Low Temperature Plasmas :

Fundamentals

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PPPL Graduate Summer School 2019

Overview of Tutorial – Low Temperature Plasmas

Jose L. Lopez

- Fundamentals of Low Temperature Plasmas
- Plasma Generation & Chemistry
- Low-Pressure vs. High-Pressure Plasmas

Igor Kaganovich

- Computational, Modelling, and Simulations of Low Temperature Plasmas

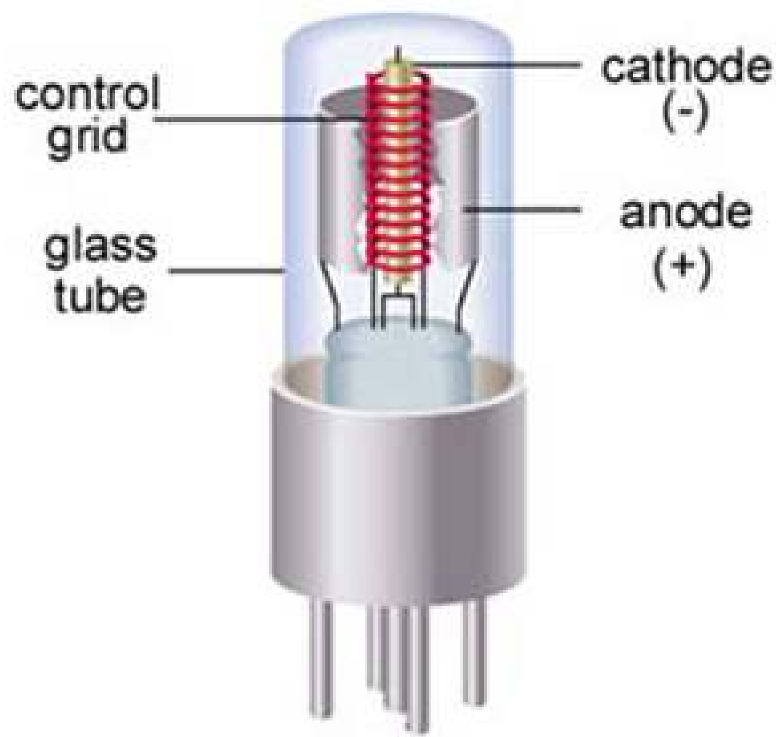
Yevgeny Raitses

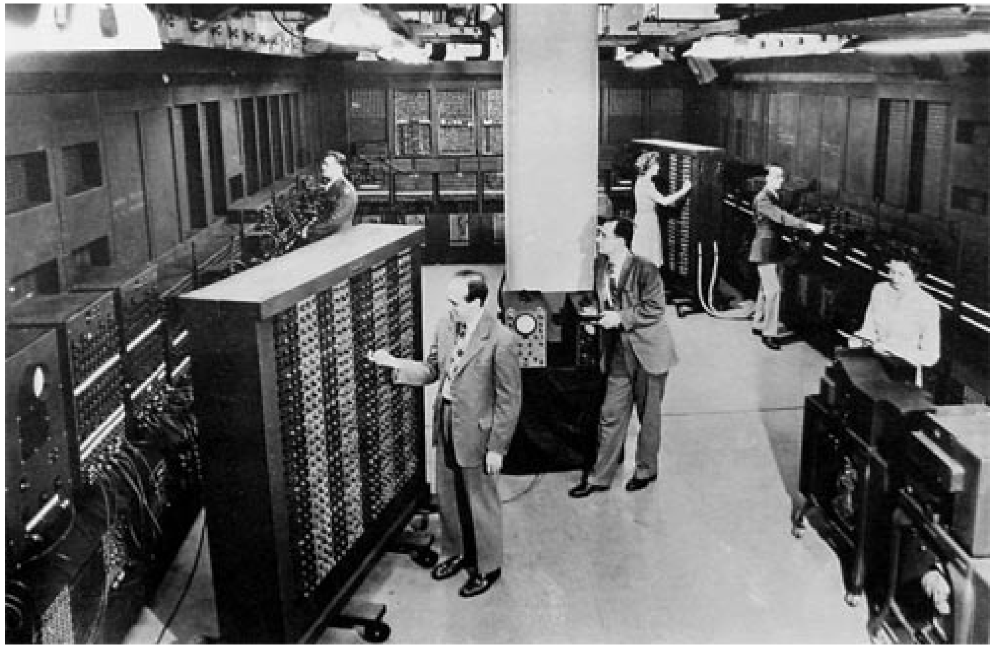
- Diagnostics
- Low Temperature Plasma applications & technologies

What are these devices?

Photo courtesy of Shutterstock user SPbPhoto

Vacuum tubes…

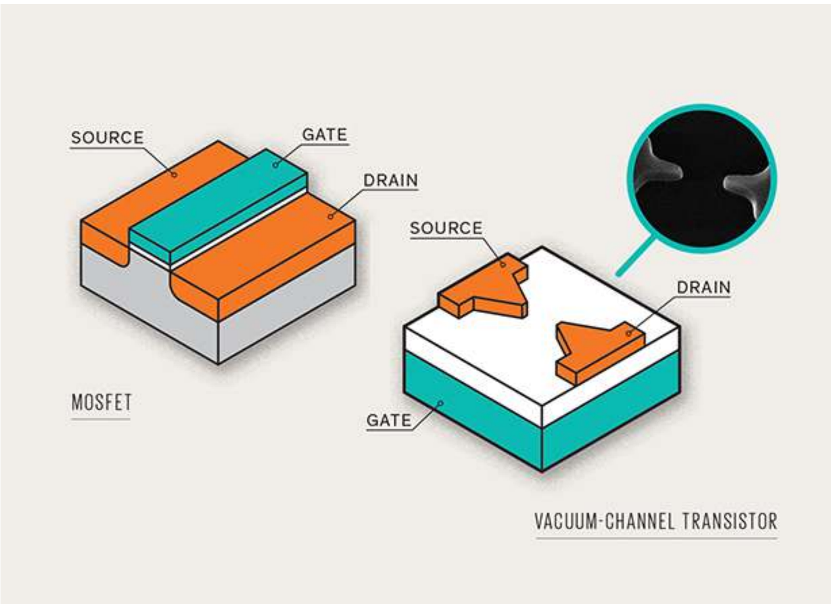




Programming the ENIAC - J. Presper Eckert (the man in the foreground turning a knob) served and John Mauchly (center) designed ENIAC to calculate the trajectory of artillery shells. The machine didn't debut until February 1946, after the end of World War II, but it did launch the computer revolution.

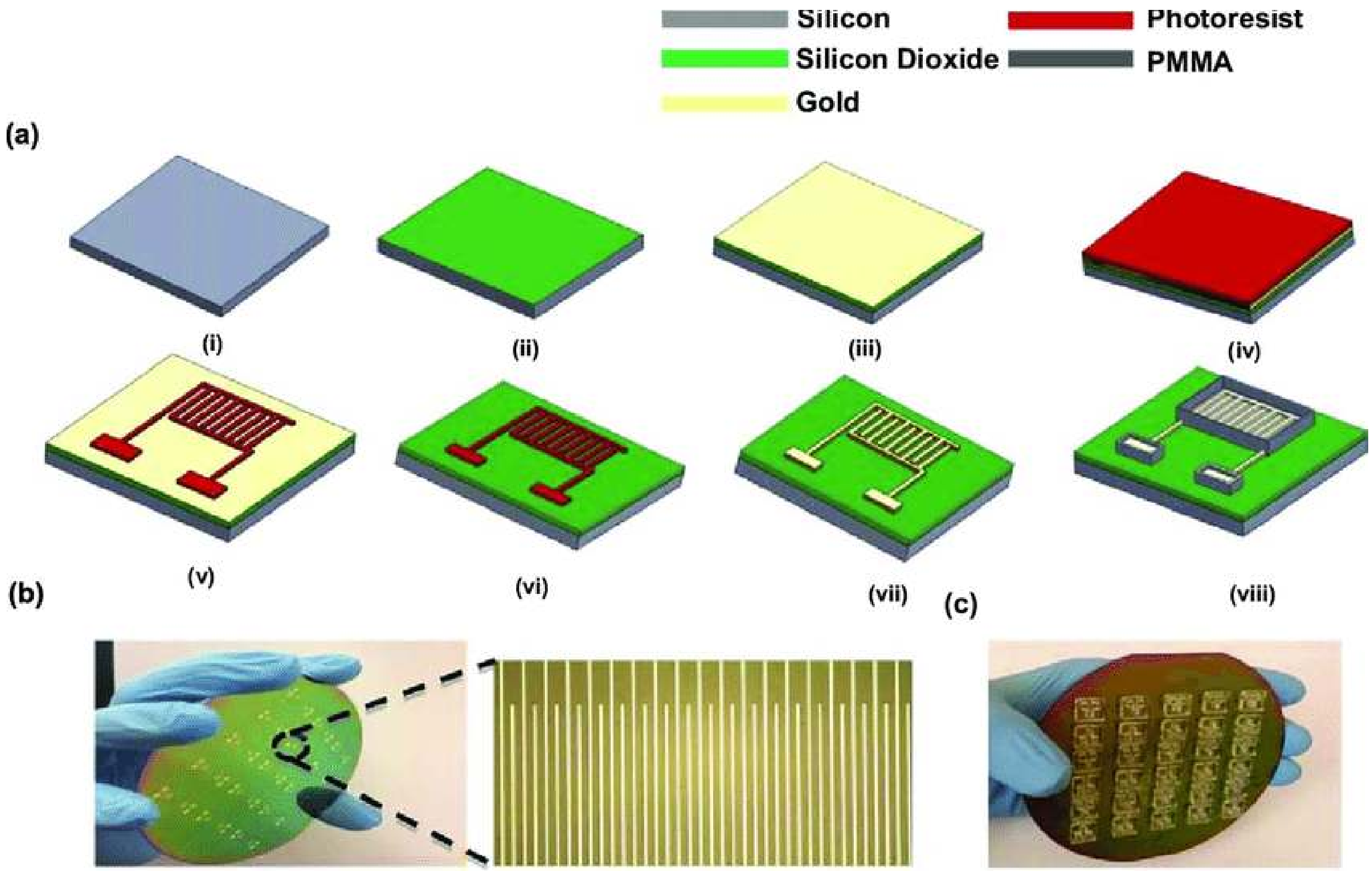
Reference: https://defence.pk/pdf/threads/the-return-of-the-vacuum-tube-computer.388381/

Vacuum tubes evolve into solid-state transistors which leads to personal computers

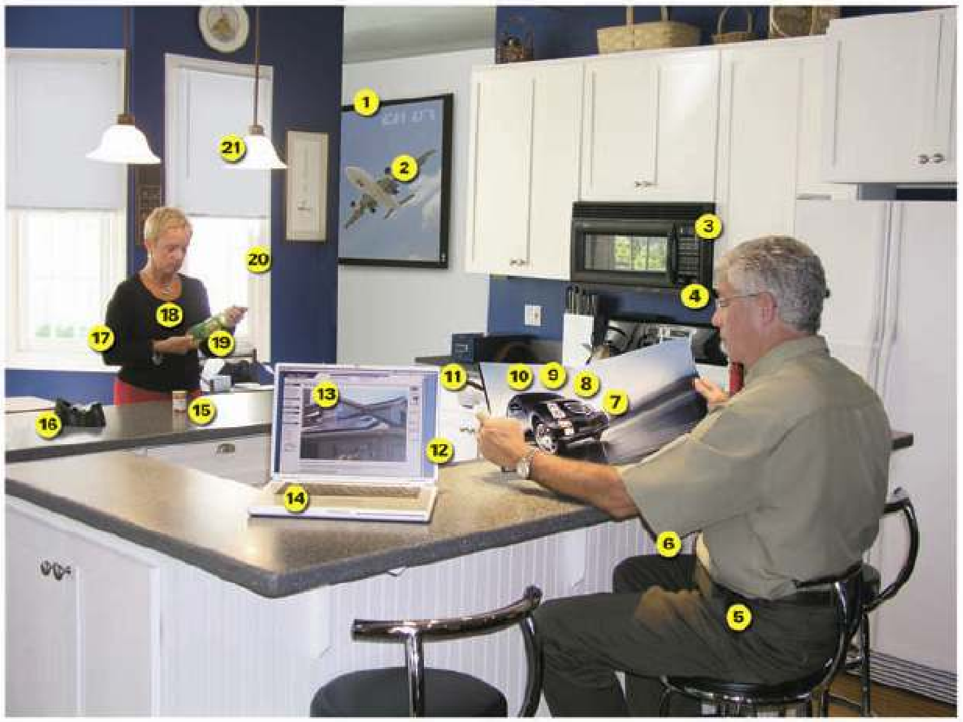


Reference: https://defence.pk/pdf/threads/the-return-of-the-vacuum-tube-computer.388381/

Low- Temperature Plasma enabled Microchip Fabrication



Plasma enabled technology



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

Plasmas in the kitchen. Plasmas and the technologies they enable are pervasive in our everyday life. Each one of us touches or is touched by plasma-enabled technologies every day.

