Plasma Material Interactions

Daniel Andruczyk

ILLINOIS

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

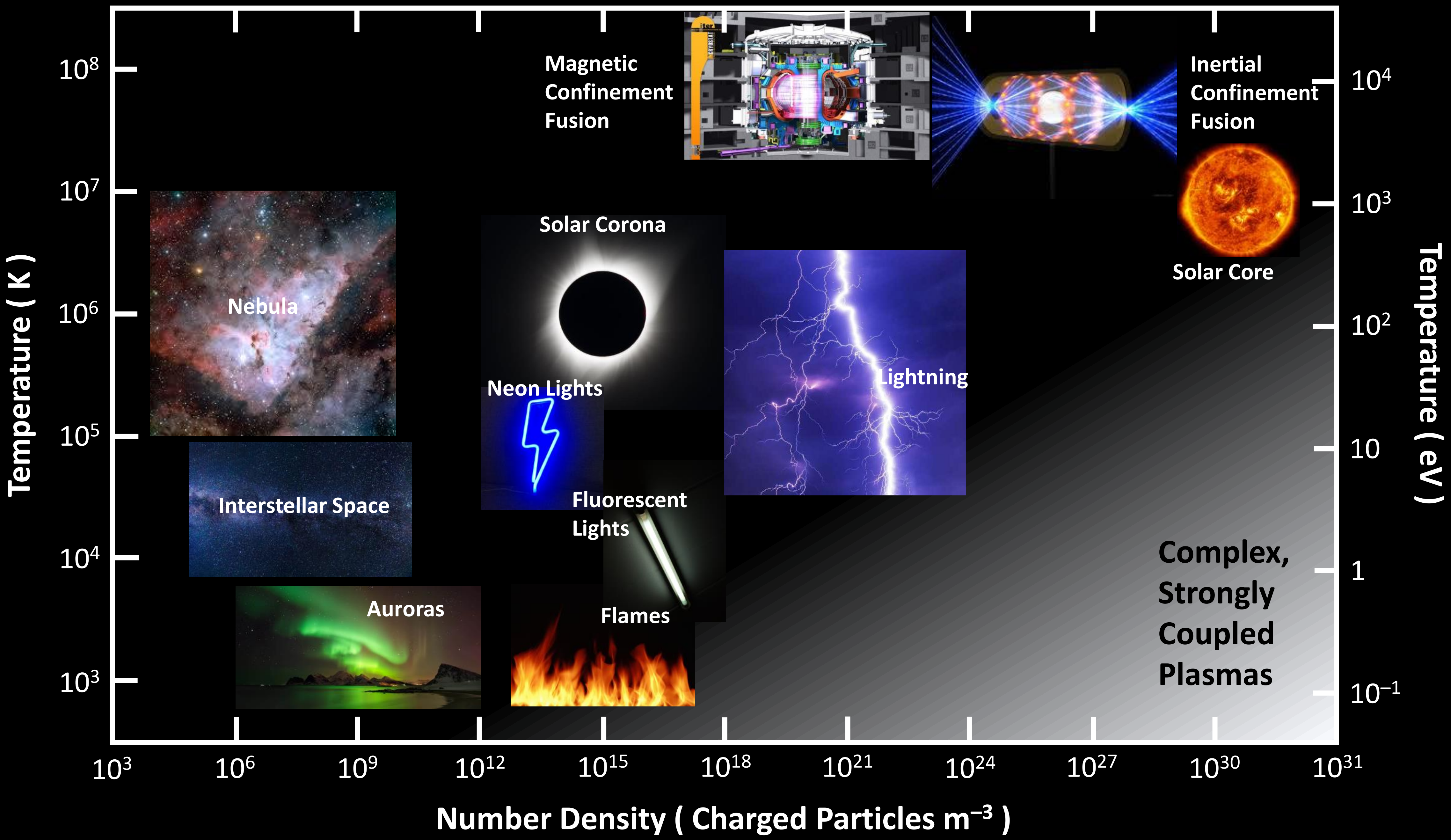
Email contact: andruczy@Illinois.edu

Outline

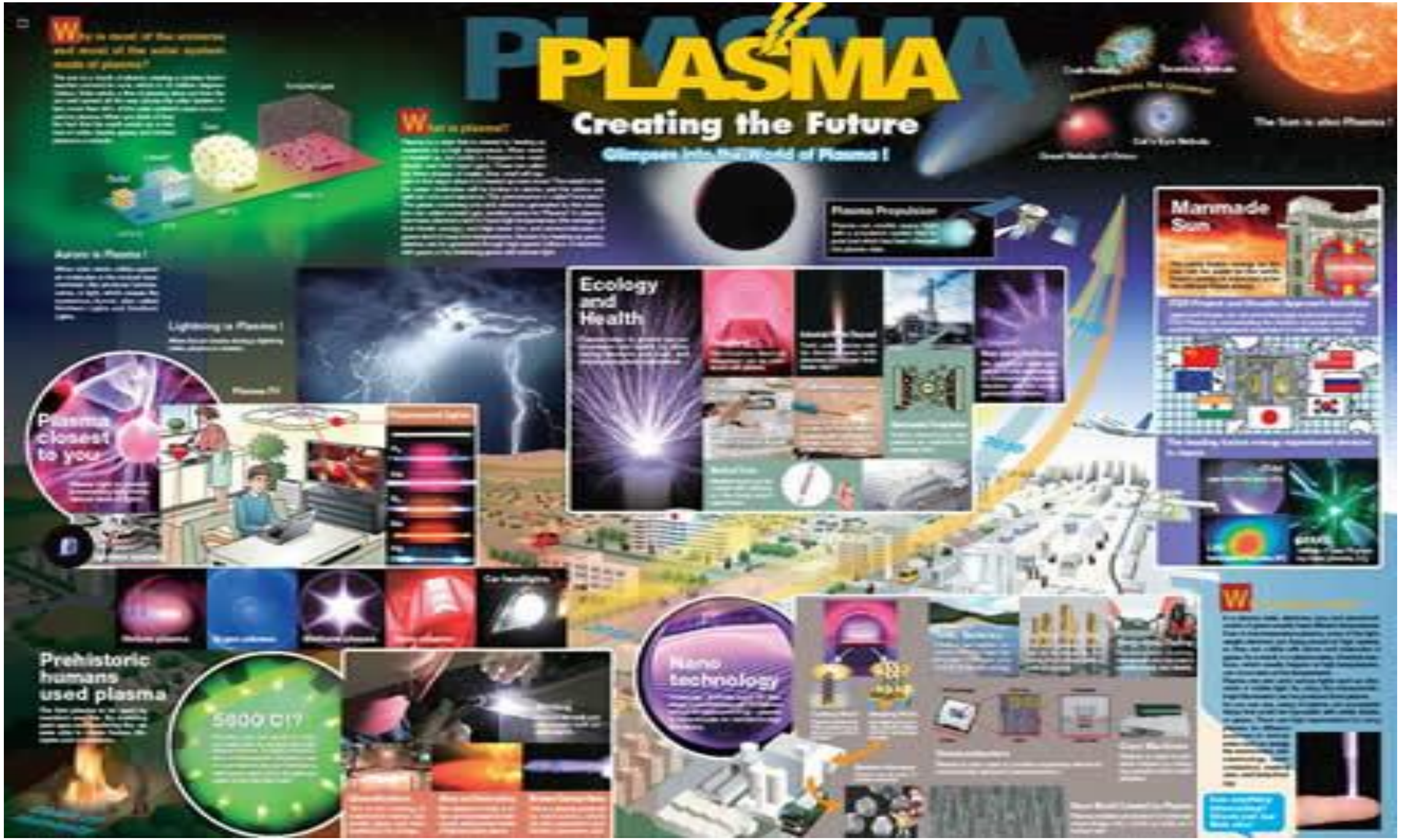
- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84

Outline

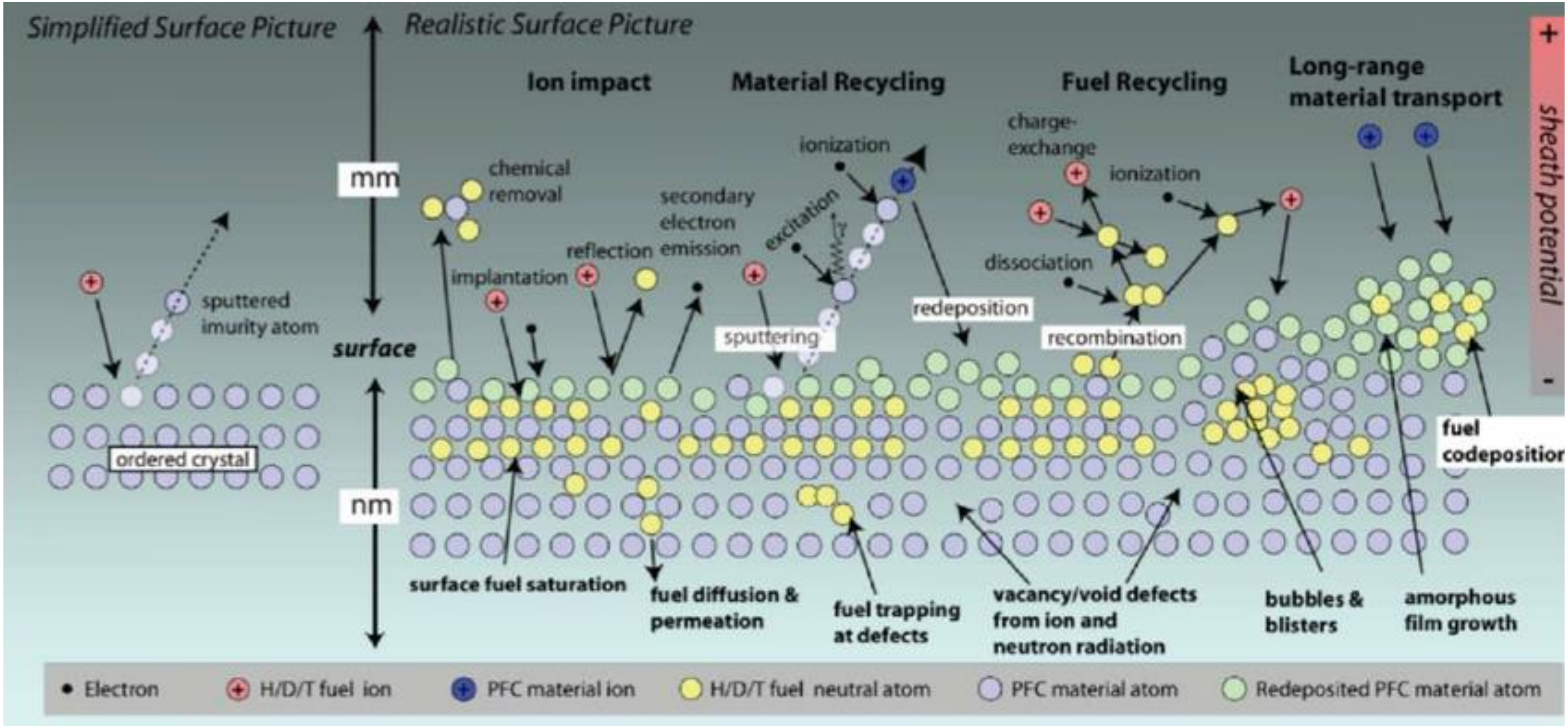
- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84


Magnetic Confinement Fusion
Inertial Confinement Fusion
Solar Core
Nebula
Solar Corona
Neon Lights
Lightning
Interstellar Space
Fluorescent Lights
Auroras
Flames
Complex, Strongly Coupled Plasmas
Temperature (K)
10^8
10^7
10^6
10^5
10^4
10^3
Temperature (eV)
10^4
10^3
10^2
10
1
10^{-1}
10^3
10^6
10^9
10^{12}
10^{15}
10^{18}
10^{21}
10^{24}
10^{27}
10^{30}
10^{31}
Number Density (Charged Particles m^{-3})

Plasmas have an impact everywhere in everyday life!



Plasma material interactions are extremely complex



Outline

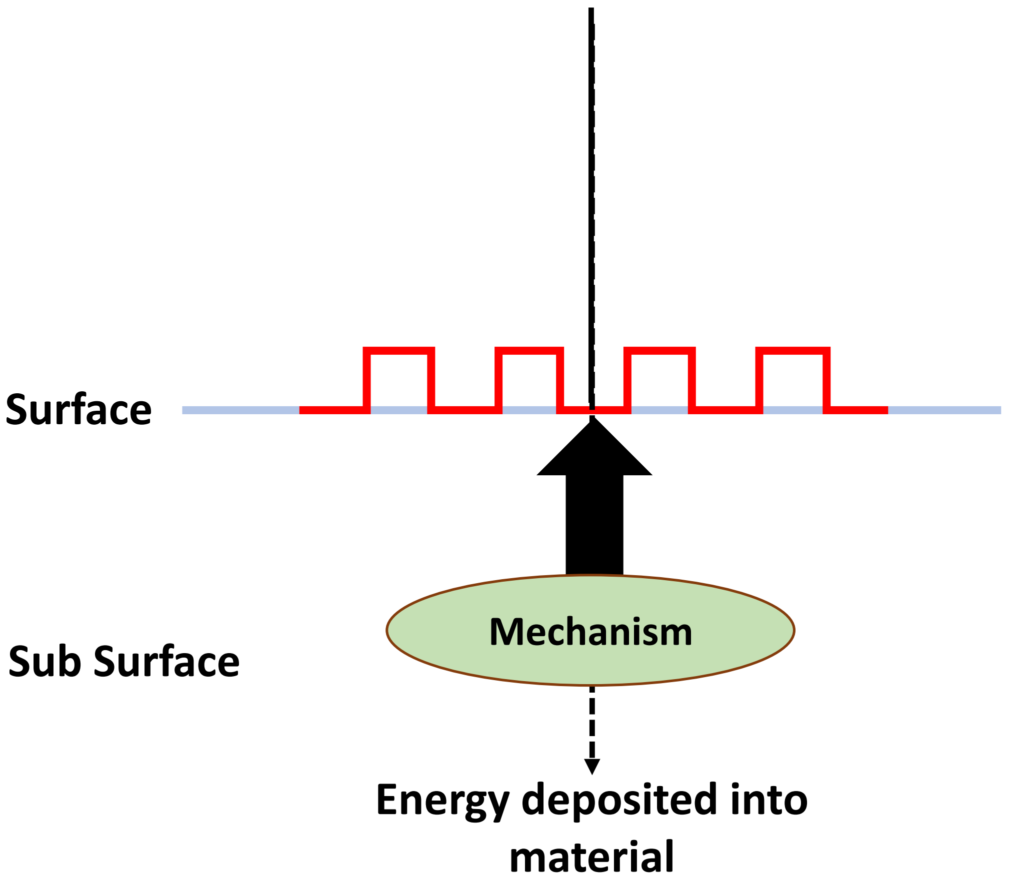
- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84

Damage and modification production mechanisms

- **Ballistic damage**
  - Displacement from collisions
  - Surface structures develop
  - No special role of surface in this mechanism.

- **Viscous flow**
  - Local volume expansion
  - Adatom production on surface
  - Cavitation
  - High atomic numbers, low melting temperature

- **Micro-explosions**
  - Cascade near surface
  - Pressure wave ruptures near surface
  - Adatom production on surface
  - Cavity production on surface
  - Surface vacancy production



Surface Science

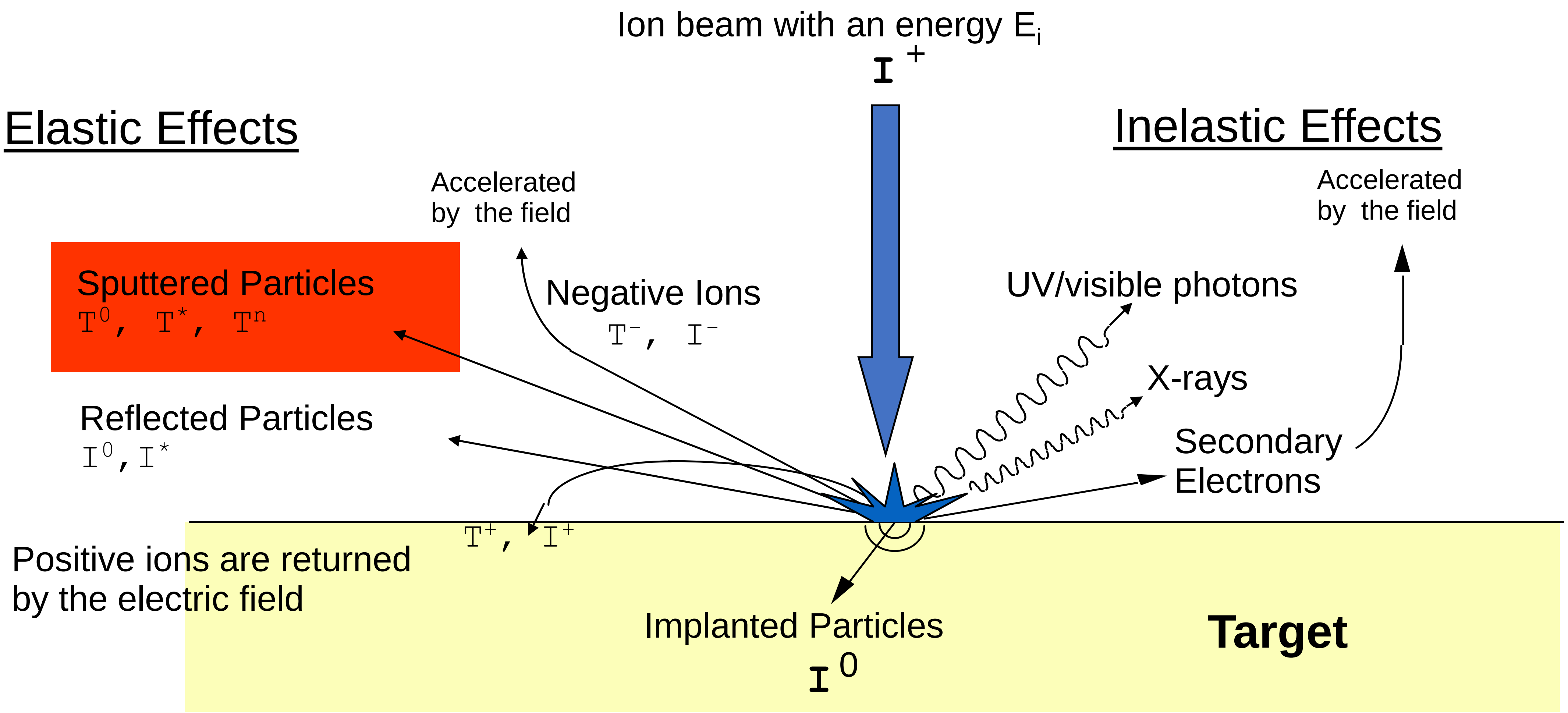
- What are the fundamental aspects of a surface that need to be considered?
  - Surface tension
  - Surface stress
  - Thermal vibration of atoms
  - Surface electro dynamics
  - Surface activated mechanisms
    - Surface diffusion
  - Structure and reconstruction of atoms
  - Surface defects
    - Adsorbed atoms (adatoms)
    - Surface vacancies

- **How does interaction with the plasma change the surface?**

What PMI effects do we need to worry about?

- Reflection
- Implantation
- Sputtering
- Electron Emission

Surface interactions



Ion beam with an energy E_i

I^+

Elastic Effects

Inelastic Effects

Accelerated
by the field

Sputtered Particles
T^0, T^*, T^n

Negative Ions
T^-, I^-

Accelerated
by the field

UV/visible photons

X-rays

Secondary
Electrons

Reflected Particles
I^0, I^*

T^+, I^+

Positive ions are returned
by the electric field

Implanted Particles
I^0

Target

Figure after G.M. McCracken, Rep. Prog Phys. 28, 241 (1975).

Reflection

- Ions almost always reflect as neutrals.
  - Exception is reflection from "alkali" metals, such as lithium. (The last electron is so loosely bound the atom can be ionized by its last collision on the way out of the material).
  - Note you will never see a reflected ion because it can not escape the sheath.

- Coefficients can be gotten from simulations e.g SRIM.
  - It is called backscattering.
  - A number of around 30% with the backscattered particles having around 30% of their energy is a good rule-of-thumb.

- Clearly though mass difference is important.
  - Light on heavy always reflects.
  - Heavy on light does not.

Implantation: Stopping cross-section

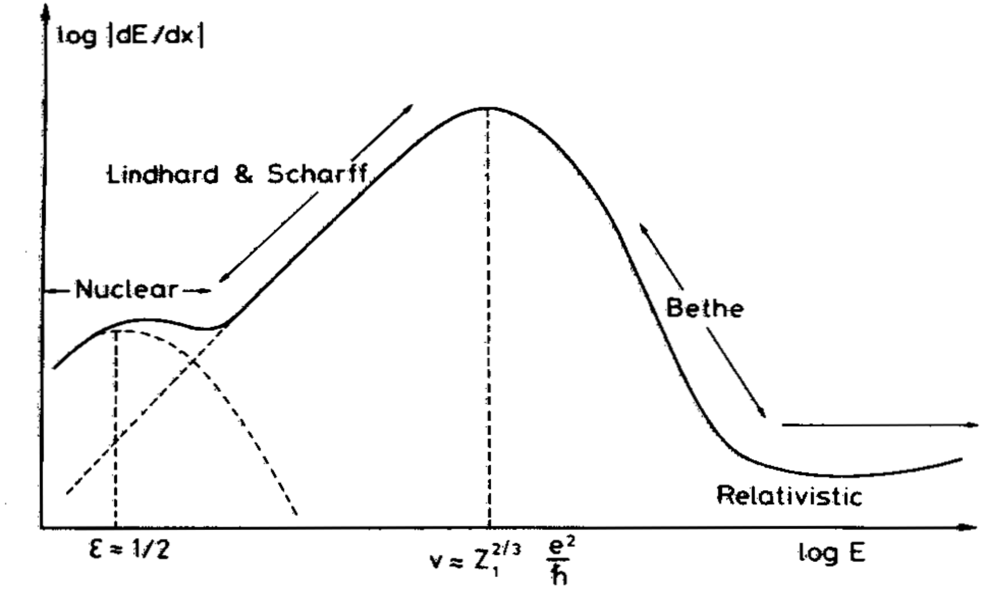
- Nuclear vs. electronic stopping powers depend on incident particle energy

$$\frac{dE}{dx} = -NS(E) = -N\left[S_n(E) + S_e(E)\right]$$

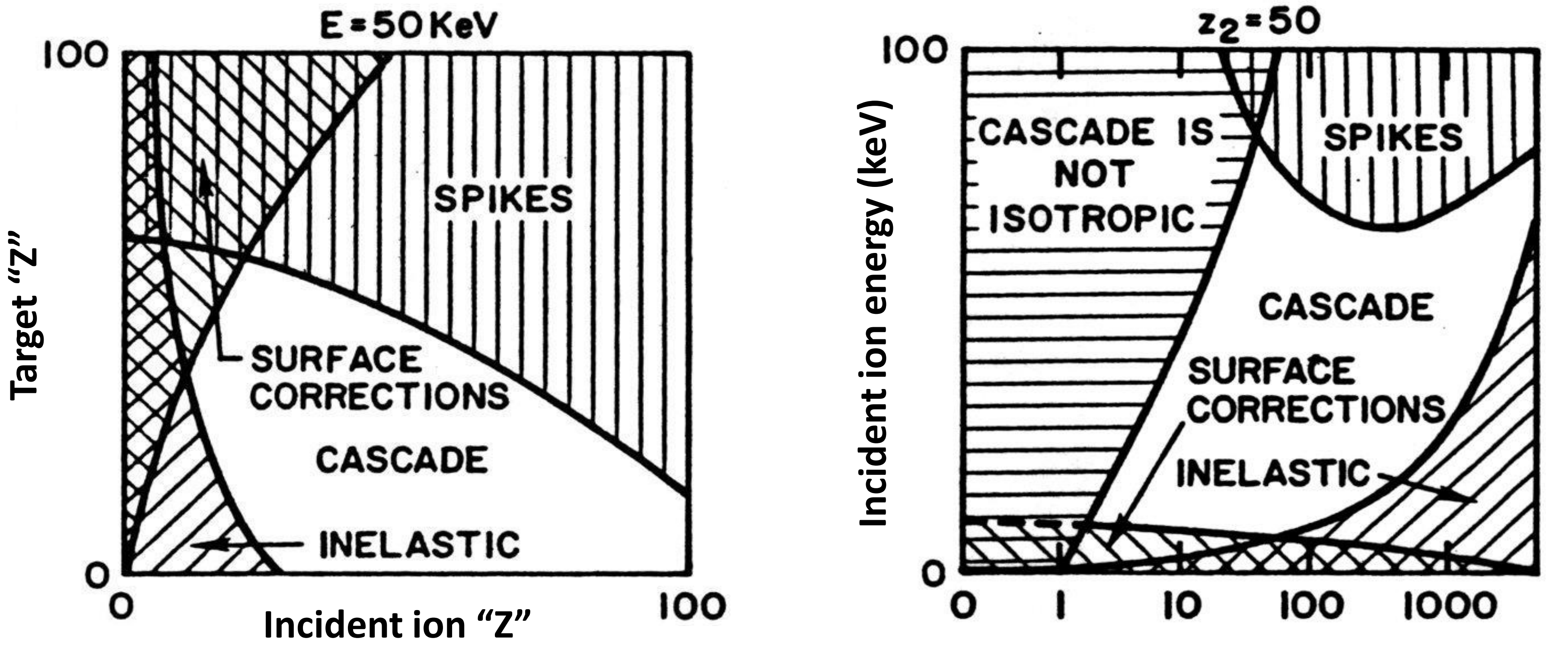
- Transition depends on particle-material combination

$$Range = \int_0^E \frac{dE'}{NS(E')}$$

- Typical energies:
  - Below ~ 1-10-keV *nuclear stopping energy loss is dominant*
  - Losses due to *electronic stopping* more dominant for most particle target systems at high energies (e.g. > 10 keV)
  - Electronic losses mostly to energy loss via electron-phonon coupling (heat).



Fundamentals of sputtering



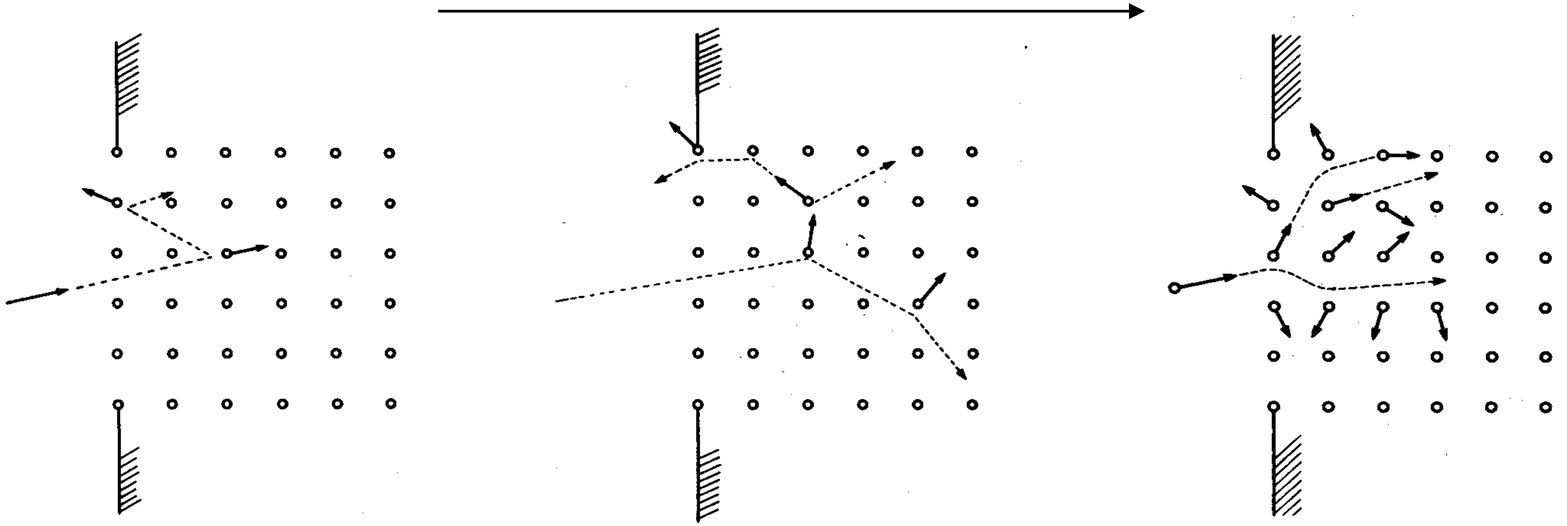
- The exact type of interaction depends on
  - Incident ion atomic number, "Z"
  - Target atomic number
  - Incident energy

From D. N. Ruzic, "Fundamentals of Sputtering", in Plasma Handbook of Processing Technology, Ed. S.Rossnagel et. al., 1990

- For Argon on most metals in most sputtering devices, we are in the "non-isotropic cascade" regime.

