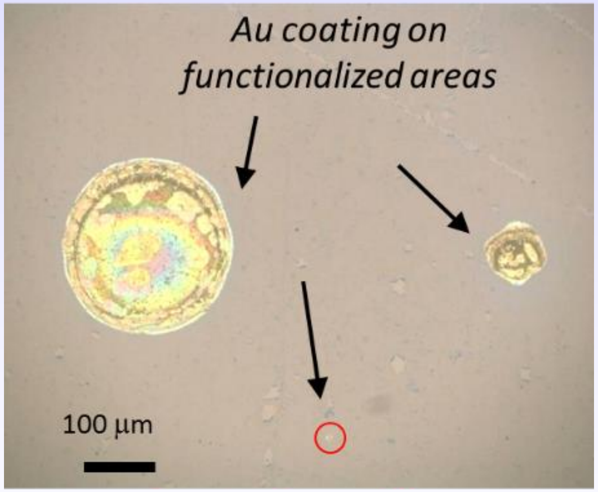
S. C. Hernández et al., Carbon 60, 84 (2013)

Chemical Patterning of Graphene

Local control over conductivity

Local control over reactivity





electrodeposition

S. C. Hernández et al., Carbon 60, 84 (2013)

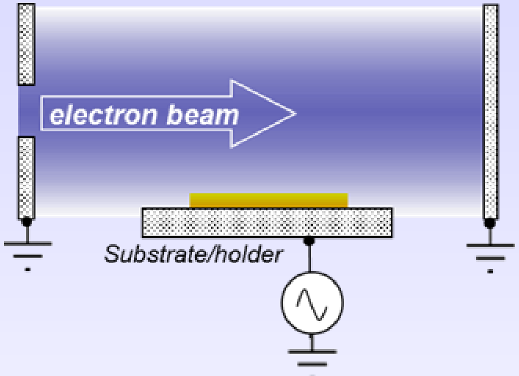
“Atomic Layer Etch”

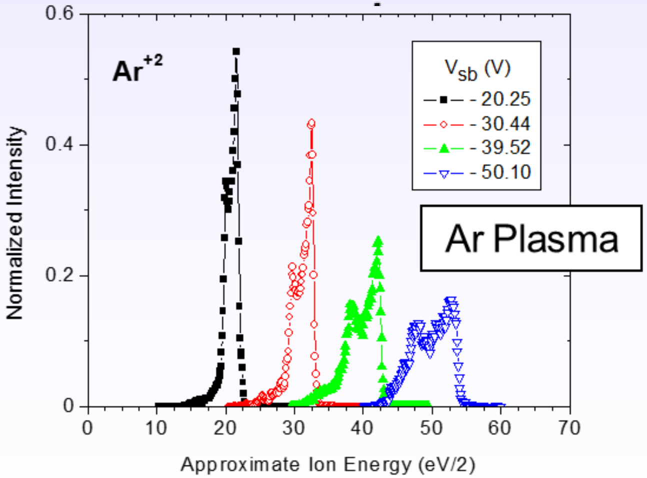
(The advantage of the broad ion energy window)