Plasma Science: Advancing Knowledge in the National Interest. Plasma 2010 Committee, Plasma Science Committee, National Research Council. ISBN: 0-309-10944-2, 280 pages, (2007)

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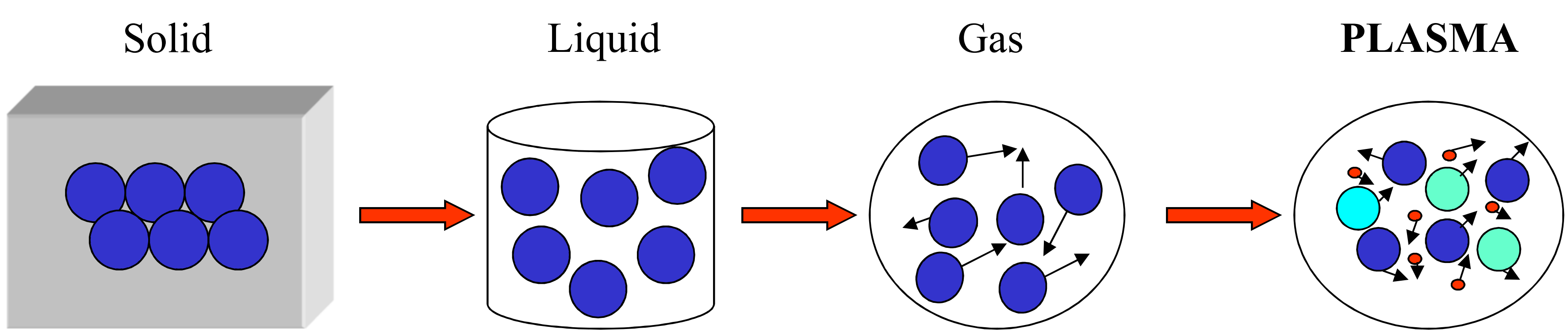
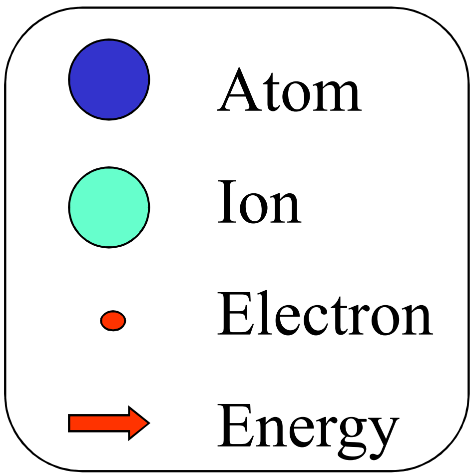
What is a Plasma?

The *Plasma* state is 'The Fourth State of Matter' (99%)

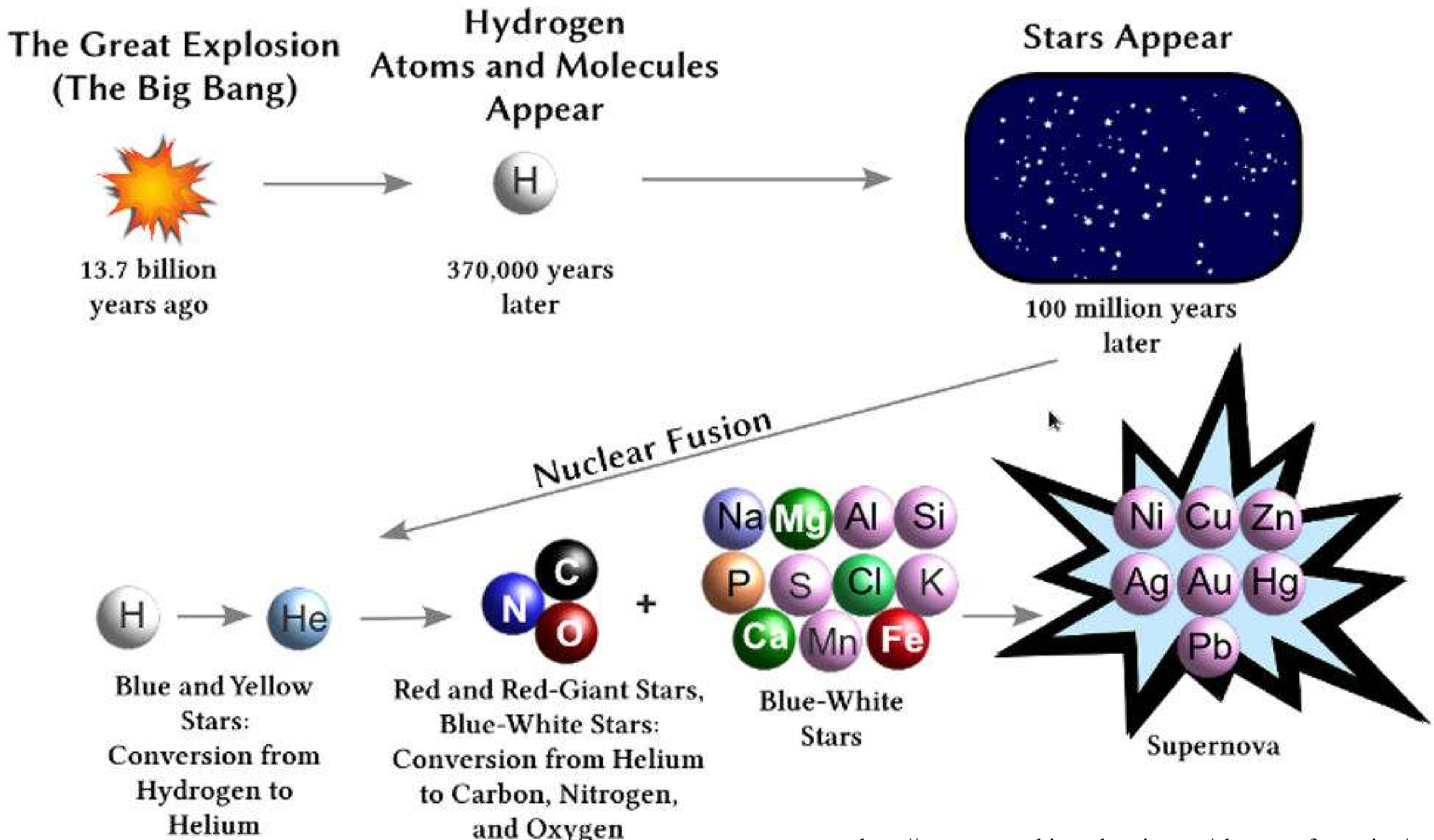




A *Plasma* is a collection of neutrals, ions, and electrons characterized by a *collective behavior*.

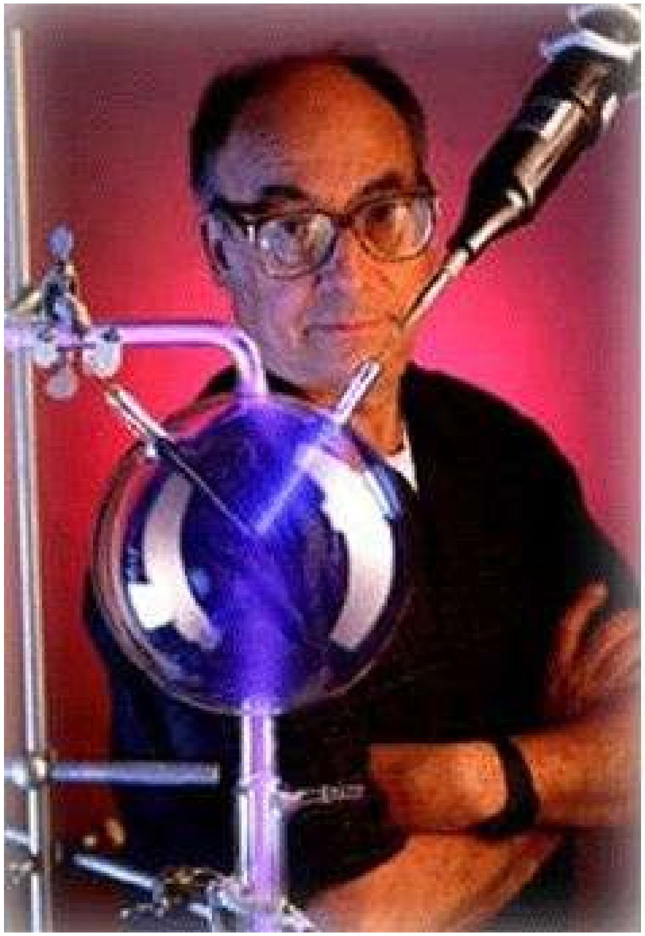
S. Eliezer and Y. Eliezer. *The Fourth State of Matter: An Introduction to Plasma Science. Bristol, UK: IOP Publishing (2001)*

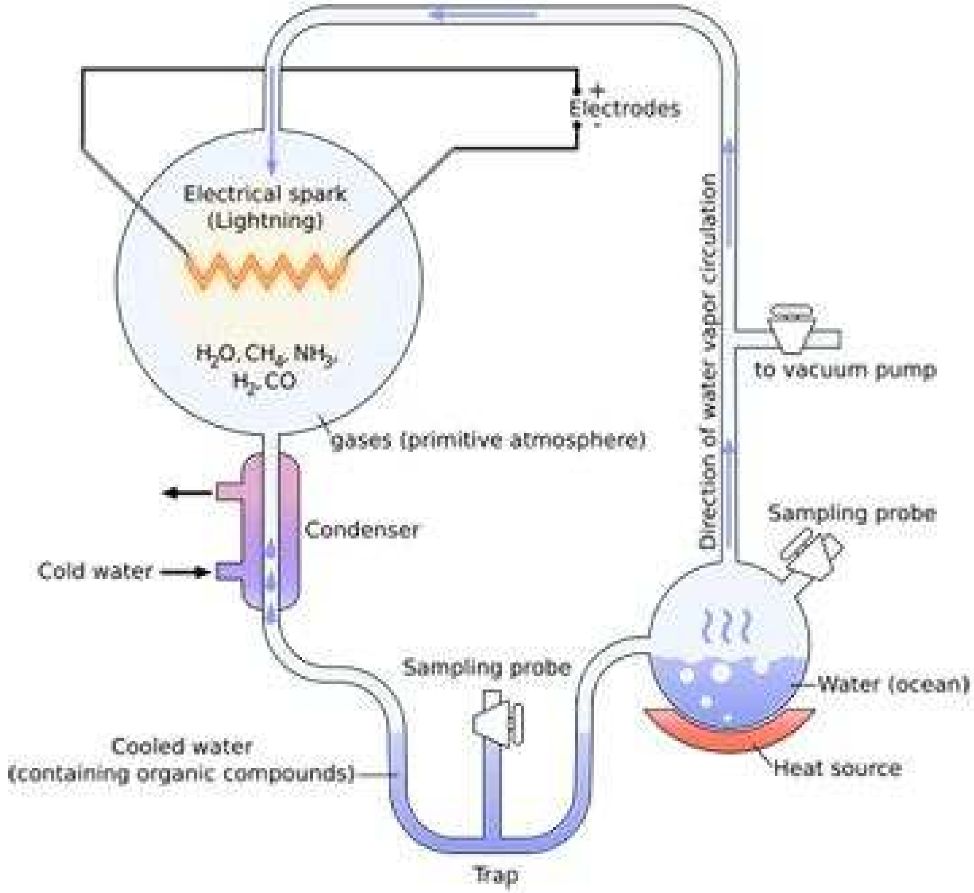
Plasma – 1st State of Matter



http://www.everythingselectric.com/elements-formation/

Plasma – Spark of Life?