Non – isotropic collision cascade

Energy increasing (dependent on M_i/M_t)



Threshhold regime
recoils sputtered, but
no (limited) cascades

Linear cascade
a series of binary collisions

Spike regime
high density of recoils

P.Sigmund, “Sputtering by ion bombardment: theoretical concepts”, in *Sputtering by particle bombardment* I, edited by R. Behrish, Springer-Verlag, 1981

- Ions striking a surface interact with a number of atoms in a series collisions.
- recoiled target atoms in turn collide with atom at rest generating a collision cascade.
- The initial ion energy and momentum are distributed to among the target recoil atoms.
- When $E_i > 1$ keV, the cascade is “linear”, i.e. approximated by a series of binary collisions in a stationary matrix.

Sputtering

- 1950's and 60's sputtering first described
  - **P. Sigmund, Phys Rev. 184 383 (1969)**
- Assumptions in sputter theory
  - Linear transport
  - Lattice is random
  - Collision cascades are isotropic
  - Stopping power described by elastic nuclear collisions.

Sputter yield

$$Y(E_i,\theta)=\Lambda F_D(E_i,\theta,x)$$

Material factor

Energy density deposited per ion

$$\boxed{Y=\frac{\Gamma_{sputtered}}{\Gamma_{incident}}}$$

$$\Lambda=\frac{\Gamma}{4}\int\frac{dE_0}{E_0 dE_o/dx}\int d\cos^2\theta_0 P(E_0,\theta_0)$$

Geometric Factor

Stopping power at E_0

Ejection Probability

Assumption in classical sputtering theory

- If these assumptions hold, then one can simplify the sputter yield expression
  - Linear transport theory (i.e. all collisions are between moving projectiles
  - and lattice atoms at rest; each collision is an independent binary event)
  - Lattice is random
  - Collision cascade is isotropic
  - Stopping power described by elastic nuclear collisions

$$\Lambda = \left(\frac{3}{4\pi^2}\right)\left(\frac{1}{N_S C_0 U_0}\right)$$

Target Density

Constant ~ 15.6

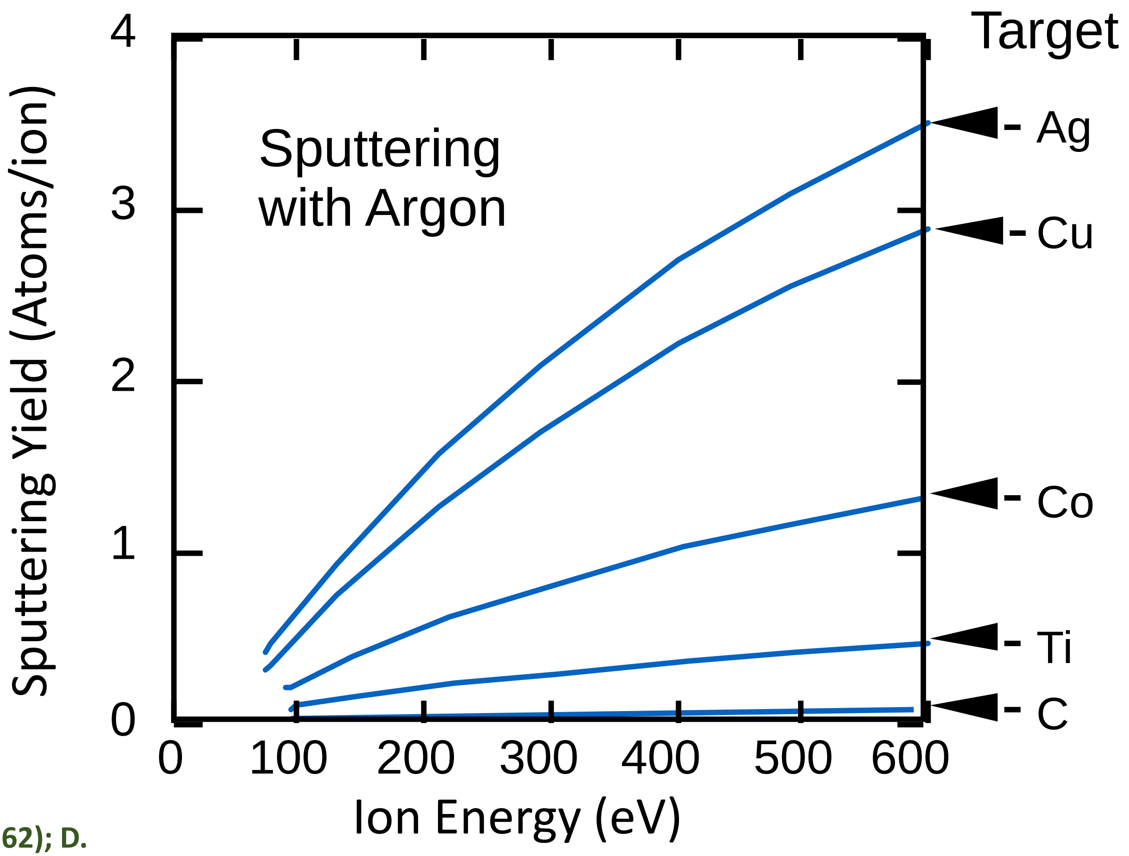
Surface Binding Energy

Sputtering Yield (γ)

Sputtering begins at an **energy threshold**

Increases rapidly.

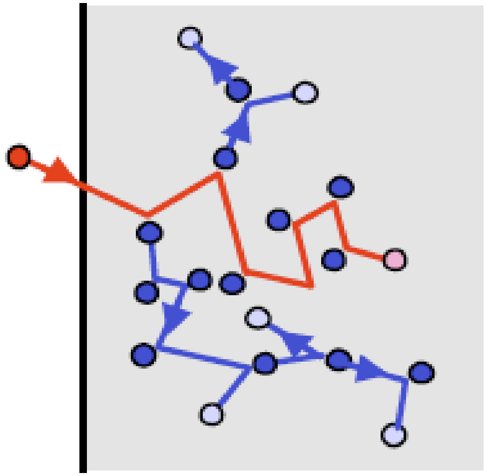
As the energy increases the curve levels off.

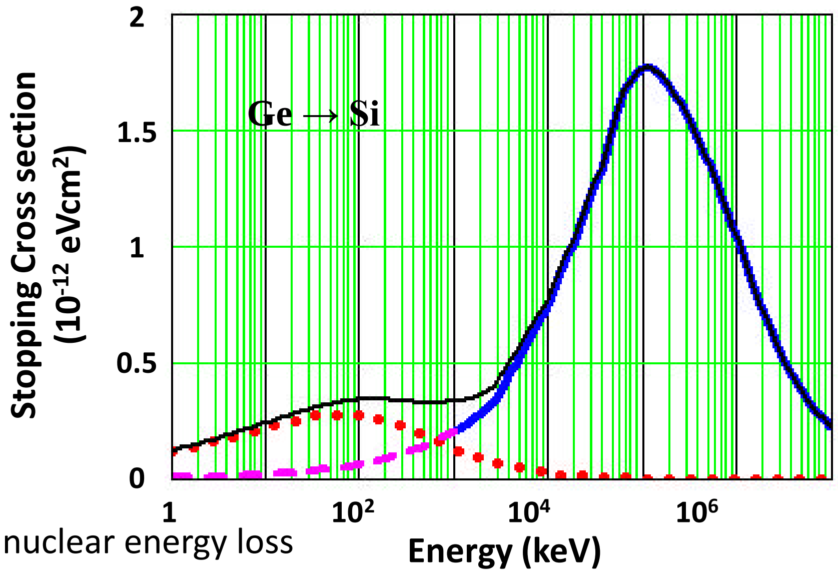


Data from R.Y. Stuart and G.K. Wehner, J. Appl. Phys. 33, 2351 (1962); D. Rosenberg and G.K. Wehner, J. Appl. Phycs. 33, 1842 (1962); and R. Behrisch, Exakt. Naturw. 35, 295 (1964).

Sputtering and recoil displacement

- The sputtering yield is proportional to the number of displaced or recoil atoms
- Energy density deposited per ion, $F_D(E)$, *depends on nuclear stopping* cross section at low energies, $S_n(E)$
- Nuclear stopping is the average energy loss which results from *elastic collisions* with target atoms
- The nuclear stopping power or nuclear energy-loss rate is the energy lost by a moving particle *due to elastic collisions per unit length travelled in the target*





H on Ni case: Thick solid blue line is electronic energy loss, dotted (red) is nuclear energy loss and thin black line is total energy loss (compared to Ge on Si)

Sputtering Threshold

- The sputtering threshold, U_{th}, is approximately the surface binding energy, E_{sbe}, divided by the maximum energy transfer function (γ)

$$U_{th} = \frac{E_{sbe}}{\gamma} \qquad \gamma = \frac{4 m_i m_t}{\left(m_i + m_t\right)^2}$$

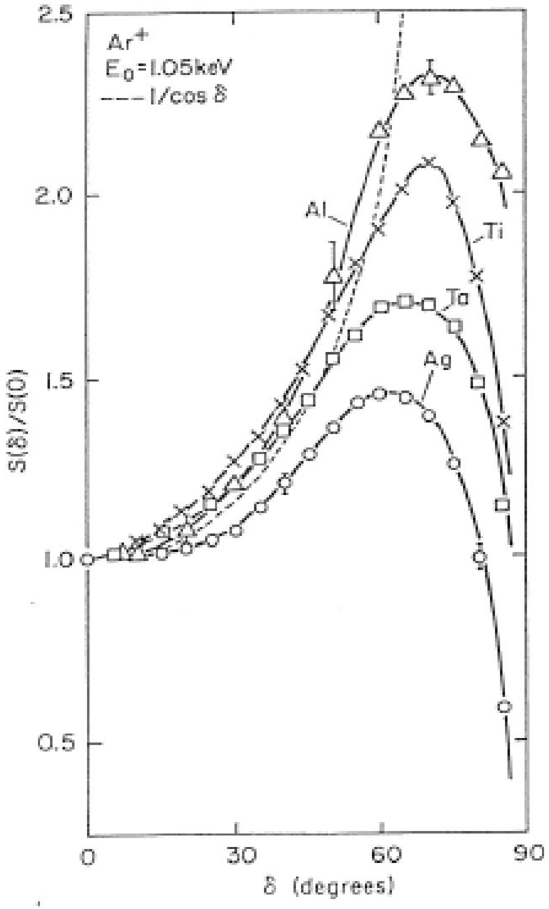
- m_i, is the incident mass, m_t, is the target mass. Note that if, $m_i = m_t$, then, $\gamma = 1$. For Ar on Si it is 0.969.

- Surface binding energies are 3 to 7 eV.

- Note though, while sputtering physically can happen at threshold it is **very, very small**.

Angular dependence for incident ion

For most sputtering devices, the angle is zero, normal to the surface. Higher angle lets one “get underneath”. Too high of angle means incident particle may just skip off the surface



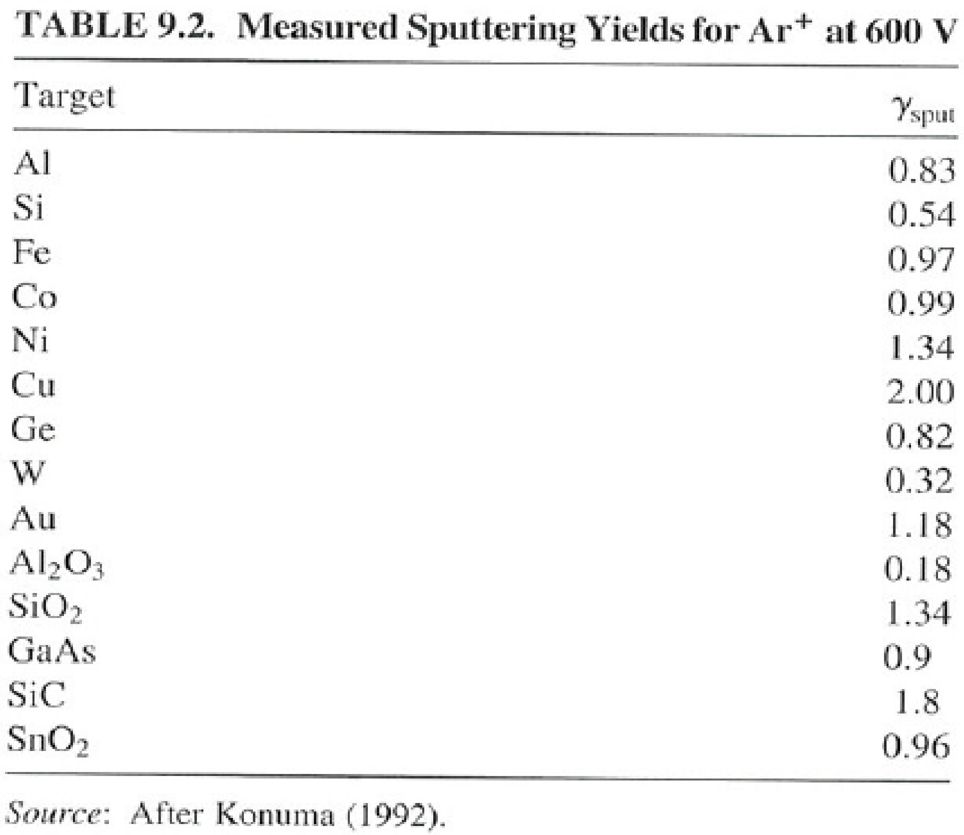


TABLE 9.2. Measured Sputtering Yields for Ar^+ at 600 V

Target	γ_{sput}
Al	0.83
Si	0.54
Fe	0.97
Co	0.99
Ni	1.34
Cu	2.00
Ge	0.82
W	0.32
Au	1.18
Al_2O_3	0.18
SiO_2	1.34
GaAs	0.9
SiC	1.8
SnO_2	0.96

Source: After Konuma (1992).

Note

Copper (Cu) is easy to sputter.

Tungsten (W) is not easy to sputter.

Alumina (Al_2O_3) is really tough

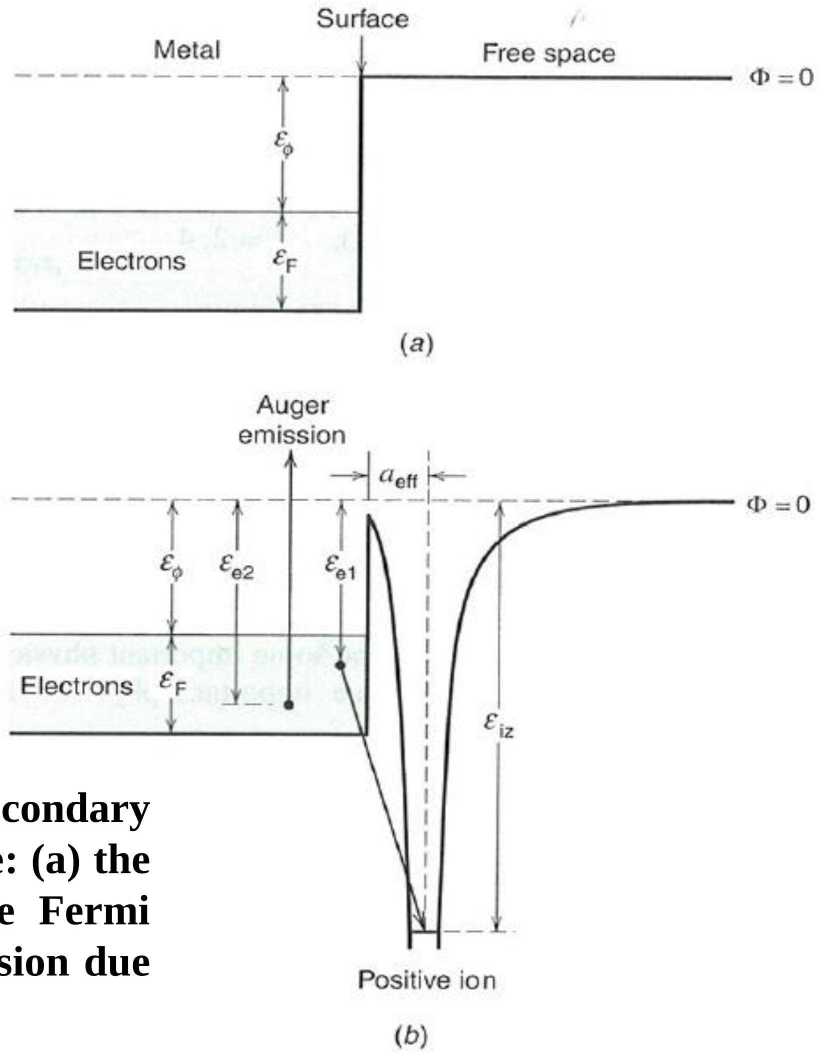
Potential electron emission

As an ion approaches a surface, it becomes energetically favorable for an electron to tunnel over to the ion and neutralize it.

THIS ALWAYS HAPPENS

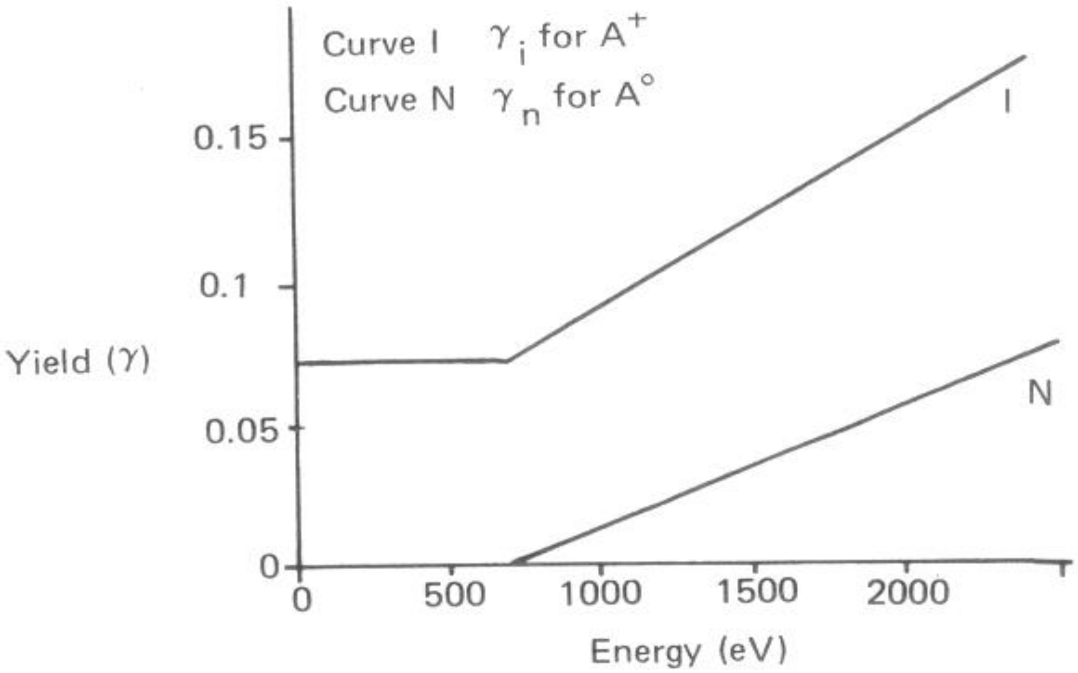
– an ion never actually hits a surface

Then, that extra energy can manifest itself in a number of ways. If the ionization potential is greater than 2 times the work function of the material, an electron from the surface to be emitted. This is “potential emission”.



Ion neutralization and secondary emission at a metal surface: (a) the work function E_0 and the Fermi energy E_F: (b) Auger emission due to electron tunnelling.

Ion induced secondary electron emission



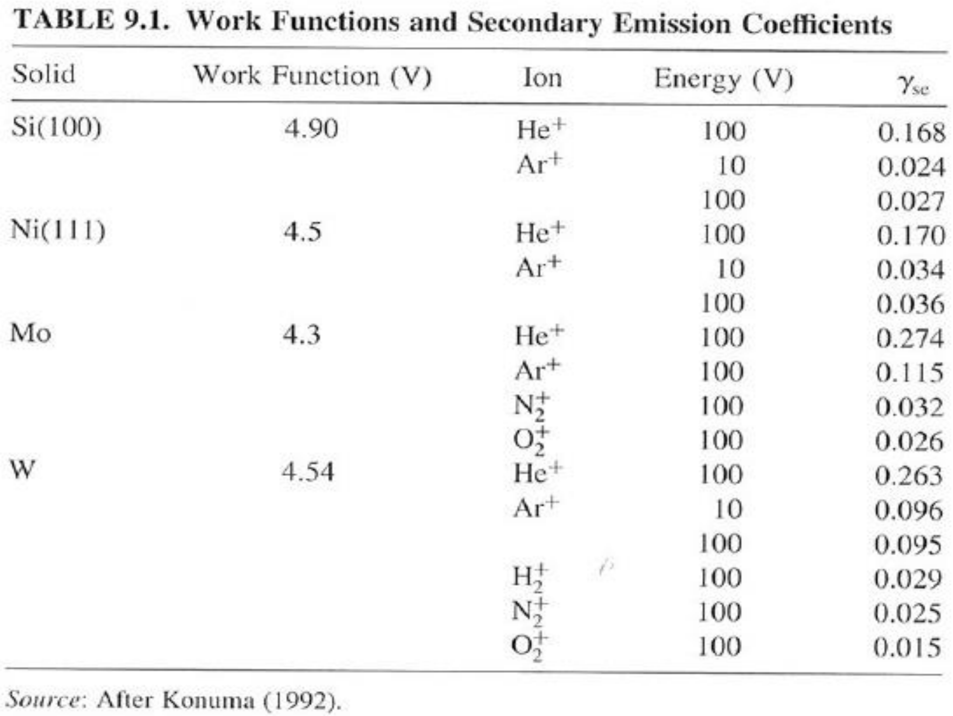


TABLE 9.1. Work Functions and Secondary Emission Coefficients

Solid	Work Function (V)	Ion	Energy (V)	γ_{se}
Si(100)	4.90	He^+	100	0.168
		Ar^+	10	0.024
			100	0.027
Ni(111)	4.5	He^+	100	0.170
		Ar^+	10	0.034
			100	0.036
Mo	4.3	He^+	100	0.274
		Ar^+	100	0.115
		N_2^+	100	0.032
		O_2^+	100	0.026
W	4.54	He^+	100	0.263
		Ar^+	10	0.096
			100	0.095
		H_2^+	100	0.029
		N_2^+	100	0.025
		O_2^+	100	0.015

Source: After Konuma (1992).

- **Higher energy ions or neutrals can liberate electrons through "kinetic emission" – basically impact ionizing the solid.**

- He^+ is always higher since ionization potential is higher.
- Note small effect of kinetic emission in energy range in fusion plasmas.
- Surfaces with low work functions (e.g. alkali metals) will emit more electrons.

