F4280 Technology of Thin Film Deposition & Surface Treatments
7. Plasma Fundamentals

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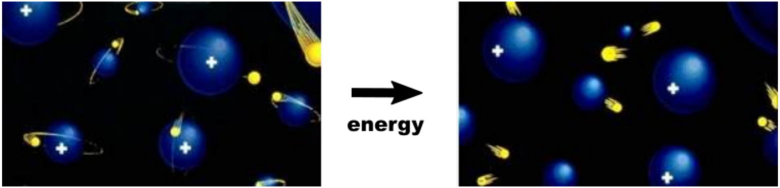
Outline

7.1 Conditions for Plasma as Ionized Gas

Plasma is created from gas by adding sufficient energy (**4th state of matter**). Added energy leads to **ionization of neutral gas**, i. e. generation of electron-ion pairs:



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**

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

- 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

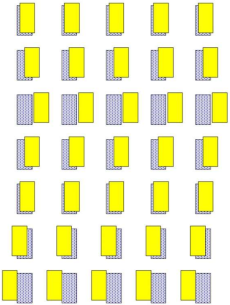
- Plasma contains **many interacting charged particles**. Condition: $n_e \lambda_D^3 \gg 1.$

- 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

7.2 Plasma in Thermal Equilibrium

Plasma can be created by **adding sufficient thermal energy** $\Rightarrow$ the system is in thermodynamic equilibrium, characterized by one T
- fusion plasma, Sun's plasma, not in laboratory

- Considering the system of N weakly interacting particles that is closed (does not exchange energy with its surroundings), the average number of particles in the states with energy E_i is given by **Boltzmann factor**

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

  where C is constant determined by $N = C\sum_i \exp(-E_i/kT)$

  We assumed above that the number of states is the same for each group of states with energy E_i. If we have to take into account the statistical weight of the states g_i

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

- Temperature T and **degree of ionization** $\alpha_\mathrm{i} = n_\mathrm{i}/(n_\mathrm{i} + n_\mathrm{g})$ are binded by **Saha equation**

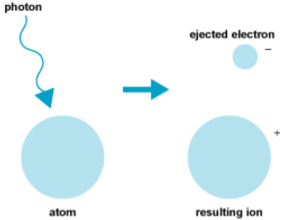
$$\frac{\alpha^2}{1-\alpha} = \frac{1}{n} C' \left(-\frac{E_\mathrm{ioniz.}}{kT}\right)$$

  where $n = n_\mathrm{i} + n_\mathrm{g}$

7.3 Non-equilibrium Plasmas

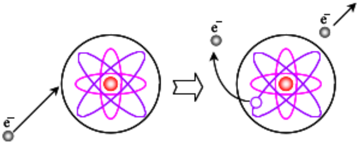
Many plasmas are created out of thermodynamic equilibrium by increasing the **ionization degree** α above the equilibrium value with an **additional ionization source**

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



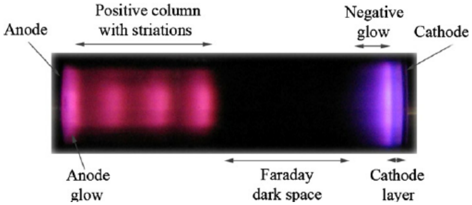
example: Earth ionosphere - natural photoionized plasma

ionization by electron impact



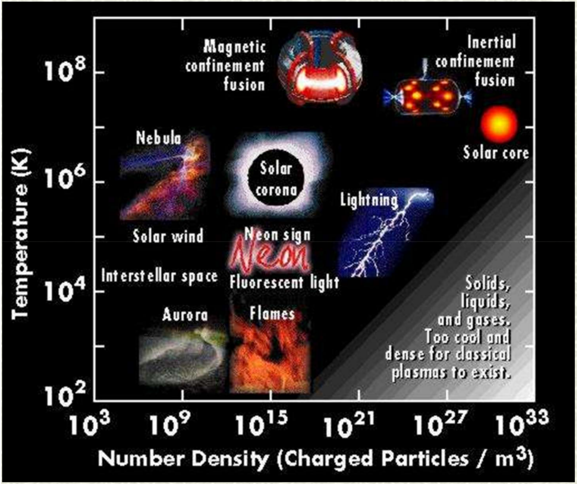
in **gaseous electrical discharges** - el. field accelerates free electrons to ionization energies

example: d.c. glow discharge

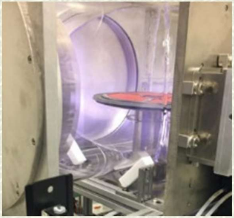


Switching off the ionization source leads to plasma extinction due to the recombination.

