Plasma and Dry Micro/Nanotechnologies

1. Introduction to Plasma Processing

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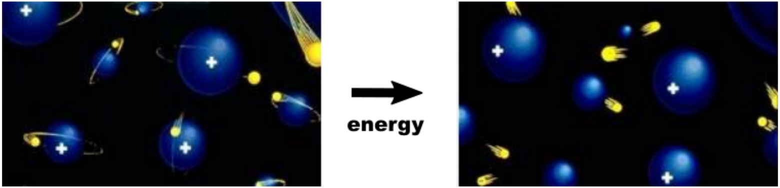
- What is plasma? The 4th state of matter: **the gas containing electrons and ions, fulfilling some special conditions** ⇒ ionization processes, ionization degree
- Fundamental plasma parameters: **electron temperature** and **density**. What about parameters of other particles?
- **Quantities and terms** important for plasma physics: Debye length, plasma frequency, cyclotron frequency, Larmor radius.
- **Plasma interacting with solid matter** - plasma sheath (Boltzmann relation for electron density, Bohm velocity), plasma potential, floating potential.
- Why plasma in material processing?
- Many existing methods: **plasma treatment, magnetron sputter-deposition, plasma enhanced CVD, plasma polymerization, plasma synthesis of nanoparticles, plasma etching**.

1.1 How to Create Plasma?

Plasma is 4th state of matter (created from neutral gas by ionization, i. e. generation of electron-ion pairs):



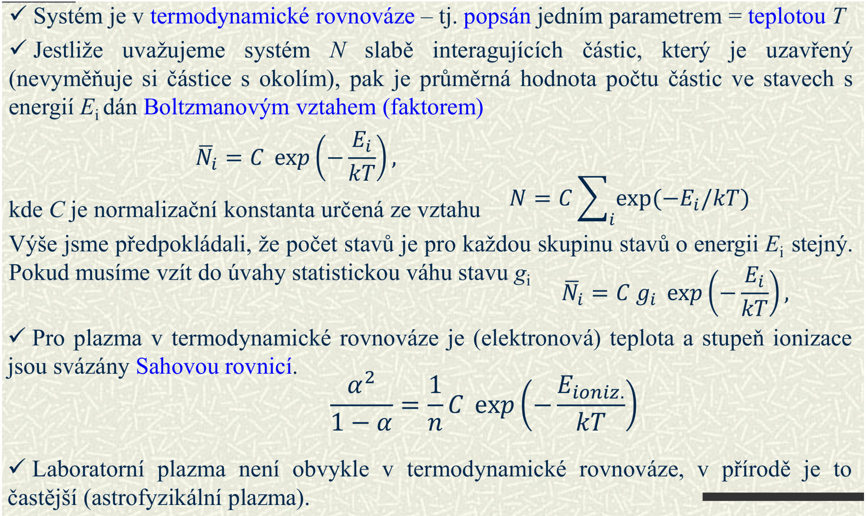
Adding sufficient energy to molecular gas leads to the **dissociation of molecules** into atoms due to collisions of the particles having energies higher than bond energy.

If the particles have even higher energie, the collisions leads to **ionization** (electrons are set free from the atom).
$\Rightarrow$ creation of **plasma as quasineutral system of electrons, ions and neutrals**.

plasma ionization degree $\alpha = \frac{n_\mathrm{i}}{n_\mathrm{i}+n_\mathrm{g}}$
$\alpha \approx 1$ - fully ionized plasma
$\alpha \ll 1$ - weakly ionized plasma

1.1 Several Methods for Plasma Generation

- **Increase of temperature** ⇒ The system is in thermodynamic equilibrium. Electron temperature T_e and degree of ionization $\alpha_\mathrm{i} = n_\mathrm{i}/(n_\mathrm{i} + n_\mathrm{g})$ are binded by Saha equation - not usual for laboratory plasma but can be often found in nature (space plasma).



✓ Systém je v termodynamické rovnováze – tj. popsán jedním parametrem = teplotou T

✓ Jestliže uvažujeme systém N slabě interagujících částic, který je uzavřený (nevyměňuje si částice s okolím), pak je průměrná hodnota počtu částic ve stavech s energií E_i dán Boltzmanovým vztahem (faktorem)

$$\bar{N}_i = C\ \exp\left(-\frac{E_i}{kT}\right),$$

kde C je normalizační konstanta určená ze vztahu $N = C\sum_i \exp(-E_i/kT)$

Výše jsme předpokládali, že počet stavů je pro každou skupinu stavů o energii E_i stejný. Pokud musíme vzít do úvahy statistickou váhu stavu g_i

$$\bar{N}_i = C\ g_i\ \exp\left(-\frac{E_i}{kT}\right),$$

✓ Pro plazma v termodynamické rovnováze je (elektronová) teplota a stupeň ionizace jsou svázány Sahovou rovnicí.