Need to talk about the sheath

- Imagine a conductor that is immersed in a plasma
- Since electrons are much faster than the ions they will strike the surface more frequently
- Flux of electrons to the surface is much more than the ions
- Flux is given by

$$\Gamma = \frac{n\bar{v}}{4}$$

- Remember the average particle velocity

$$\bar{v} = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

- So this if we were to look at the average ratio of the ions to electrons

$$\frac{\bar{v}_e}{\bar{v}_i} = \left(\frac{T_e m_i}{m_e T_i}\right)^{1/2}$$

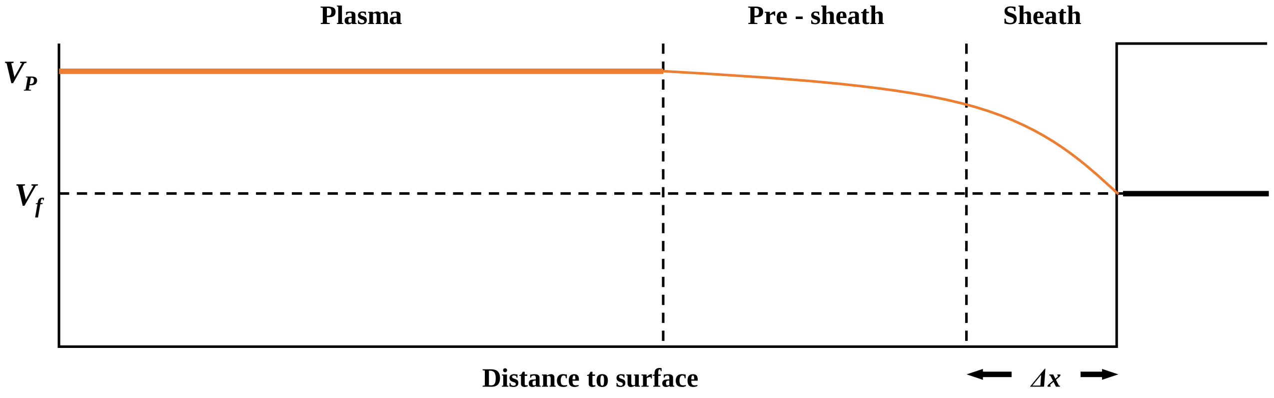
- Typical T_e = 3 eV and T_i = 0.025 eV, then find that for say an argon plasma

$$\bar{v}_e \approx 3000\bar{v}_i$$

Acceleration of ions to the surface

- What if you get both species bombarding the surface?
- Electrons will stick to the surface while the ions are mostly reflected
- Reflect as neutrals leaving their charge behind
- The conductor will pick up more negative charge than positive very quickly
- If the conductor is floating then its potential falls negative very quickly, but because of an electric field that is set up to oppose the diffusion of electrons to the surface, the electrons are repulsed

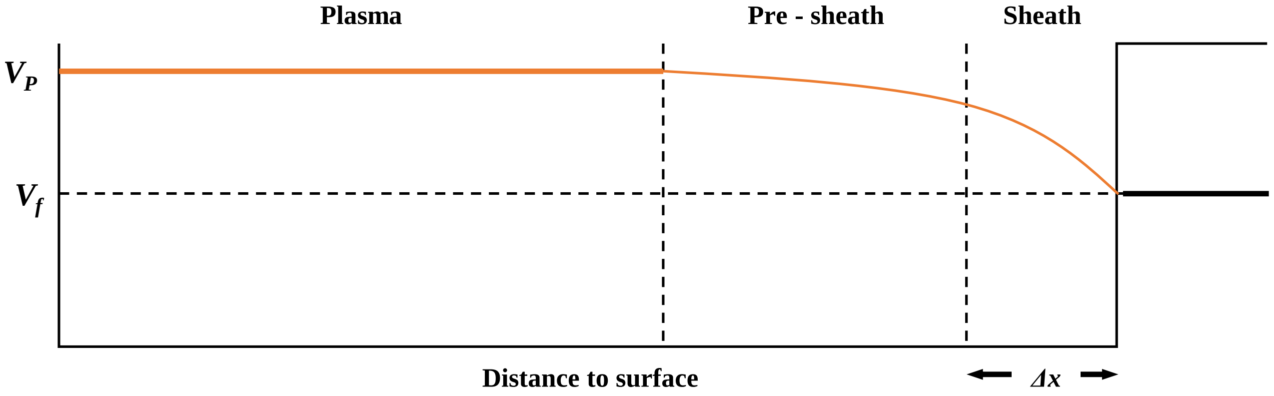
$$E = -\frac{dV}{dx}$$



- This field then accelerates ions to the surface
- Very quickly reaches a value such that the electron and ion flux is the same. This equilibrium potential is called the ***floating potential, V$_f$.***

The plasma sheath

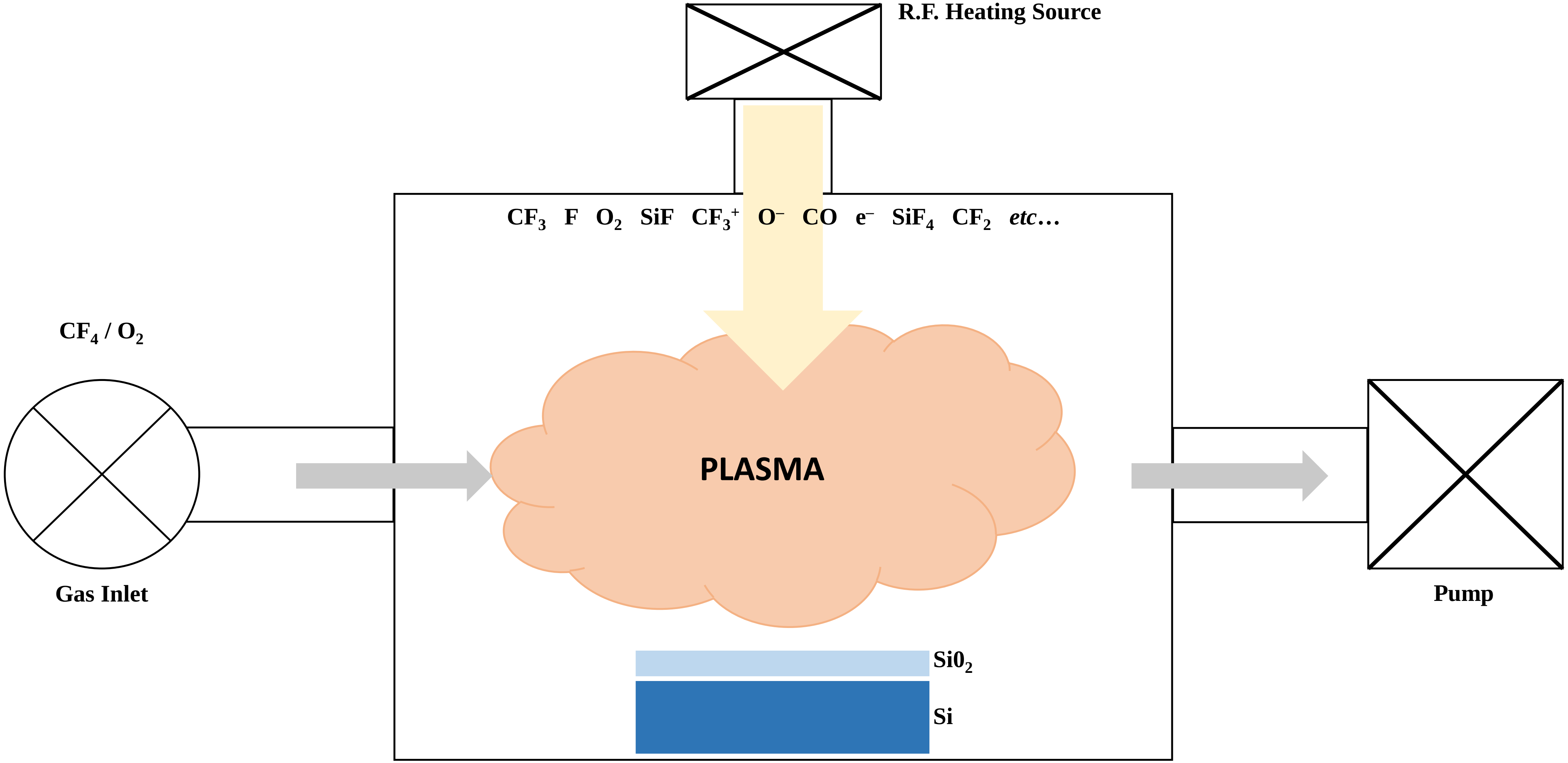
- Typically any conductor immersed inside a plasma will sit at the floating potential
- Another way to think about it, V_f, is the voltage when the current, $I = 0$ A
- Typically the plasma is only disturbed locally at the conductor surface and does not influence the rest of the plasma
- The region of the plasma, that is disturbed around the probe is called the ***plasma sheath***
- Electrons are repelled in this region. The ones with the lowest energy are repelled while the ones with highest energy can still get through



Outline

- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84

Low temperature plasma material interactions



Plasmas (and the material interactions) influence our lives everyday

01—Plasma TV
02—Plasma-coated jet turbine blades
03—Plasma-manufactured LEDs in panel
04—Diamondlike plasma CVD eyeglass coating
05—Plasma ion-implanted artificial hip
06—Plasma laser-cut cloth
07—Plasma HID headlamps
08—Plasma-produced H_2 in fuel cell
09—Plasma-aided combustion
10—Plasma muffler
11—Plasma ozone water purification
12—Plasma-deposited LCD screen
13—Plasma-deposited silicon for solar cells
14—Plasma-processed microelectronics
15—Plasma-sterilization in pharmaceutical production
16—Plasma-treated polymers
17—Plasma-treated textiles
18—Plasma-treated heart stent
19—Plasma-deposited diffusion barriers for containers
20—Plasma-sputtered window glazing
21—Compact fluorescent plasma lamp

Applications of low temperature plasmas and PMI

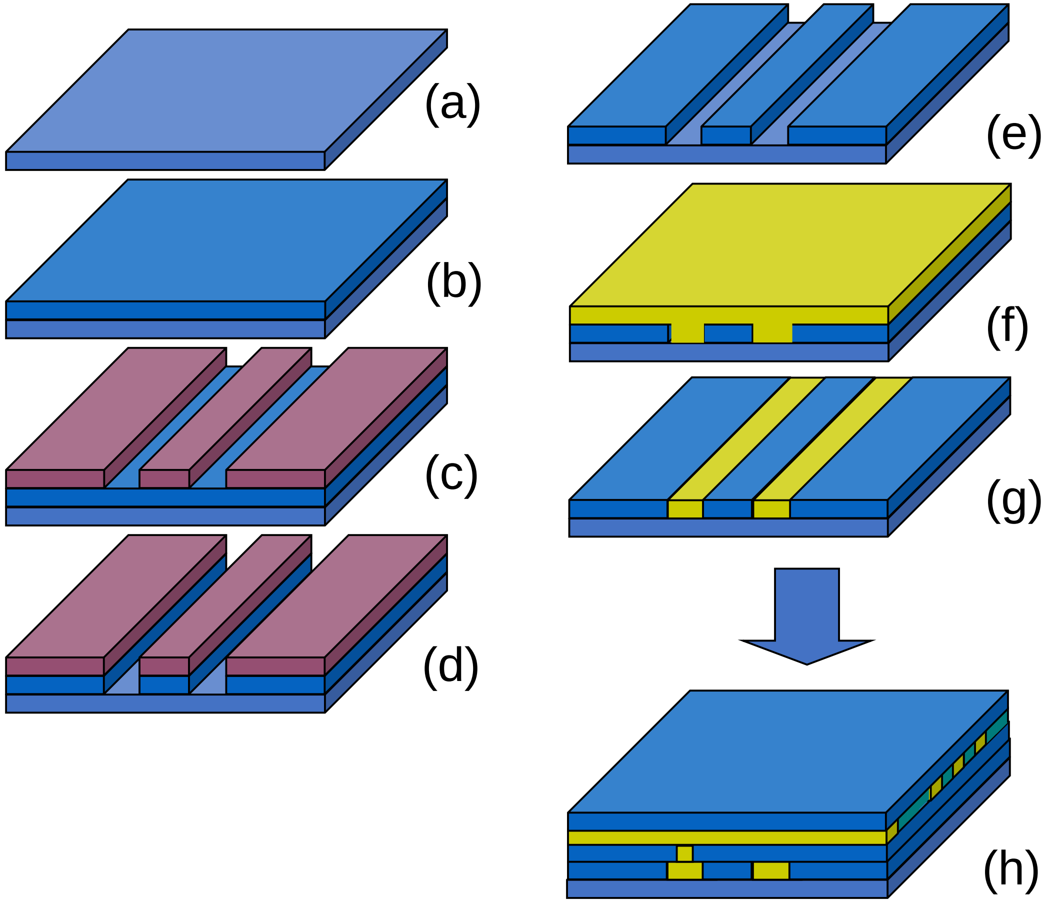
- Plasmas are used in a wide variety of places
    - Semiconductor industry
    - Surface modification
    - Treat emission and waste before entering the environment
- The plasma is a source of ions
- What is needed by industry?
    - Simple and compact plasma devices
    - Processing at high rates
    - Processing at high efficiency
    - Processing to be uniform over a large area
- Can control several parameters to produce the best type of plasma
    - Size and shape of plasma
    - Gas mixture
    - Voltage
    - Current
    - Magnetic field
    - Frequency
- These determine the ion and electron density and temperatures, ion fluxes and energies
- There will be atomic and molecular process that need to be understood as well, within the plasma and the surface

Fabrication with plasma

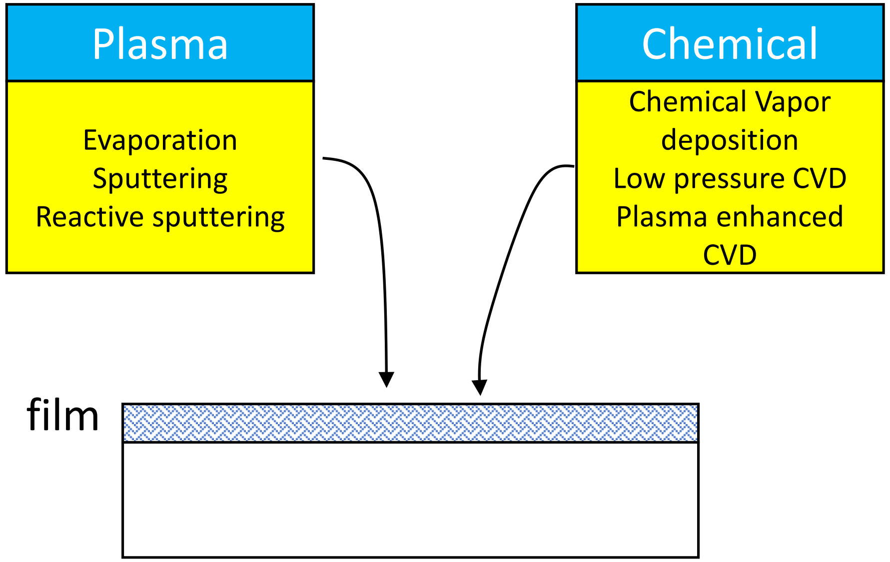
- So lets look at micro-fabrication, in particular the semi conductor industry

- In general we want to make a pattern of some kind.

- The method used is to have
  a. Lay down a substrate
  b. Deposit insulating etch material
  c. Deposit masking material with pattern
  d. Etch exposed material away
  e. Remove masking material
  f. Lay down conducting material
  g. Sputter away unwanted conductor
  h. Repeat process to get the desired pattern

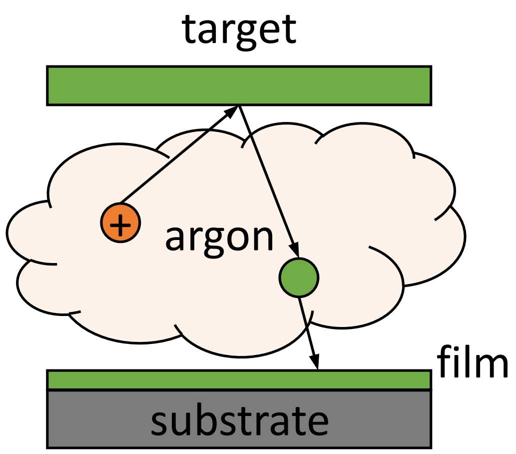


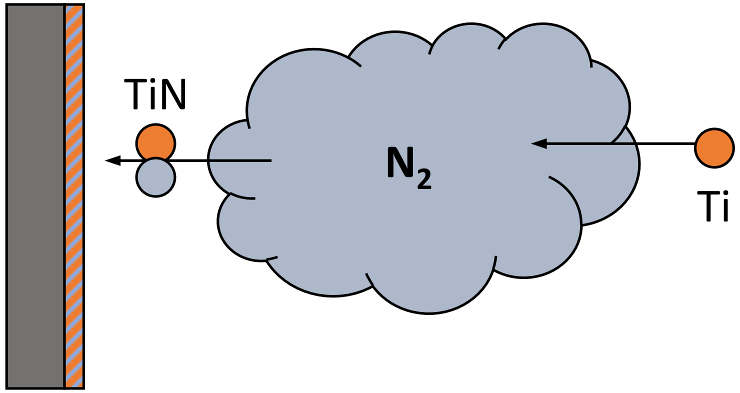
Plasma deposition



- Different types of plasmas can be used to do all these processes
- Lets look at some examples of plasmas used for deposition.
- There are in fact many different ways to do plasma deposition.
- Will cover some but not all methods here.
- So imagine there is a thin film that needs to be deposited onto a surface (substrate)
- Can do this via
  - Evaporation
  - **Using a plasma to sputter material onto the surface**
  - **Use a plasma to react with a material and deposit it on a surface**
  - Can use chemical vapor to deposit material on a surface
  - **Plasma vapor deposition where the plasma is able to enhance the chemical deposition**

Plasma deposition





- Target is the source of coating material for the substrate
- DC sputtering: metals , the target is the cathode
- RF sputtering: non conducting materials
- Ion beam sputtering
- Reactive sputtering, TiN for wear resistance, Ti + N_2 gas
- The substrate may be biased so ion bombardment modifies the film being grown
- Plasma assisted CVD, electron bombardment of atoms and molecules in the plasma volume
- Excitation and dissociation of species
- Produce variety of chemically reactive species with very different properties from the parent gas
- Lower temperatures required

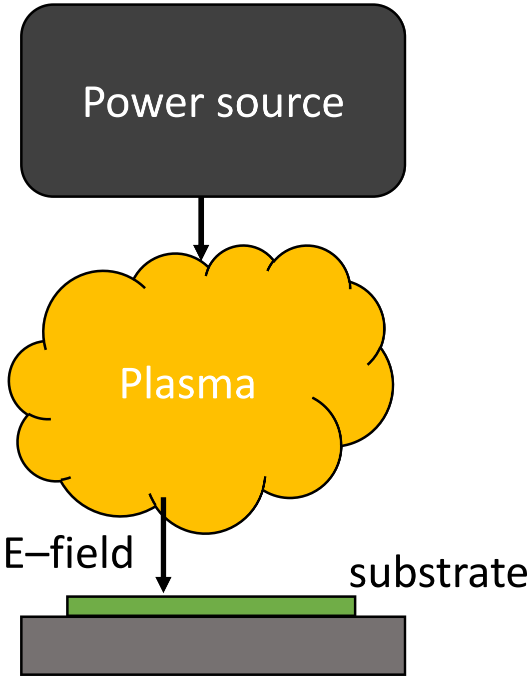
Plasma deposition

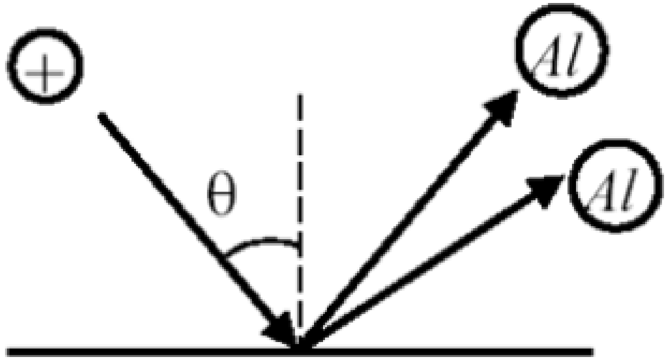
- Lets look at the plasma properties here
- Quasi neutrality needs holds
- Weak plasma containing mostly neutrals, 10^{-3} to 10^{-6} ionization
- A generic plasma reactor has a power source for the plasma, and provides an electric field for ion transport to the substrate
- So as you have a plasma hit a target, say the target has a negative bias to accelerate the ions to it
- The deposition rate, $R_{deposit}$, will be a function od

$$R_{deposit} = C\ I_i\ S$$

- Where C, is some constant, I_i, is the ion current and S is the sputtering rate
- S, which is simply just the number of atoms ejected from a surface due to a single ion bombardment

$$S = \frac{\#\ ejected\ target\ atoms}{incoming\ ions}$$

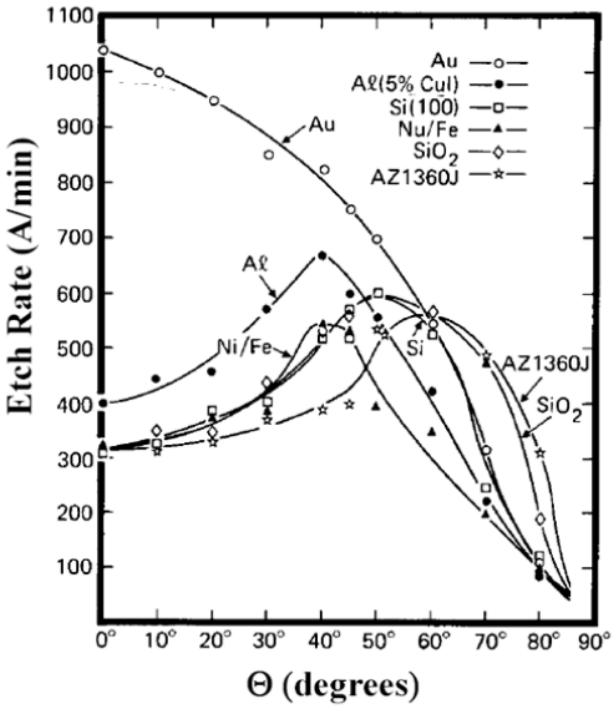


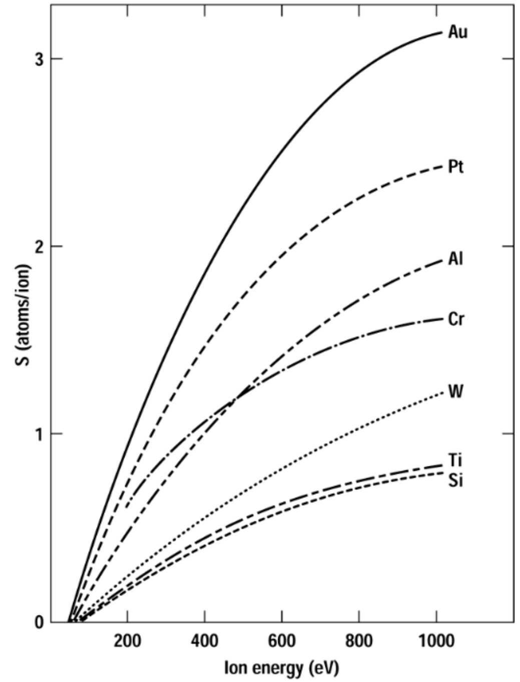


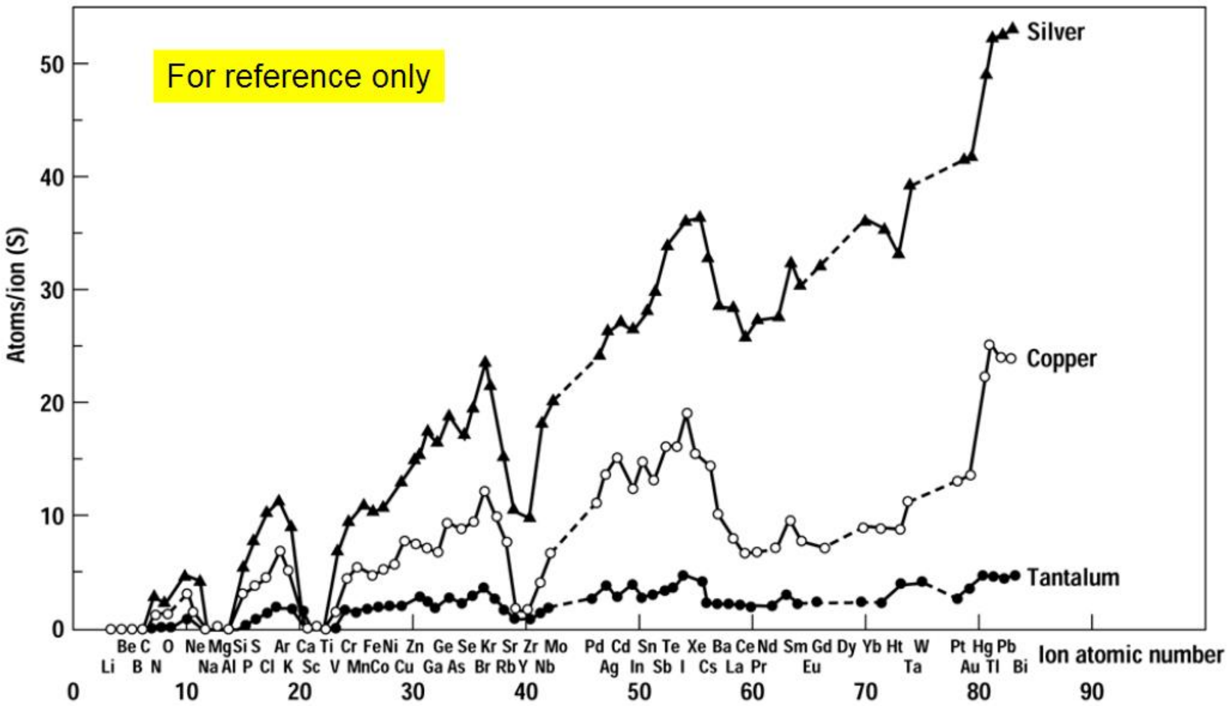
The sputtering rate is different for different surfaces

- Units: atoms/ion
- Dependent on ion energy
- Dependent on angle incident on surface

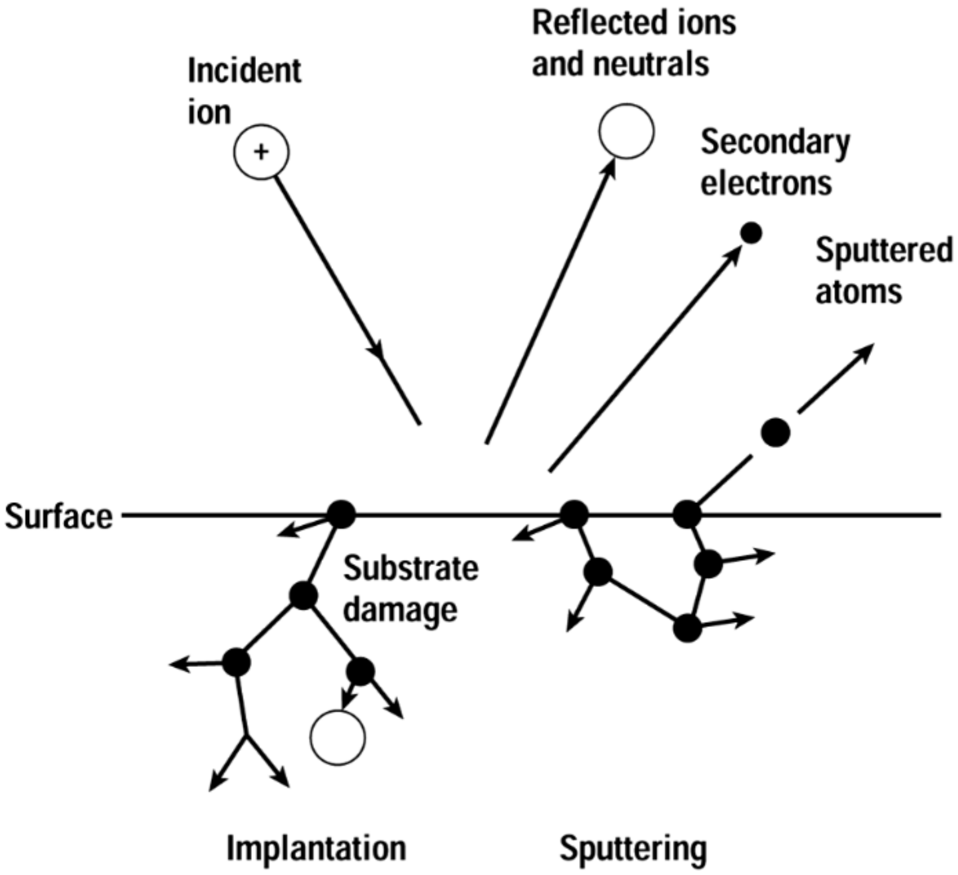
$$0.1 < S < 30$$





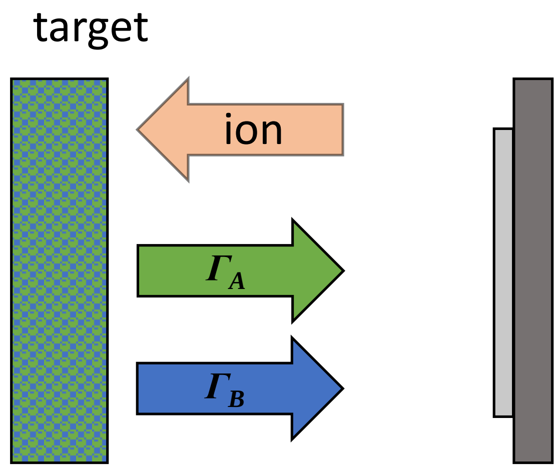

For reference only

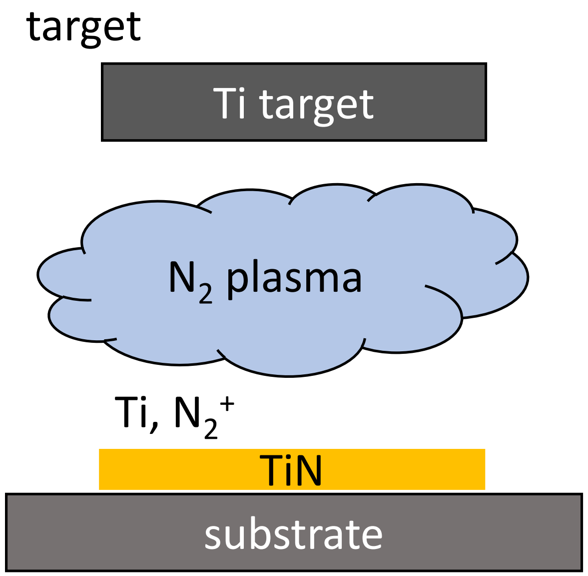
Substrate is also exposed to the plasma



- Typical gas pressure is 1 – 10 mtorr
  - What is this in Pa?
- The ejected atoms from the target then land onto the substrate and form a film
- But this is not necessarily all hunk dory
- What can happen to the substrate surface in this process?
- Remember that it is also exposed to the plasma and now there are energetic target ions, neutrals and radicals that are hitting it
  - Implantation: The incoming ion/atom is able to implant itself into the substrate, thus over time a layer gets built up
  - Sputtering: just like with the target, if there is enough energy, rather than implantation there will be surface ejection, this leads to surface damage and non-uniformity
- Secondary electrons can also be emitted as well as the incoming ions are neutralized at the surface and get "reflected back" at the temperature of the surface

Sputtering of multi-compound targets will yield a film that is made up of multi-compounds





- Target is made up of elements A and B
- Since

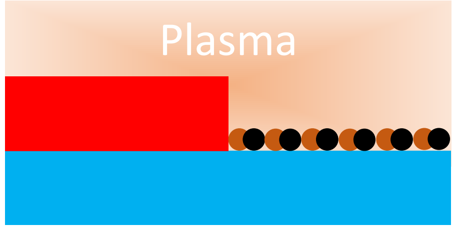
$$S_A \neq S_B$$

- then target surface will acquire a A_xB_y at steady state and so the film will be deposited with A_xB_y
- Reactive sputtering where the ejected ions from the target react with the plasma gas itself to form a new compound that coats the substrate
- Example is titanium nitride, TiN
- Sputter a Ti target with N_2 plasma
- Ti, N_2^+ will then react to form the Ti
- This is a beautiful golden color, often used to coat drill bits for increased wear resistance

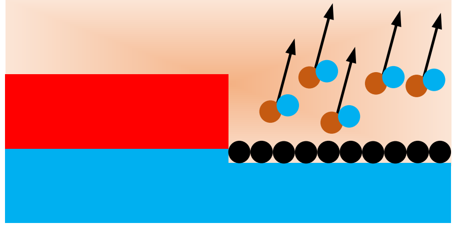
What if we want to remove material?