Where to find plasma?

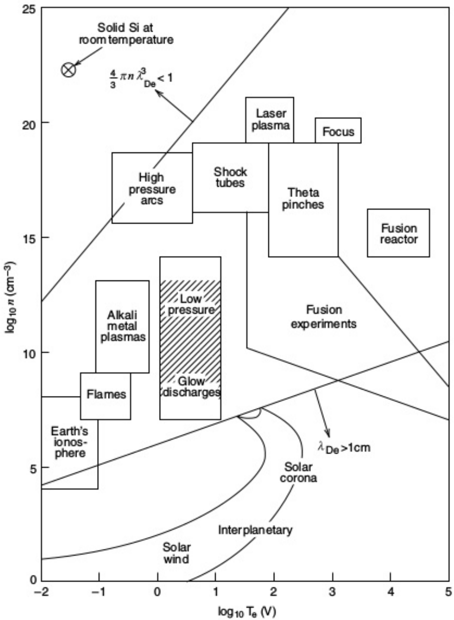


glow discharge for etching & thin film deposition (CCP) $n_e = 10^{14}$-10^{16} m^{-3} $T_e = 1$-2 eV



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

7.4 Fundamental Plasma Parameters n_e, T_e, B



Outside thermodynamic equilibrium other T appear (T_i, T_g, T_rot, T_vib)!

T_e units are rather [eV], 1 eV = 11 600 K

Other quantities are derived from the fundamental plasma parameters
Debye length

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

plasma frequency

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

cyclotron frequency $\omega_\mathrm{c} = qB/m$

Larmor radius $r_\mathrm{c} = v_\perp/\omega_\mathrm{c}$

thermal velocity $\sqrt{kT_j/m_j}$

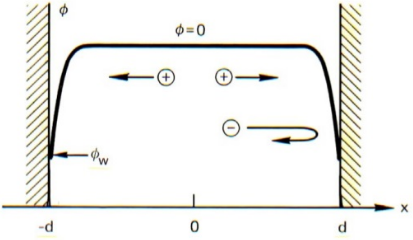
7.5 Plasma Sheath

Quasineutrality $n_e \approx n_i$ is fulfilled on the scale $L \gg \lambda_D$, i. e. on the dimensions larger than Debye length

$$\lambda_D = \left(\frac{\varepsilon_0 k T_e}{e^2 n_e} \right)^{1/2}$$

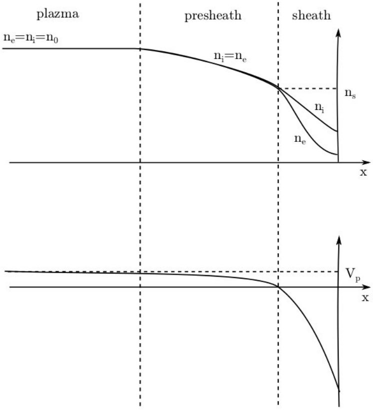
but this is violated in regions adjacent to walls and other solid objects in contact with plasma – **plasma sheath**.

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



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

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

Floating and Plasma Potentials

Electron and ion fluxes toward surface

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

$$\Gamma_\mathrm{i} = n_\mathrm{s} u_\mathrm{B}$$

have to equal at the **floating** wall (surface dielectrically disconnected from ground or electrode) $\Rightarrow$

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

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. $5\lambda_\mathrm{D} = 0.37\,\mathrm{mm}$.

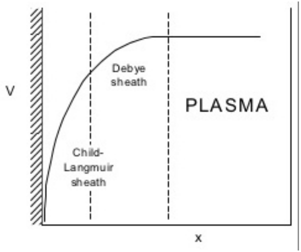
Plasma Sheath for High Voltage Drop (Applied Voltage)

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.