SiN Etch

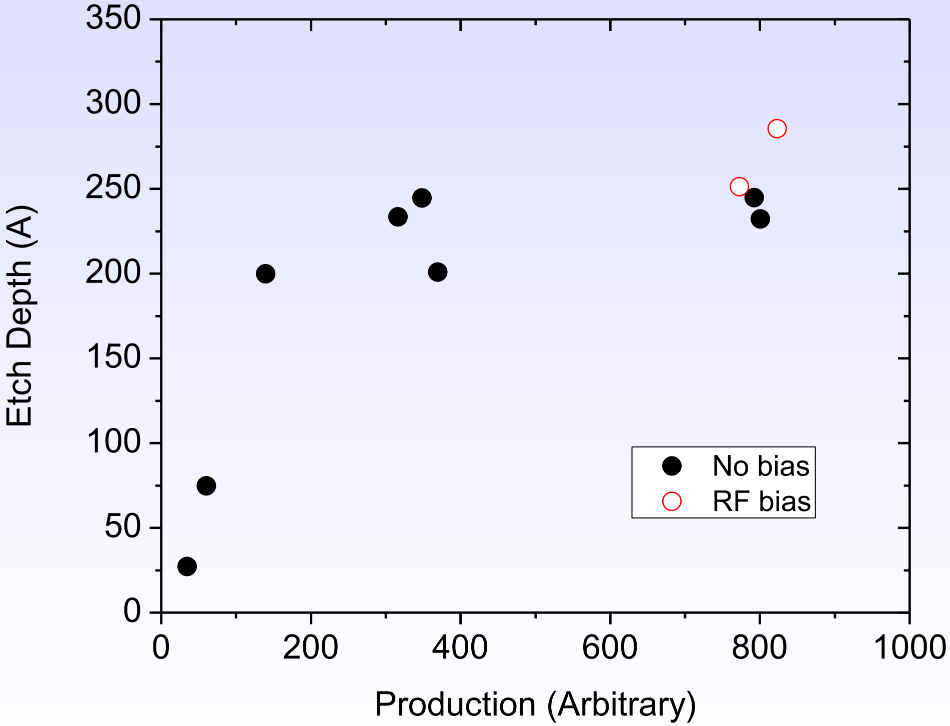
Etching is carried out in mixtures of Argon and SF_6 (5-20%)

Ion energy control with RF biasing*





Several “knobs” are available**
(SF_6 flow, RF bias, Time …)



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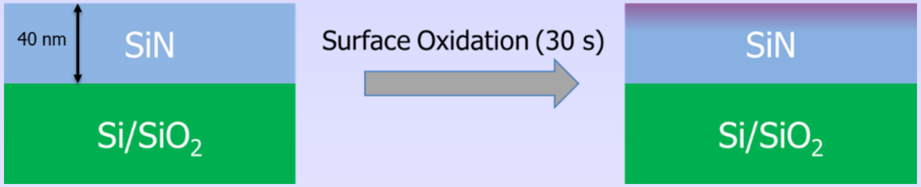
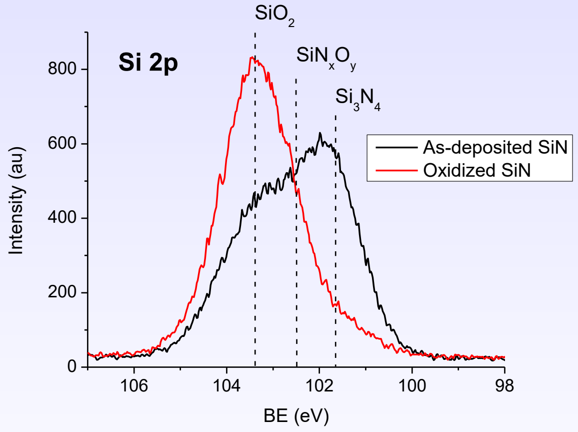
* S. G. Walton, et al., ECS Journal of Solid State Science and Technology, 4(6) N5033-N5040 (2015)

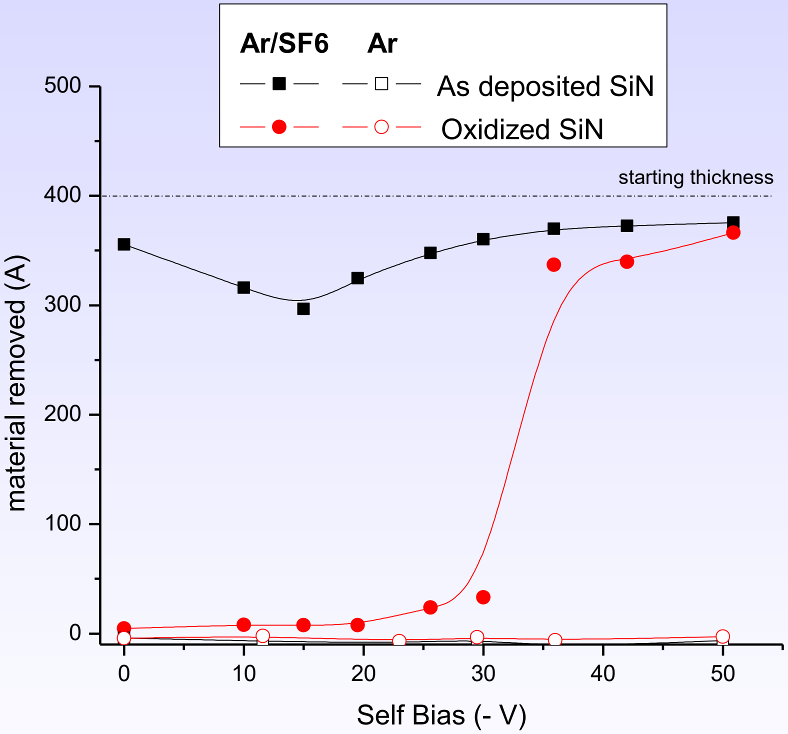
** S. G. Walton, et al., Microelectronic Engineering 168, 89-96 (2017)

