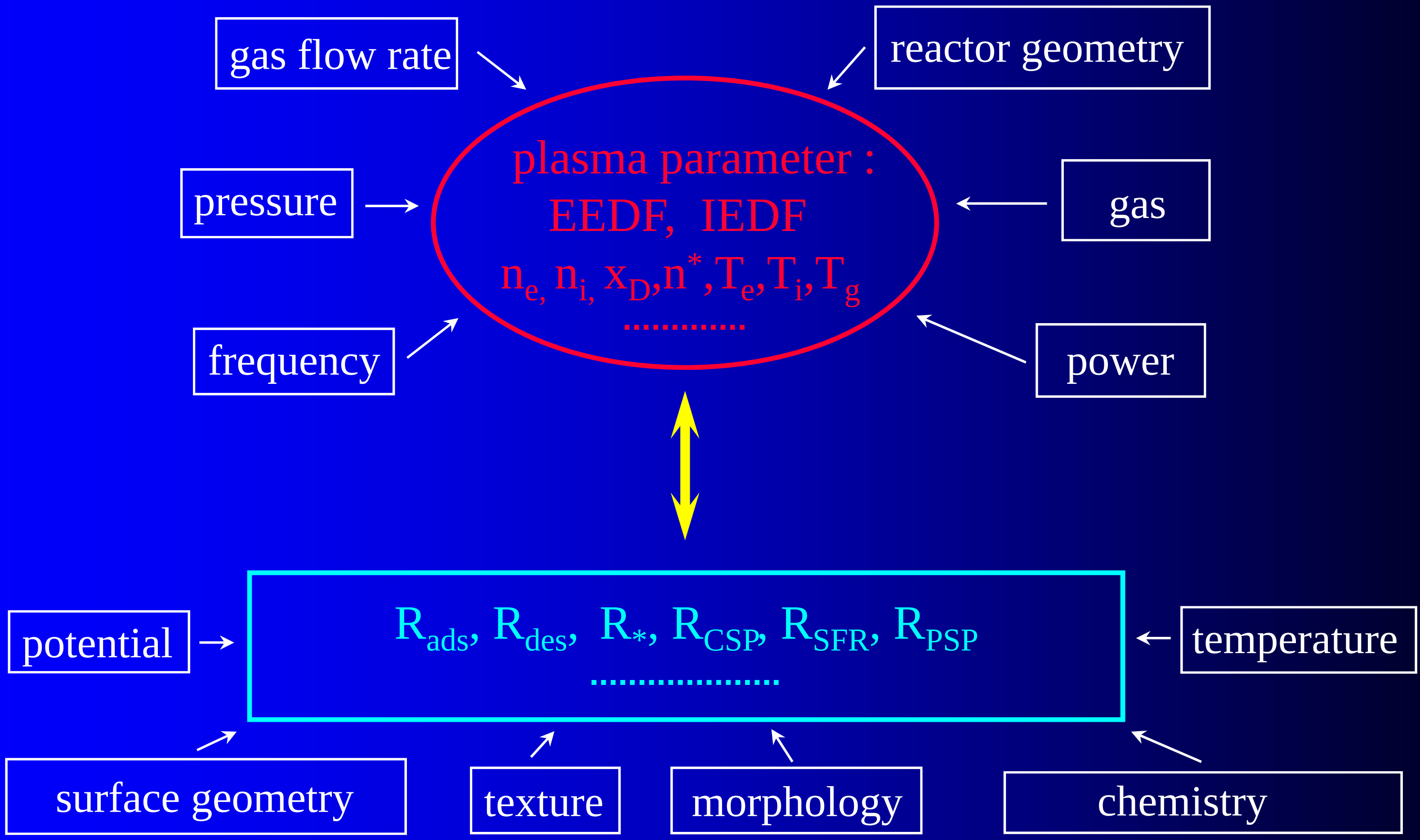
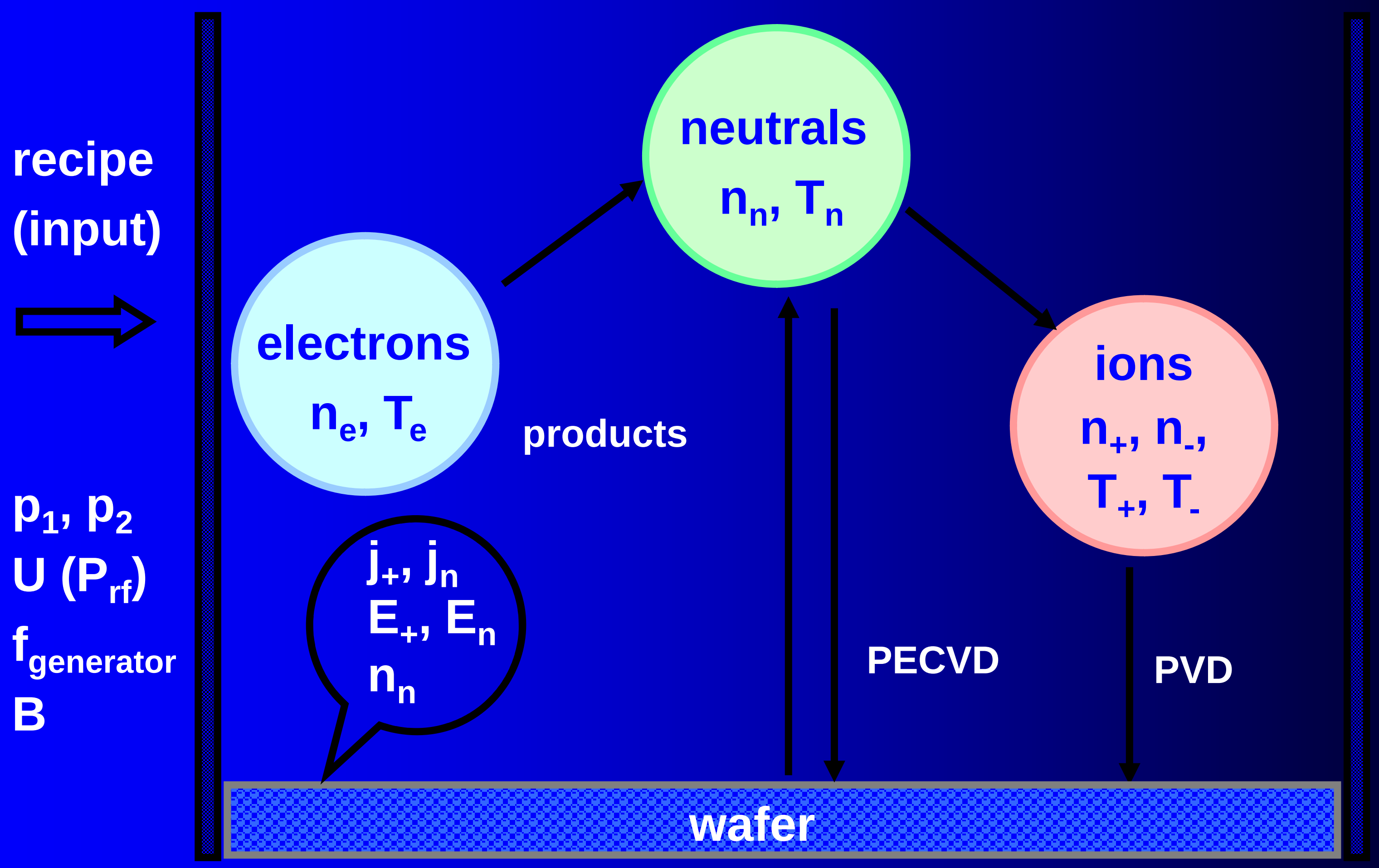
Plasma Surface Interaction
(part I: fundamentals)