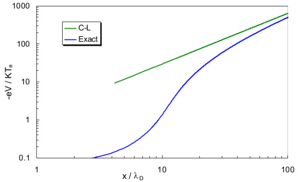
Then, current density j, voltage drop V_0 and sheath thickness d are related by the Child-Langmuir Law of Space-Charge-Limited Diodes

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



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

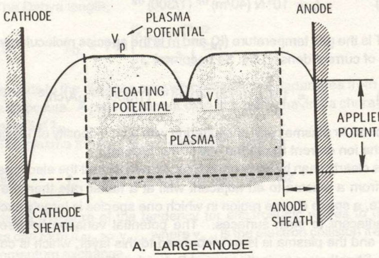
An exact calculation for a plane sheath shows that C-L scaling is not followed unless the sheath is very thick (notice log-log scale)



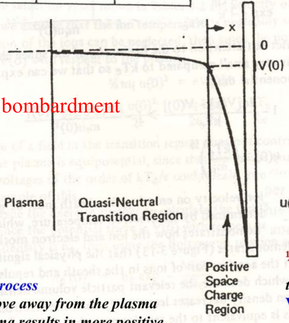
DC Plasma in Touch with Electrodes/Walls

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

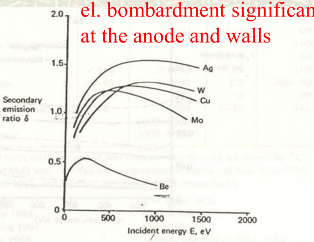


high-energy ion bombardment at the cathode



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

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)

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

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

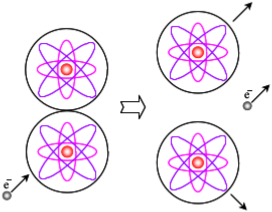
→ 3) it hinders the escape of the negative electrons

7.6 Why Plasma Is Used in Material Processing?

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

- **hot electrons** (T_e few eV, $1\mathrm{eV} = 11600$ K)
  $\Rightarrow$ dissociation of molecules into reactive species

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

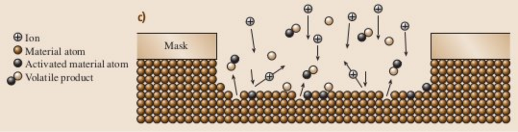


- **positive ions** that can be accelerated by $\approx$ 100 eV near solid surface
  $\Rightarrow$ sputtering of targets, implantation, modification of surfaces and growing films
- **cold neutral gas**
  $\Rightarrow$ highly energetic process can be kept in a vessel, heat sensitive materials can be treated (e. g. polymers)

7.7 Overview of Plasma Processing Methods I

Plasma etching - irreplaceable etching method

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



Plasma treatment

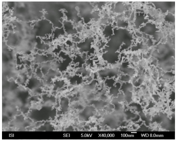
dry modification of the top surface layer (no material added, modification of existing material by oxidation, nitridation etc.) in Ar, O_2, NH_3 . . . discharges for

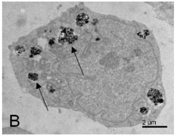
- change of roughness
- change of surface chemistry
- creation of dangling bonds

Plasma synthesis - high purity

- plasma in liquids
- plasma synthesis of nanoparticles (dry or in liquid)

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





7.7 Overview of Plasma Processing Methods II

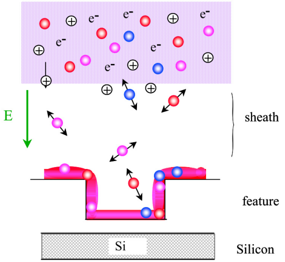
plasma enhanced chemical vapor deposition (PECVD)

- from gases and vapors
- very easy for organic materials and Si compounds (SiH_4, variety of volatile organosilicon compounds)
- for metals - necessary to find sufficiently volatile compounds (organometallic)

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

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

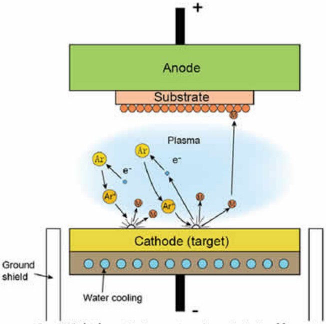
$$O + Si(OC_2H_5)_3(OH) \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_4O$$



(in various low or atm. pressure discharges)

plasma sputter-deposition - physical vapor deposition (PVD)

- gasification of solid targets by ion sputtering $\Rightarrow$ deposition
- simple method for metals
- a bit more complex for oxides, nitrides, carbides (reactive sputtering)



(dc diode sputtering, magnetron sputtering)

7.8 Reactions/Interactions in Plasma

Electrons in plasma gain high energies (in the order of 1–10 eV) due to acceleration by electric field.
Since electrons collide with heavy particles (atoms, molecules) they change direction of their velocity or even loose the energy.