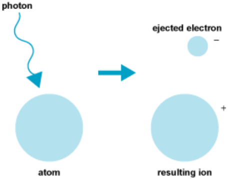
$$\frac{\alpha^2}{1-\alpha} = \frac{1}{n} C\ \exp\left(-\frac{E_{ioniz.}}{kT}\right)$$

✓ Laboratorní plazma není obvykle v termodynamické rovnováze, v přírodě je to častější (astrofyzikální plazma).

Several Methods for Plasma Generation

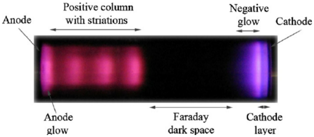
- **Using additional ionization processes** ⇒ the ionization degree is increased above its equilibrium value. When the source of additional ionization is switched off the plasma fades out due to recombination.

photoionization - ionization potential of e. g. oxygen atom is 13.6 eV ⇒ photon with 91 nm (vacuum UV)



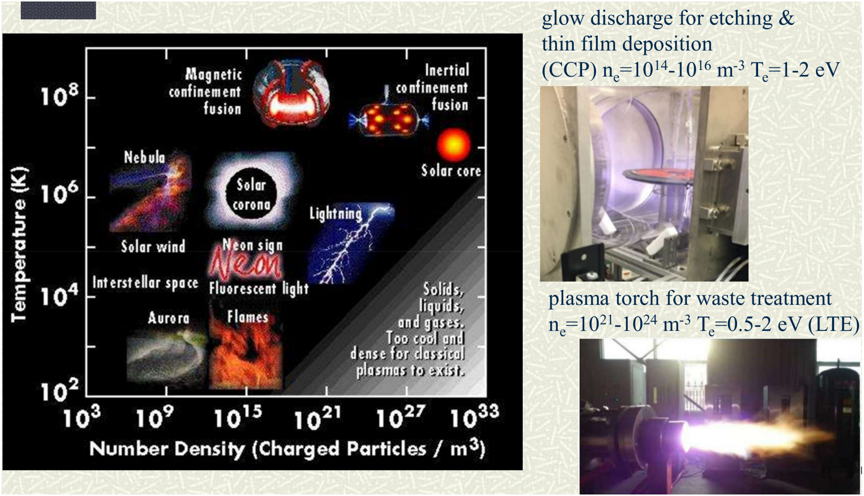
example: Earth ionosphere - natural photoionized plasma

gaseous electrical discharges - el. field accelerates free electrons to energies sufficient for ionization



example: d.c. glow discharge - laboratory plasma

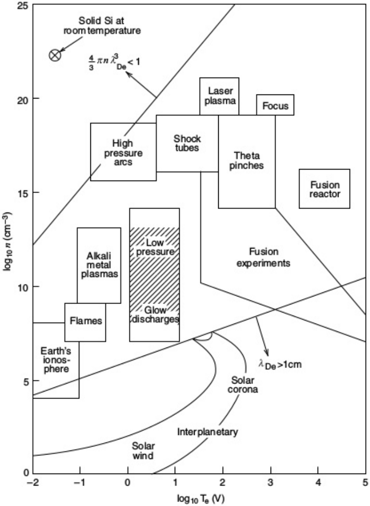
Where to find plasma?



glow discharge for etching & thin film deposition (CCP) $n_e=10^{14}$-10^{16} m^{-3} $T_e=1$-2 eV

plasma torch for waste treatment $n_e=10^{21}$-10^{24} m^{-3} $T_e=0.5$-2 eV (LTE)

1.2 Fundamental Plasma Parameters - T_e, n_e, B



electron temperature T_e in eV, 1 eV = 11 600 K
Outside thermodynamic equilibrium other temperatures discussed: ions (T_i), neutrals (T_n)

electron concentration $n_e = n_i$

magnetic field B

Other essential physical quantities are derived from T_e, n_e, B:

Debye length $\lambda_D = \sqrt{\frac{\varepsilon_0 k T_e}{e^2 n_e}}$

plasma frequency $\omega_p \approx \omega_{pe} = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}}$

cyclotron frequency $\omega_c = qB/m$

Larmor radius $r_c = v_\perp/\omega_c$

thermal velocity etc.