- Introduction
  # complexity: plasma and surface
- Elementary processes of PSI
  # adsorption, diffusion, desorption
  # chemical reactions, sputtering
- Particle and energy balances

complexity of phenomena : plasma and surface



complexity of phenomena



basic description of plasma excitation

Maxwell-Boltzmann Equation

Basic Equation $$\left[\frac{\partial}{\partial t}+\vec{v}_i\frac{\partial}{\partial \vec{r}}+\dot{\vec{v}}_i\frac{\partial}{\partial \vec{v}_i}\right]f_i=\sum_{i\in jklm}S^i_{jklm}\left(f_j,f_k\right)$$

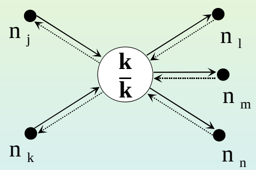
Problems: Inhomogeneities / Cross Sections

Distribution Functions

- **Electrons:** $$-\frac{e\left(\vec{E}+\vec{v}_e\times\vec{B}\right)}{m_e}\frac{\partial}{\partial \vec{v}_e}f_e=\sum_{e\in jklm}S^e_{jklm}\left(f_j,f_k\right)$$
- **Ions:** $$\frac{e\left(\vec{E}+\vec{v}_i\times\vec{B}\right)}{m_e}\frac{\partial}{\partial \vec{v}_i}f_i=\sum_{i\in jklm}S^i_{jklm}\left(f_j,f_k\right)$$
- **Neutrals:** $$0=\sum_{n\in jklm}S^n_{jklm}\left(f_j,f_k\right)$$

Chemical Reactions

Mostly Neutrals $$\sum_{i\in jklm}\dot{n}_i^{jklm}=\pm k_{jk}n_j n_k$$



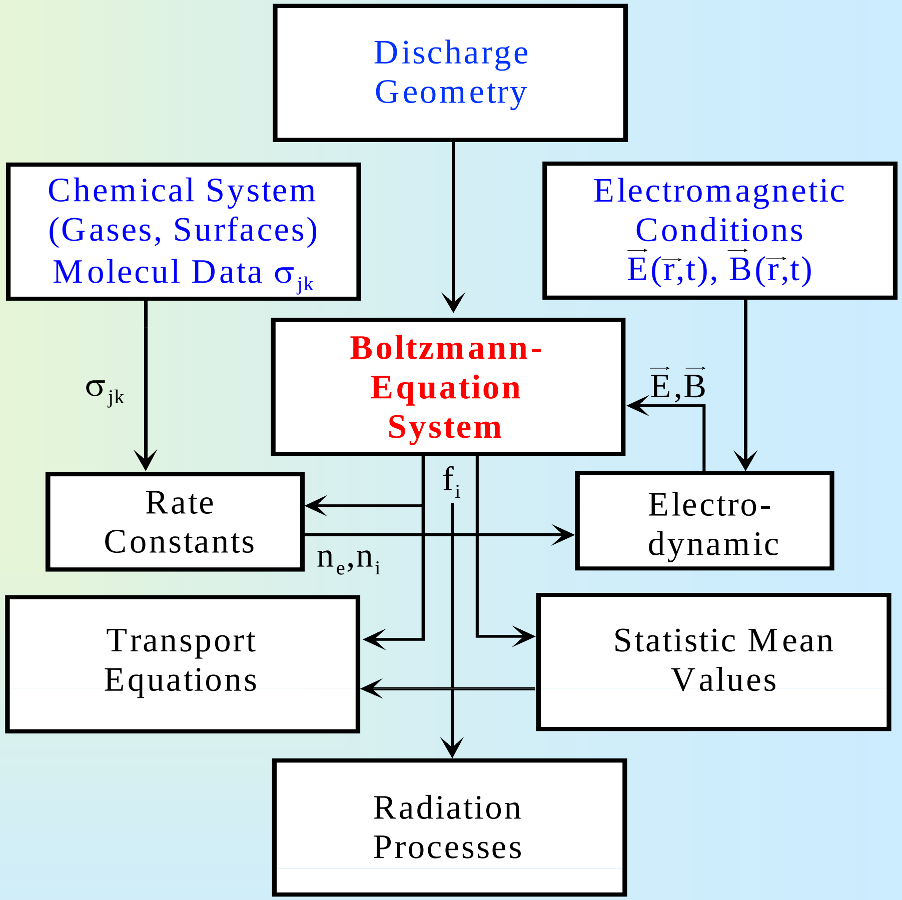
Transport Equations

Navier-Stokes Equation $$\mu_m\left(\vec{v}_s\frac{\partial}{\partial \vec{r}}\right)\vec{v}_s=-\frac{\partial}{\partial \vec{r}}p+\eta\,\Delta\vec{v}_s$$