SiN Etch

Selectivity at low energies: SiN vs oxidized SiN



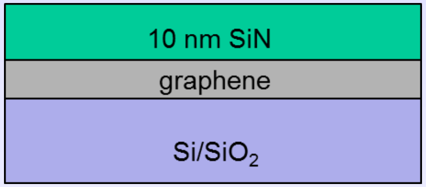


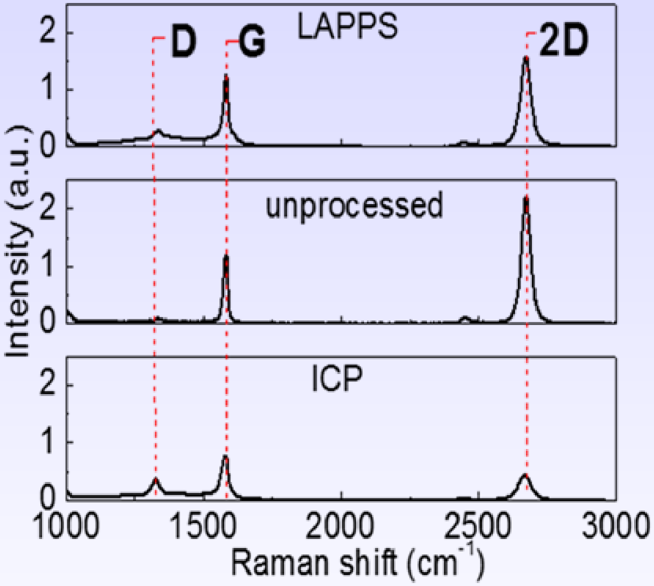


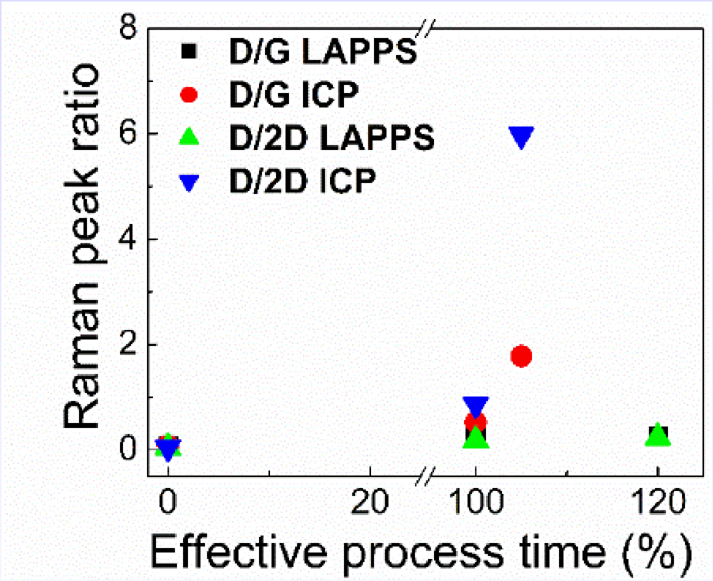
- Complete SiN removal for all conditions
- Sharp threshold for oxidized SiN etch
- “Infinite” selectivity below threshold

SiN Etch on Graphene

Selectivity at the monolayer scale





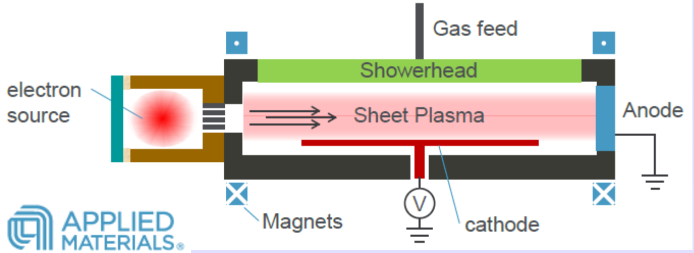


Results show less damage (D/G ratio) to the graphene after e-beam plasma etch compared to ICP etching