Urey-Miller Experiment – Origin of Life

The Plasma State – New Jersey

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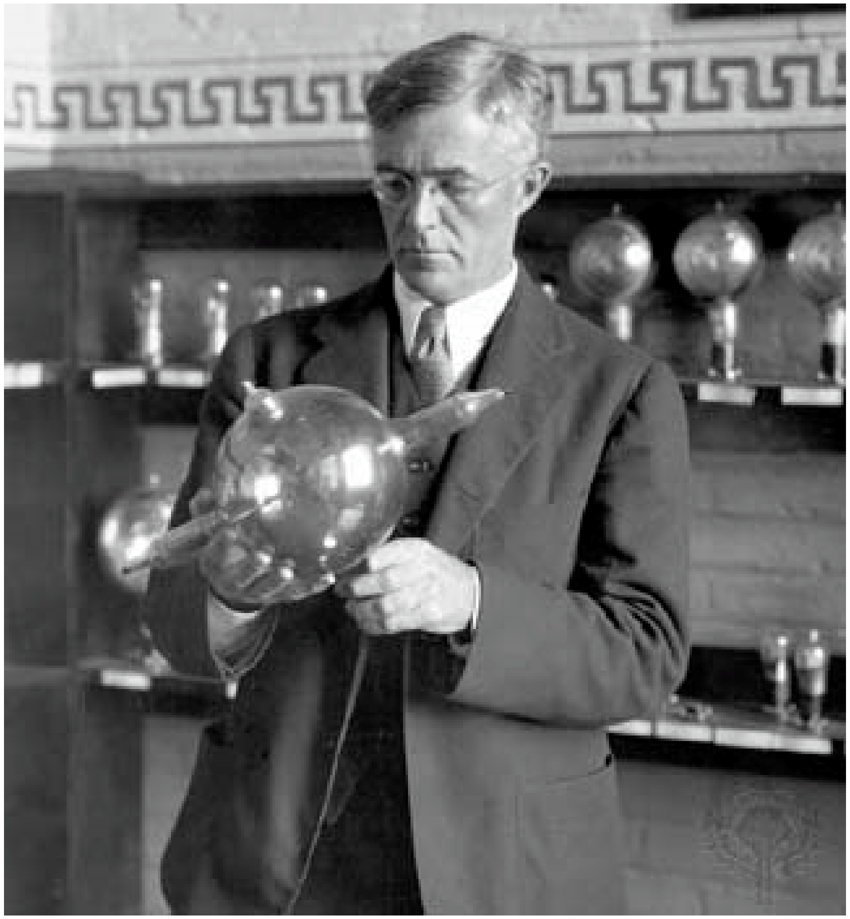
New Jersey – The birth place of Plasma Science



Irving Langmuir

Birth of Plasma Science

Birthplace: Hoboken, New Jersey

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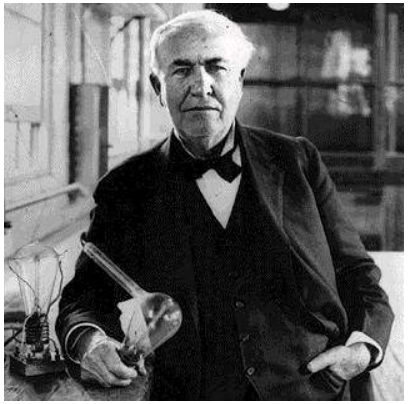
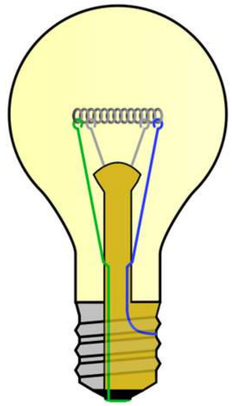
Irving Langmuir was one of the first scientists to work on plasmas and the first to refer to this 4th state of matter as ***plasmas***, because their similarity to blood plasma

Plasma Lighting Technology



Thomas Edison



Daniel McFarlan Moore

Birthplace of the Fluorescent Light Bulb: Edison (Menlo Park) / West Orange, NJ

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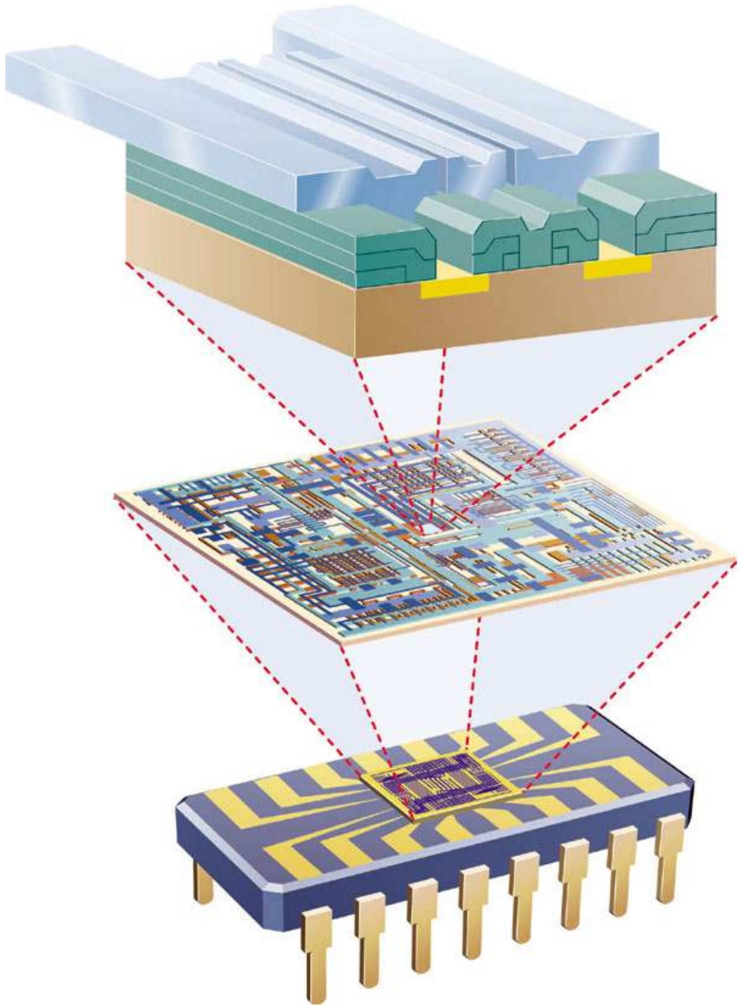
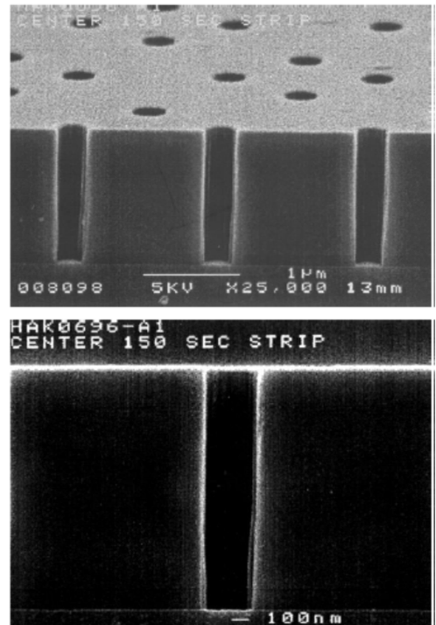
Plasma Enhanced Technology





A small section of a

Bell Laboratories

Birthplace of solid-state microelectronics: Bell Laboratories, Murray Hill, NJ

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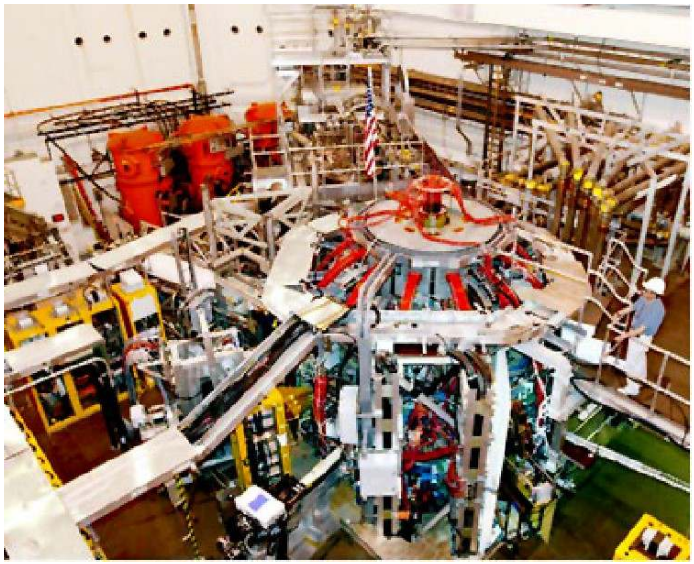
PPPL
PRINCETON PLASMA PHYSICS LABORATORY

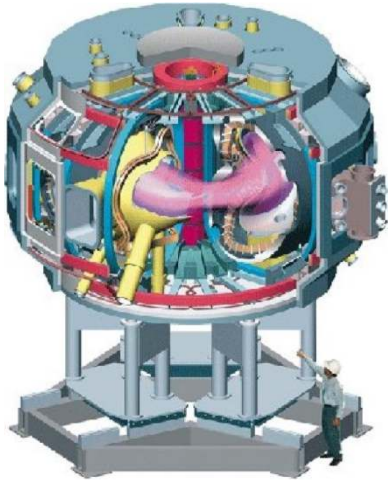
PRINCETON UNIVERSITY

U.S. DEPARTMENT OF ENERGY

The U.S. Department of Energy's Princeton Plasma Physics Laboratory (PPPL) is a collaborative national center for plasma and fusion science. Its primary mission is to develop the scientific understanding and the key innovations which will lead to an attractive fusion energy source. Associated missions include conducting world-class research along the broad frontier of plasma science and technology, and providing the highest quality of scientific education.

Prof. Lyman Spitzer and the first stellarator





National Spherical Torus Experiment (NSTX)

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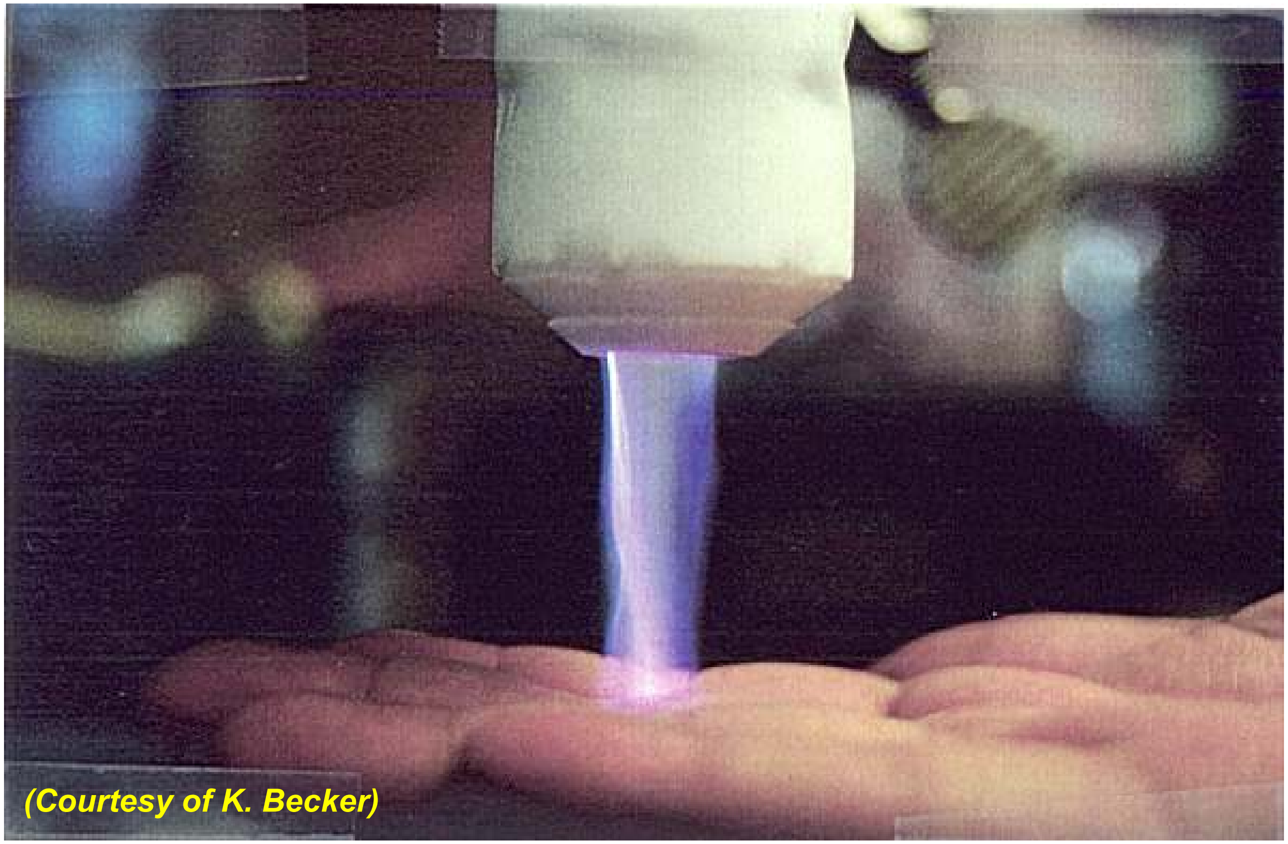
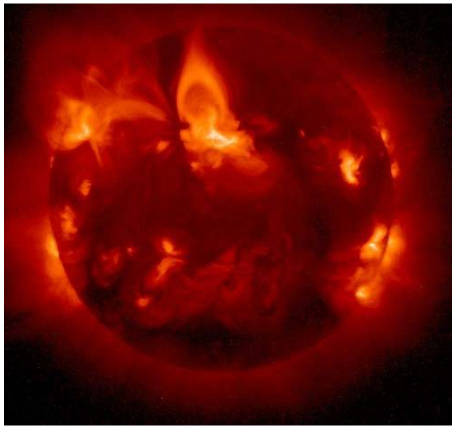