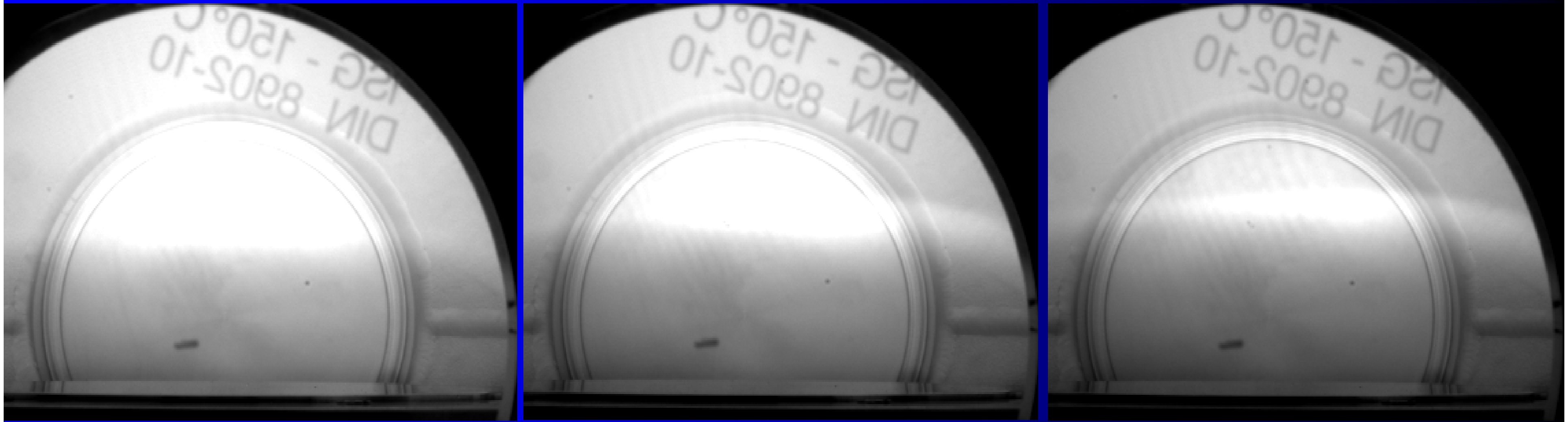
Maxwell Equations / Plasma Sheath

Wave and space charge phenomana

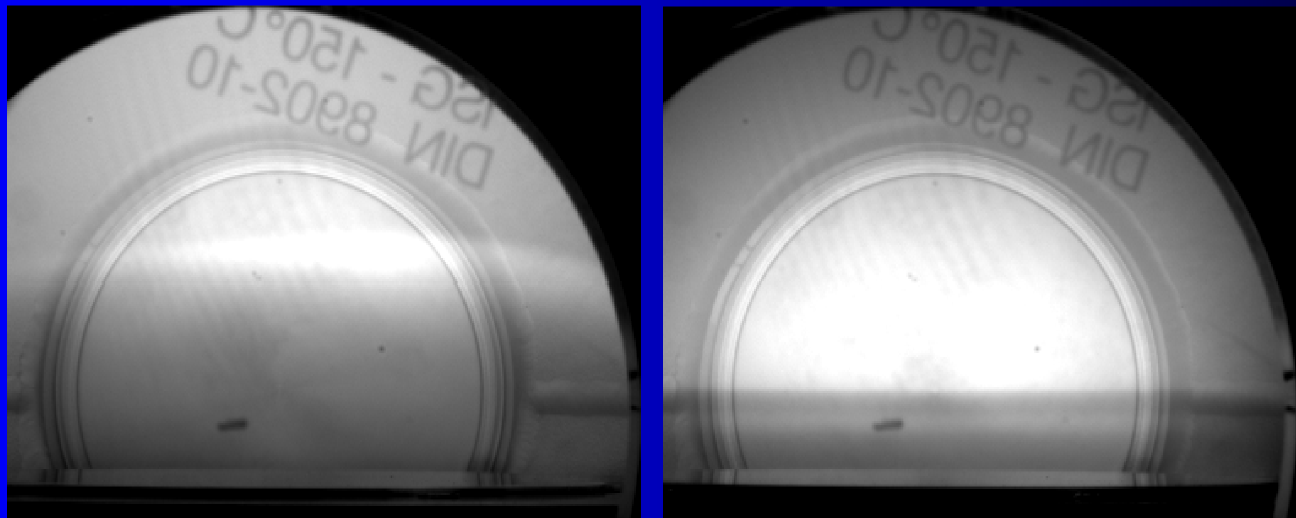
Plasma sheath important for surface reactions ! $$\frac{d^2V(\vec{r})}{d\vec{r}^2}=-\frac{e\,n_i(\vec{r},t)}{\varepsilon_0}$$



plasma sheath (dark space) at surfaces affects the PSI ...
... and depends on discharge power and pressure