Collisions between electrons and heavy particles (according to the electron energy E_e):

- $E_\mathrm{e} < 2\,\mathrm{eV}$ (depending on the atom/molecule): elastic collisions with very small fractional energy transfer (see next slide).
- $2\,\mathrm{eV} < E_\mathrm{e} < 15\,\mathrm{eV}$ (approx.): variety of inelastic collisions $\Rightarrow$ E_e is partially converted into internal energy of the target molecule (atom)
- $E_\mathrm{e} > 15\,\mathrm{eV}$ (approx.): ionization (sustains the discharge)

Rate constant k for reaction of two particles with velocities $\vec{v}_1$, $\vec{v}_2$ can be calculated from **cross section** σ

$$K = \langle \sigma(v_\mathrm{R}) v_\mathrm{R} \rangle_{v_1, v_2} = \int \sigma(v_\mathrm{R}) v_\mathrm{R} f_1(\vec{v}_1) f_2(\vec{v}_2) \mathrm{d}v_1^3 \mathrm{d}v_2^3$$

where $v_\mathrm{R} = |\vec{v}_1 - \vec{v}_2|$ and $f_1(\vec{v}_1)$, $f_2(\vec{v}_2)$ are velocity distribution functions.

Elastic and Inelastic Collisions

Elastic scattering (momentum and energy are conserved):

- **Coulomb** collisions - between two charged particles (e-e, e-ion, ion-ion)
- polarization scattering with **permanent dipole** (for molecules with permanent dipole)
- polarization scattering with **induced dipole** (e-neutral for electrons with low energies, ion-neutral collisions)
- **hard sphere** - between neutrals, e-neutral for very low electron energies (approx.)

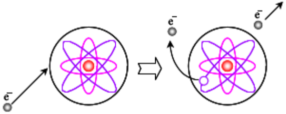
TABLE 3.1. Scaling of Cross Section σ, Interaction Frequency ν, and Rate Constant K, With Relative Velocity v_R, for Various Scattering Potentials U

Process	$U(r)$	σ	ν or K
Coulomb	$1/r$	$1/v_R^4$	$1/v_R^3$
Permanent dipole	$1/r^2$	$1/v_R^2$	$1/v_R$
Induced dipole	$1/r^4$	$1/v_R$	const
Hard sphere	$1/r^i,\ i \to \infty$	const	v_R

after Lieberman & Lichtenberg 1994

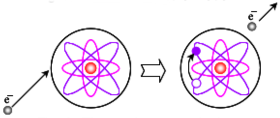
Inelastic scattering: ionization, recombination, excitation, dissociation . . .

Atomic Processes - Excitation Processes



Electron impact ionization

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



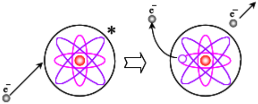
Electron impact excitation

$$\mathrm{e}^- + \mathrm{A} \longrightarrow \mathrm{e}^- + \mathrm{A}^*$$

A^* can have quite different chemical reactivity towards the surface. Some excited atoms have very long lifetimes ($\approx$ 1–10 ms) $\Rightarrow$ **metastables**

Electron-metastable ionization

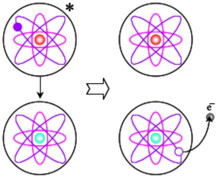
$$\mathrm{e}^- + \mathrm{A}^* \longrightarrow \mathrm{e}^- + \mathrm{e}^- + \mathrm{A}^+$$



Since the metastable atom is already excited, less energy is required.