An Atmospheric Pressure Plasma Generated with a Capillary-Plasma-Electrode Discharge

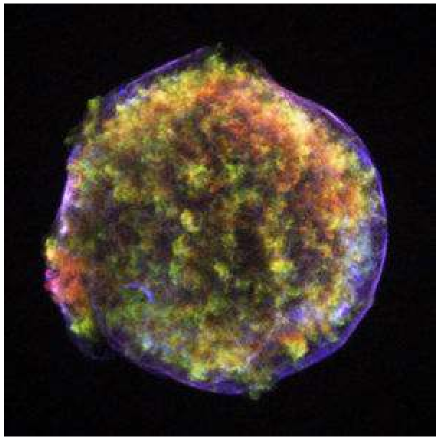
Plasmas in Nature


The Sun

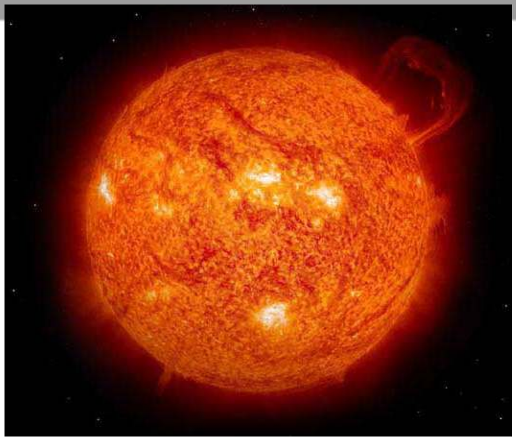

Aurora


Lightning


The Comet


Supernova

Plasmas are everywhere!!!



Sun

Aurora Borealis (Northern Lights)

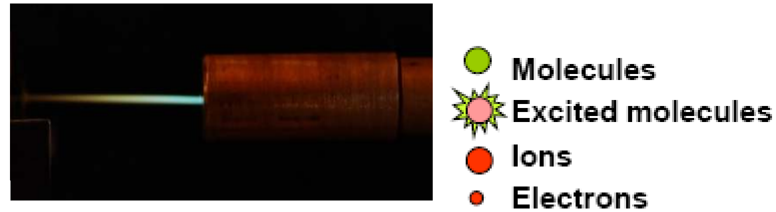
Lightning

Fluorescent Lamps

Plasma Display Televisions

Plasmas 101

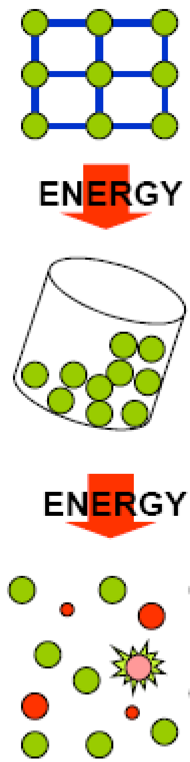
Solid, Liquid, Gas and ...Plasma
-The 4th State of Matter



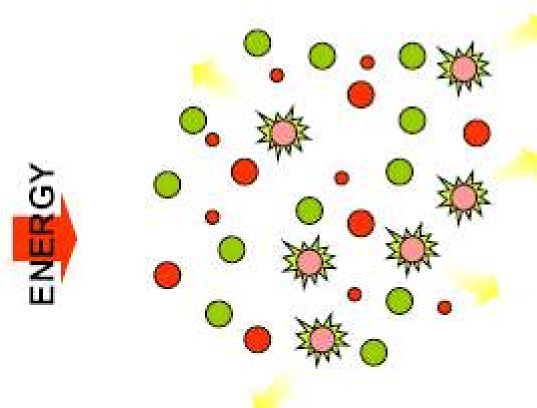
SOLID
- Molecules fixed in lattice
- Electrons bound to molecules or lattice

LIQUID
- Molecule bonds are flexible
- Electrons close to molecules

GAS
- Molecules free to move
- Few electrons and ions that are free to move
- Some excited molecules are present



PLASMA
- Molecules free to move
- Many electrons, ions and excited molecules, all free to move
- often accompanied by light



>99% in Universe

What is a Plasma?

- A *Plasma* is more than a collection of neutrals, ions, and electrons!

- What characterizes a plasma?
  - Quasi-neutral state of existence
  - Collective behavior due to Coulomb forces
  - Energy distribution
  - Collisional and radiative processes

Quasi-neutral state

- In the quasi-neutral state of the plasma the densities of the electrons and of the ions are usually equal.

$$n_e \cong n_i$$

- The *plasma density*, *n* is the density of electrons and ions in the plasma.

$$n_e = n_i = n$$

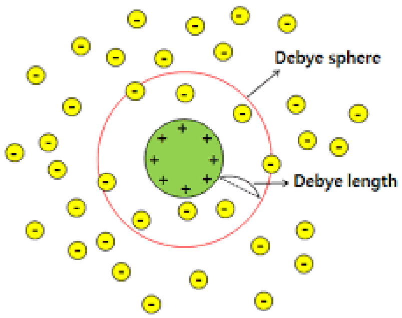
- The density of the neutral particles is much greater than of the charged species.

$$n < n_n$$

Debye Shielding

- To prevent deviations from quasi-neutrality, the charged particles in the plasma respond to reduce any effect of local electric fields by *Debye shielding*.
- If an external charge is introduced in the plasma, a *Debye sphere* (sheath) is created to shield the plasma from the perturbation.
- The *Debye shielding distance* or *Debye length* is given by:

$$\lambda_d = \left(\frac{kT_e \varepsilon_0}{n_e e^2} \right)^{\frac{1}{2}}$$



- The Debye length is the characteristic thickness of the sheaths which form between a plasma and an electrode or a plasma and a wall.

Plasma Frequency

- Due to their smaller mass, the electrons will respond faster than ions to the electric forces generated by the perturbations from neutrality.
- The response to the perturbation will be through oscillations.
- The frequency of these electron oscillations is called the *plasma frequency*, ω_p, and is given by the relation:

$$\omega_p = \left(\frac{n_e e^2}{m_e \varepsilon_0} \right)^{\frac{1}{2}}$$

Energy Distribution

- The individual plasma species (neutrals, ions, and electrons) do not all move with the same velocity.
- If these plasma particles are allowed to interact and equilibrate, their velocities and energies become distributed over a range of values described by the *Maxwell-Boltzmann distribution function*.
- For simplicity very often the average energy, E_{av} of a plasma is expressed in terms of a *temperature*.

$$\overline{E}_e = \frac{3}{2}kT_e \qquad \overline{E}_i = \frac{3}{2}kT_i \qquad \overline{E}_g = \frac{3}{2}kT_g$$

Plasma Classifications

- Thermodynamic equilibrium or *Thermal (hot) plasmas*

$$T_g \approx T_i \approx T_e \leq 10^4 - 10^8 K$$

- Non-equilibrium *or Low Temperature (cold) Plasmas*

$$T_g \approx T_i \approx 300 - 1000K$$

$$T_i << T_e \leq 10^5 K \left(\approx 10eV\right)$$

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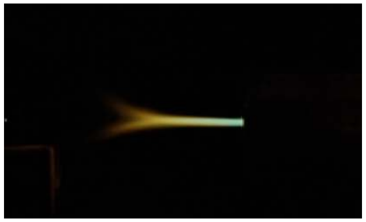
Types of Collisions

A number of different processes may result from the collision of an electron with an atom or molecule. These processes may be classified as elastic or inelastic collisions.

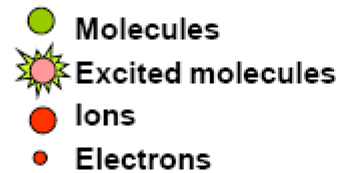
Elastic collisions are those, like the interaction of billiard balls, in which the total kinetic energy of the two particles is conserved, such that no energy exchange takes place between the internal motion of the atom or molecule and the electron.

Inelastic collisions are those in which the initial kinetic energy is greater than the kinetic energy after the collision due to some kinetic energy being transferred from the electron to internal energy of the target.

Collisions generate the plasma

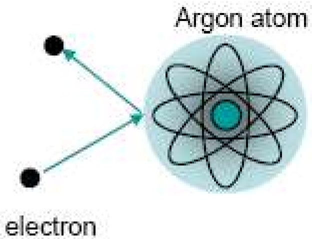


Collisions in plasmas



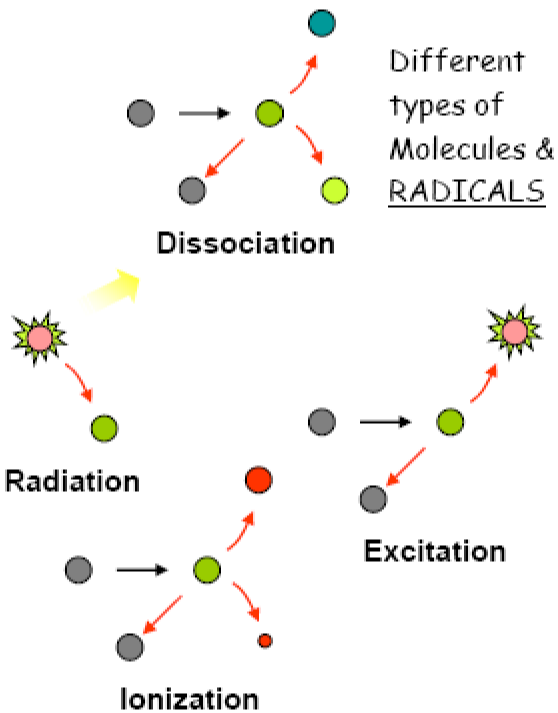
Elastic collisions

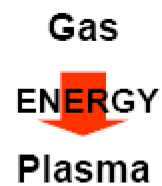
Elastic collision are frequent in gases
No energy exchange



essentially no exchange of energy ($m_{Ar} >> m_e$)

Inelastic collisions





Therefore more and stronger collisions leading to more

ionization, excitation, dissociation and radiation

Collisional and radiative processes

- The processes that determine the properties of low temperature plasmas are collisions involving the plasma electrons and other plasma constituents.

- The charge carrier production is governed by
  - Direct ionization of ground state atoms and/or molecules
  - Step-ionization of an atom/molecule that is already in an excited and, in particular, a long-lived metastable state

- The generation of chemically reactive free radicals by electron impact dissociation in molecular plasmas is an important precursor for plasma chemical reactions.