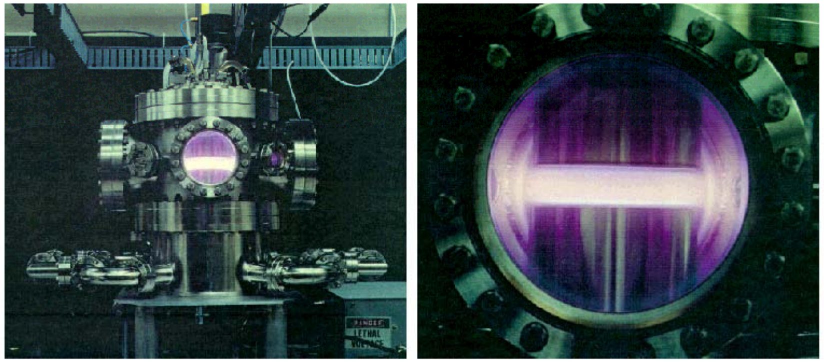
Argon, 0.005mbar, 10W 30W 50W

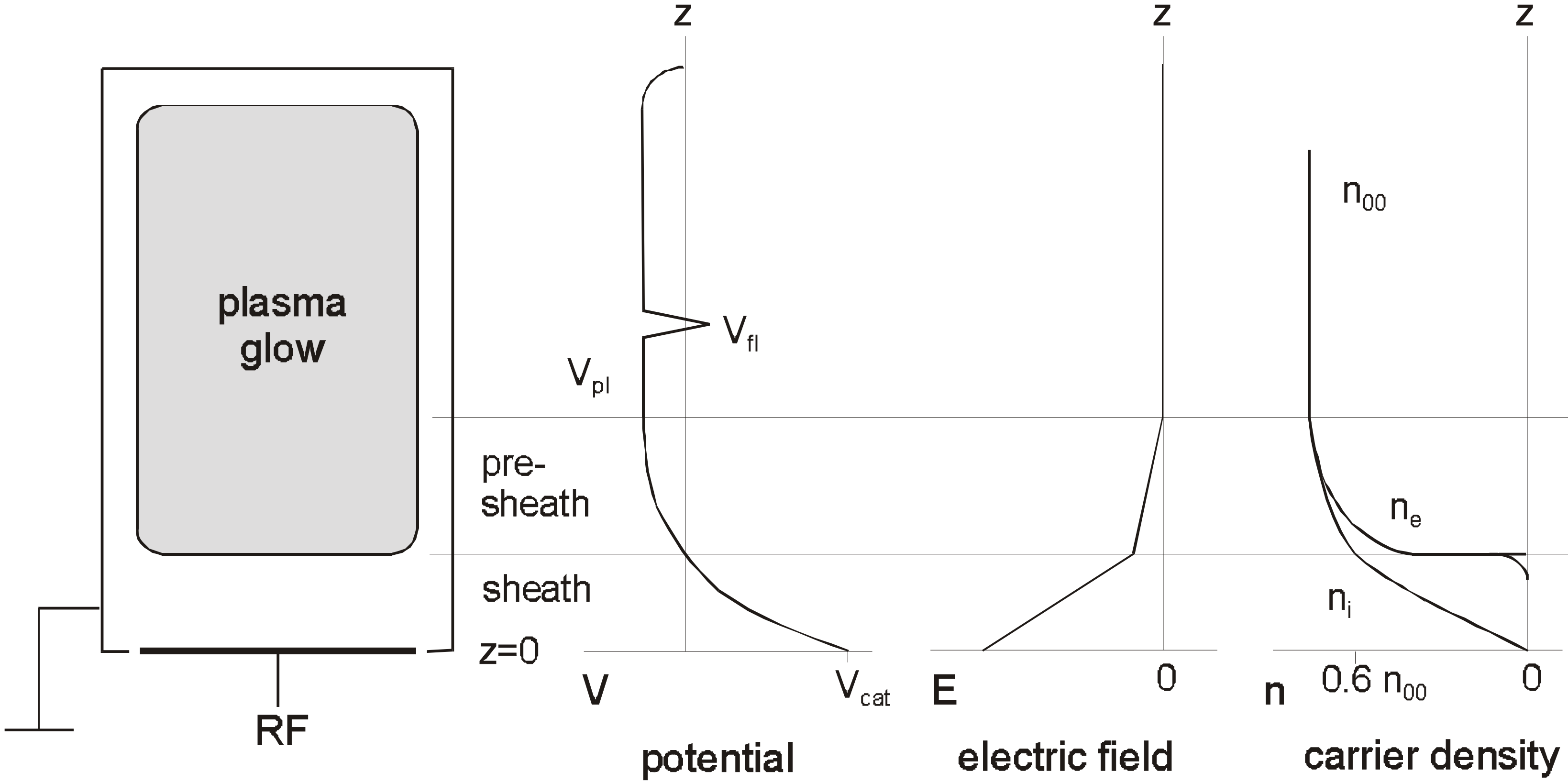


Argon, 50W 0.005mbar 0.01mbar

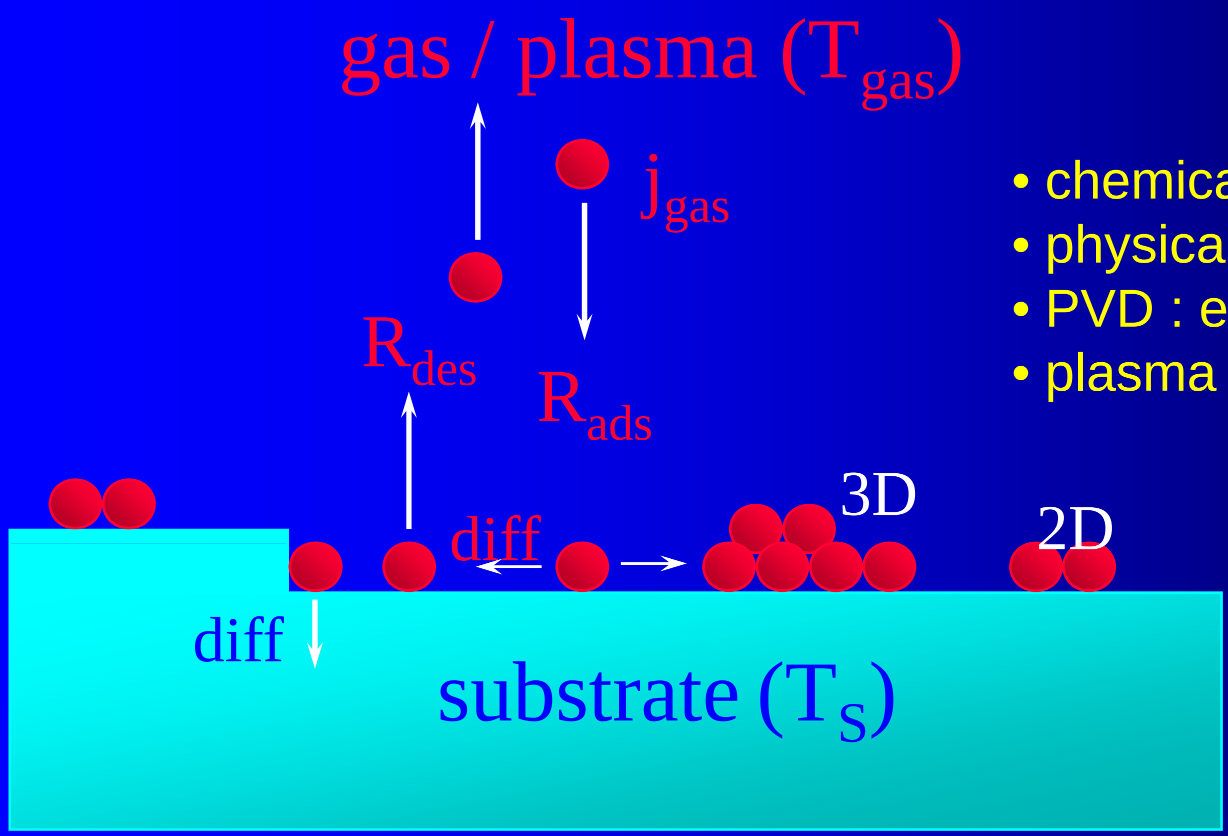
plasma bulk and plasma sheath

Gaseous Electronics Conference Reference Cell

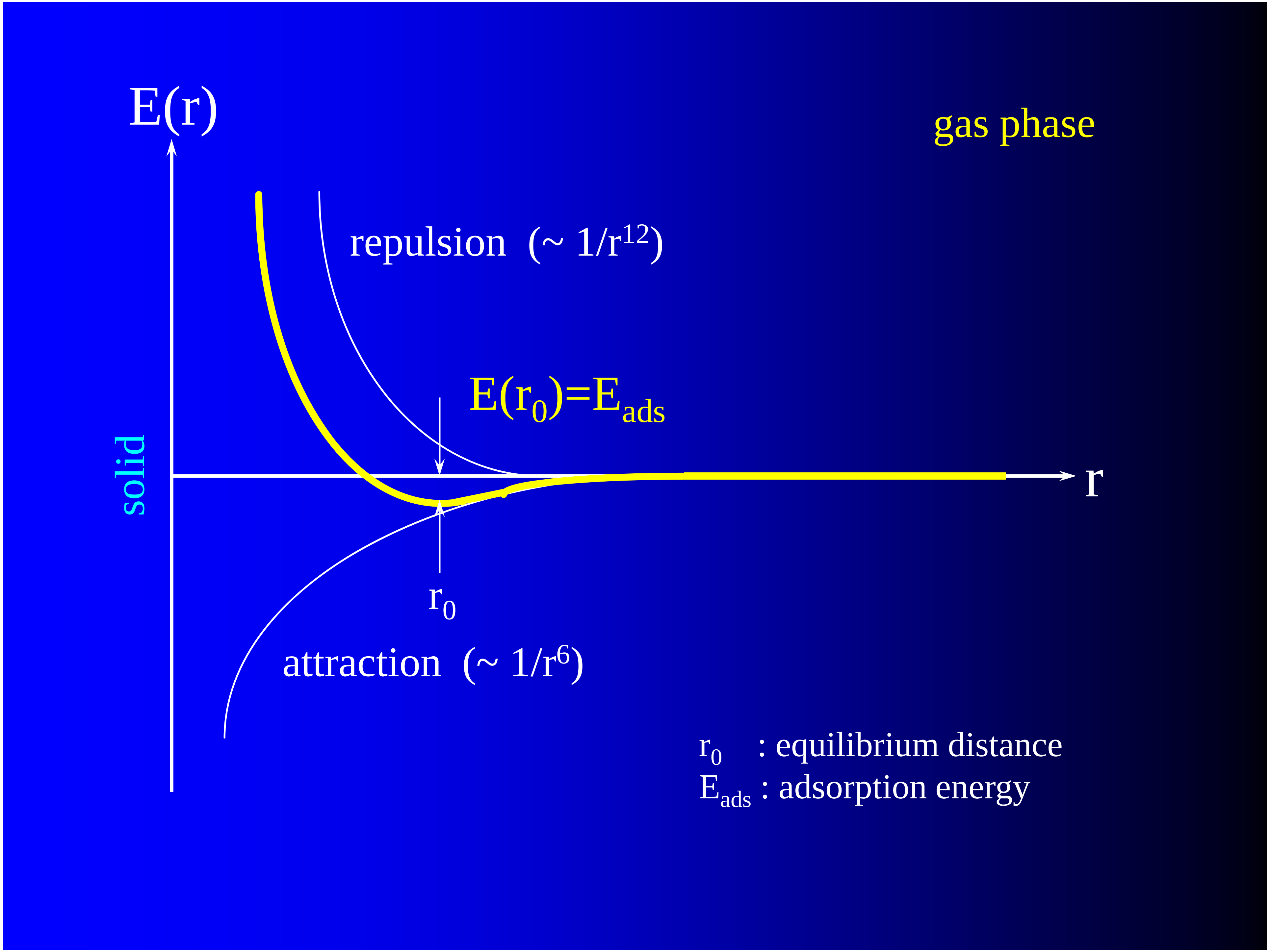




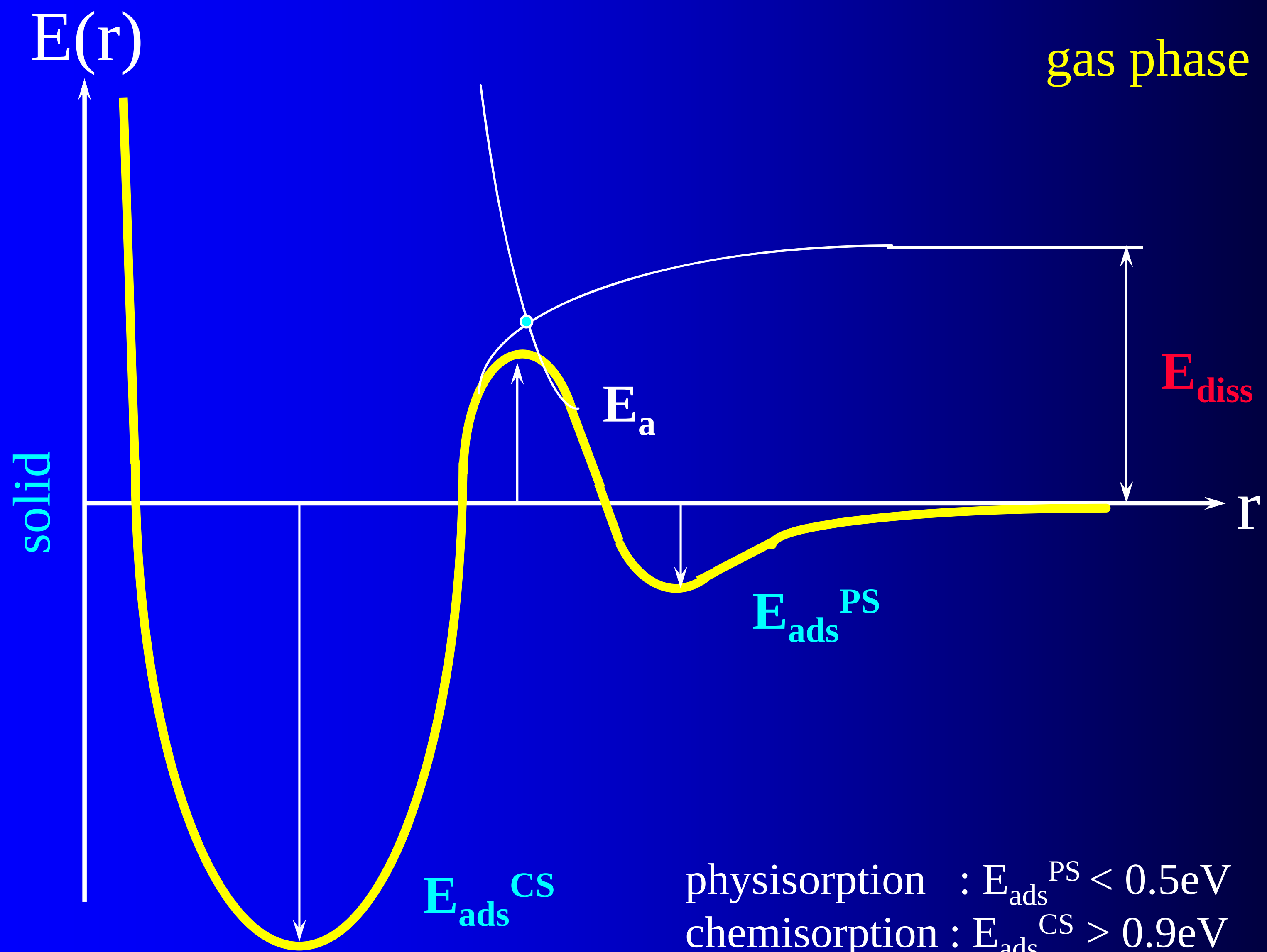
elementary processes at substrate : plasma methods :



- chemical methods (CVD, MOCVD)