1.3 Conditions for Plasma as Ionized Gas

Natural length scale in plasma is **Debye length**

$$\lambda_\mathrm{D} = \left(\frac{\varepsilon_0 k T_\mathrm{e}}{n_\mathrm{e} e^2} \right)^{1/2}$$

Natural frequency (time) scale in plasma is **plasma frequency**

$$\omega_\mathrm{p} = \left(\frac{n_\mathrm{e} e^2}{m_\mathrm{e} \varepsilon_0} \right)^{1/2}$$

- Ionized gas is the plasma namely if $n_\mathrm{e} = n_\mathrm{i}$ on the scales of $L \gg \lambda_\mathrm{D}$.
- Plasma contains many interacting charged particles, condition: $n_\mathrm{e} \lambda_\mathrm{D}^3 \gg 1$
- Plasma exhibits collective behavior of electrons that is not much disturbed by electron-neutral collisions (collision frequency ν_en), conditions: $\omega_\mathrm{pe}/(2\pi) > \nu_\mathrm{en}$

Plasma Conditions - Collective Behaviour

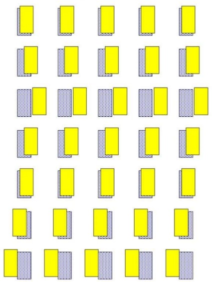
- Plasma contains **many interacting charged particles**. Condition: $n_e \lambda_D^3 \gg 1.$

- Plasma exhibits **collective behavior of electrons** (plasma frequency)

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

that is not much disturbed by electron-neutral collisions:

$$\omega_{pe}/(2\pi) > \nu_{en}$$



A plasma oscillation: displaced electrons oscillate around fixed ions. The wave does not necessarily propagate.

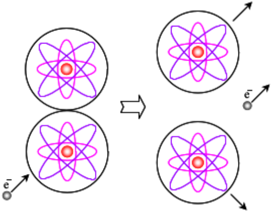
podle Chen & Chang 2003

1.4 Why Plasma in Material Processing?

Low temperature plasma of gaseous discharges provides unique environment for material processing:

- **hot electrons** (T_e few eV, 1 eV = 11 600 K)
  ⇒ dissociation of molecules into reactive species

$$\mathrm{e}^- + \mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}^-$$



- **positive ions** that can be accelerated to hundreds of eV near solid surface
  ⇒ sputtering of targets, implantation, modification of surfaces and growing films
- **cold neutral gas**
  ⇒ highly energetic process can be kept in a vessel, heat sensitive materials can be treated (e. g. polymers)

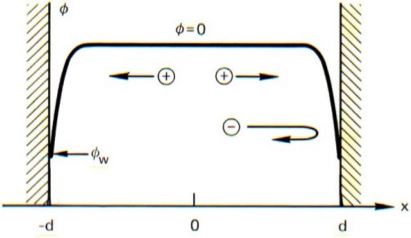
1.5 Plasma Sheath

Quasineutrality $n_\mathrm{e} \approx n_\mathrm{i}$ is fulfilled on the scale $L \gg \lambda_\mathrm{D}$, i. e. on the dimensions larger than Debye length

$$\lambda_\mathrm{D} = \left(\frac{\varepsilon_0 k T_\mathrm{e}}{e^2 n_\mathrm{e}} \right)^{1/2}$$

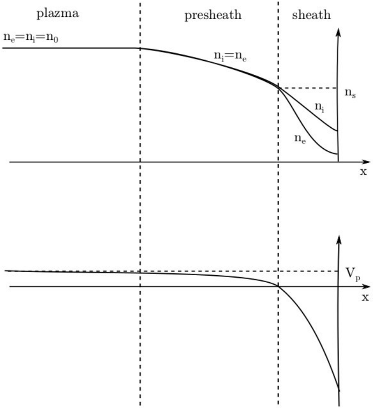
but this is violated in regions adjacent to walls and other solid objects in contact with plasma – **plasma sheath**.

Plasma sheath regions are very important for plasma processing. Plasma potential is always the most positive potential ⇒ electrons are repelled by a Coulomb barrier, ions accelerated towards solid surfaces.



1.5 Plasma Sheath for Low Voltage Drop

Charge densities and potential in bulk plasma, presheath and sheath adjacent to the wall or electrode



Relations valid for

- low sheath voltage (at floating or grounded walls)
- weakly ionized plasmas $T_\mathrm{e} \approx \mathrm{few\ eV}$, $T_\mathrm{i} \approx 0$

Densities of electrons and positive ions are expressed as

$$n_\mathrm{e} = n_\mathrm{s} \mathrm{e}^{\frac{eV}{kT_\mathrm{e}}} \qquad n_\mathrm{i} = n_\mathrm{s} \left(1 - \frac{2eV}{Mv_\mathrm{s}^2}\right)^{-1/2}$$

where v_s is ion velocity at the sheath edge, approximated by so called Bohm velocity u_B