Electron-Atom collision processes in plasmas

$e + A \rightarrow A^{*/m} + e'$ $A^* \rightarrow A + h\nu$	Excitation of atoms Spontaneous de-excitation
$e + A^{*/m} \rightarrow A + h\nu + e'$	Collision-induced de-excitation
$e + A \rightarrow A^+ + e'$	Ionization of atoms
$e + A^{*/m} \rightarrow A + e' + E_{kin}$	Super-elastic collisions
$e + A^m \rightarrow A^* + e'$	Step-wise excitation
$e + A^m \rightarrow A^+ + e'$	Step-wise ionization

K. Becker and A. Belkind. 'Introduction to Plasmas'. *Vacuum Technology & Coating (September 2003)*

Electron-Molecule collision processes in plasmas

$e + AB \rightarrow AB^{*/m} + e'$ $AB^* \rightarrow AB + h\nu$	Excitation of molecules Spontaneous de-excitation
$e + AB^{*/m} \rightarrow AB + h\nu + e'$	Collision-induced de-excitation
$e + AB \rightarrow A^{*/m} + B + e'$	Dissociation of molecules
$e + AB \rightarrow AB^+ + e'$	Ionization of molecules
$e + AB \rightarrow A^+ + B + e'$	Dissociative ionization of molecules
$e + AB \rightarrow A^+ + B + e'$	Dissociative attachment of molecules
$e + A^+ \rightarrow A + h\nu$	Radiative recombination of an atomic ion
$e + A^+ + e' \rightarrow A + e'$	3-body dielectronic recombination
$e + A^+ + M \rightarrow A + M + e'$	3-body heavy particle recombination
$e + AB^- \rightarrow A + B$	Dissociative attachment of molecular negative ions

Heavy particle collision processes in a plasma

$A + B^+ \rightarrow A^+ + B$	Charge transfer
$A + B^m \rightarrow A^+ + B + e$	Penning ionization
$A^m + A^m \rightarrow A^+ + A + e$	Pair ionization
$A^* + A \rightarrow A_2^+ + e$	Hornbeck-Molnar ionization
$A^+ + BC \rightarrow AC^+ + B$	Ion-molecules reaction
$A^{*/m} + BC \rightarrow AC + B$	Chemical reaction
$R + BC \rightarrow RC + B$	Chemical reaction with plasma radical, R

What is a collision cross-section?

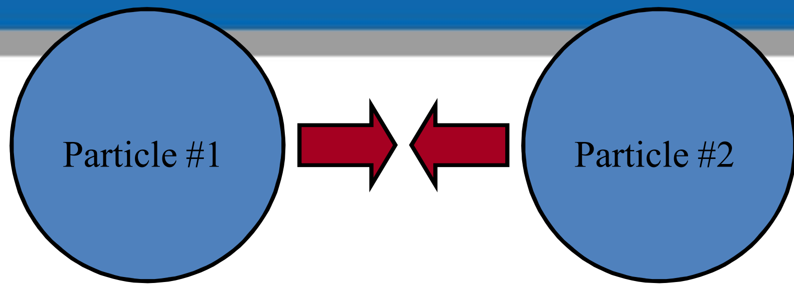


Figure 1. Particle #1 and #2 are on a path toward a collision.

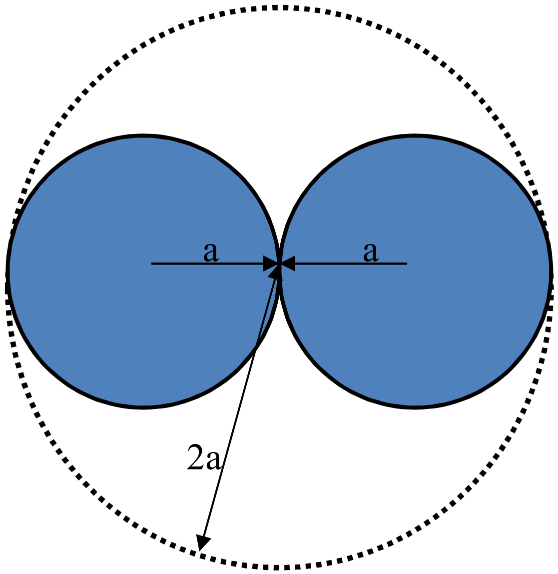
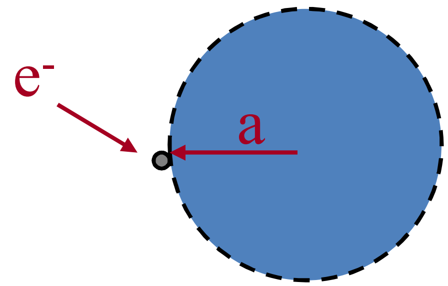


Figure 2. Particle #1 and #2 impact and the total cross section, σ, for this process is the area of the dotted circle.

Mathematically:

$$\sigma = \pi(2a)^2 = 4\,\pi a^2 \quad (cm^2)$$

The concept of collision cross-section



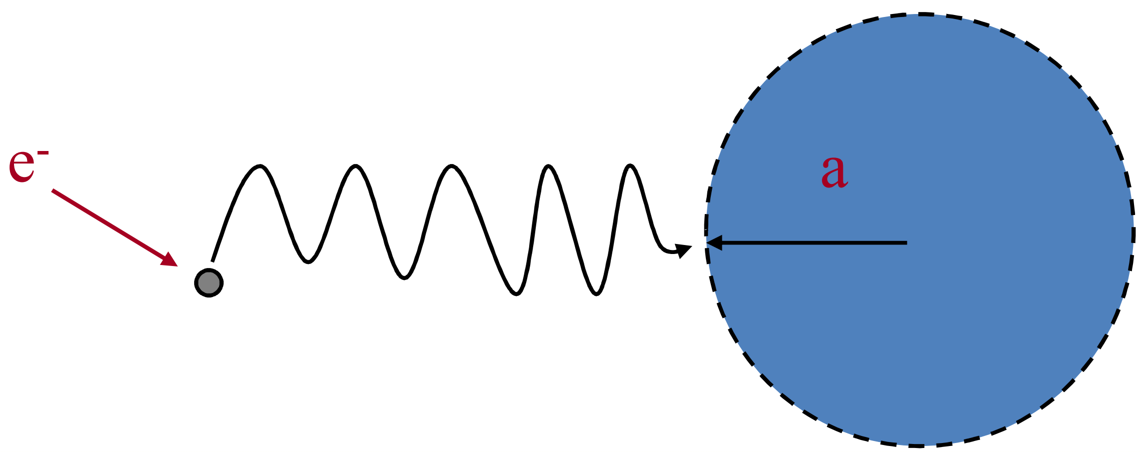
Similarly, if the electron is represented as a classical point mass and the target is seen as a rigid sphere with a radius *a*, the collision cross-section is simply given by the geometrical cross section $\pi \mathbf{a}^2$.

The collision cross-section is a constant!?

The concept of collision cross-section

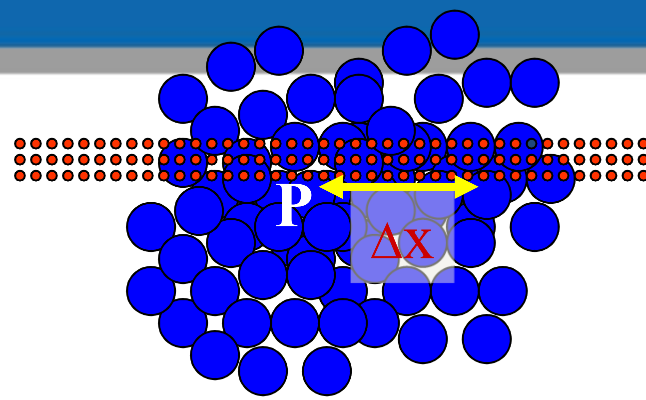
A real electron, however follows quantum mechanics.

This means that the wave nature of the electron motion comes into play. For these reasons, the collision cross-section is not a constant and can subsequently be measured, since it depends on the collision energy or the kinetic energy of the relative motion of the electron to the target.



The concept of collision cross-section

electron beam



An atom of cross sectional area σ cm^2

Electrons

The amount of the electron beam current lost in traveling a small distance Δx from a point P is

$$\Delta I = I_P N \sigma \Delta x$$

$$I_P = I_0 e^{-N \sigma X}$$

$$\sigma = -\ln (I_P / I_0) / Nx$$

If I_p/I_0 is measured as a function of x and N, σ can be found and it is known as the collision cross-section. This gives us a convenient measure to represent the collision probability for all types of collisions between the electron beam and the targets. The collision cross-section has a dimension of the area or cm^2.

Total ionization collision cross-section

$$e^- + NO \longrightarrow NO^+ + 2e^-$$ **(partial ionization)**

$$\longrightarrow N^+ + \text{other fragments} + 2e^-$$ **(dissociative ionization)**

$$\longrightarrow O^+ + \text{other fragments} + 2e^-$$ **(dissociative ionization)**

Total ionization cross-section, σ_T, is a sum of all the above processes

$$\sigma_p + \sigma_d = \sigma_T$$ (total ionization cross-section)

J.L. Lopez, V. Tarnovsky, M. Gutkin, and K. Becker. *Electron-impact ionization of NO, NO_2, and N_2O.* **International Journal of Mass Spectrometry** 225 (1) 25-37 · February 2003. DOI: 10.1016/S1387-3806(02)01042-4

Fast-Neutral-Beam Apparatus

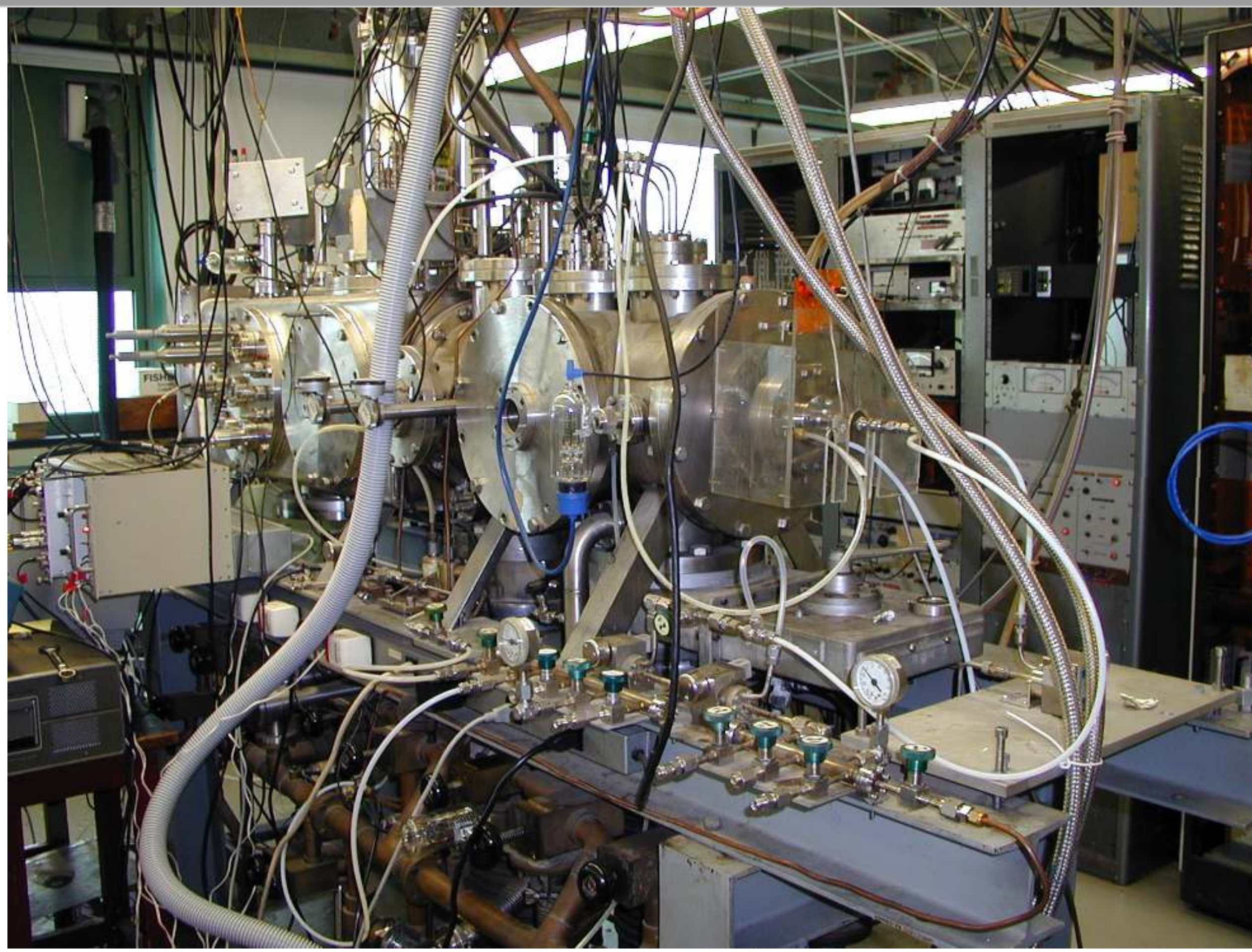


Figure 1. Picture of the Fast-Neutral-Beam Apparatus.