- physical methods : PECVD, *PVD*
- PVD : evaporation, *plasma*, ions
- plasma : PSP, IP/PL, PP, ME



E(r)
gas phase
repulsion (~ 1/r^12)
E(r0)=Eads
solid
r
r0
attraction (~ 1/r^6)
r0 : equilibrium distance
Eads : adsorption energy



physisorption : $E_{ads}^{PS} < 0.5eV$

chemisorption : $E_{ads}^{CS} > 0.9eV$

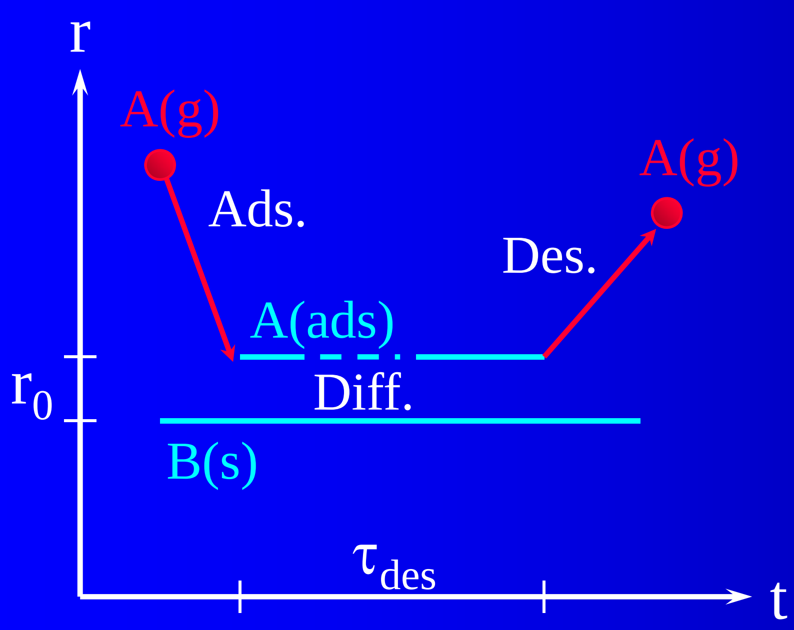
$E_a > 0$: activated CS

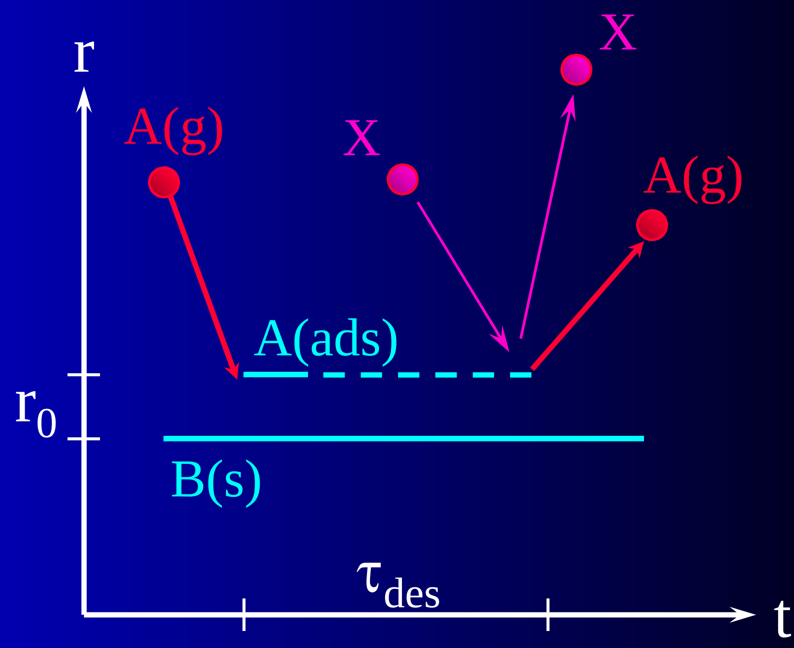
$E_a < 0$: non-activated CS

Adsorption :