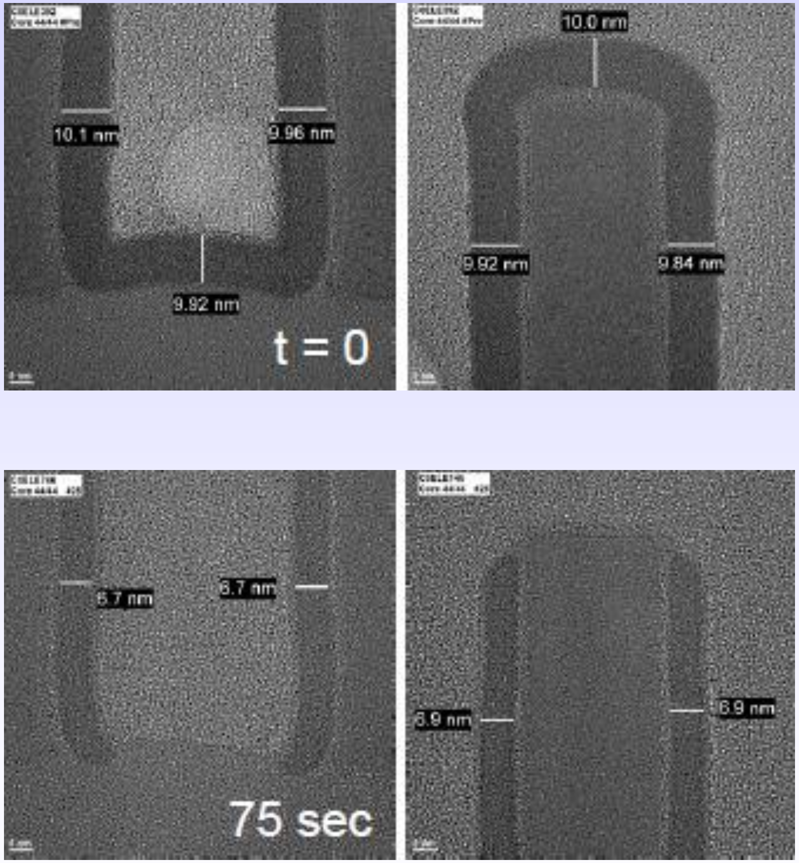
A. V. Jagtiani, et al,J. Vac. Sci. Technol. A 34, 01B103 (2016).

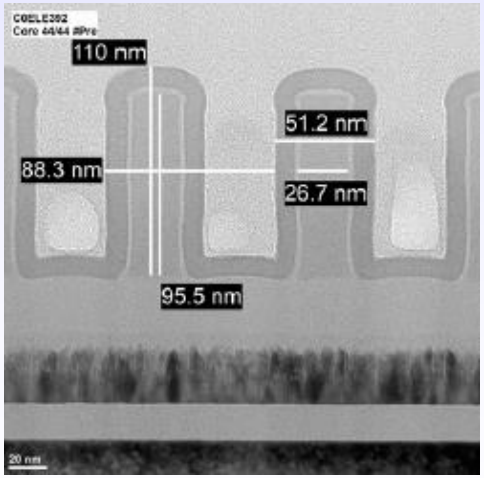
Feature etching

AMAT Etch Tool



Selective etch at top and bottom of trenches





Operating Parameters
Beam Energy: 1.5 – 2.5 keV
Beam Current: 120 – 180 mA
Pressure: 5 – 80 mTorr

Courtesy Applied Materials: L. Dorf, et al. 61st AVS International Symposium and Exhibition, Baltimore, MD (Nov 9-14, 2014); J. Phys. D: Appl. Phys. **50** (2017) 274003

Summary

- For processing application (present and future), managing flux of species and ion energy is critical
- For atomic layer processing applications, the lower the ion energy the better (you can always raise it).
- Electron beam generated plasmas are an attractive approach.

Thank you

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