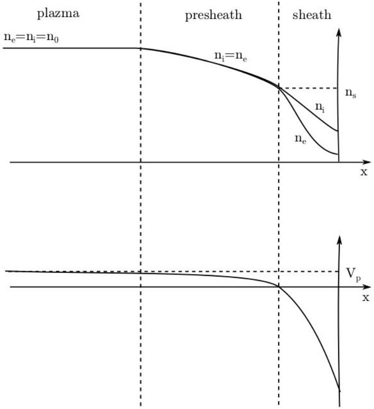
$$v_\mathrm{s} \geq u_\mathrm{B} = \sqrt{\frac{kT_\mathrm{e}}{M}}$$

Charge density at the sheath edge is

$$n_\mathrm{s} \approx 0.5 n_0 .$$

1.5 Plasma Sheath at Floating Wall

Charge densities and potential in bulk plasma, presheath and sheath adjacent to the wall or electrode



Electron and ion fluxes

$$\Gamma_\mathrm{e} = \frac{1}{4} n_\mathrm{s} \sqrt{\frac{8kT_\mathrm{e}}{\pi m}} \mathrm{e}^{\frac{eV}{kT_\mathrm{e}}} \qquad \Gamma_\mathrm{i} = n_\mathrm{s} u_\mathrm{B}$$

have to equal at the floating wall $\Rightarrow$

$$V_\mathrm{float} - V_\mathrm{plasma} = \frac{kT_\mathrm{e}}{2e} \ln\left(\frac{2\pi m}{M}\right)$$

For a typical low pressure discharge:

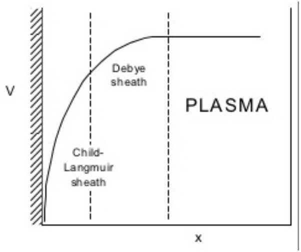
- $T_\mathrm{e} = 2\,\mathrm{eV}$, $n_\mathrm{e} = 10^8\ \mathrm{cm}^{-3}$
- in argon

floating potential is approx. $5T_\mathrm{e} = 10\,\mathrm{V}$
sheath thickness is approx. $5\lambda_\mathrm{D} = 0.37\,\mathrm{mm}$.

1.5 Plasma Sheath for High Voltage Drop (Applied Voltage)

High-voltage sheath (a voltage is applied) can be approximated by a model with **Child-Langmuir sheath**:

Sheath is artificially divided into **Debye sheath** which contains electrons and high-voltage **Child-Langmuir** sheath which has ions only.

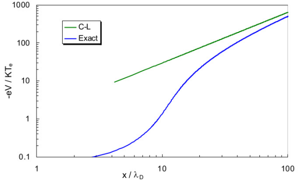


Then, current density j, voltage drop V_0 and sheath thickness d are related by the Child-Langmuir Law of Space-Charge-Limited Diodes

$$j = \frac{4}{9}\left(\frac{2e}{m_\mathrm{i}}\right)^{1/2}\frac{\varepsilon_0 V_0^{3/2}}{d^2} \qquad d = \frac{2}{3}\left(\frac{2V_0}{kT_\mathrm{eV}}\right)^{3/4}\lambda_\mathrm{D}$$

following previous example
with assumption $V_0 = 400\,\mathrm{V} \Rightarrow$
$d = 30\lambda_\mathrm{D}$, total sheath thickness $35\lambda_\mathrm{D}$,
i.e. about 1 cm

An exact calculation for a plane sheath shows that C-L scaling is not followed unless the sheath is very thick (notice log-log scale)



DC Plasma in Touch with Electrodes/Walls

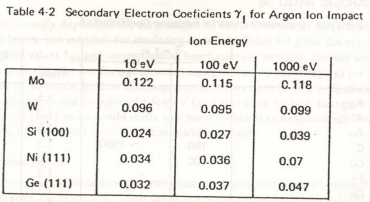
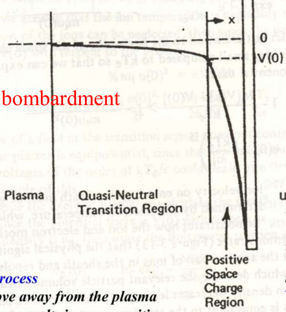