$$A(g) + B(s) \xrightarrow{\ \gamma_A\ } A(ads) + B(s)$$

$$R_{ads} = \frac{dn_{ads}}{dt} = \gamma_A \, j_A \, f(\Theta)$$





Desorption :

thermal

$$A(ads) \xrightarrow{\ \tau_{des}\ } A(g)$$

$$\tau_{des} = \tau_{des}^{0} \exp\{-E_{des}/kT_S\}$$

collision

$$A(ads) + X \xrightarrow{\ \sigma_{des}\ } A(g) + X$$

$$\tau_{des} = 1 / \sigma_{des} \, j_X$$

$$R_{des} = \frac{dn_{ads}}{dt} = -\frac{n_{ads}}{\tau_{des}}$$

sticking coefficient γ : $\gamma = n_{ads} / n_{in}$

$\gamma = \gamma_0 \exp(-E_a/kT)$ (PS: $\gamma = \gamma_0$)

degree of coverage Θ : $\Theta = n_{ads} / n_0$

equilibrium of adsorption - desorption :

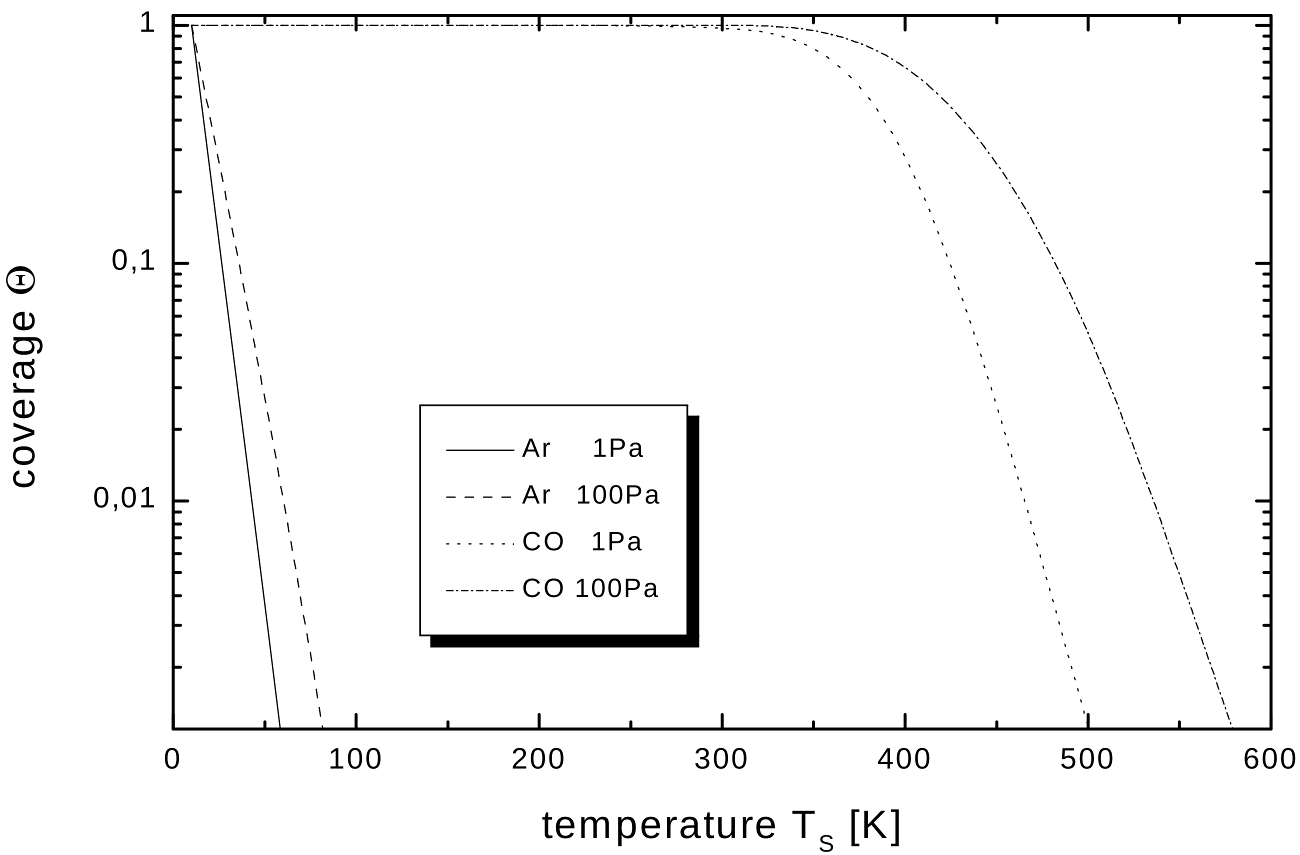
$$\frac{dn_{ads}}{dt} = \gamma\, j\, f(\Theta) - \frac{n_{ads}}{\tau_{des}} , \qquad \frac{dn_{ads}}{dt} = 0 \longrightarrow \gamma\, j\, f(\Theta) = \frac{n_{ads}}{\tau_{des}}$$

$f(\Theta) = 1 - \Theta$, T = const. Langmuir-adsorption isotherm : $n_{ads} = n_{ads}(p)$