- This is called ***plasma etching***
- Etching is the removal of “unwanted” material off a surface
- Lets look at something like etching away silicon (Si) to make patterns in micro chips
- CF_4 gas is used to do the etching. By itself the CF4 will not etch but if the bonds can be broken through the generation of a plasma now the free F atoms can react with the Si
- Creates a volatile gas SiF_4 and can be pumped away.
- However what happens to the C? It can be left on the surface thus “protecting” any further Si to be etched away
- Solution: have a bit of O_2 in the plasma and this will react with the C to form CO and CO_2 and can be pumped away

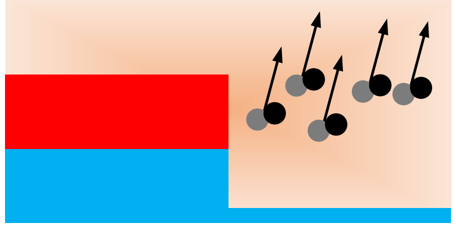
Start with a silicon etch substrate with a mask to protect any area needed



Generate a plasma with volatile gas such as CF_4. This will etch away the Si by forming SiF_4



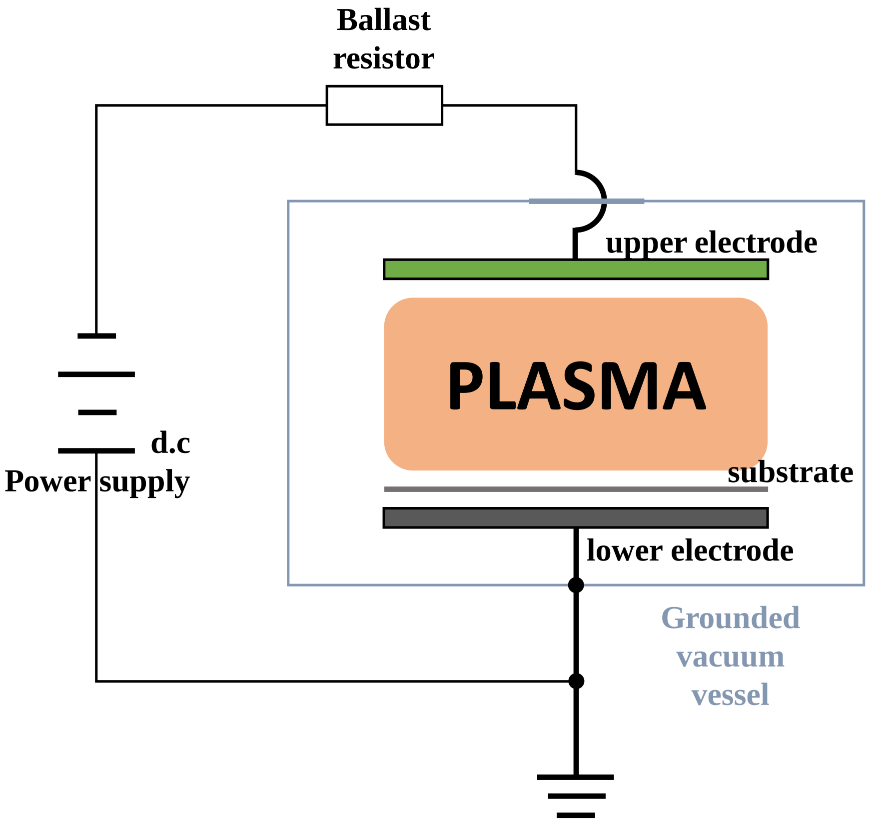
The SiF_4 gas is pumped away, however, the remaining carbon is left behind on the surface



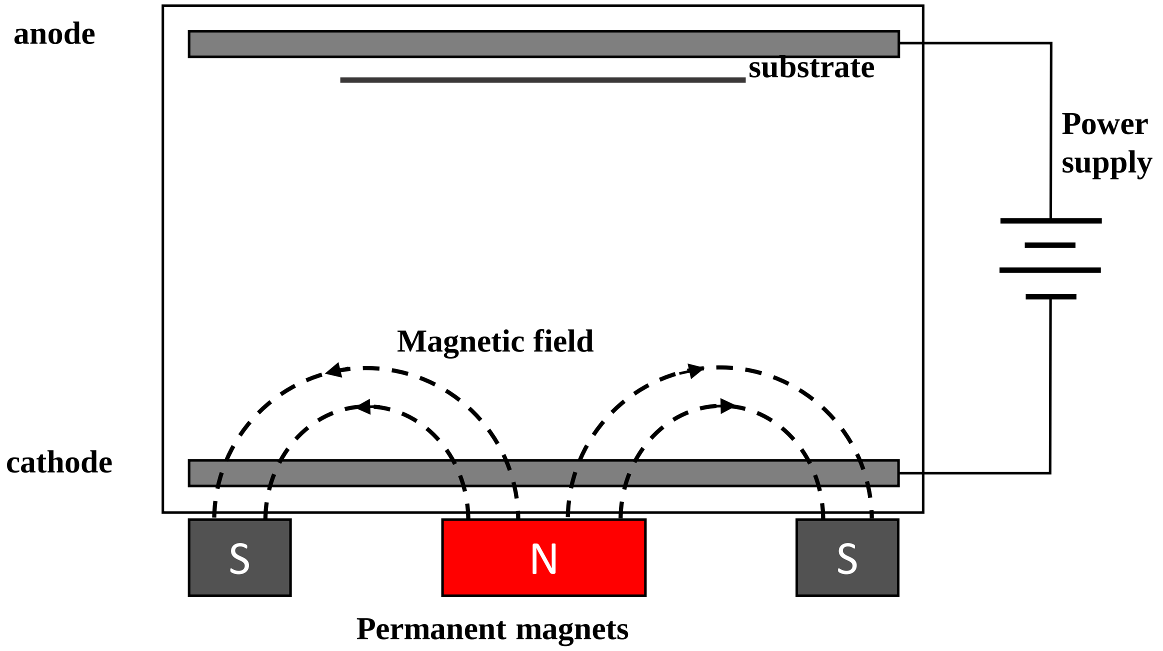
By having some O_2 in the plasma, will react with the carbon, forming CO, CO_2 and pump away leaving a clean surface

Types of plasma sources – DC Plasma (*DCP*)

- There are many different types of plasma sources that can be used to do plasma processing.
- Advantages and disadvantages
- Simplest type is the direct current (DC) plasma source
- This simply has two electrodes where a potential is applied.
- The E – field that is generated accelerates and stray electrons and if sufficient voltage will cause enough cascading break downs
- Advantages
  - simple to set up, not very complicated to use
  - quick turn around
- Disadvantages:
  - low density
  - low temperature
  - high pressure
  - Lots stray contamination



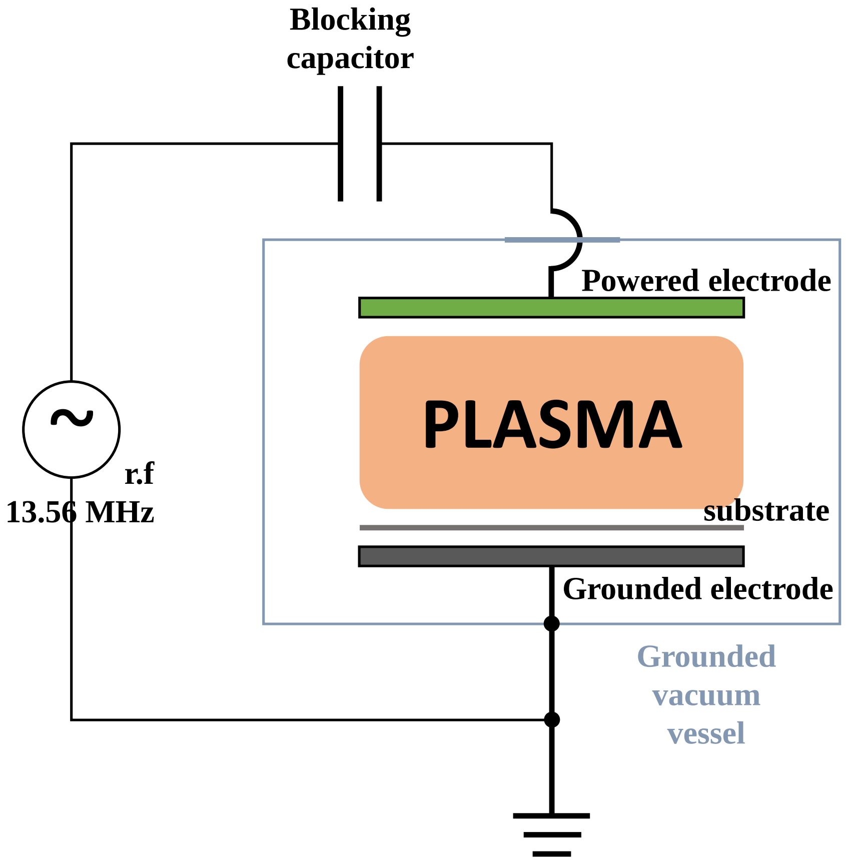
DC magnetron (*DCMP*) plasma



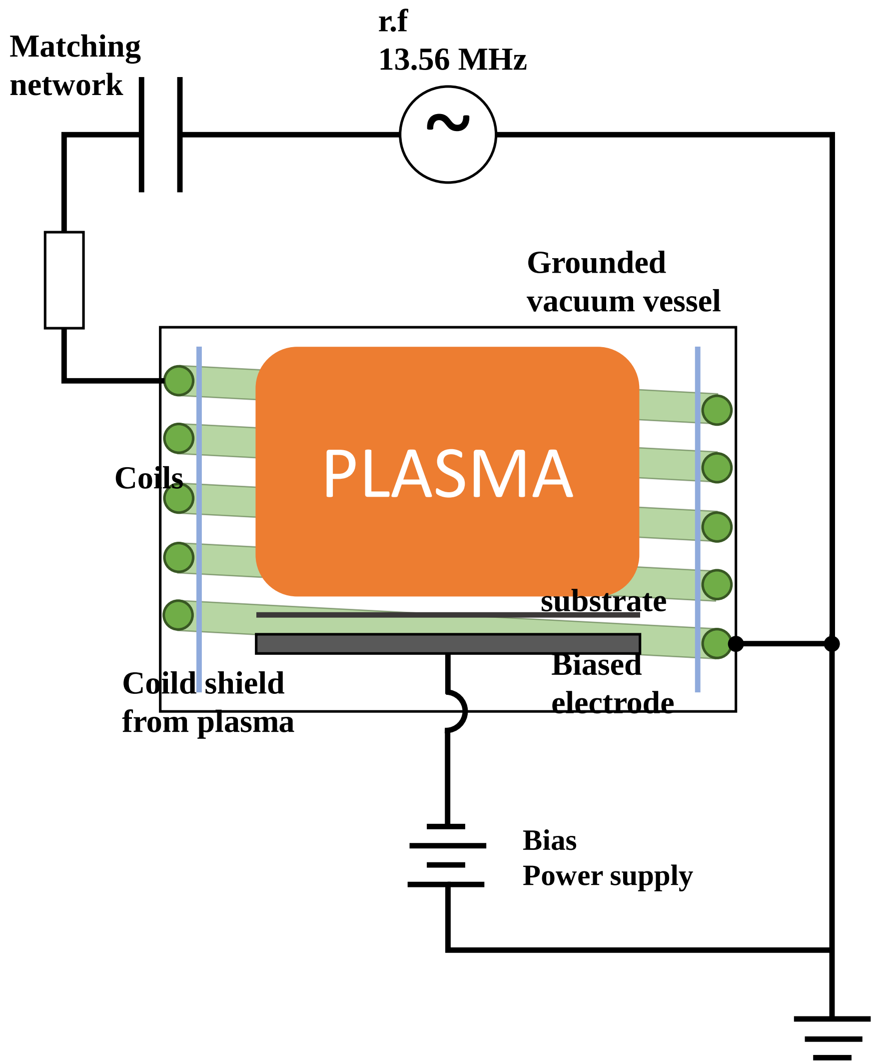
- Capable of high current densities and fast processing
- A magnetic field (0.02 T) is able to confine secondary electrons
- Bright ring that sits above the cathode
- The ions are still able to reach the cathode and bombard it
- The material on the cathode can be just about anything
  - Metallic
  - Oxides
  - Insulating material
- Advantages
  - Almost any metallic target material can be sputtered without decomposition
  - Non-conductive materials can be sputtered
  - Oxide coatings can be sputtered (reactive sputtering)
  - Excellent layer uniformity
  - Very smooth sputtered coatings (no droplets)
  - high flexibility of sputtering equipment design
- Disadvantages
  - Lower plasma density (~5%)
  - adhesion of coatings is lower
  - density of the sputtered layers may be lower

Capacitively couples plasma (*CCP*)

- Under applied r.f. voltage the plasma sheath boundary oscillated up and down while the bulk plasma remains uniform
- Low pressure discharge can provide high ion energies for etching
- High pressure discharge low ion energies for deposition
- Heating mechanism, ohmic heating
- Ohmic current is capacitively coupled across sheath
- Since the sheaths are oscillating the electron velocities are changed over 1 period
- Advantages
  - Simple construction
  - No B – fields required
- Disadvantages
  - Low Ion flux
  - high ion energy
  - Surface damage likely
  - Geometry sensitive
- Typical Frequency is *f* = 13.56 MHz



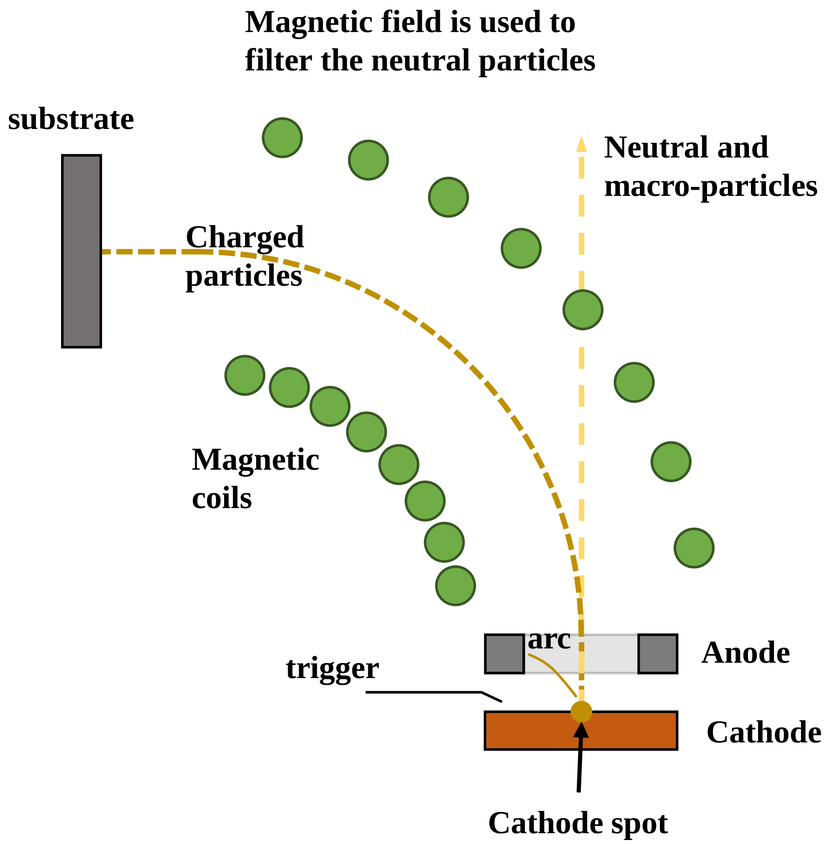
Inductively coupled plasma (*ICP*)



- Think of a transformer, there is a coil that is the primary and the plasma is the secondary
- The plasma is generated within the coils, again think of the fact that there are stray electrons that a plasma will ignite
- Coils need to be shielded from the plasma by an insulator
  - Glass
  - Ceramic
- Bias on the substrate will form an electric field between plasma and substrate
- Accelerate ions in
- Advantages
  - Ions energy can be independently controlled
  - Ion energies much less, less surface damage
- Disadvantages
  - Tend to be large machines, cooling and pumping an issue
  - Non uniform density profile

Vacuum Arc Plasma (*VAP*)

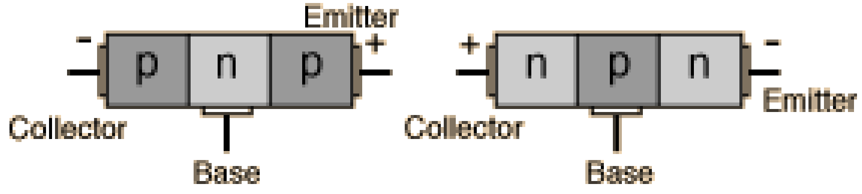
- This is a very particular type of discharge that uses a low pressure arc to create the plasma
- Neutral particles are formed so a linear device is not desirable
  - Substrate damage
  - contamination
- Use a magnetic filter to transport ions (and electrons)
  - ¼ tokamak essentially
- Advantages
  - Fully ionized plasma
  - High deposition rate
  - Low substrate temperature
- Disadvantages
  - Formation of macro-particles
  - Contamination
  - Slightly more complicated design

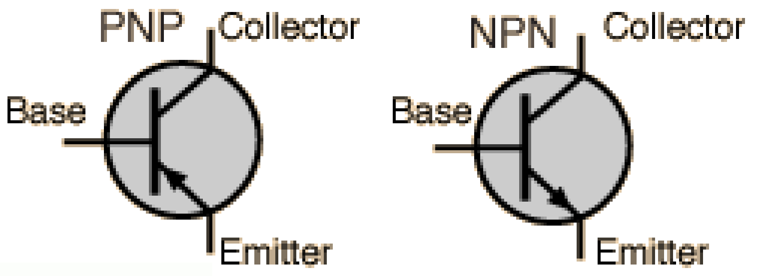


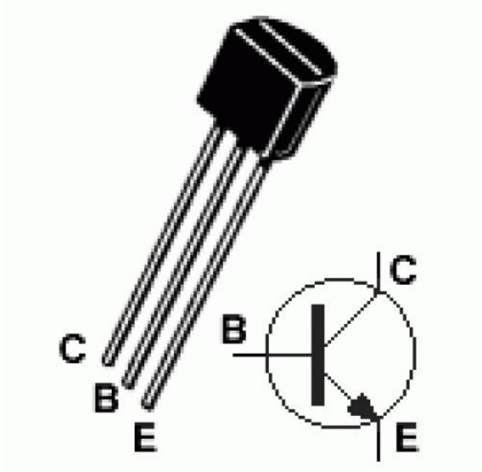
The Transistor

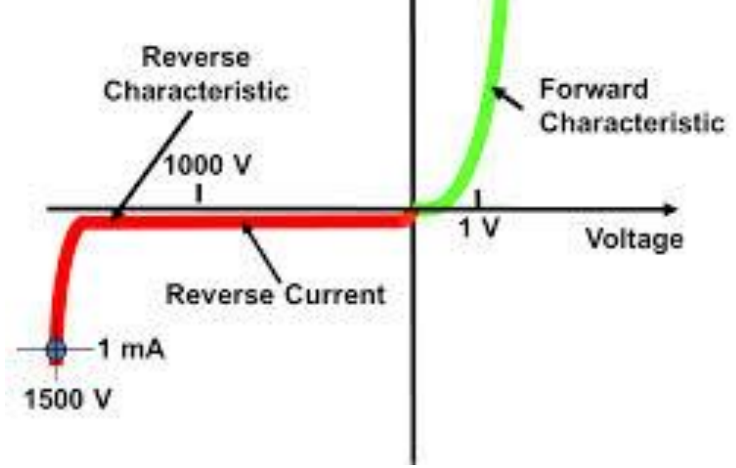
- No voltage to the "base", and no current flows from the "emitter" to the "collector". It is OFF. Value is "0"

- Add a small voltage to the "base", and a large current can flow. It is ON. Value is "1"



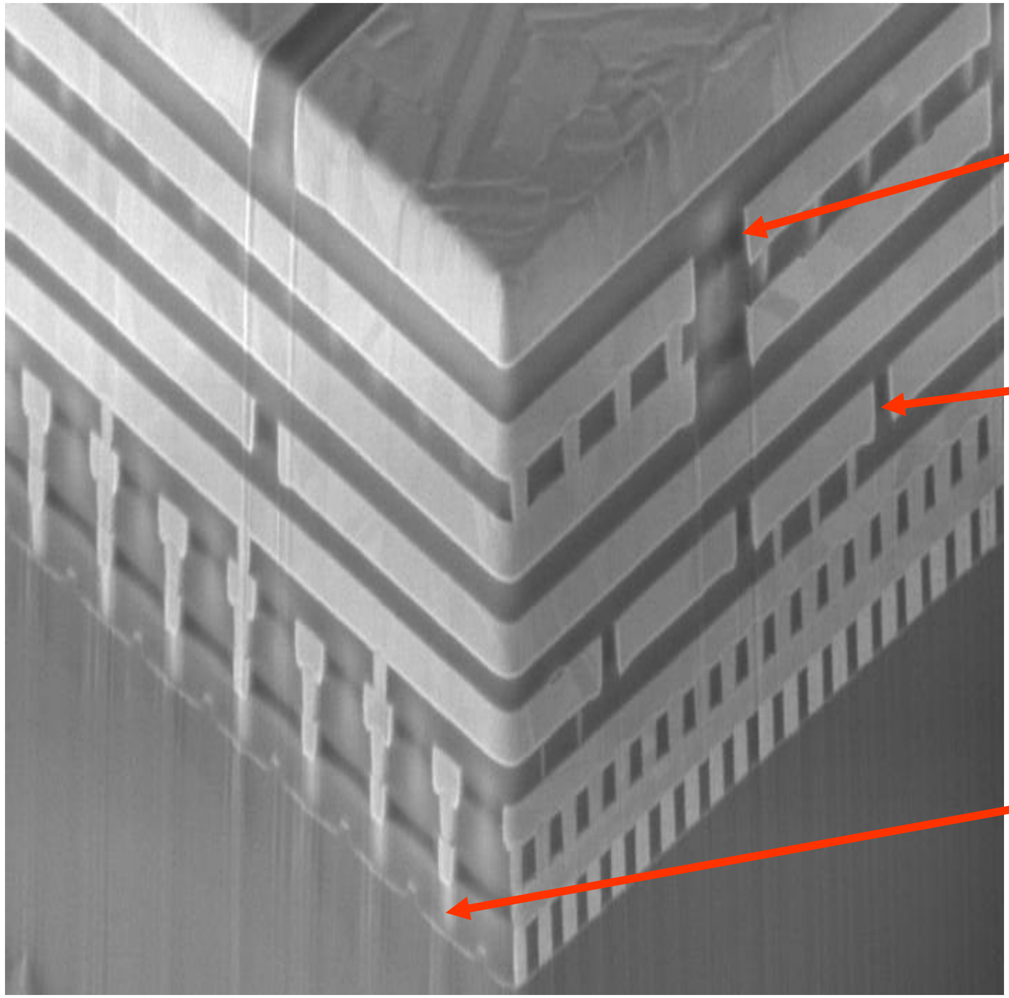




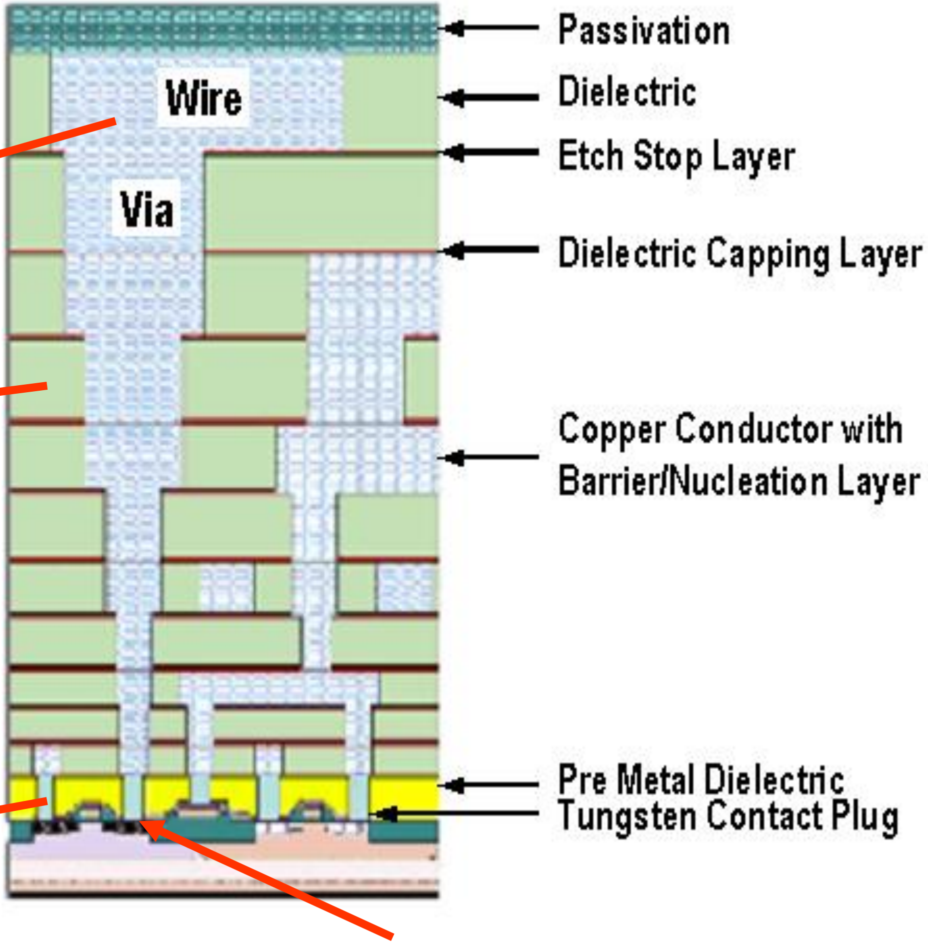


Radios used to only have a few transistors

50 years later, look how far we have come!