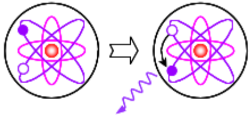
Metastable-neutral ionization

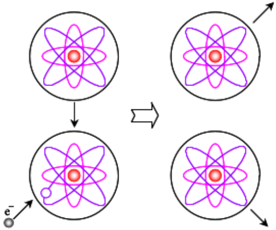
$$\mathrm{A}^* + \mathrm{B} \longrightarrow \mathrm{A} + \mathrm{e}^- + \mathrm{B}^+$$



If the ionization energy of the neutral B is less than the excitation energy of the metastable A^* $\Rightarrow$ **Penning ionization** (He* 19.8, Ne* 16.7, Ar* 11.7 eV)

Atomic Processes - Relaxation and Recombination





De-excitation

$$\mathrm{A}^* \longrightarrow \mathrm{A} + \mathrm{h}\nu$$

In most cases, the relaxation of electronically excited states is practically instantaneous ($\approx$ 10 ns).

Electron-ion recombination

$$\mathrm{e}^- + \mathrm{A}^+(+\mathrm{C}) \longrightarrow \mathrm{A}^*(+\mathrm{C})$$

A third-body (neutrals, reactor walls) must be involved to conserve energy and momentum.

Radiative recombination

$$\mathrm{e}^- + \mathrm{A}^+\,(+\mathrm{C}) \longrightarrow \mathrm{A} + \mathrm{h}\nu\,(+\mathrm{C})$$

Electron attachment

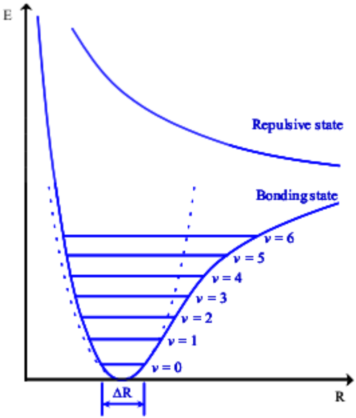
$$\mathrm{e}^- + \mathrm{A}\,(+\mathrm{C}) \longrightarrow \mathrm{A}^-(+\mathrm{C})$$

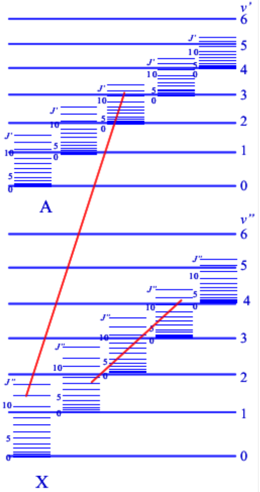
Ion-ion recombination

$$\mathrm{A}^+ + \mathrm{A}^- \longrightarrow \mathrm{A} + \mathrm{A}$$

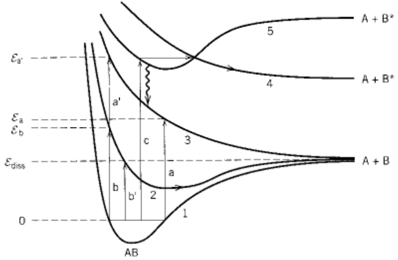
Processes Involving Molecules

In molecules, **excitation of vibrational and rotational states** (besides electronic states) are possible:





Electron Collisions with Molecules - Dissociation



Dissociation cross section rises linearly from threshold $\varepsilon_{\rm thr} \approx \varepsilon_1$ to a max. value (typically 10^{-15} cm^2) at ε_2 and then falls off as $1/\varepsilon$:

$$\sigma_{\rm diss} = 0 \quad \varepsilon < \varepsilon_1$$

$$\sigma_{\rm diss} = \sigma_0 \frac{\varepsilon - \varepsilon_1}{\varepsilon_1} \quad \varepsilon_1 < \varepsilon < \varepsilon_2$$

$$\sigma_{\rm diss} = \sigma_0 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon} \quad \varepsilon > \varepsilon_2$$

$$\sigma_0 = \pi \left(\frac{e}{4\pi\epsilon_0\varepsilon_1} \right)^2$$

Dissociation

key role for plasma chemistry of low pressure discharges:

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

Collisions *a* and *a'*: ground state $v = 0$ excited to repulsive state of AB, energy $\langle \varepsilon_{\rm a} - \varepsilon_{\rm diss}, \varepsilon_{\rm a'} - \varepsilon_{\rm diss} \rangle$ shared among the dissociation products A and B.
Typically, $\varepsilon_a - \varepsilon_{diss} \approx$ few eV
$\Rightarrow$ **hot neutral fragments** (profound effect on plasma chemistry of growing films if hitting the substrate surface)

Collisions *b* and *b'*: ground state excited to an attractive state of AB but energy exceeds $\varepsilon_{\rm diss}$ $\Rightarrow$ dissociation of AB resulting in fragments having energies from thermal up to $\varepsilon_{\rm b} - \varepsilon_{\rm diss} \approx$ few eV.

Collision *c*: excitation to bound state AB* that radiates creating $\mathrm{A} + \mathrm{B}$ or

$$\mathrm{AB}^*(\mathrm{bound}) \longrightarrow \mathrm{AB}^*(\mathrm{unbound}) \longrightarrow \mathrm{A}{+}\mathrm{B}^*$$

Complex reaction schemes for O_2 plasma - 2^{nd} order reactions

Number	Reaction	Rate Constant (cm^3/s)
Reactions among e, O_2, O_2^+, O, *and* O^-		
1	$e + O_2$ momentum transfer	$4.7E{-}8T_e^{0.5}$
2	$e + O_2 \rightarrow O^- + O$	$1.07E{-}9T_e^{-1.391}\exp(-6.26/T_e)$
3	$e + O_2 \rightarrow 2O + e$	$6.86E{-}9\exp(-6.29/T_e)$
4	$e + O_2 \rightarrow O_2^+ + 2e$	$2.34E{-}9T_e^{1.03}\exp(-12.29/T_e)$
5	$e + O^- \rightarrow O + 2e$	$5.47E{-}8T_e^{0.324}\exp(-2.98/T_e)$
6	$e + O_2^+ \rightarrow 2O$	$2.2E{-}8/T_e^{1/2}$
7	$O^- + O_2^+ \rightarrow O + O_2$	$2.6E{-}8(300/T)^{0.44}$
8	$O^- + O \rightarrow O_2 + e$	(1.9, 3, 5)E−10
9	$O^- + O_2^+ \rightarrow 3O$	$2.6E{-}8(300/T)^{0.44}$
Addition of O^+		
10	$e + O_2 \rightarrow O^- + O^+ + e$	$7.1E{-}11T_e^{0.5}\exp(-17/T_e)$
11	$e + O_2 \rightarrow O + O^+ + 2e$	$1.88E{-}10T_e^{1.699}\exp(-16.81/T_e)$
12	$e + O \rightarrow O^+ + 2e$	$9.0E{-}9T_e^{0.7}\exp(-13.6/T_e)$
13	$O^- + O^+ \rightarrow 2O$	$4.0E{-}8(300/T)^{0.44}$
14	$O^+ + O_2 \rightarrow O + O_2^+$	$2.0E{-}11(300/T)^{0.5}$
Addition of metastable $O_2^*(^1\Delta_g)$; *see note f below*		
15	$e + O_2 \rightarrow O_2^* + e$	$1.37E{-}9\exp(-2.14/T_e)$
16	$e + O_2^* \rightarrow e + O_2$	$2.06E{-}9\exp(-1.163/T_e)$
17	$e + O_2^* \rightarrow O + O^-$	$4.19E{-}9T_e^{-1.376}\exp(-5.19/T_e)$
18	$O_2^* + O_2 \rightarrow 2O_2$	$2.2E{-}18(T/300)^{0.8}$
19	$O_2^* + O \rightarrow O_2 + O$	(1.0, 7)E−16
20	$O^- + O_2^* \rightarrow O_3 + e$	2.2E−11
21	$O^- + O_2^* \rightarrow O_2^- + O$	1.1E−11
Addition of metastable $O(^1D)$		
22	$e + O_2 \rightarrow O + O^* + e$	$3.49E{-}8\exp(-5.92/T_e)$
23	$e + O \rightarrow O^* + e$	$4.54E{-}9\exp(-2.36/T_e)$
24	$e + O^* \rightarrow e + O$	$8.17E{-}9\exp(-0.4/T_e)$
25	$e + O^* \rightarrow O^+ + 2e$	$9.0E{-}9T_e^{0.7}\exp(-11.6/T_e)$
26	$O^* + O \rightarrow 2O$	8.0E−12
27	$O^* + O_2 \rightarrow O + O_2$	$(6.4, 7.0)E{-}12\exp(67/T)$
28	$O^* + O_2 \rightarrow O + O_2^*$	1.0E−12
Addition of selected reactions for O_2^- *and* O_3		
29	$O^- + O_2 \rightarrow O_3 + e$	5E−15
30	$e + O_3 \rightarrow O_2^- + O$	1E−9
31	$e + O_3 \rightarrow O^- + O_2$	$2.12E{-}9T_e^{-1.058}\exp(-0.93/T_e)$
32	$O_2^- + O_2^+ \rightarrow 2O_2$	$2E{-}7(300/T)^{0.5}$
33	$O_2^- + O^+ \rightarrow O_2 + O$	$(1, 2)E{-}7(300/T)^{0.5}$
34	$O_3 + O_2 \rightarrow O_2 + O + O_2$	$7.3E{-}10\exp(-11400/T)$
35	$O_3 + O \rightarrow 2O_2$	$1.8E{-}11\exp(-2300/T)$