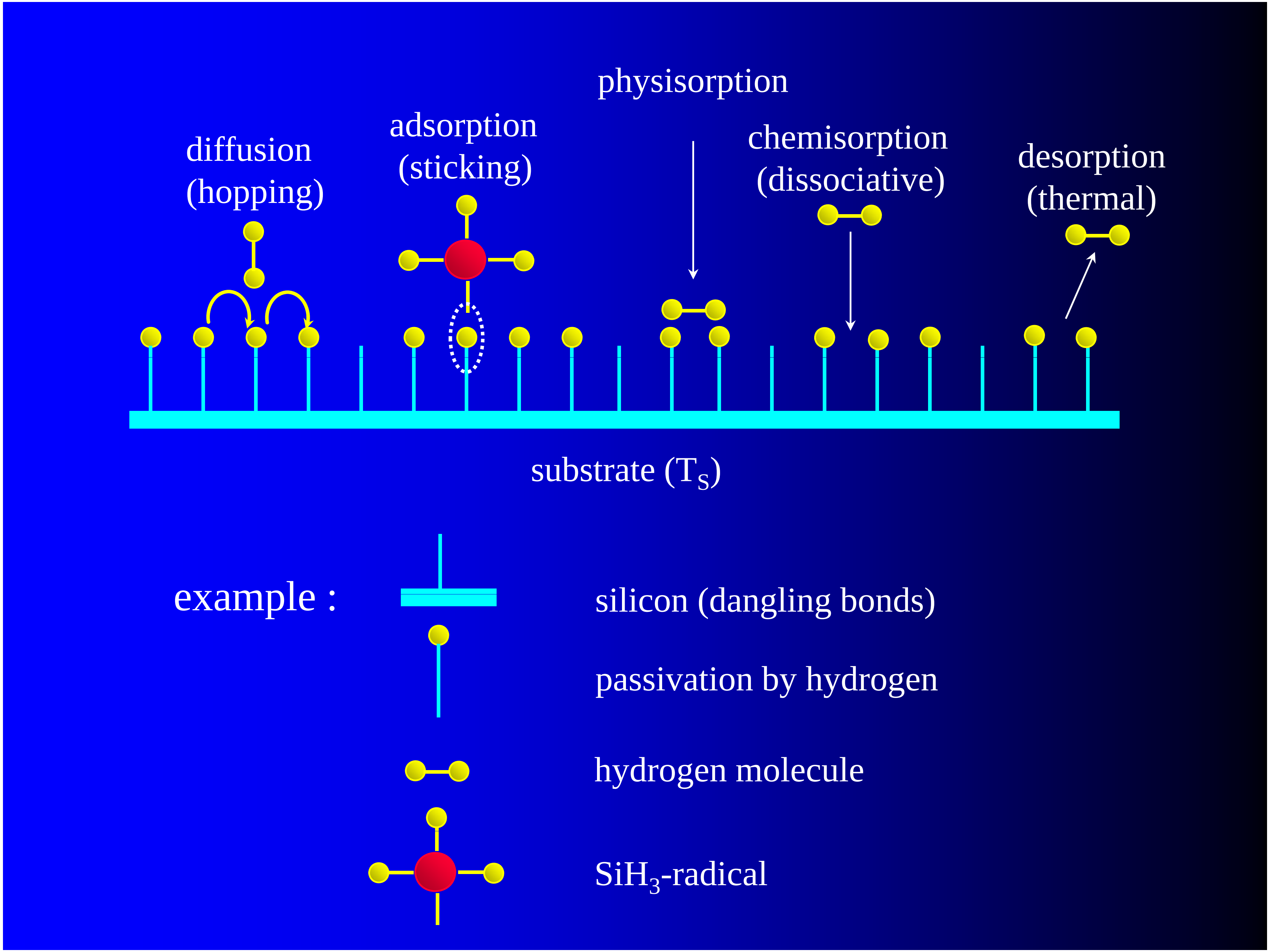
$$\longrightarrow \quad n_{ads} = n_0 \frac{1}{1 + \dfrac{n_0}{\gamma\, j\, \tau_{des}}}$$

$f(\Theta) \sim (1 - \Theta)^2$, e.g. if dissociative adsorption

(Freundlich, BET, ...)



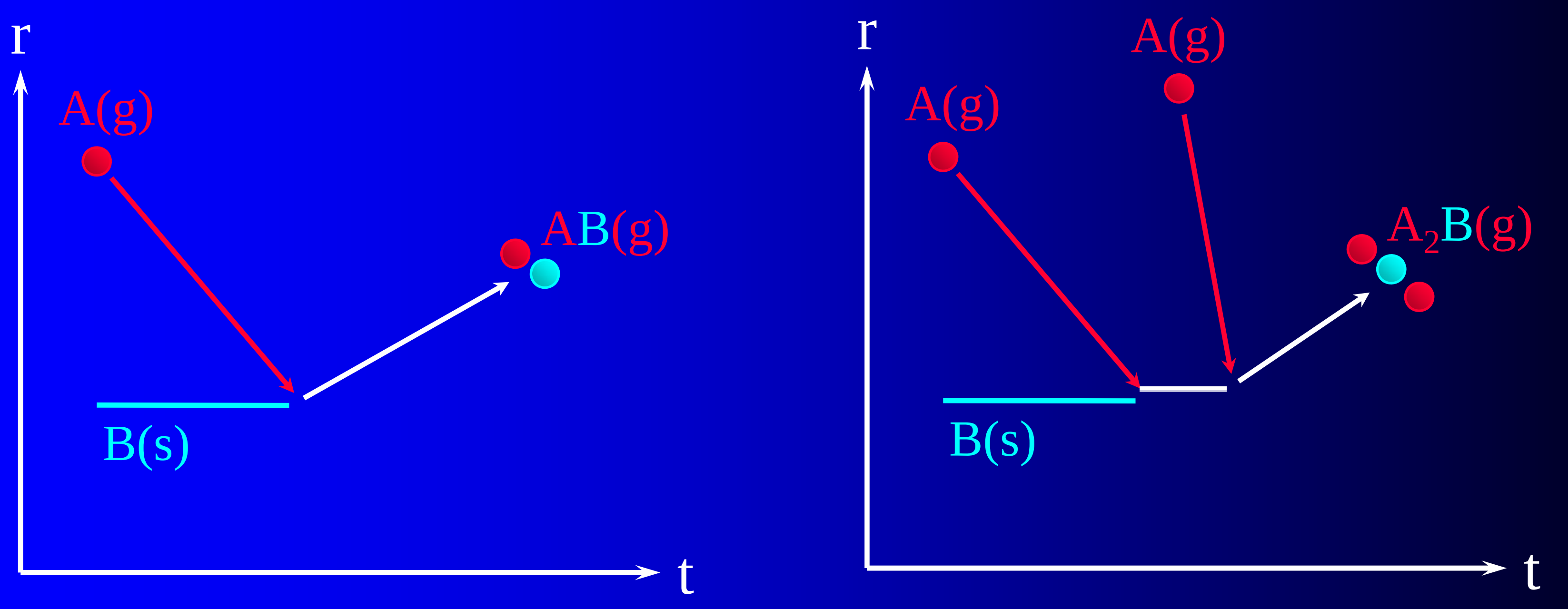
The initial coverage of Ar on Zr ($E_{des}=0.24eV$) and CO on Pd ($E_{des}=1.43eV$) in dependence on the surface temperature.
The surface density is assumed to $n_0=6\cdot10^{14}cm^{-2}$.


physisorption
diffusion
(hopping)
adsorption
(sticking)
chemisorption
(dissociative)
desorption
(thermal)
substrate (T_S)
example :
silicon (dangling bonds)
passivation by hydrogen
hydrogen molecule
SiH_3-radical