SEM cross-section, courtesy of AMD

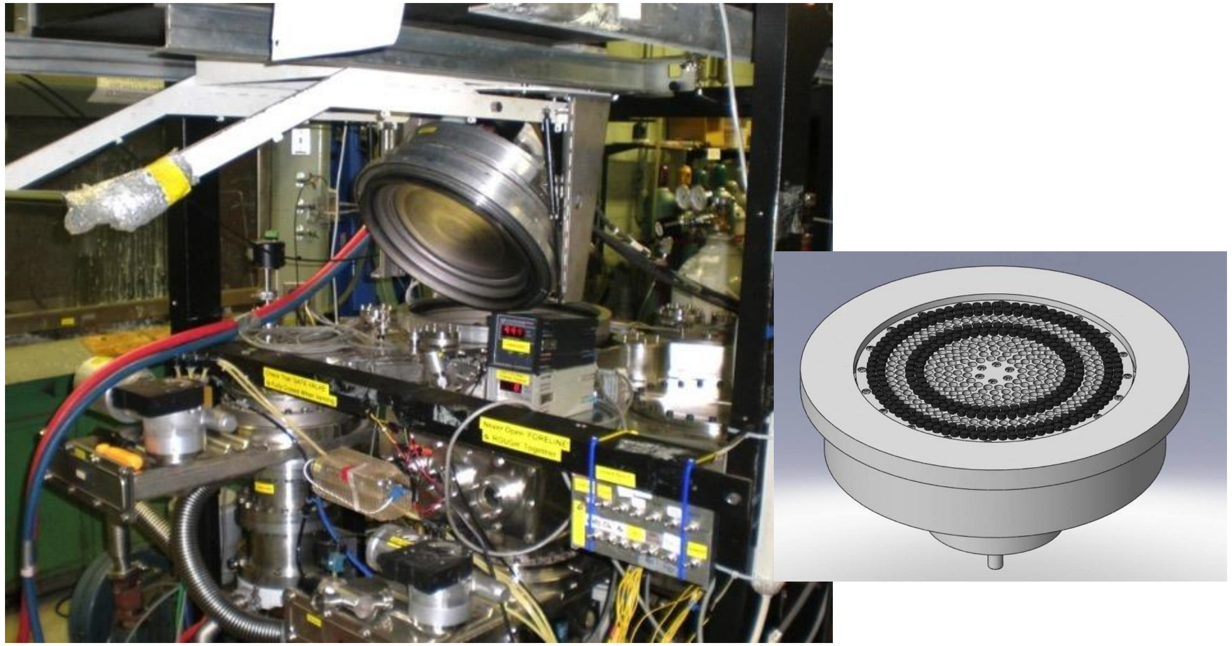


Here is the N-P-N transistor

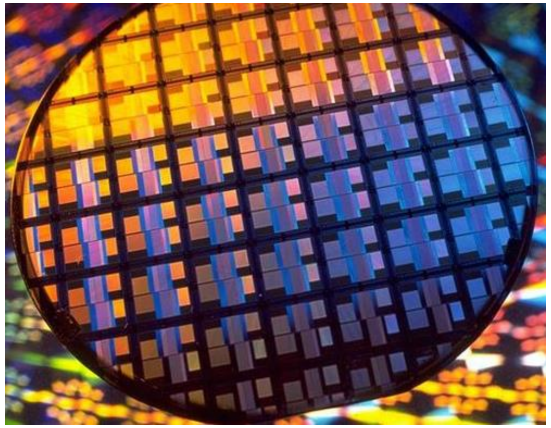
layout, courtesy of International Sematech

With the different plasma techniques now have millions of transistors on a single chip.

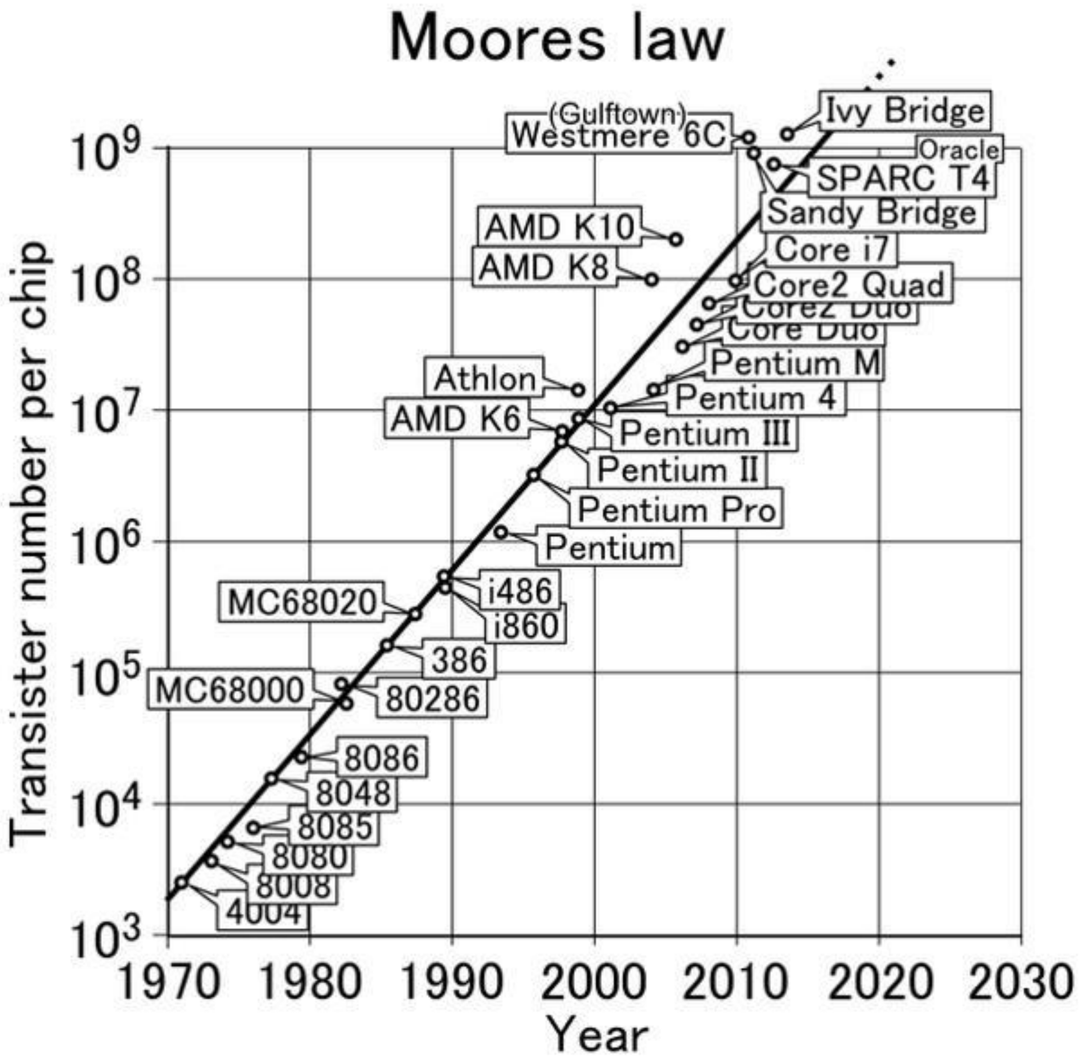
- Spin Coating
- Evaporation
- Physical Vapor Deposition (PVD)
- Chemical Vapor Deposition (CVD)
- Plasma-Enhanced CVD (PECVD)
- Atomic Layer Deposition (ALD)



Each technique has particular uses depending on size of feature and type of material



Moore’s law has pushed chip technology to its physical limits

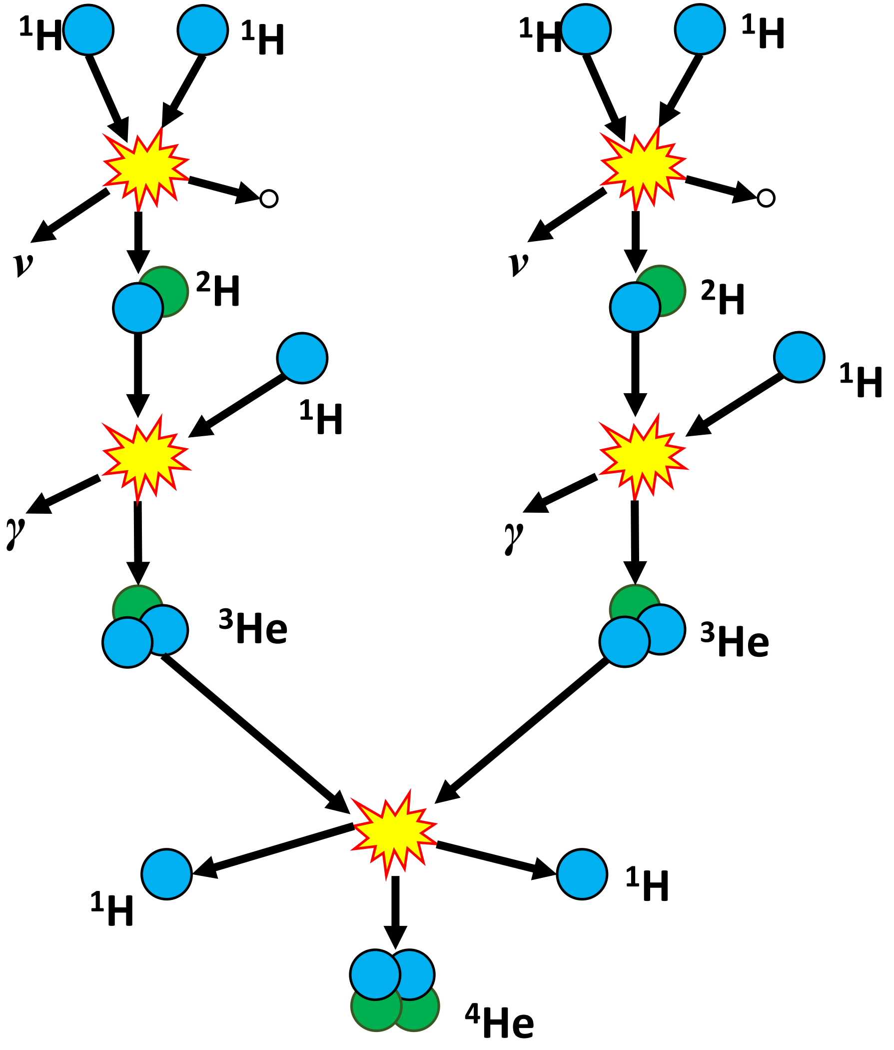


- Moore’s Law: The cost effective number of transistors that can be placed on an integrated circuit will double every two years.
- Emphasis is on *cost effective* implementation, because making a higher transistor count does no good if no one can afford to buy the devices!

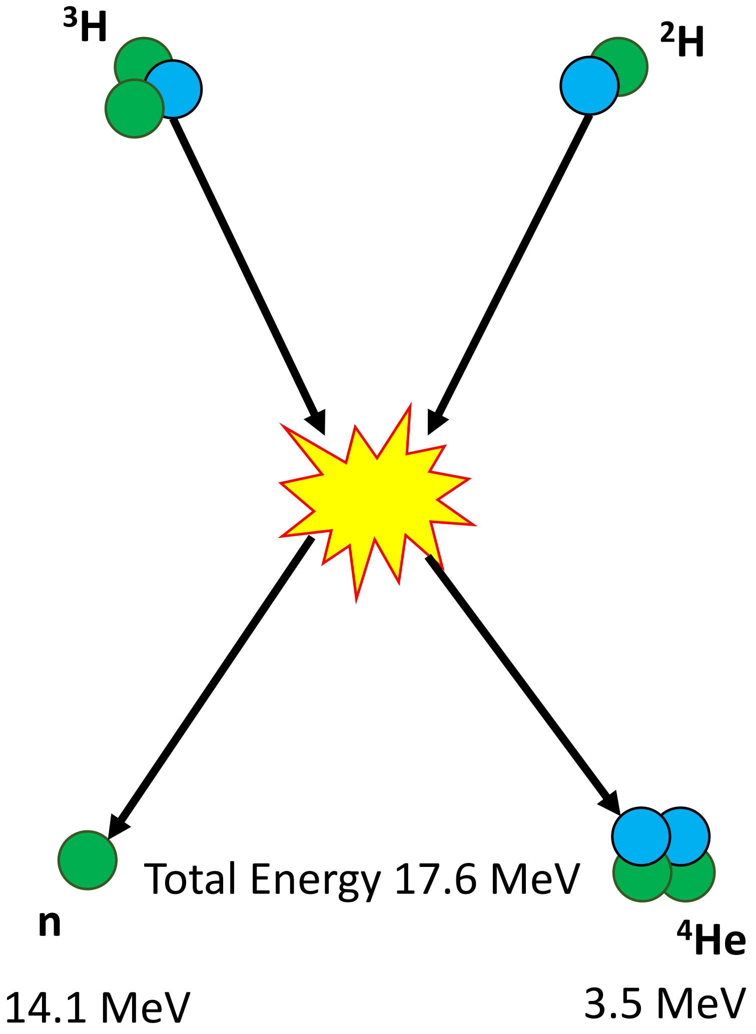
Outline

- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84

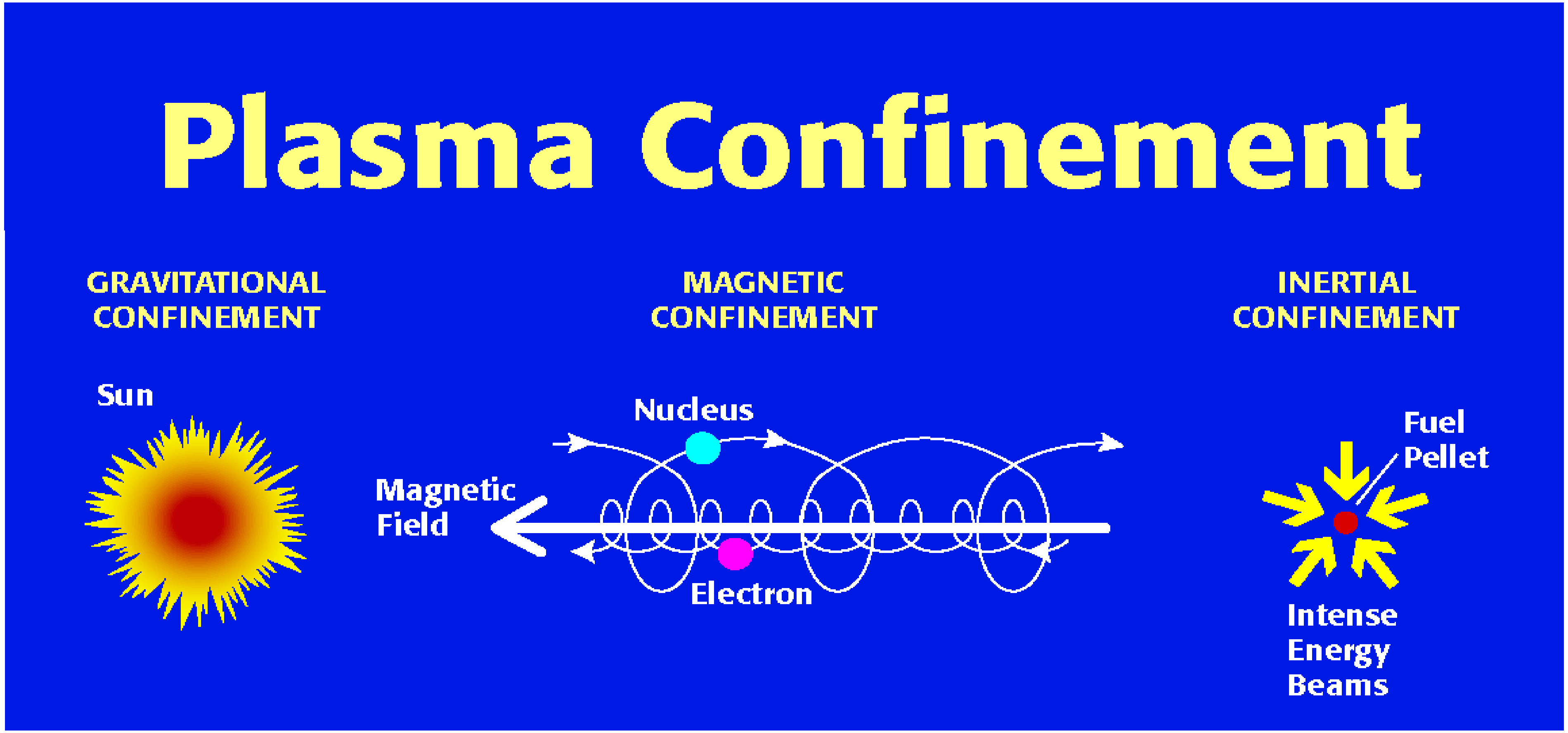
Fusion reactions – how does it impact plasmas



🔵 Proton
🟢 Neutron
○ Positron
ν Neutrino
γ Gamma Ray



Confining a hot fusion plasma

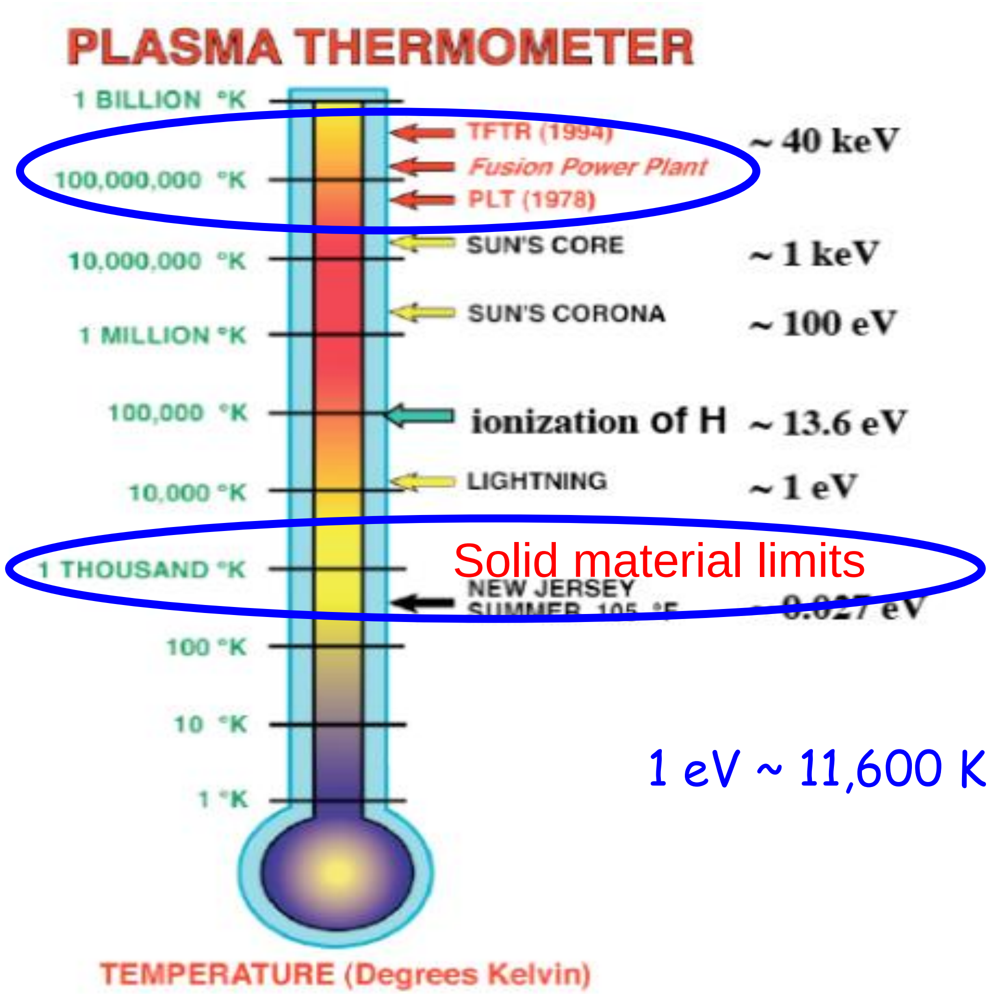


Requires large amounts of masss!

Confines the plasma in the direction across the magnetic field

Energy and defense relevant

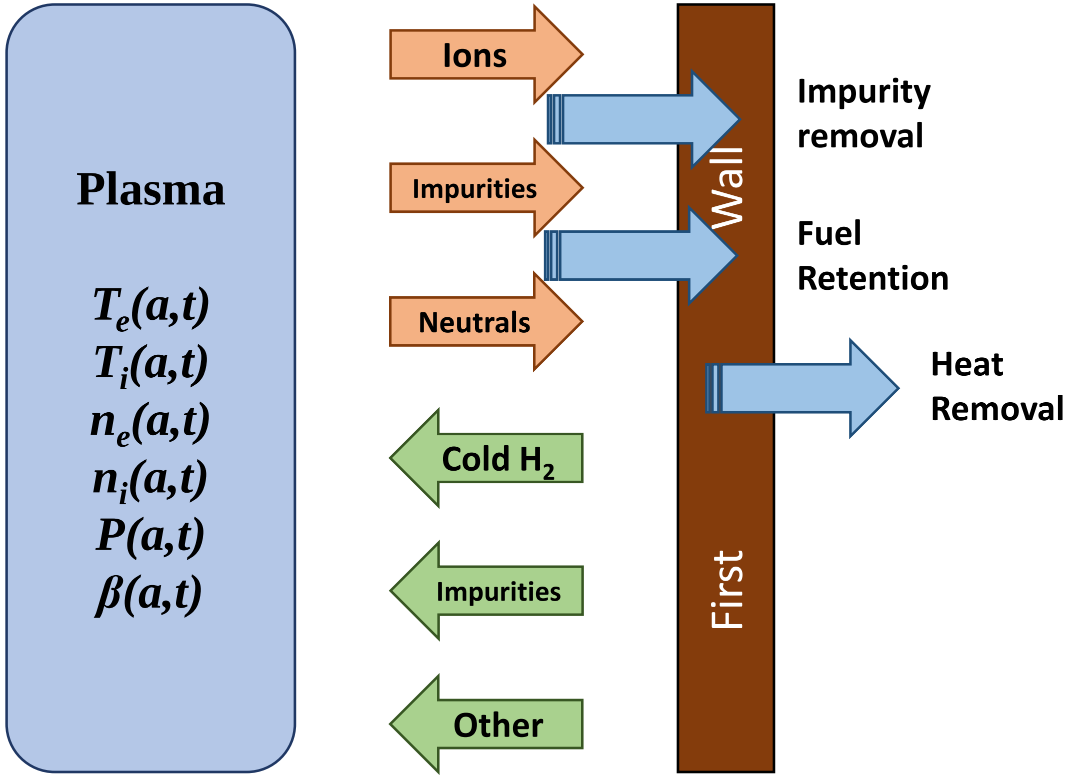
Challenge for fusion: Keeping the core hot and the plasma facing components (PFC) cold



1 eV ~ 11,600 K

Complex behavior of materials and plasmas

- Incident high energy ions and neutral will have a significant impact on the reactor surface
- Damage
  - Displacement of atoms within the lattice structure of the materials
  - Leads to embrittlement
- Surface structure formation
  - Fuzz
  - Blisters and bubbles
  - Fuel retention within the structure
- Recycling
  - Cold hydrogenic species
  - Impurity atoms
  - Secondary electron emission
  - other



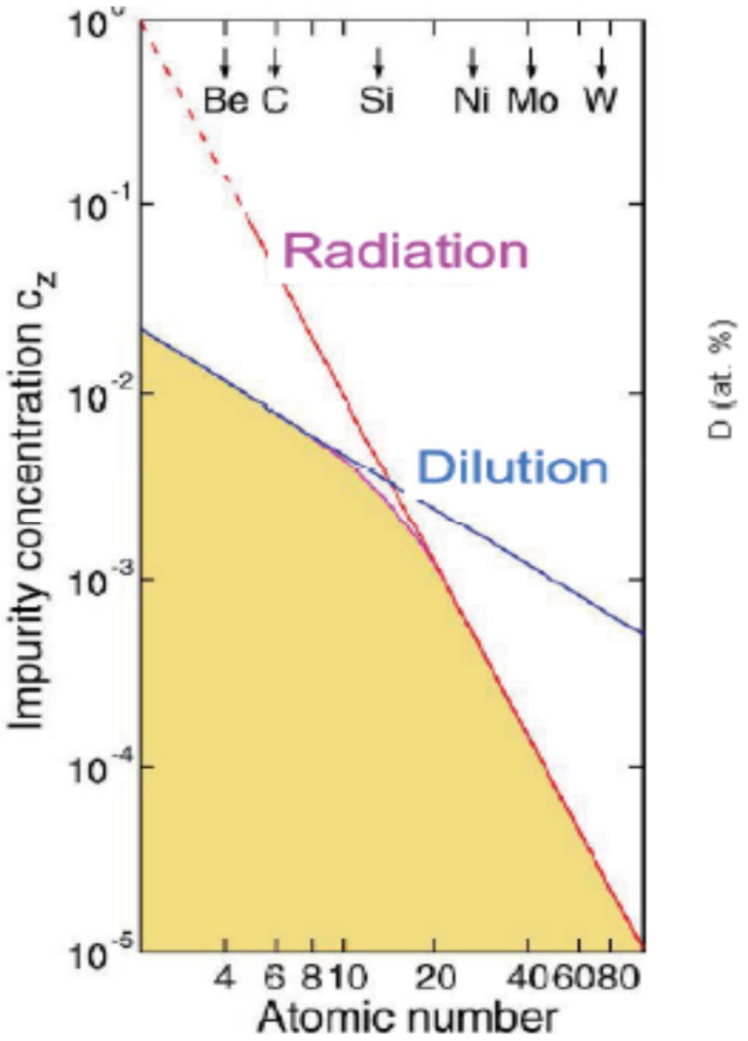
Minimization and control of impurities in the plasma

- There is a maximum level of impurity allowed inside a fusion reactor

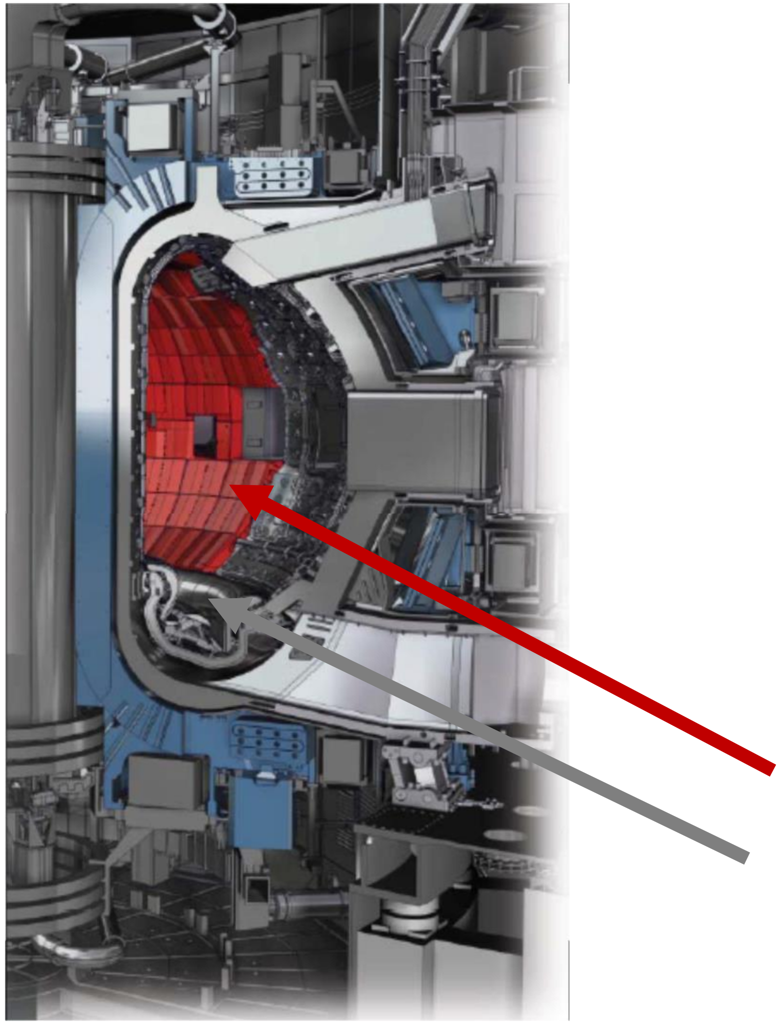
- Tolerances for High-z are much stricter than for low Z