Table 4-2 Secondary Electron Coeficients γ_i for Argon Ion Impact

	Ion Energy		
	10 eV	100 eV	1000 eV
Mo	0.122	0.115	0.118
W	0.096	0.095	0.099
Si (100)	0.024	0.027	0.039
Ni (111)	0.034	0.036	0.07
Ge (111)	0.032	0.037	0.047

high-energy ion bombardment at the cathode



$$u(0) > \left(\frac{kT_e}{m_i}\right)^{1/2}$$

$$\frac{1}{2} m_i u(0)^2 = eV(0)$$

therefore,

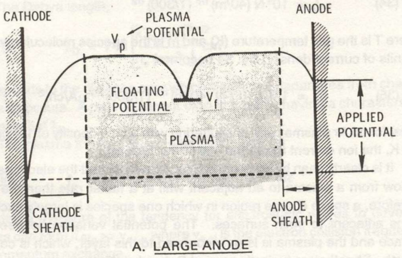
$$V(0) = m_i u(0)^2 / 2e$$
$$= (m_i/2e)\,(kT_e/m_i)$$
$$= kT_e/2e$$

Self-limiting process

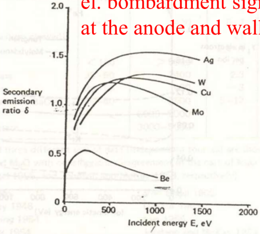
: 1) electron move away from the plasma

→ 2) the plasma results in more positive

→ 3) it hinders the escape of the negative electrons



el. bombardment significant at the anode and walls

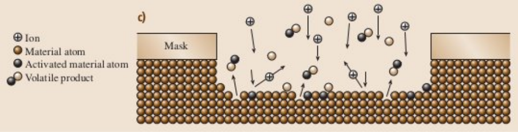


Secondary emission coefficient δ of different metals as a function of the energy of incident electrons (Hemenway et al. 1967)

1.6 Overview of Plasma Processing Methods

Plasma etching - irreplaceable

anisotropic dry etching: combination of chemistry and effect of ions (reactive ion etching)



Plasma treatment

dry modification of the top surface layer (no material added)

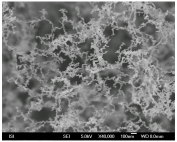
- roughness
- surface chemistry
- dangling bonds

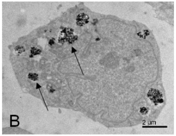
in Ar, O_2, NH_3 . . . discharges

Plasma synthesis - high purity

- plasma in liquids
- plasma synthesis of nanoparticles

e. g. iron oxide superparamagnetic NPs - (minimum toxic effects for cells)





Plasma deposition of thin films

see next slide

Plasma Deposition

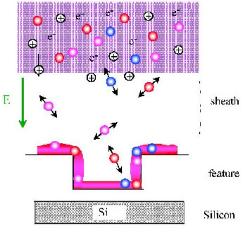
Plasma deposition of thin films

- plasma enhanced chemical vapor deposition (PECVD)

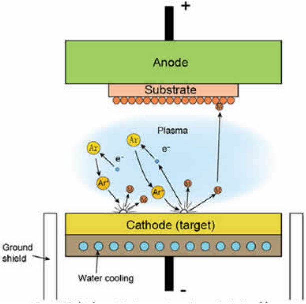
$$Si(OC_2H_5)_4 + e^- \rightarrow Si(OC_2H_5)_3(OH) + C_2H_4 + e^-$$

$$O_2 + e^- \rightarrow 2O + e^-$$

$$O + Si(OC_2H_5)_3(OH) \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_4O$$



- physical vapor deposition (PVD) - dc diode sputtering, magnetron sputtering



Applications of Plasma Treatment and Deposition

Material surface can be **plasma treated** or **plasma coated with a thin film** thickness of the plasma modified layer ranges from **few nm to tens of μm**.

- hydrophilic surfaces for improved painting, printing, lacquering
- surfaces for improved adhesion of coatings or strength of adhesive bonds
- hydrophobic surfaces for nonadhesive, self-cleaning or antifouling applications
- thin films for electronic applications (a-Si:H, Si-based dielectric films)
- thin films for optical applications (low and high refractive index oxides)
- hard and tribological coatings (metal nitrides, metal carbides, diamond like carbon)
- barrier coatings (a-C:H, organosilicon plasma polymers)
- bioapplications such as biosensors, drug immobilization, tissue engineering (surface functionalization, plasma polymers)




Unique Features of Plasma Technologies:

- dry process (gas phase), i.e. with low consumption of chemicals,
- offering replacement of toxic and explosive reactants, i.e. environmentally and user friendly
- irreplaceable for anisotropic etching required in microelectronics or MEMS applications
- preparation of new materials that cannot be obtained by pure chemical methods

How it can be used?

- in vacuum reactor (at low pressure) - excellent control over the process
- at atmospheric pressure with no need of vessel (except because of safety reasons in case of toxic chemicals)