Complex reaction schemes for O_2 plasma - 3^{rd} order reactions

Number	Reaction	Rate Constant (cm^6/s)
Reactions among e, O_2, O_2^+, and O^-		
1	$e + e + O_2^+ \rightarrow e + O_2$	$1E-19(0.026/T_e)^{4.5}$
2	$e + O_2^+ + O_2 \rightarrow O_2 + O_2$	$6E-27(0.026/T_e)^{1.5}$, $1E-26$
3	$e + O + O_2 \rightarrow O^- + O_2$	$1E-31$
4	$O^- + O_2^+ + O_2 \rightarrow O + O_2 + O_2$	$2E-25(300/T)^{2.5}$
5	$O + O + O_2 \rightarrow O_2 + O_2$	$2.45E-31T^{-0.63}$
		$1.3E-32(300/T)\exp(-170/T)$
6	$O + O + O \rightarrow O_2 + O$	$6.2E-32\exp(-750/T)$
Addition of O^+		
7	$e + e + O^+ \rightarrow e + O$	$1E-19(0.026/T_e)^{4.5}$
8	$e + O^+ + O_2 \rightarrow O + O_2$	$6E-27(0.026/T_e)^{1.5}$, $1E-26$
9	$O^- + O^+ + O_2 \rightarrow O_2 + O_2$	$2E-25(300/T)^{2.5}$, $2E-25$
10	$O^- + O^+ + M \rightarrow O + O + M$	$2E-25(300/T)^{2.5}$
11	$O^+ + O + O_2 \rightarrow O_2^+ + O_2$	$1E-29$
Addition of metastable $O(^1D)$		
12	$O + O^* + O_2 \rightarrow O_2 + O_2$	$9.9E-33$
Addition of selected reactions for metastable $O_2^*(^1\Delta_g)$, O_2^-, *and* O_3		
13	$e + O_2 + O_2 \rightarrow O_2^- + O_2$	$1.4E-29(0.026/T_e)$
		$\times \exp(100/T - 0.061/T_e)$
14	$e + O_2 + O \rightarrow O_2^- + O$	$1E-31$
15	$O^- + O_2^+ + O_2 \rightarrow O_3 + O_2$	$2E-25(300/T)^{2.5}$
16	$O + O_2 + O_2 \rightarrow O_3 + O_2$	$6.9E-34(300/T)^{1.25}$,
		$6.4E-35\exp(663/T)$
17	$O + O_2 + O \rightarrow O_3 + O$	$2.15E-34\exp(345/T)$
18	$e + O_2^* + O_2 \rightarrow O_2^- + O_2$	$1.9E-30$
19	$e + O_2^* + O \rightarrow O_2^- + O$	$1E-31$
20	$O_2^- + O^+ + M \rightarrow O_3 + M$	$2E-25(300/T)^{2.5}$
21	$O_2^- + O_2^+ + O_2 \rightarrow O_2 - O_2 + O_2$	$2E-25(300/T)^{2.5}$