- Anything the plasma touches will almost most definitely end up the fusion reactor and plasma

- So as low-Z as possible is desired



Maximum level of impurities allowed inside a reactor



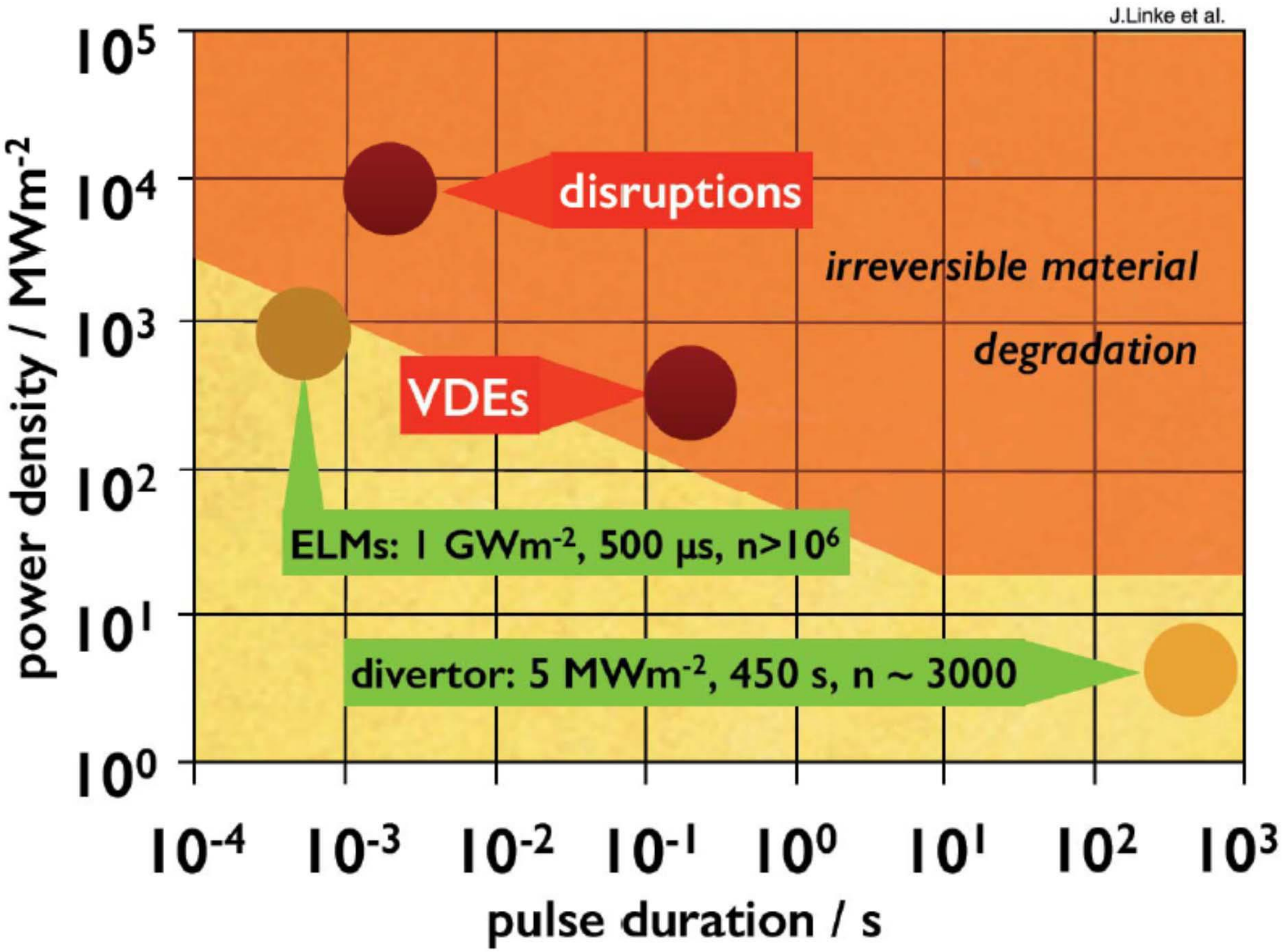
- Fuel Dilution
  - Power from the reactor is proportional to $n_D \times n_T$
  - Density of the electron is fixed:
    - e.g. 1 W atom fully stripped replaces 37 D and 37 T
  - Fusion power goes down from $50 \times 50 = 2500$ to $13 \times 13 = 169$
    - 1% impurity cuts the power by over 90%!
- Energy Loss from radiation
  - Bremsstrahlung radiation ∝ to Z^2
  - Takes a lot of energy to strip off all the electrons
  - Wasted energy

- First wall tiles are **Be**
- The divertor is **W**
  - Scale lengths are so large
  - Any eroded material should not make it back into the core

Heat flux limits - tungsten

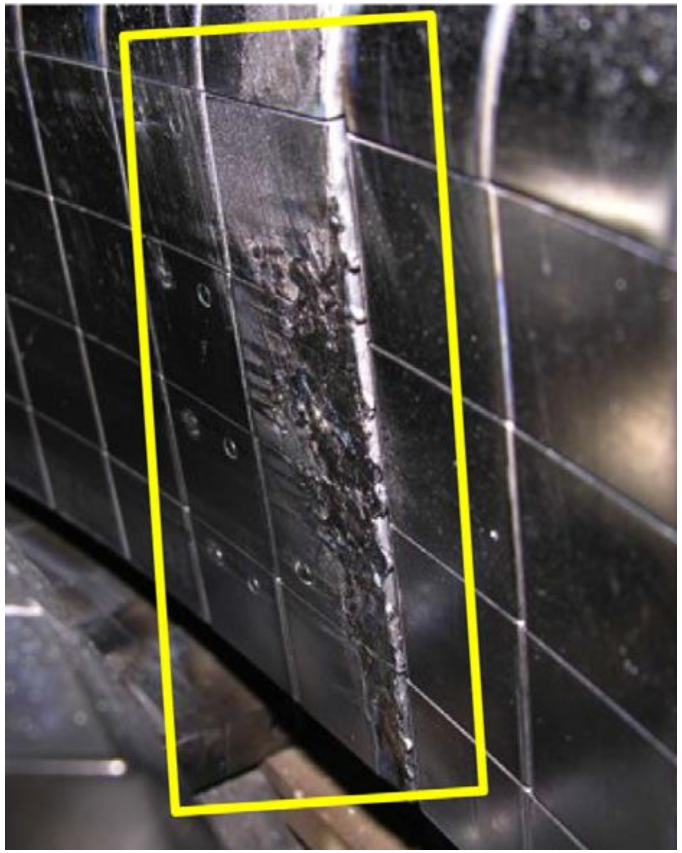
- Plasma stored energy $\propto R^5$
- Energy deposition area on plasma wetted surface $\propto R\lambda_q$
  - As seen earlier, λ_q, will potentially be very small in ITER and larger machines
  - Large uncertainties on wetted area at the transient time
  - Surface temperature rise due to transients:

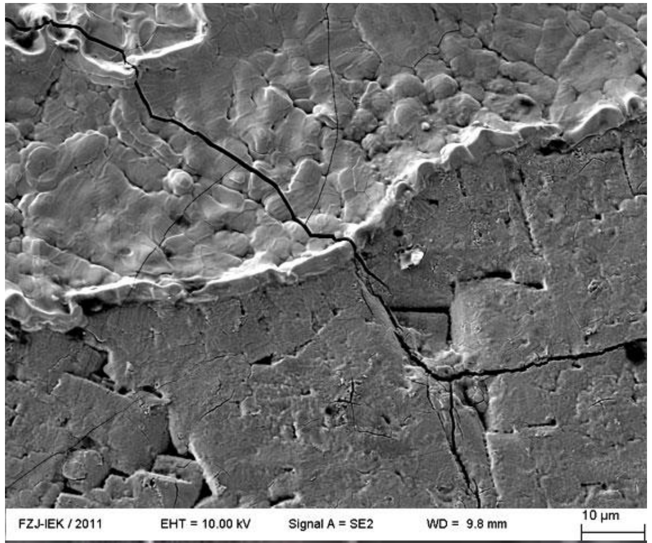
$$\Delta T \propto \frac{E_{trans}}{A_{wet} t^{1/2}}$$



Heat flux is one of the most critical areas for future devices

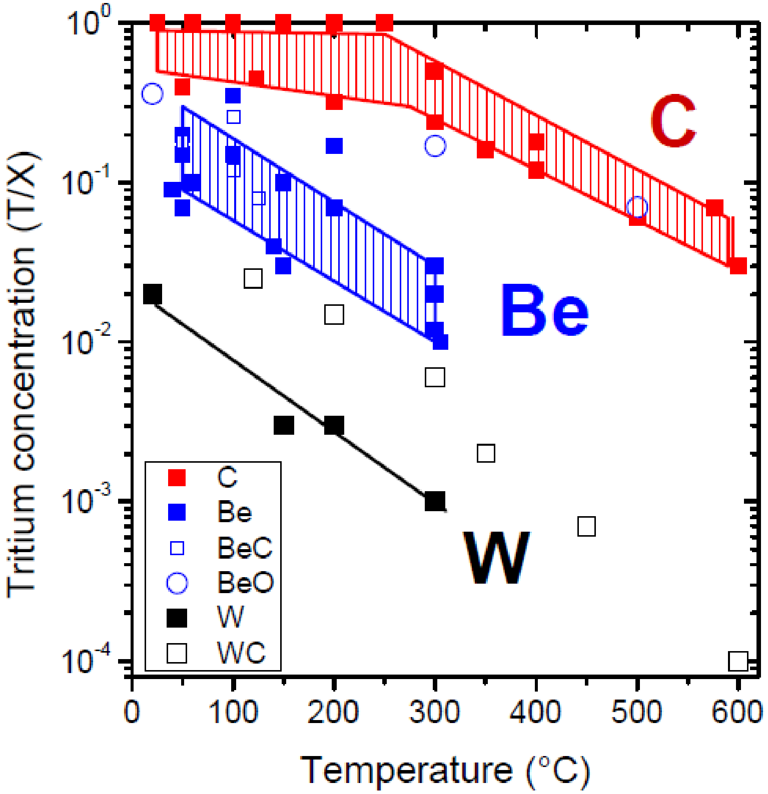
- Need to manage:
  - Stationary heat fluxes at the limit of cooling technology
  - Near complete mitigation of transients
  - Low tritium retention
  - High throughput fuel cycle
  - Material migration and erosion rates on a scale never seen before
- Cracked, arced and melted tungsten
  - Like being in an arc-welder (heat flux 40 MW/m^2)
  - Surface of the Sun, 63 MW/m^2





Tritium (fuel) retention at the surface and boundary

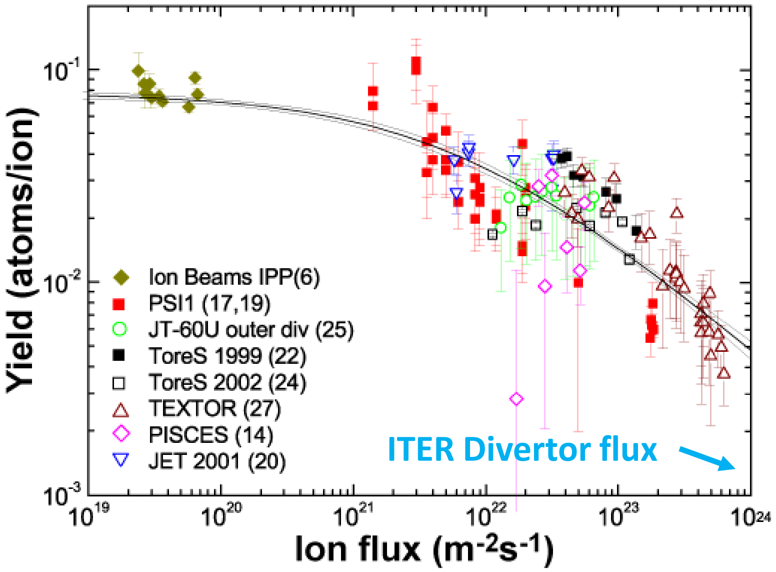
- A 400 s $Q_{DT} = 10$ ITER discharge will require ~100 g of tritium fueling
- Maximum in-vessel mobilisable T in ITER limited to 1kg
  - This is a safety issue
- In practice, administrative limit of ~700 g
  - 120 g in cryopumps
  - 180 g uncertainty
- Predicting the expected retention in ITER is fraught with uncertainty but progress is being made



- For C, complex interplay between erosion → hydrocarbons → dissociation / ionization → transport → re-deposition → migration to remote areas with high sticking coefficients and retention in co-deposits
  - Carbon traps D, T very efficiently
  - D/C ratio can be in the range ~0.4 → > 1
- For Be, co-deposition of T also possible - large potential source of Be from first wall
- For W, most of retention will be from implantation → not thought to constitute a large reservoir
- BUT effects of increased trapping due to neutron irradiation of metals – does not look like an issue from recent results

Cold and Neutral Atoms Coming off the Wall Surface will Interact with the Plasma

Chemical Sputtering



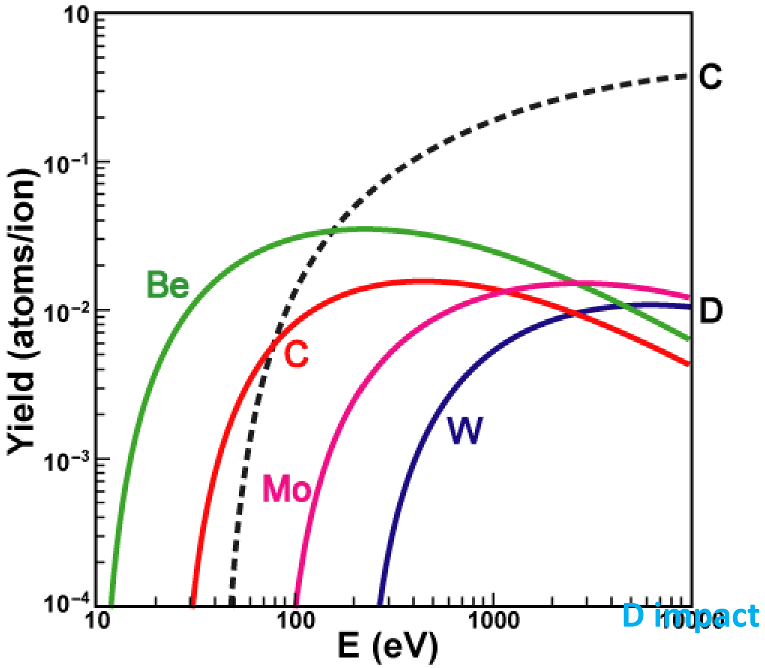
ITER Divertor flux

- Recycling rate

$$R = \frac{\Gamma_{wall\rightarrow plasma}}{\Gamma_{plasma\rightarrow wall}}$$

- Steep pressure gradients
  - Pedastal
- Surfaces will have different sputtering yields
- Higher Z have higher sputtering thresholds
  - Much higher yield for high-Z projectiles
  - Important if using seed gasses

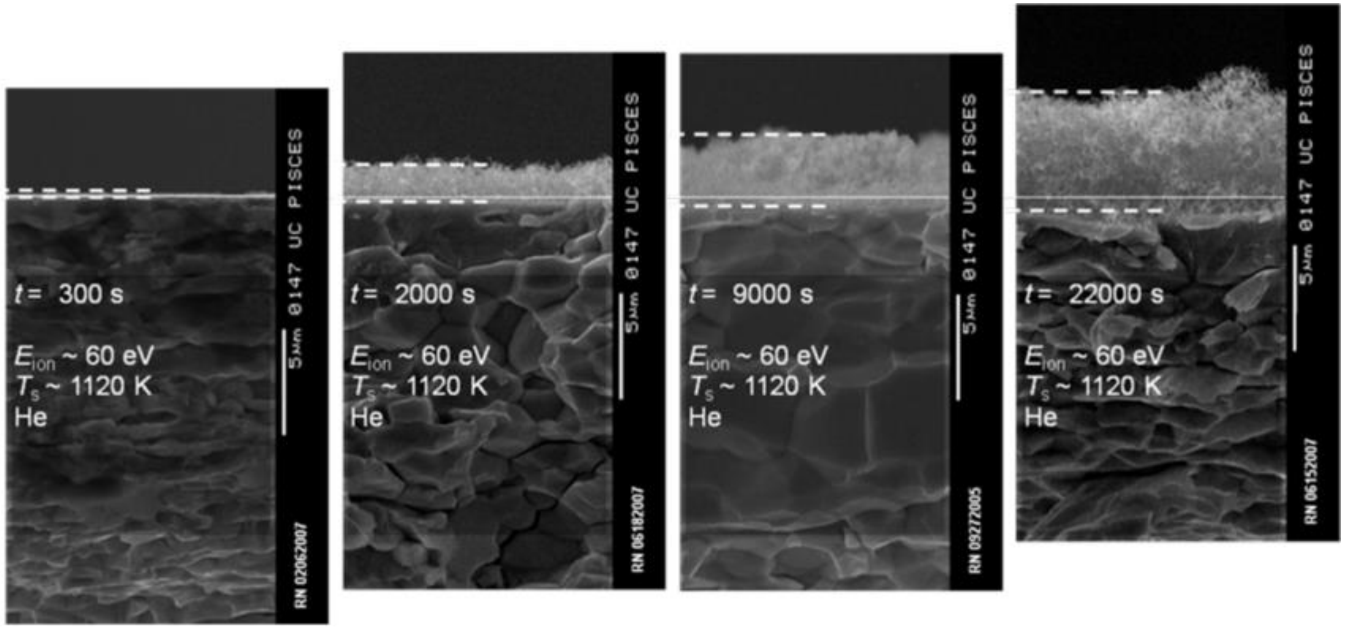
Physical Sputtering



D impact

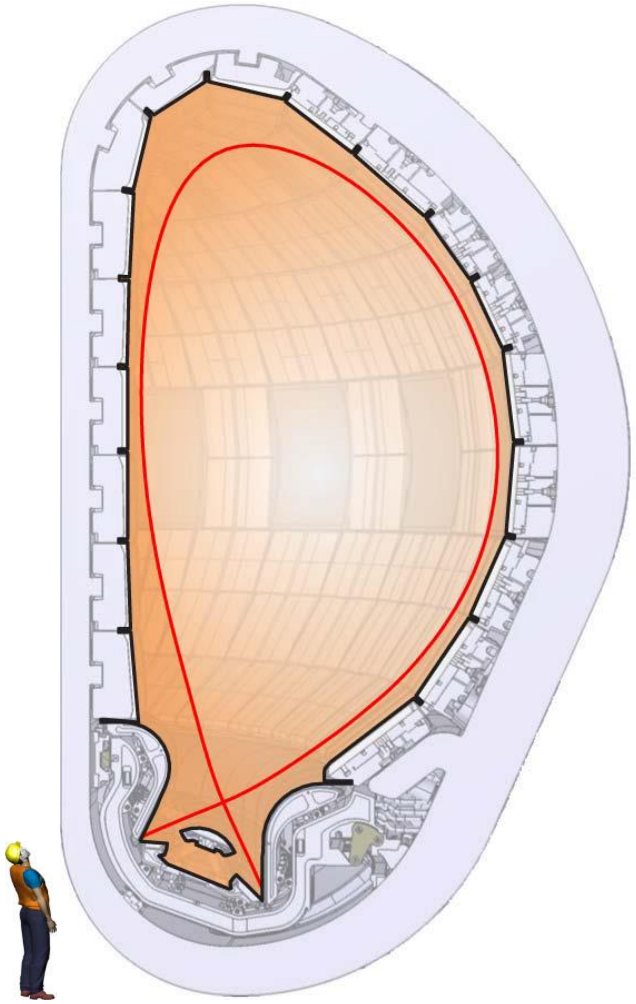
Surface modification can Lead to Dust and Safety Issues

- Hydrogenic species can form blisters and bubbles on a surface
- Tendril Growth/Fuzz with helium exposure
  - Seen not just on W but other metals as well
- Erosion of the fuzz leading to impurities, causing large losses in fusion power.

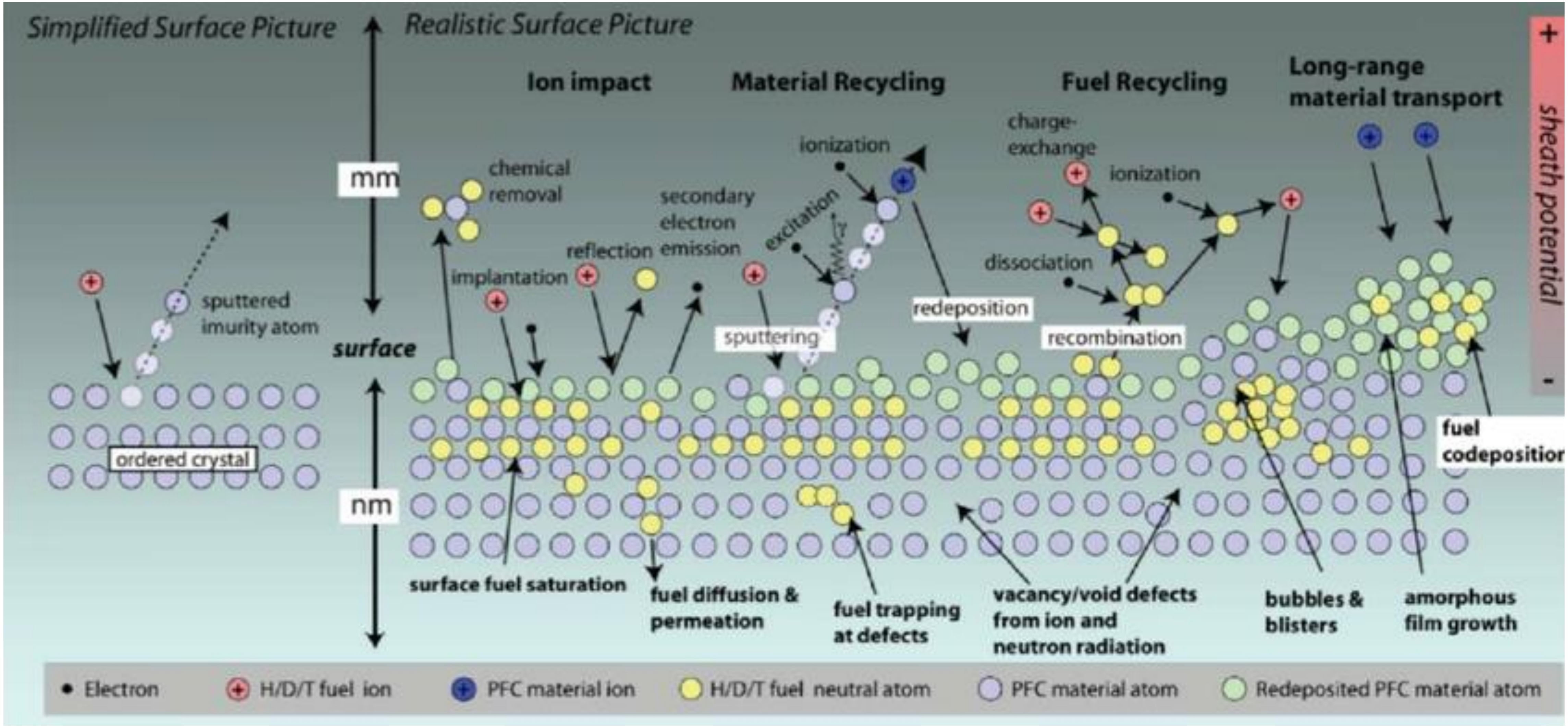


Surface modification can Lead to Dust and Safety Issues

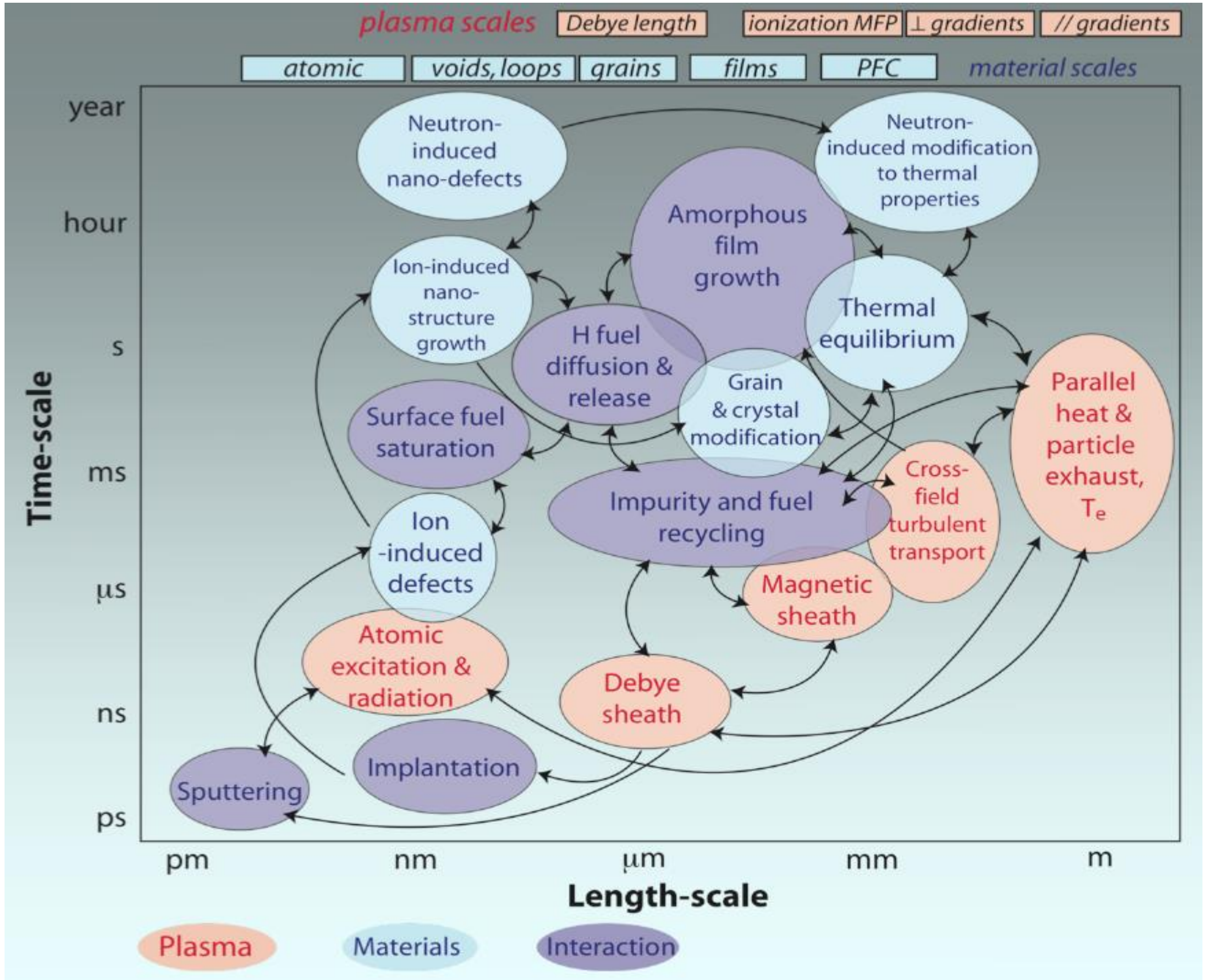
- Expectation is that increase in duty cycle and erosion in ITER will lead to large scale-up in quantity of dust particles produced
- Like T-retention, dust is a safety issue
  - dust particles radioactive (tritium + activated metals)
  - potentially toxic (Be)
  - potentially responsible for a large fraction of in-VV mobilisable tritium
  - chemically reactive with steam or air
- Radiological or toxic hazard depends on how well dust is contained in accident scenarios and whether it is small enough to remain airborne and be respirable
  - size needs to be <~ 100 μm
  - depends on how dust is produced, e.g. crumbling of co-deposited layers or destruction (thermal overload) of tritiated layers during off-normal events
  - tritiated dust can levitate in electric fields as a result of self-charging due to emission of beta electrons