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Fast-Neutral-Beam Apparatus

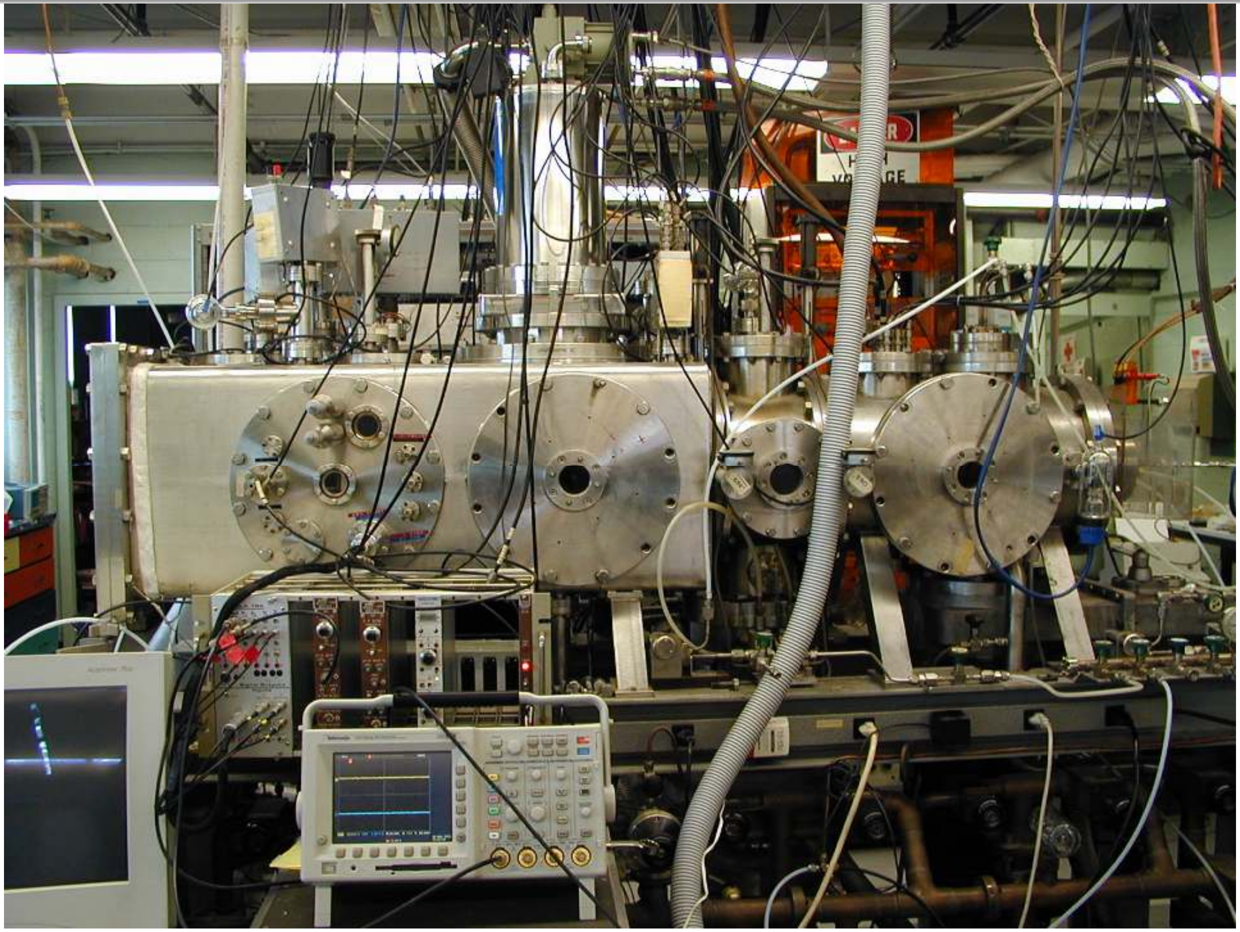

Figure 2. Side view of the Fast-Neutral-Beam Apparatus.

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Fast-Neutral-Beam Apparatus

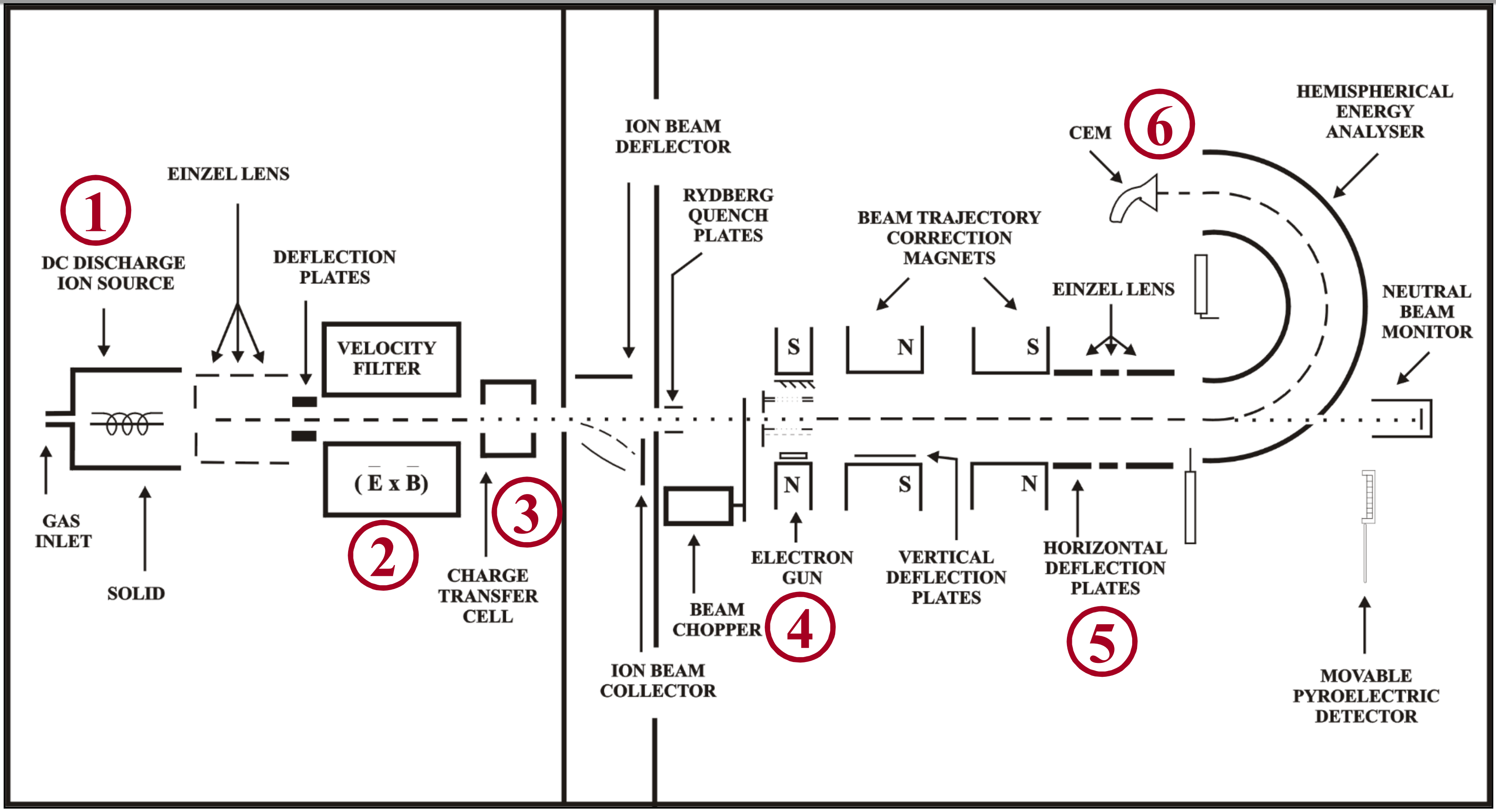


Figure 3. Schematics of the Fast-Neutral-Beam Apparatus.

Total ionization cross-section

In the case of the fast-neutral-beam configuration that was used in this work, the ionization cross-section σ(E) is given by an expression

$$\sigma(E) = \frac{I_i(E)\upsilon_e\upsilon_n}{I_e(E)RF(\upsilon_e^2 + \upsilon_n^2)^{1/2}}$$

where

$I_i(E)$ – ion current
$I_e(E)$ – electron current
υ_n – neutral beam velocity
υ_e – electron beam velocity
R – neutral beam flux (atoms/sec)
F – measure of the overlap between the neutral and electron beams

Total ionization collision cross-section

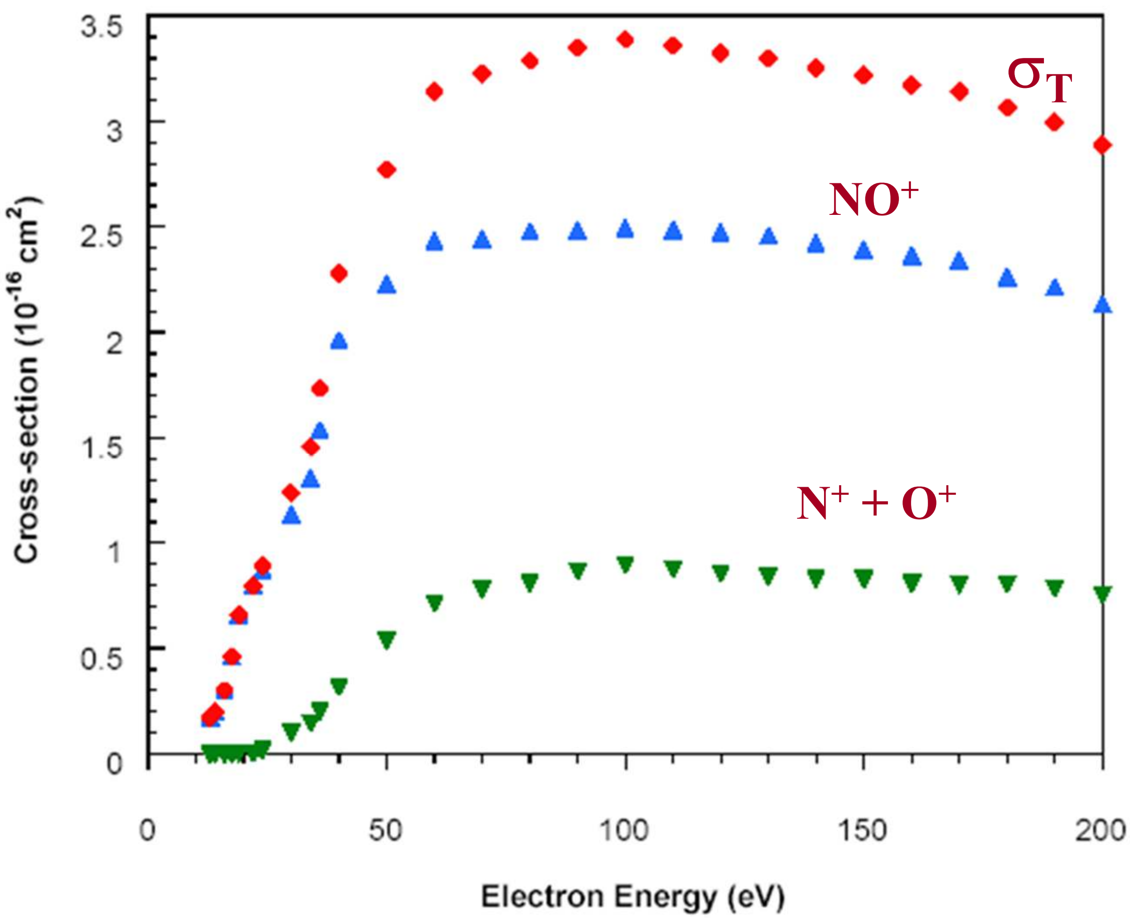
$$
\begin{aligned}
e^- + NO &\longrightarrow NO^+ + 2e^- && \text{(partial ionization)} \\
&\longrightarrow N^+ + \text{other fragments} + 2e^- && \text{(dissociative ionization)} \\
&\longrightarrow O^+ + \text{other fragments} + 2e^- && \text{(dissociative ionization)}
\end{aligned}
$$

Total ionization cross-section, σ_T, is a sum of all the above processes

$$\sigma_p + \sigma_d = \sigma_T \quad \text{(total ionization cross-section)}$$

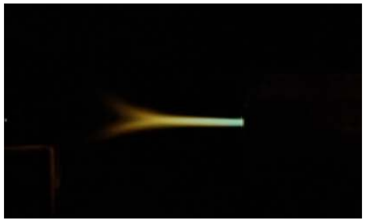
J.L. Lopez, V. Tarnovsky, M. Gutkin, and K. Becker. *Electron-impact ionization of NO, NO_2, and N_2O.* **International Journal of Mass Spectrometry** 225 (1) 25-37 · February 2003. DOI: 10.1016/S1387-3806(02)01042-4

Electron-impact ionization cross-sections of NO



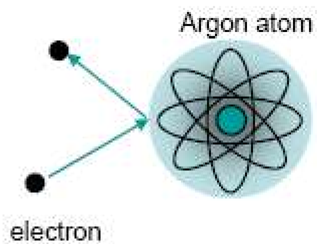
Present NO^+ (▲) and combined ($N^+ + O^+$) (▼) partial electron-impact ionization cross-sections of NO as a function of electron energy from threshold to 200 eV. Also shown is the sum of the two cross-sections (♦), which represents the total single NO ionization cross- section, which is essentially identical to the total NO ionization cross-section.