Remember the summary of all these interactions



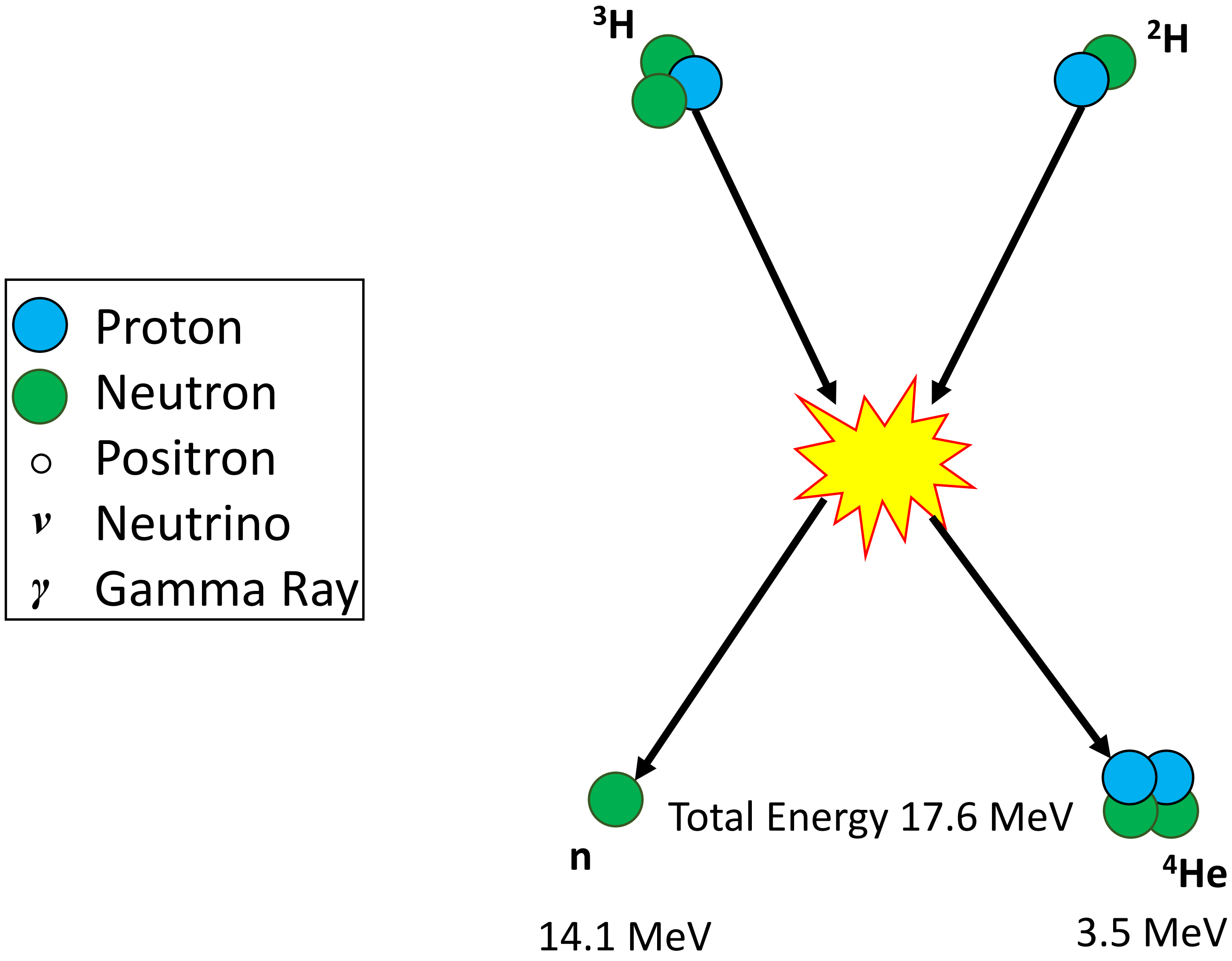
Time and temperature scale makes it even more complex



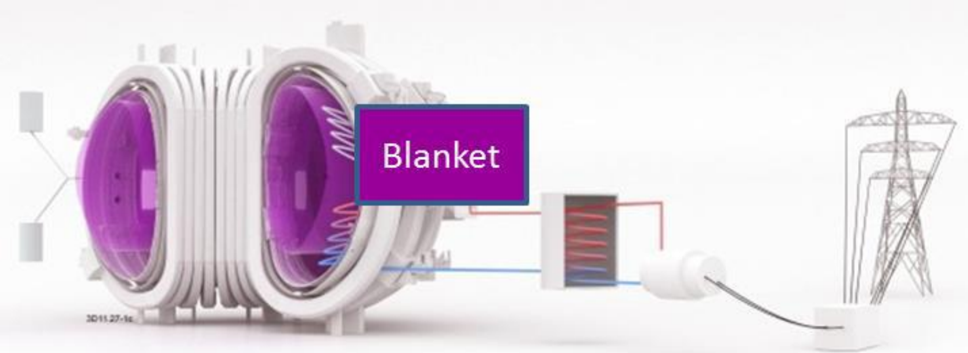
Unidentified flying objects (UFO)

A failure in materials can have spectacular results!

Final note on neutron material interactions



Remember, neutrons will also change materials & surfaces



The D-T fuel reacts inside the fusion reactor

Neutrons that are produced from the fusion reaction are stopped in the blanket.

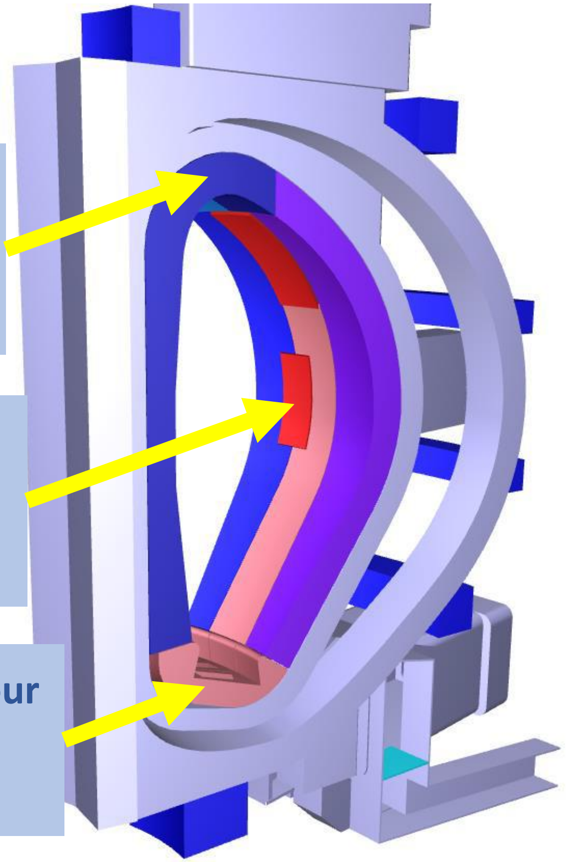
This heats it up and also generates tritium (breeding)

HOWEVER

F. Maviglia ITER School talk, 2019

He/dpa ≤ 1 (fission); > 10 (fusion)

H/dpa = 10 (fission); > 40 (fusion)



Ferritic – Martensitic Steel Li – ceramic or LiPb (breeder)

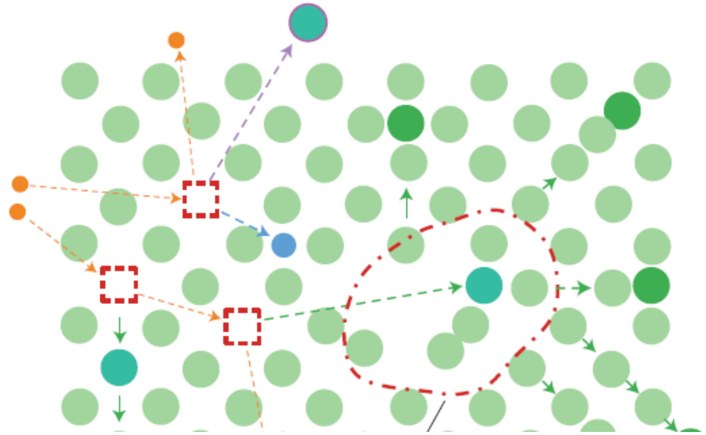
Tungsten – Carbon – stainless steel – (Plasma facing components)

Tungsten armour - copper alloys (heat sink)

n-damage in materials
- Creates disorder
- Vacancies
- Transmutations
- helium

Severity of damage measured by dpa (displacement per atom)
- **ITER ~1 dpa**
- **DEMO 20-50 dpa**

This damage is studied in irradiation experiments in material testing reactors



If the plasma is liquifying solid metals… lets start off with a liquid metal!

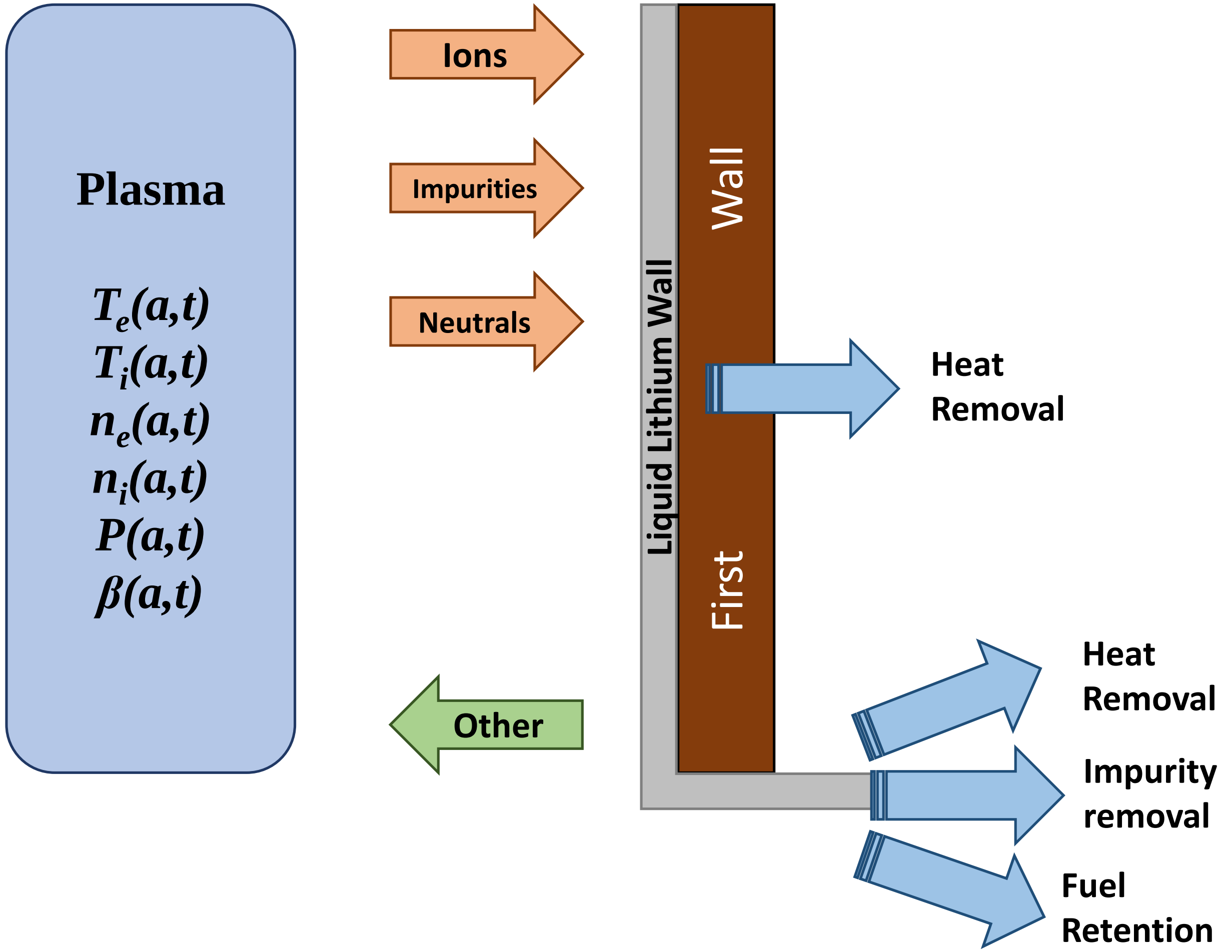
- ELM’s, VDE’s and other instabilities will eventually turn any surface into a liquid metal

- So why not start out with a liquid metal from the get go

- Several options to look at:
  - **Lithium**
  - Tin
  - Gallium
  - Tin-Lithium

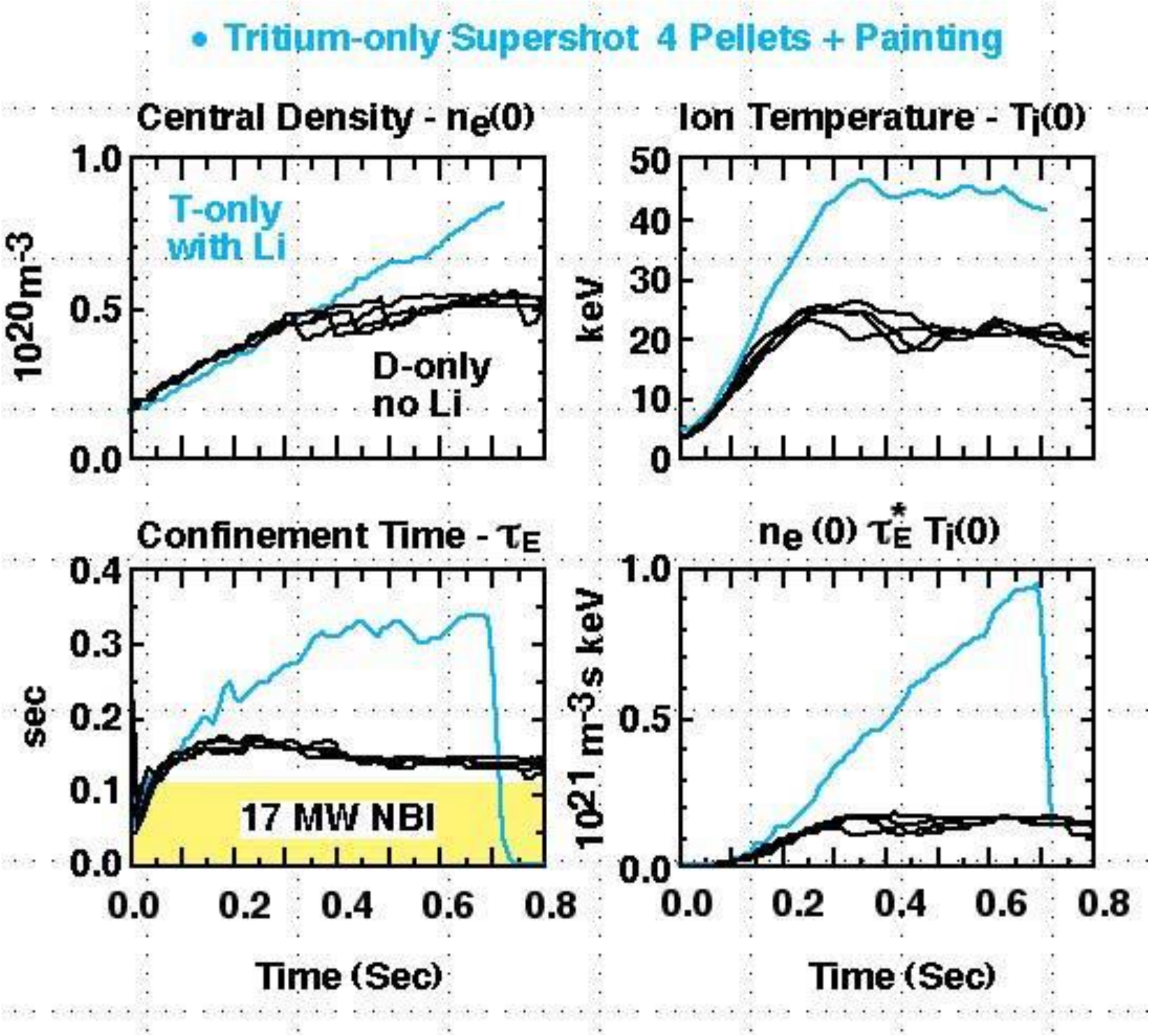
Complex behavior of materials – liquid metals

- As low-Z as possible:
  - Minimise power losses by reducing high-Z impurities entering the core.
- High affinity for ionised fuel species:
  - Mitigates instabilities and eliminates ELMs, Increases cross-sectional T_i while reducing particle wall flux.
- Constantly refreshing:
  - Removes impurities and products (if flows outside chamber) + minimises erosion
- Stable flow
  - Need to avoid any dry out or lack of wetting
  - Damage to the substructure
- Neutron tolerant



Liquid lithium has Become the more Studied Liquid Metal for Fusion

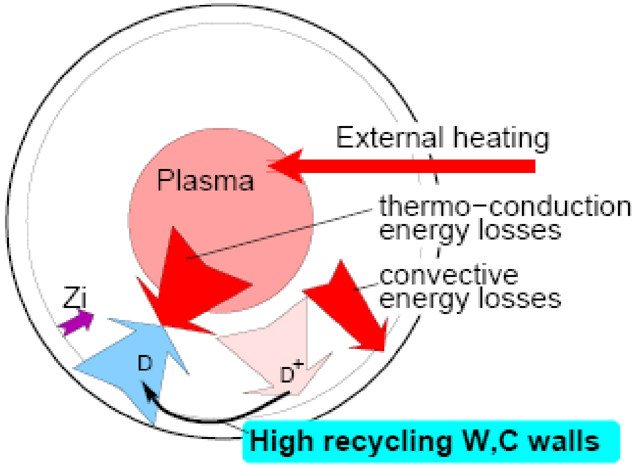
- First evidence for lithium were the TFTR super shots in 1994!
- Low Z
- Tends to stay in the edge
- Can be used for instability control
- Not to say that it has its own issues and challenges

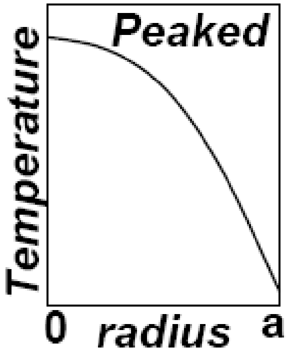


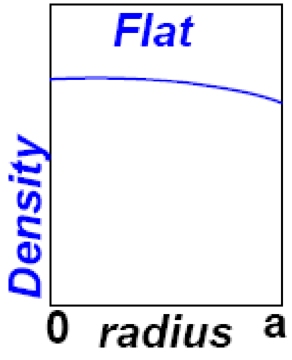
What Low recycling does for fusion – Lithium Wall Fusion (LiW)

- No cold hydrogen returns from the wall – Plasma stays hot

- Standard case





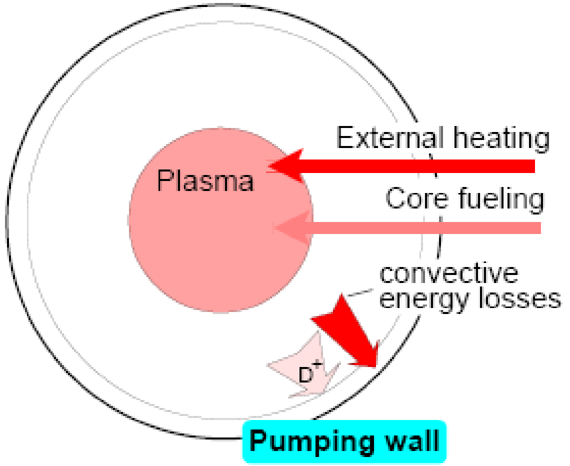


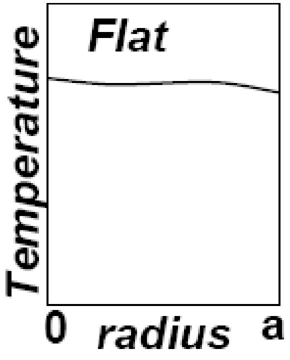
Plasma Physics and alpha heating get ion and electron temperature gradient turbulent transport for stability

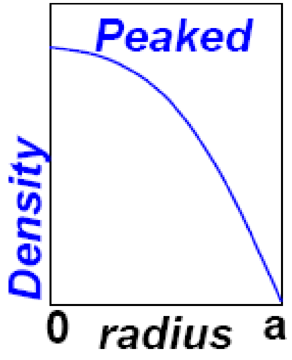
Bad core and edge stability (sawteeth, ELMs etc…)

Most of the plasma volume does not produce fusion

- Lithium case:
  - The radius needed is only 1/3
  - Volume, and the cost of fusion power reduced
  - Factor ~ 27!





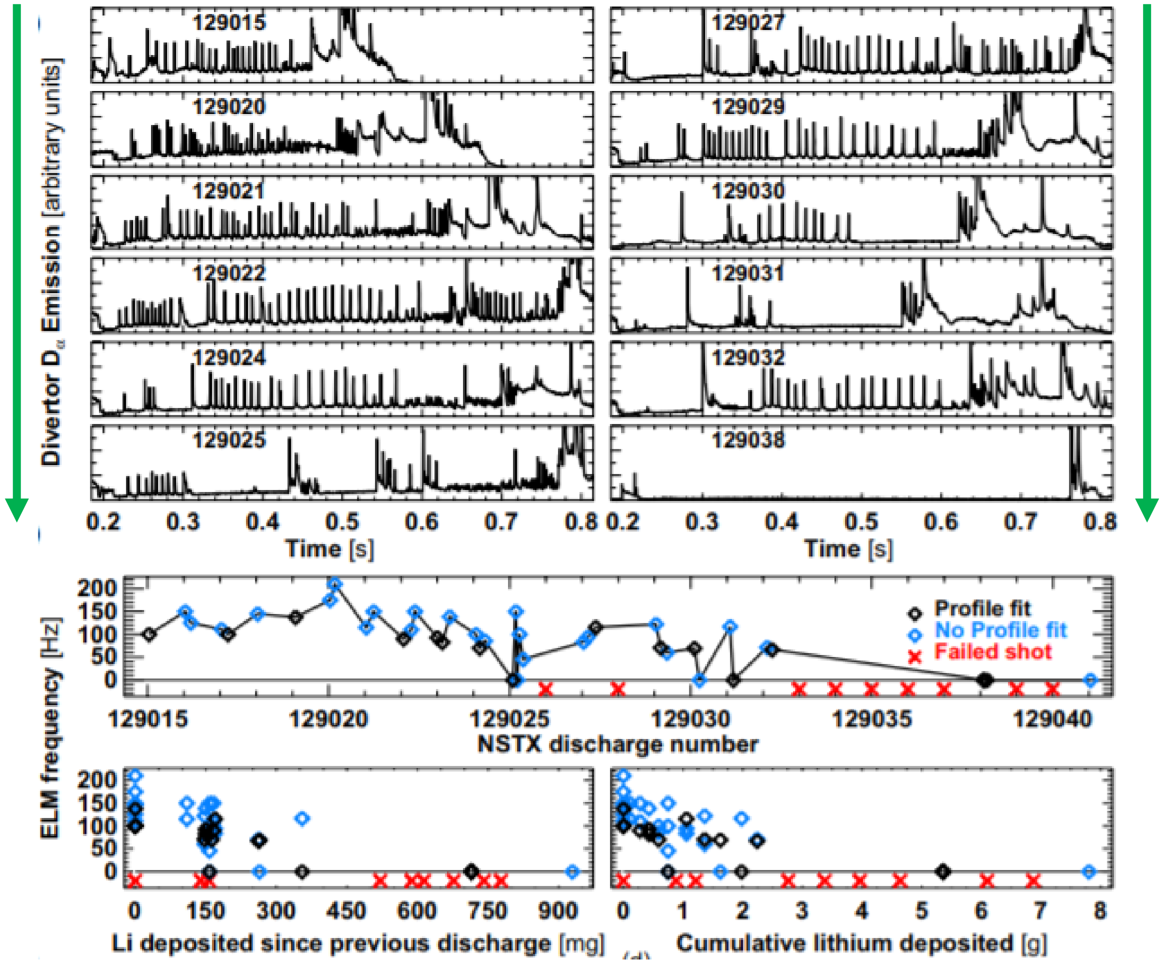


Nothing from the physics expected or accepted

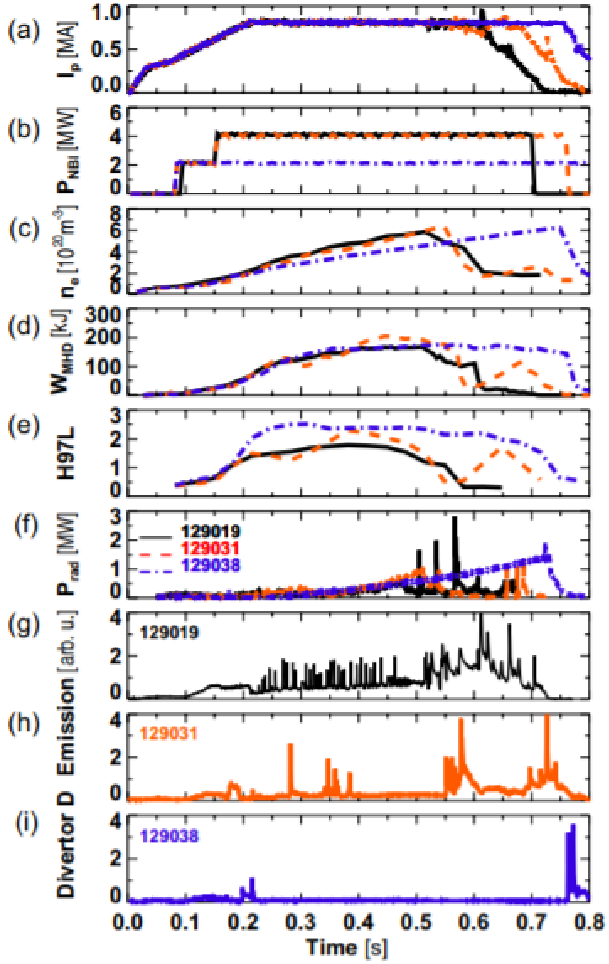
Stability is excellent, no instabilities, external control

The whole plasma volume produces fusion

Lithium coatings reduce the D recycling, reduces H-mode power threshold, broadens T_e profile, reduces electron thermal diffusivity, improves confinement and ELM Suppression