Collison sustain the plasma



Elastic collisions

Elastic collision are frequent in gases
No energy exchange

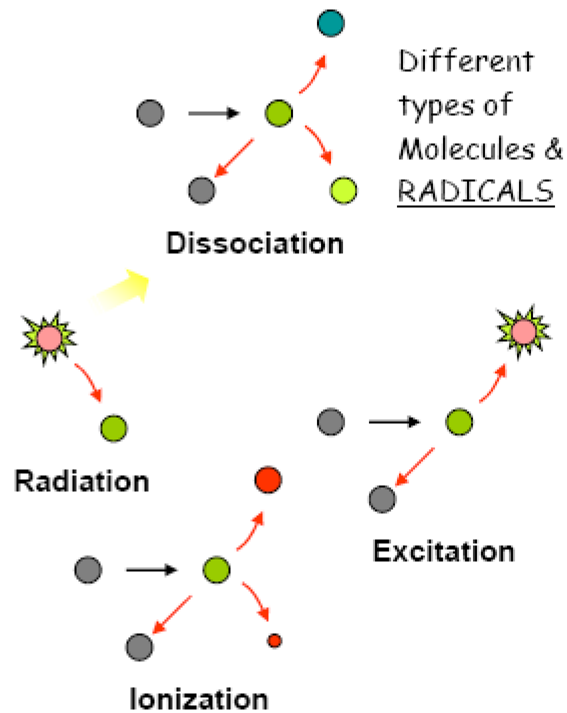


essentially no exchange of energy ($m_{Ar} >> m_e$)

Collisions in plasmas

- Molecules
- Excited molecules
- Ions
- Electrons

Inelastic collisions



Gas

ENERGY

Plasma

Therefore more and stronger collisions
leading to more

ionization,
excitation,
dissociation and
radiation

Plasma generation

- A plasma is generated by supplying energy to a volume of gas to produce pairs of electrons and ions (charge carriers).
  - most commonly electrical energy is supplied

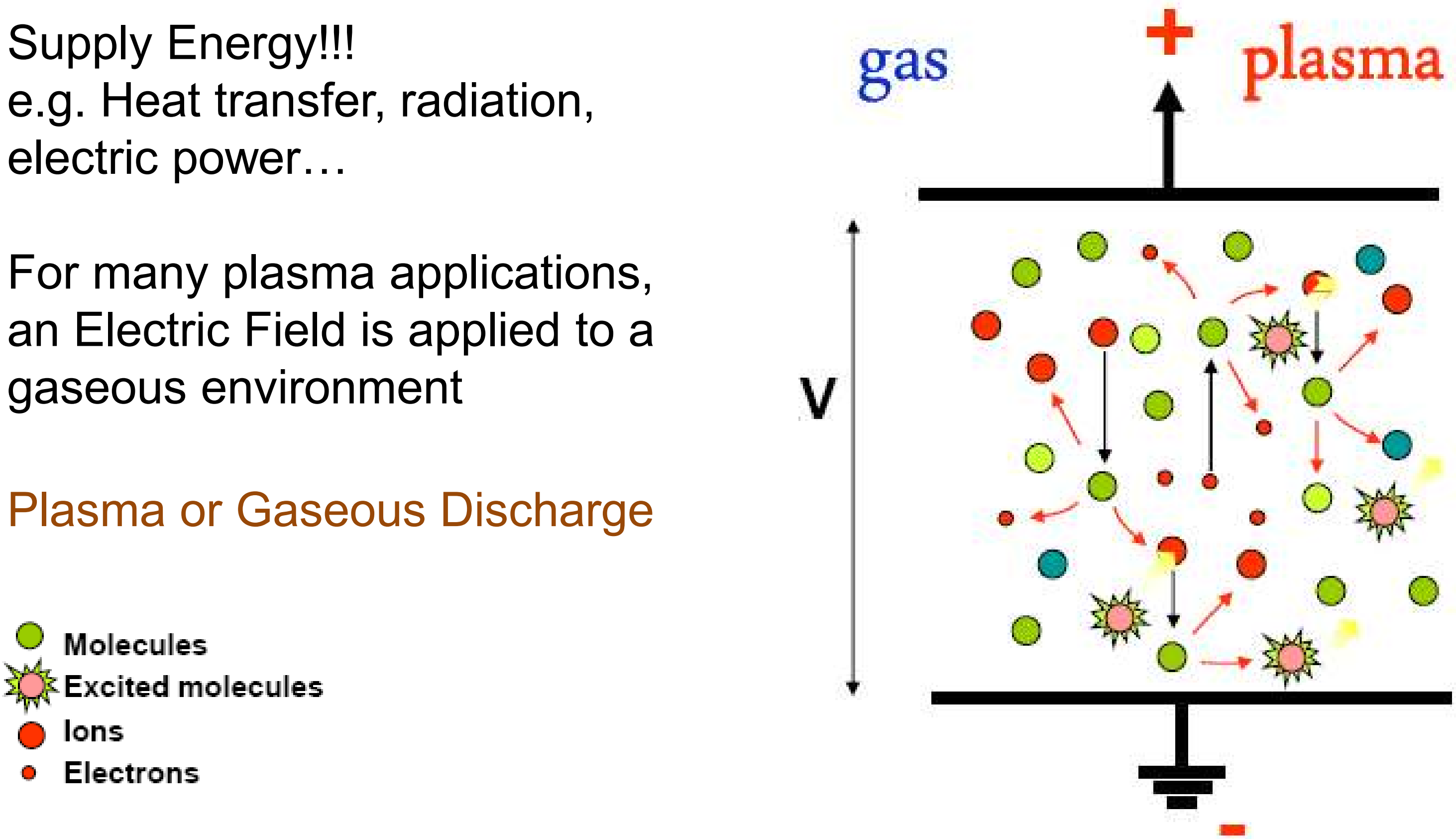
- Low temperature plasmas are usually excited and sustained electrically by applying
  - Alternating Current (AC) power
  - Radio Frequency (RF) power
  - Microwave (MW) power
  - Direct Current (DC) power
    - Pulsed DC power

How do we make plasmas?

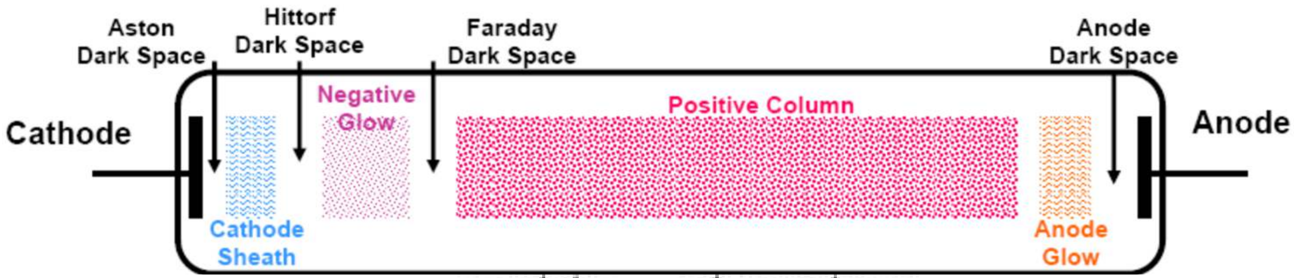
Supply Energy!!!
e.g. Heat transfer, radiation, electric power…

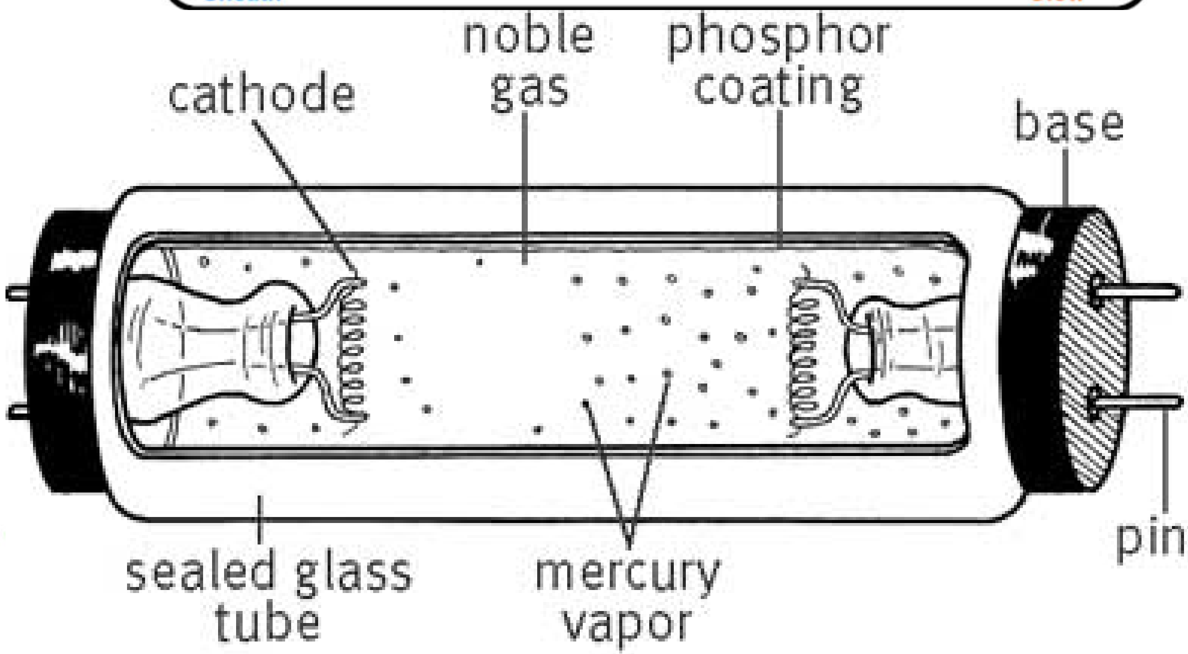
For many plasma applications, an Electric Field is applied to a gaseous environment

Plasma or Gaseous Discharge



Low-Pressure Glow Discharge Plasmas





Two Types of plasmas

High-temperature plasmas or Hot (Thermal) plasmas

$T_i \approx T_e \geq 10^7$ K

e.g., fusion plasmas

$T_i \approx T_e \approx T_g \leq 2 \times 10^4$ K

e.g. arc plasma at normal pressure

Low-temperature plasmas or Cold (Non-thermal Plasmas)

$T_i \approx T_g \approx 300$ K

$T_i << T_e \leq 10^5$ K

e.g. low-pressure glow discharge

high-pressure cold plasma

Hot vs. Cold Plasmas

Thermal vs. Non-Thermal Plasmas

The plasma components (electrons, ions, neutrals) are characterized by energy distribution functions or alternatively by an "average" energy or temperature (T_e, T_i, T_n) – not quite correct, only true for Maxwell-Boltzmann distributions !!!

Electrons in general have more complicated energy distributions !!!

<u>Thermal Plasma:</u> $T_e \approx T_i \approx T_n$ (a few thousand Kelvin for e.g. torches to $>10^6$ Kelvin for e.g. fusion plasmas)

<u>Non-Thermal Plasma:</u> $T_e >> T_i, T_n$ with $T_i \approx T_n$

- high electron temperature (10,000 – 50,000 K)
- low gas temperatures (300 – 1,500 K)
- "high-temperature chemistry" at low ambient temperatures

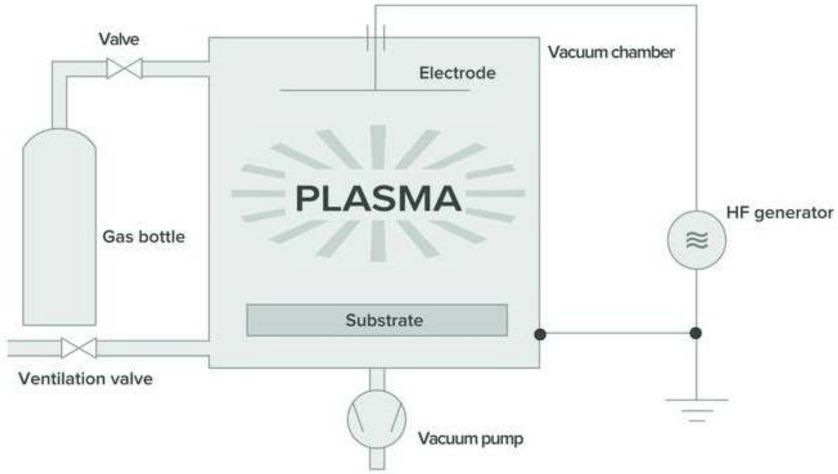
(through dissociation and ionization & vibrational non-equilibrium)

Low-Temperature ("Cold") Plasmas [Non-equilibrium, Non-Thermal]

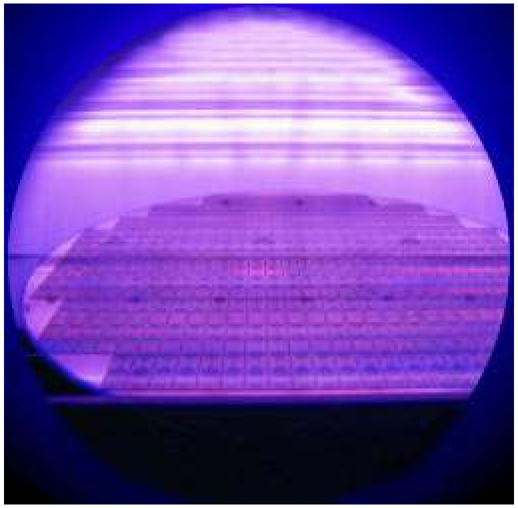
$T_e >> T_i, T_n$ with $T_i \approx T_n$

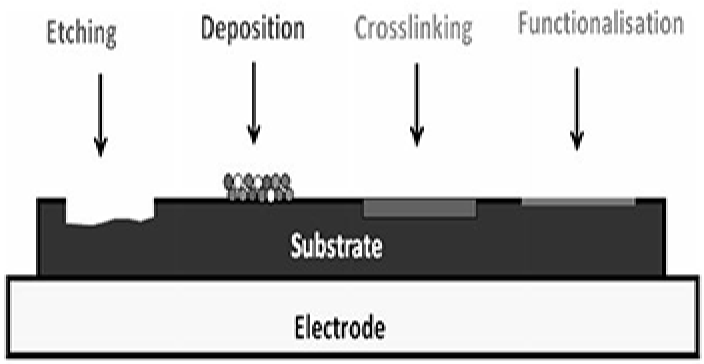
- High "electron temperature" (10,000 – 100,000 K)
  - T_e from 0.5 eV to 10 eV
  - Often highly non-Maxwellian EEDF; "bulk" and "beam" electrons
- Low gas temperature (350 – 2,500 K)
- "High-temperature chemistry" at low ambient temperatures
  - Electron-driven ionization and dissociation (in molecular plasmas) create reactive radicals
  - Electron interactions (in molecular plasmas) create a vibrational non-equilibrium

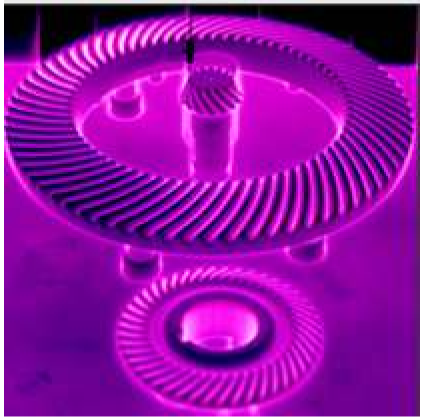
Low-Pressure, Low-Temperature Plasma Processing



Plasma processing of silicon for semiconductor manufacturing.





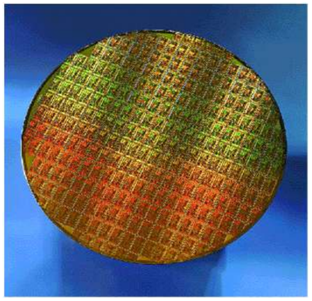


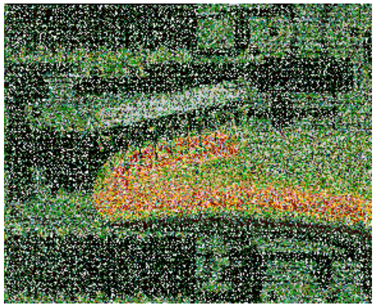
Plasma processing to harden or coat materials.

Plasmas are easier to be generated at low pressures

Low pressure plasmas
(1 mTorr ~ a few Torr)

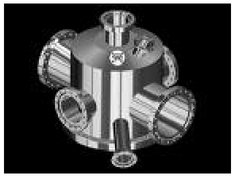
- are well understood
- are used extensively nowadays (e.g. in semiconductor industry for computer chips manufacturing)





However, to generate low pressure plasmas:

- vacuum chambers
- expensive vacuum pumps
- pressure monitoring and pressure control devices

 +  +  = 

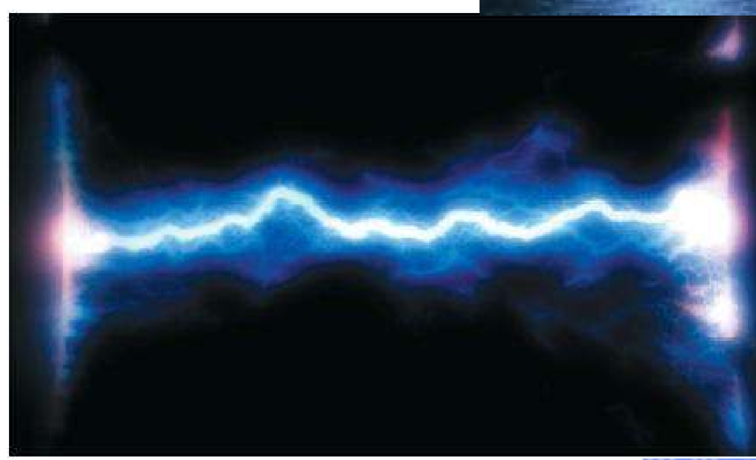
Generate Plasmas at Atmospheric Pressure!!

What happens at air pressure?

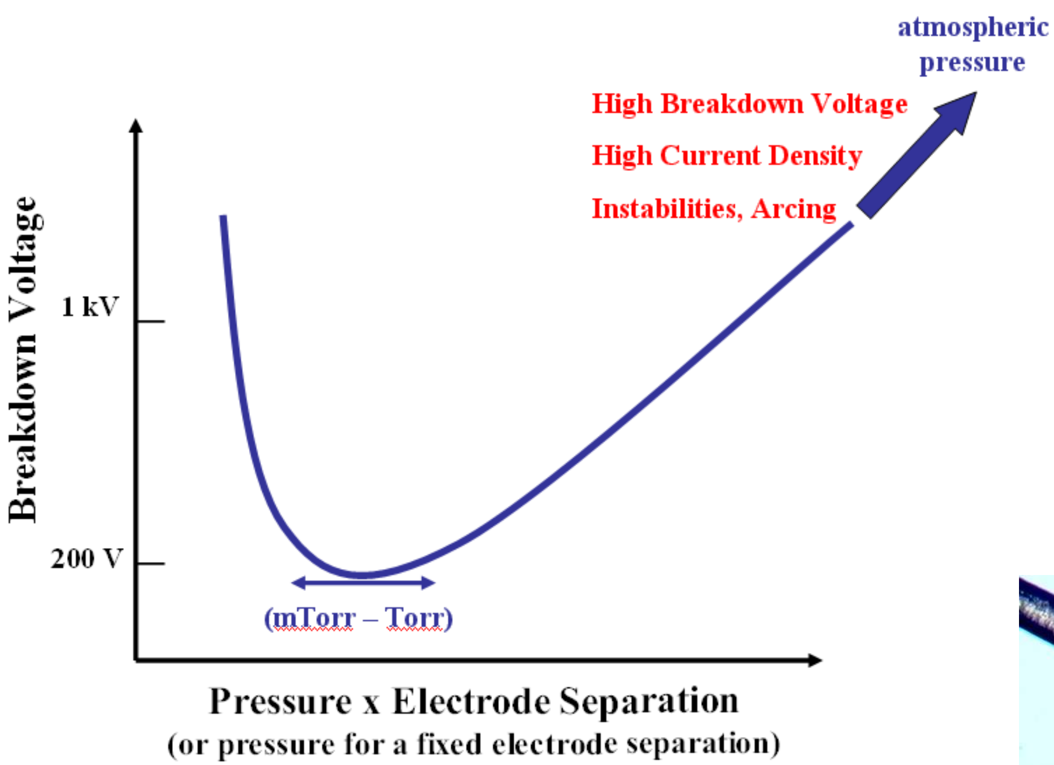
- No vacuum is involved
- Difficult to generate and sustain
- Run into some challenges such as glow to ***arc*** transition – Non controllable

Arc Discharge: thermal plasma

- It's hot and detrimental
- Gas temperature can reach as high as $2x10^4$ K
- Low voltage drop at cathode
- High cathode current density



Atmospheric (or higher) Pressure: Microplasmas



Paschen Breakdown Curve

Stabilization of high-pressure plasmas: "pd scaling": "p" ↑, so "d" ↓ to keep breakdown voltage low and minimize instabilities after breakdown -

Microplasmas

Dimension: a few millimeter down to and below **100 μm**

Human Hair: 60 – 100 μm

How do we create stable atmospheric pressure, low temperature plasmas?

Transient (pulsed) plasmas: *In atmospheric* plasmas, *for efficient gas heating at least 100-1000 colli*sions are necessary. Thus, if the plasma duration is shorter than 10^{-6} – 10^{-5} s, *gas* heating is limited. Of course, for practical purposes such plasma has to be operated in a repetitive mode, e.g., in trains of microsecond pulses with millisecond intervals.

Micro-confinement: Gas heating occurs in the plasma volume, and the energy is carried away by thermal diffusion/convection to the outside. If the plasma has a small volume and a relatively large surface, gas heating is limited.

Dielectric Barrier Discharges: These plasmas are typically created between metal plates, which are covered by a thin layer of dielectric or highly resistive material. The dielectric layer plays an important role in suppressing the current: the cathode/anode layer is charged by incoming positive ions/electrons, which reduces the electric field and hinders charge transport towards the electrode. DBD also has a large surface-to-volume ratio, which promotes diffusion losses and maintains a low gas temperature.

a.k.a **Microplasmas**

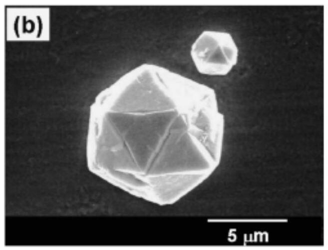
Advantages of Microplasmas

- Low-cost of implementation
- System flexibility
- Atmospheric pressure operation
- High densities and high reaction rates
- Fast and efficient processes
- Easy to generate and sustain for a variety of gas mixtures
- Glow-like and diffuse
- Non-equilibrium ($T_e > T_g$) *to thermal*
- Unique chemistry

… a new realm of low temperature plasma science

What can we do with low temperature plasmas?

Material Synthesis

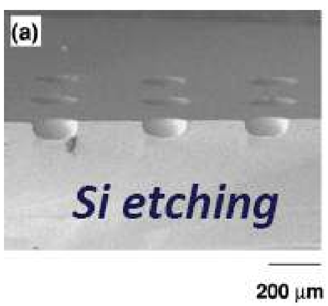


Plasma display

Surface Treatment

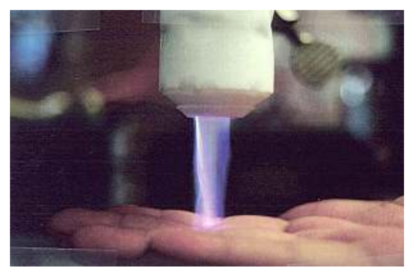
Lighting

Material processing

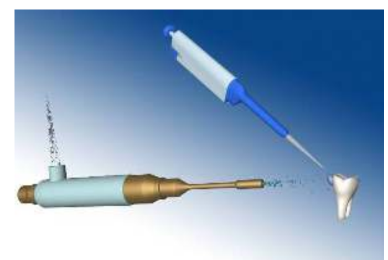


Ozone generation for water cleaning

Bio-application



Dental application



and many more…

SETON HALL UNIVERSITY

Questions???

Thank You!

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