Increasing Lithium
Up to 600 mg



– **No Li**

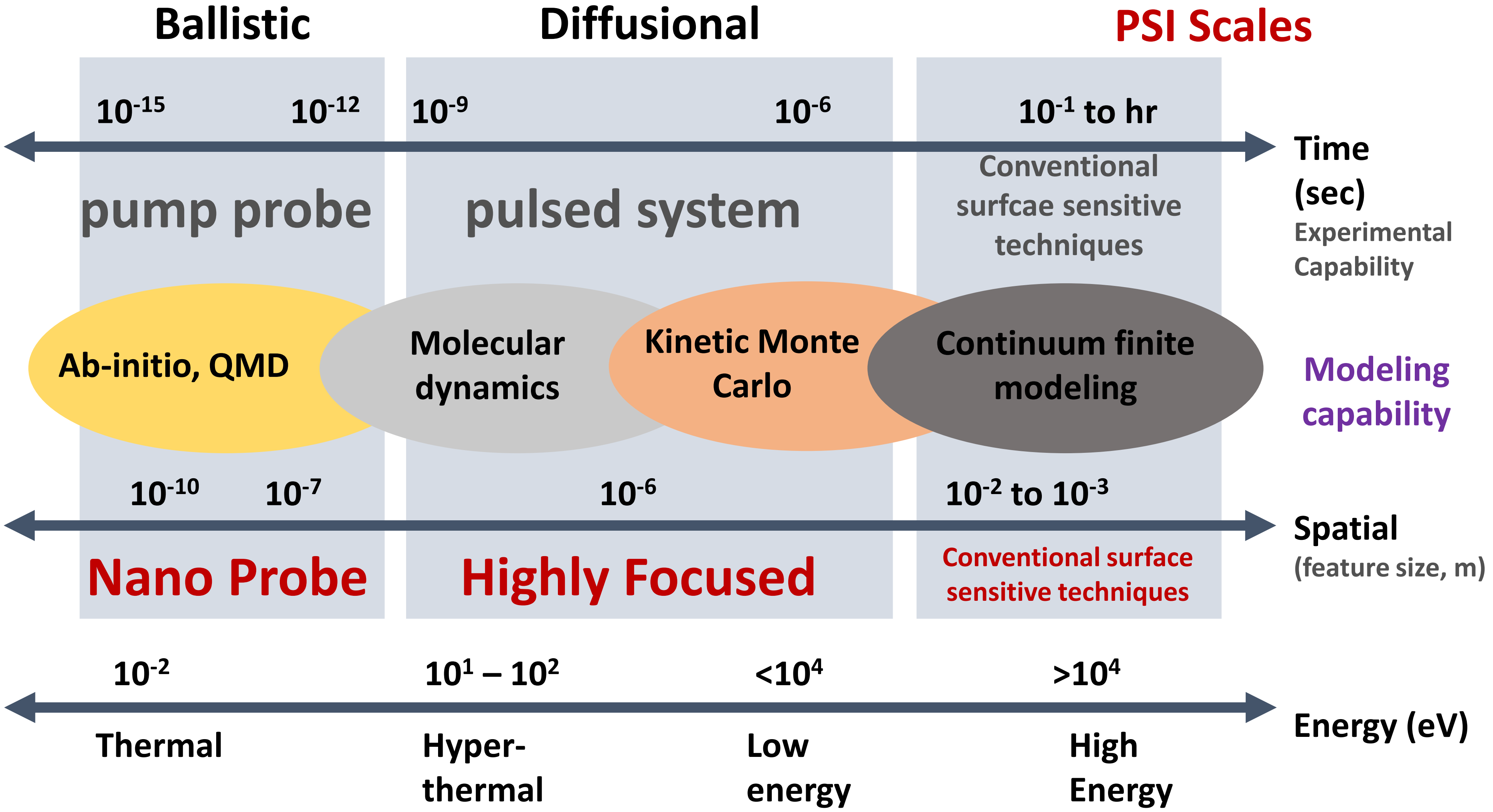
– **Medium Li coating**

– **Thick Li coating**

Outline

- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84

PMI experiment and theory



Ballistic **Diffusional** **PSI Scales**

10^{-15} 10^{-12} 10^{-9} 10^{-6} 10^{-1} to hr

Time (sec)

pump probe

pulsed system

Conventional surfcae sensitive techniques

Experimental Capability

Ab-initio, QMD

Molecular dynamics

Kinetic Monte Carlo

Continuum finite modeling

Modeling capability

10^{-10} 10^{-7} 10^{-6} 10^{-2} to 10^{-3}

Spatial (feature size, m)

Nano Probe

Highly Focused

Conventional surface sensitive techniques

10^{-2} $10^{1} – 10^{2}$ $<10^{4}$ $>10^{4}$

Energy (eV)

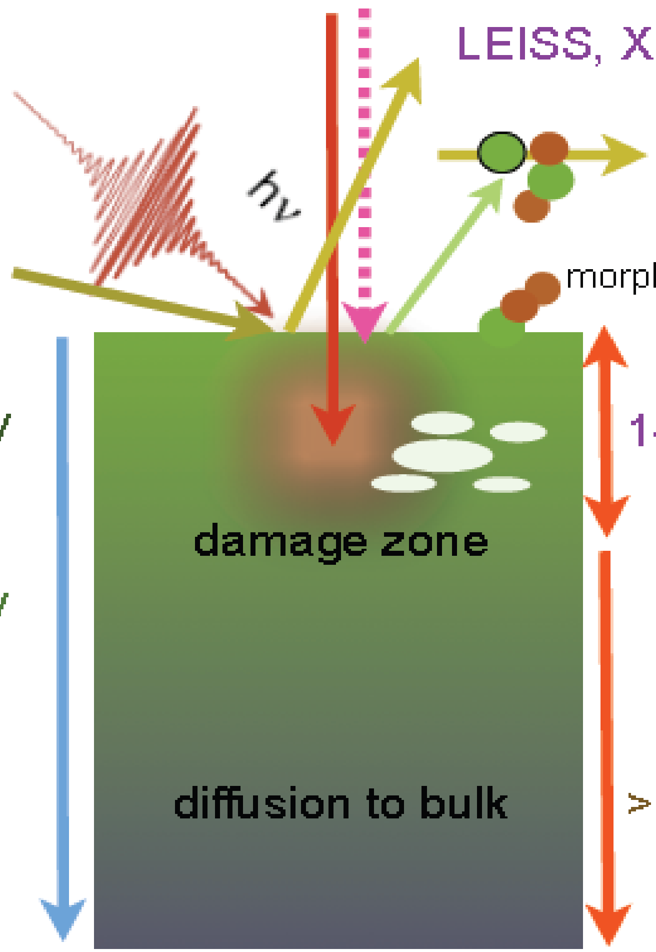
Thermal

Hyper-thermal

Low energy

High Energy

Plasma material interface diagnostics



Computational Modeling

Synergistic radiation sources (e.g. ion *and* atom)

Experimental Techniques

Ab-initio, MD, QMD

LEISS, XPS, UPS, HR-EELS, SANS

PI-SNMS, vis spec, QCM, mass spectrometry

morphology, phase transformations

Surface Techniques

energy

1-100 eV

> 100 eV

Bulk Techniques

> 1 keV

Ab-initio, MD, QMD
(bulk damage zone)

spatial

1-50 nm

Surface Techniques

Bulk Techniques

> 50 nm

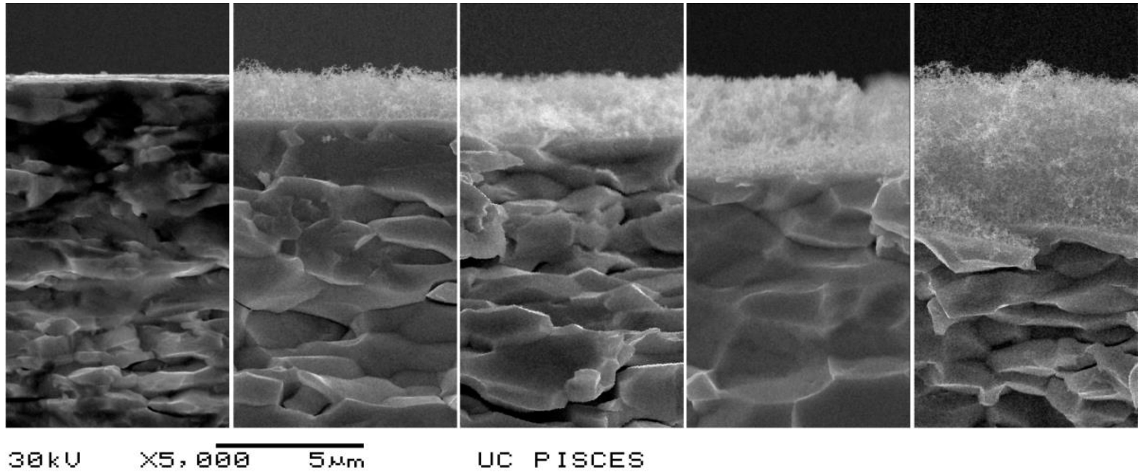
RBS, ERD, IBA, XRF, XRD

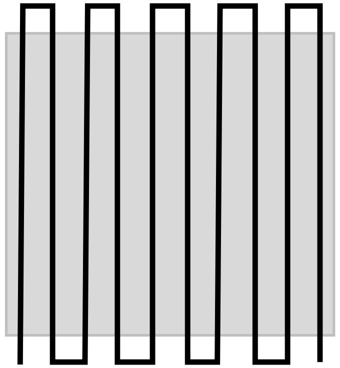
Surface diagnostics

- Scanning Electron Microscope (SEM)
- Auger Electron Microscope (AEM)
- X-ray Photon Spectroscopy (XPS)
- Low Energy Ion Scattering Spectroscopy (LEISS) and Direct Recoil Spectroscopy (DRS)
- Thermal Desorption Spectroscopy (TDS)
- Laser Induced Breakdown Spectroscopy (LIBS)

Scanning electron microscope (SEM)

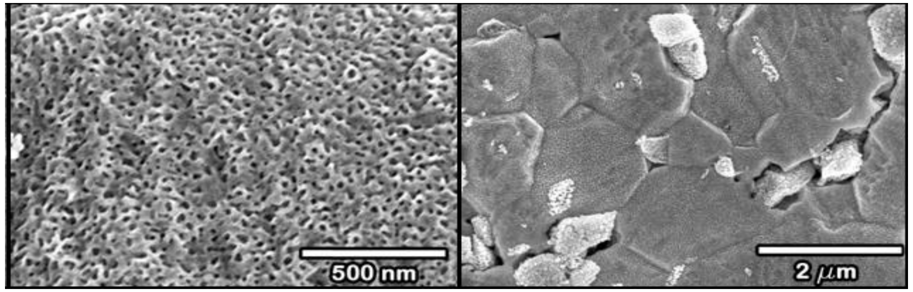
- SEM is a type of electron microscope
  - Scans a focused beam of electrons over a surface
  - Electrons interact with atoms
  - Various signals produces that are detected
- A topographical and compositional map of the surface is generated
  - Raster pattern used
  - Beam position with detected signal used to build up the image
- Excellent resolution, better than 1 nm.





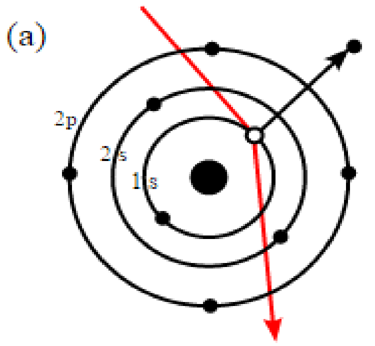
Left: Raster Pattern scans up and down the sample building up the image.

Bottom: SEM with an opened sample chamber

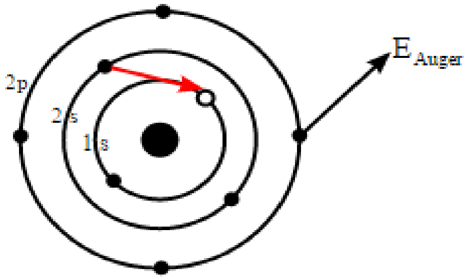


Auger electron spectroscopy (AES)

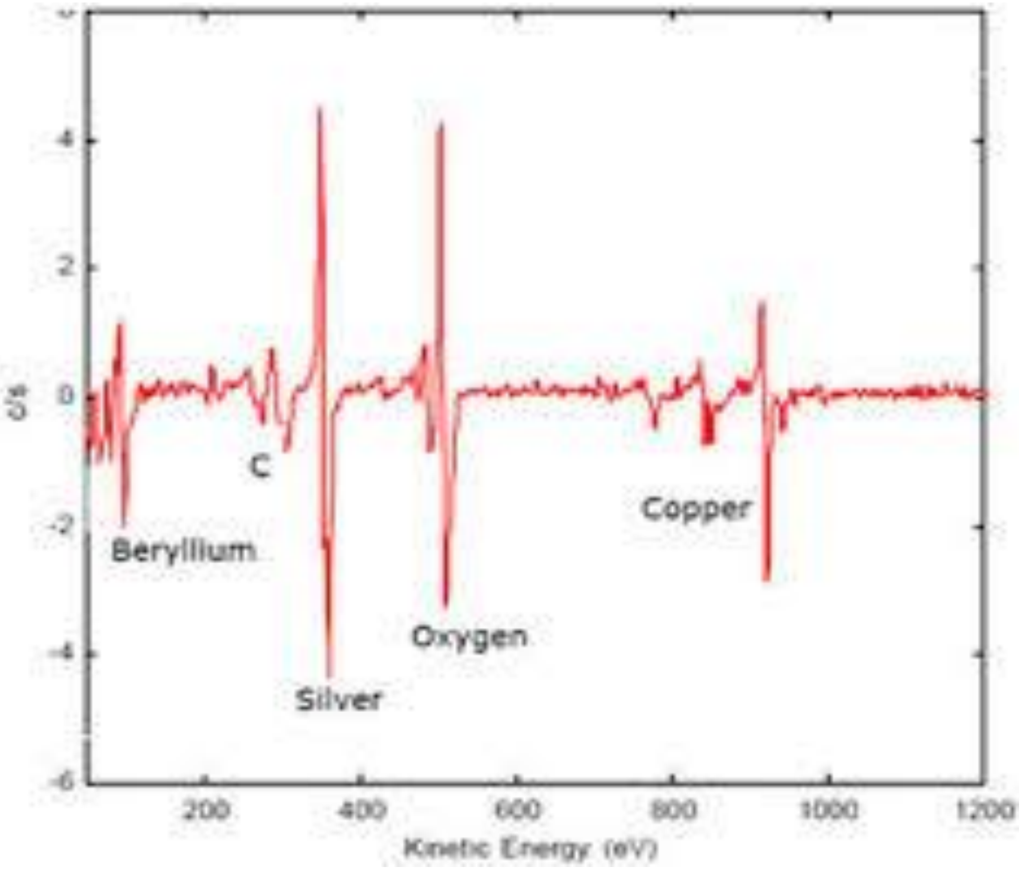
- This is a surface sensitive analytical technique used to determine the elemental compositions of materials.
  - Can be used to potentially get the chemical state of surface atoms too.
- The information depth for Auger analysis is the top 2-20 atomic layers.
- When an atom is probed by a photon or electrons with energies of several eV → 50 keV
  - Core electron removed leaving behind a hole.
  - Unstable state, the core hole can filled by an outer shell electron
- Electron moving to the lower energy level loses an amount of energy equal to the difference in orbital energies.
  - The transition energy coupled to a second outer shell electron
  - emitted from atom if the transferred energy is greater than the orbital binding energy.



Electron collision

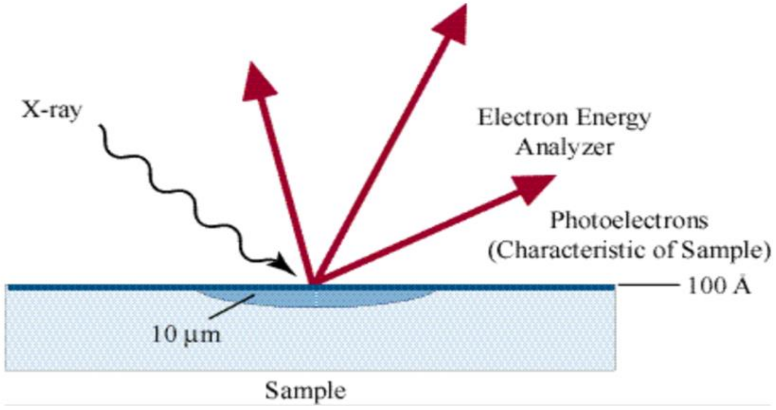


Auger electron emission



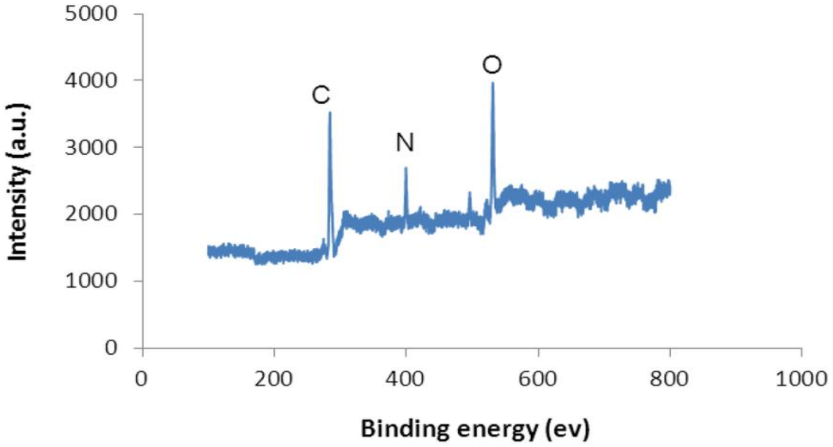
X-ray photon spectroscopy (XPS)

- XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material
- As-received state, or after some treatment
  - for example: fracturing
  - cutting or scraping in air
  - UHV to expose the bulk chemistry
- XPS is used to measure:
  - elemental composition of the surface (top 0–10 nm usually)
  - Empirical formula of pure materials
  - elements that contaminate a surface
  - chemical or electronic state of each element in the surface
  - uniformity of elemental composition across the top surface (or line profiling or mapping)
  - uniformity of elemental composition as a function of ion beam etching (or depth profiling)



$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$

- $E_{binding}$, is the binding energy of the electron, E_{photon}, is the energy of the X-ray, $E_{kinetic}$, is the kinetic energy of the electron as measured and, ϕ, is the work function.



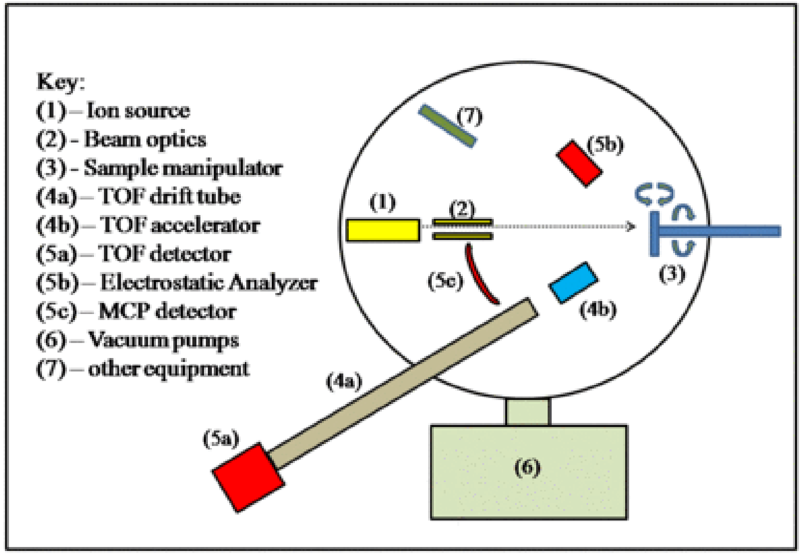
Low energy ion scattering spectroscopy (LEISS) and direct recoil spectroscopy (DRS)

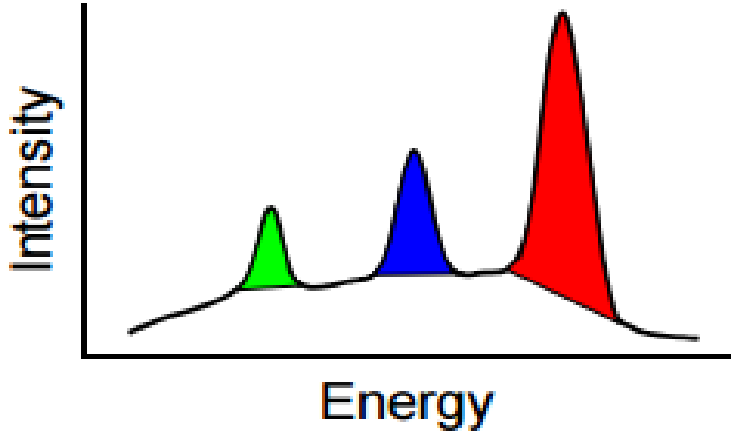
- Sometimes referred to as ion scattering spectroscopy (ISS),
  - Surface sensitive analytical technique
  - Characterises chemical and structural make up of a material

- Directs a beam of ions at a surface
  - Makes observations of the ions that interact with the surface.
  - Can detect metal impurities and sputtered .
  - He, Ne, Ar typically used

- Sensitive to first surface layer of a material

- Under the right conditions
  - Direct Recoil Spectroscopy (DRS)
  - Sensitive to hydrogen and deuterium that is on the surface

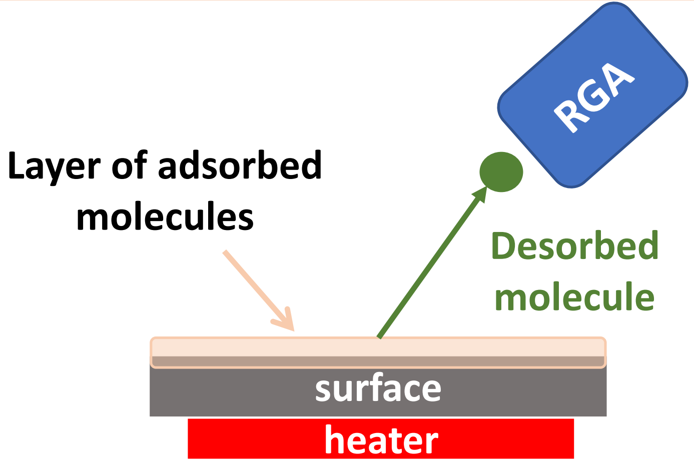


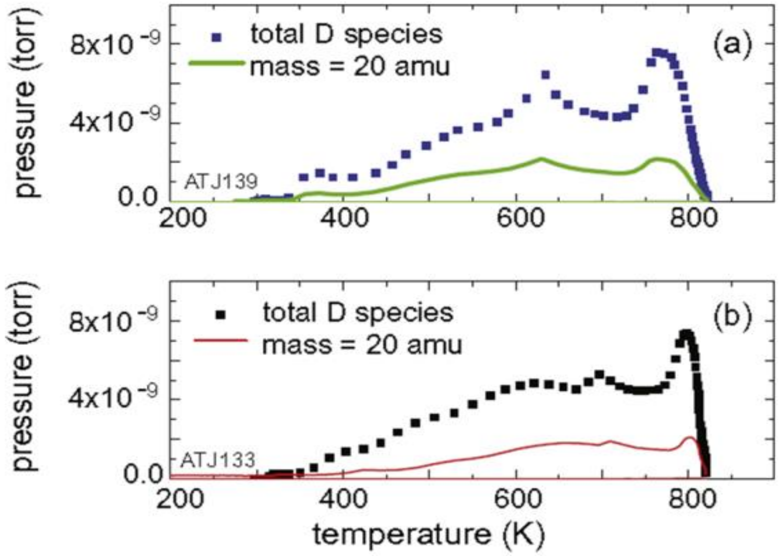


The energy after a collision with a heavy atom is high (red) while with a light atom is low (green).

Thermal desorption spectroscopy (TDS)

- Also known as temperature programmed desorption (TPD).
  - Observing of desorbed atoms/molecules from the surface when the temperature is increased.
  - Not really a spectroscopy technique hence why some like to use TPD.
- When molecules or atoms come in contact with a surface the absorb onto it forming a bond with the surface.
- Binding energy varies with the adsorbed molecule and surface combination.
  - Surface is heated, at a point, the energy transferred to the adsorbed species will cause it to desorb.
  - Temperature which happens is known as the desorption temperature.
- TDS shows information on the binding energy.
- Typically a RGA or a QMS or TOF mass spectrometer used to detect the adsorbed molecules/atoms.



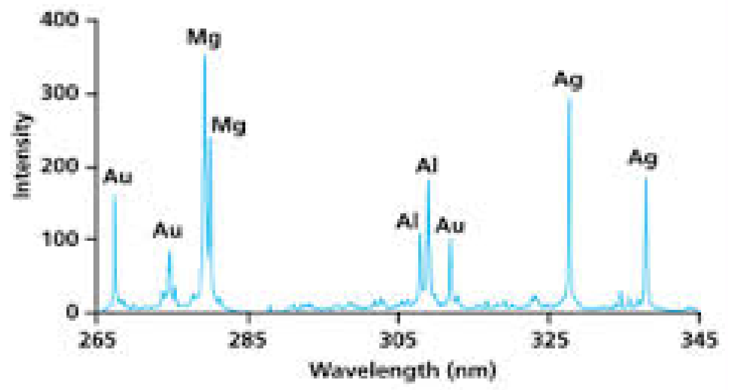


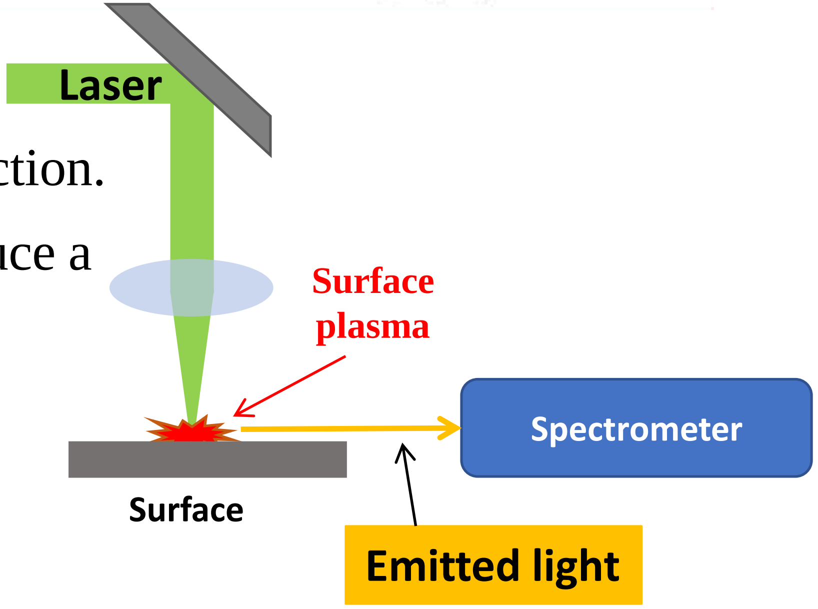
C. H. Skinner, JNM 2011

TDS of ATJ graphite exposed via MAPP in NSTX. (a) without lithium and (b) with lithium.

Laser induced breakdown spectroscopy (LIBS)

- Type of atomic emission spectroscopy.
  - Energetic laser pulse as the excitation source.
  - Focused to form a plasma
  - Atomizes and excites atoms/molecules from the surface.
- In principle does not discriminate to the state of matter
  - Solid, liquid and gas
- Can detect all elements
  - Limited by the power of the laser.
- Destructive technique, however such a small amount used – minimal destruction.
- Uses a focused laser beam from a high power pulsed Nd:YAG laser to produce a "plume" at the surface.
- Temperature can reach around 5,000 – 20,000 K
  - Breaks down into atomic and ionic species
  - Excited state
- Safer than portable X-ray fluorescence since no ionizing radiation.





Outline

- Introduction 3
  - Basics of plasma material interactions 7
  - Low temperature plasma material interactions 28
  - High temperature plasma material interactions 50
  - Plasma surface diagnostics 74
- Summary 84

Summary

- The intimate play between plasma – material interactions is critical to the understanding how we can control material deposition
  - Low temperature / plasma processing – manufacture and surface modification
  - Fusion plasmas – Plasma control and survivability of plasma facing surfaces
- Many mechanisms of particles from the plasma modify the surface and the plasma itself
  - Implantation
  - Reflection
  - Electron emission
  - Sputtering
    - Redeposition of material
    - Impurities
- What is the influence of materials on the plasma itself?
- Many of these question hang on understanding the surface morphology and how it modifies under plasma exposure

These are rich and important areas of work and research whether its for using plasma to manufacture a microchip or to finally have a fusion reactor work!