Chemical Sputtering (CSP) :

$$B(s) + nA(g) -\sigma_{CSP}\rightarrow A_nB(g)$$

$$R_{CSP} = \frac{dn_B}{dt} = -\, n_B \sigma_{CSP} j_A$$



direct CSP

delayed CSP

$$\sigma_{CSP} = \sigma_{CSP}{}^0 \exp\{-E_{CSP}/kT\}$$

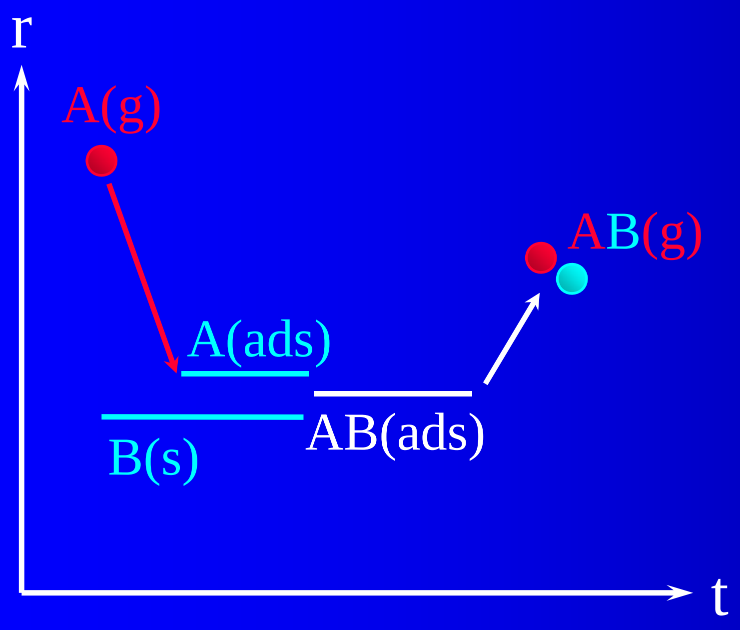
surface film reaction (SFR) :

$B(s) + A(ads) - k_{SFR} \rightarrow AB(ads)$

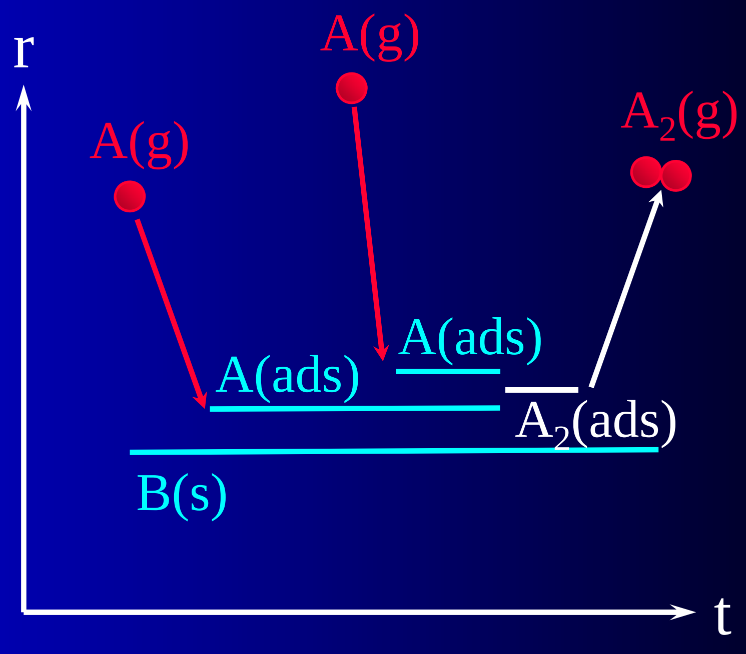
$$R_{SFR} = \frac{dn_{AB}}{dt} = k_{SFR} n_A n_B$$

$A(ads) + A(ads) + B - k_{SFR} \rightarrow A_2(ads) + B$

$$R_{SFR} = \frac{dn_{A2}}{dt} = k_{SFR} n_A^2$$

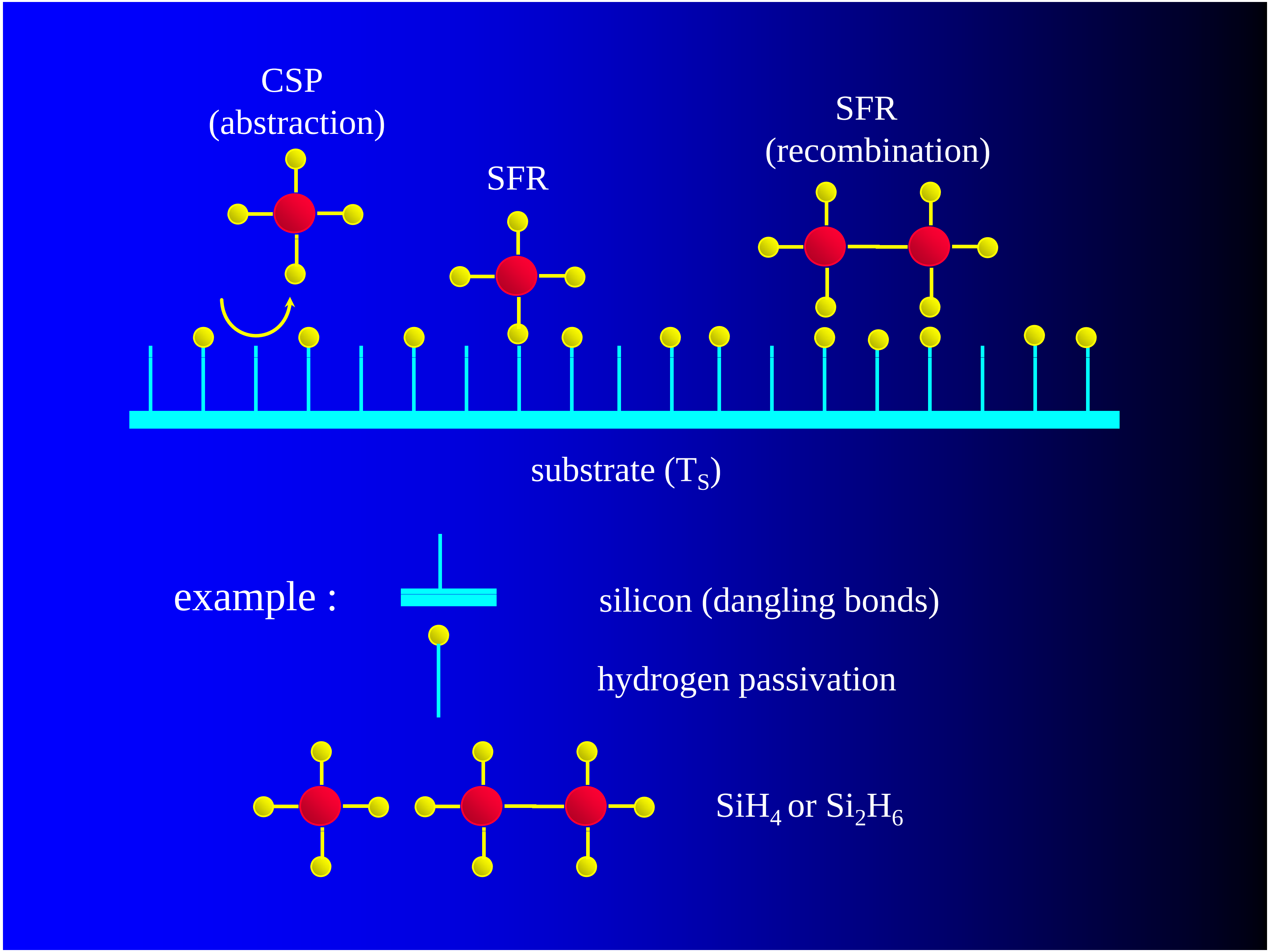


SFR with solid

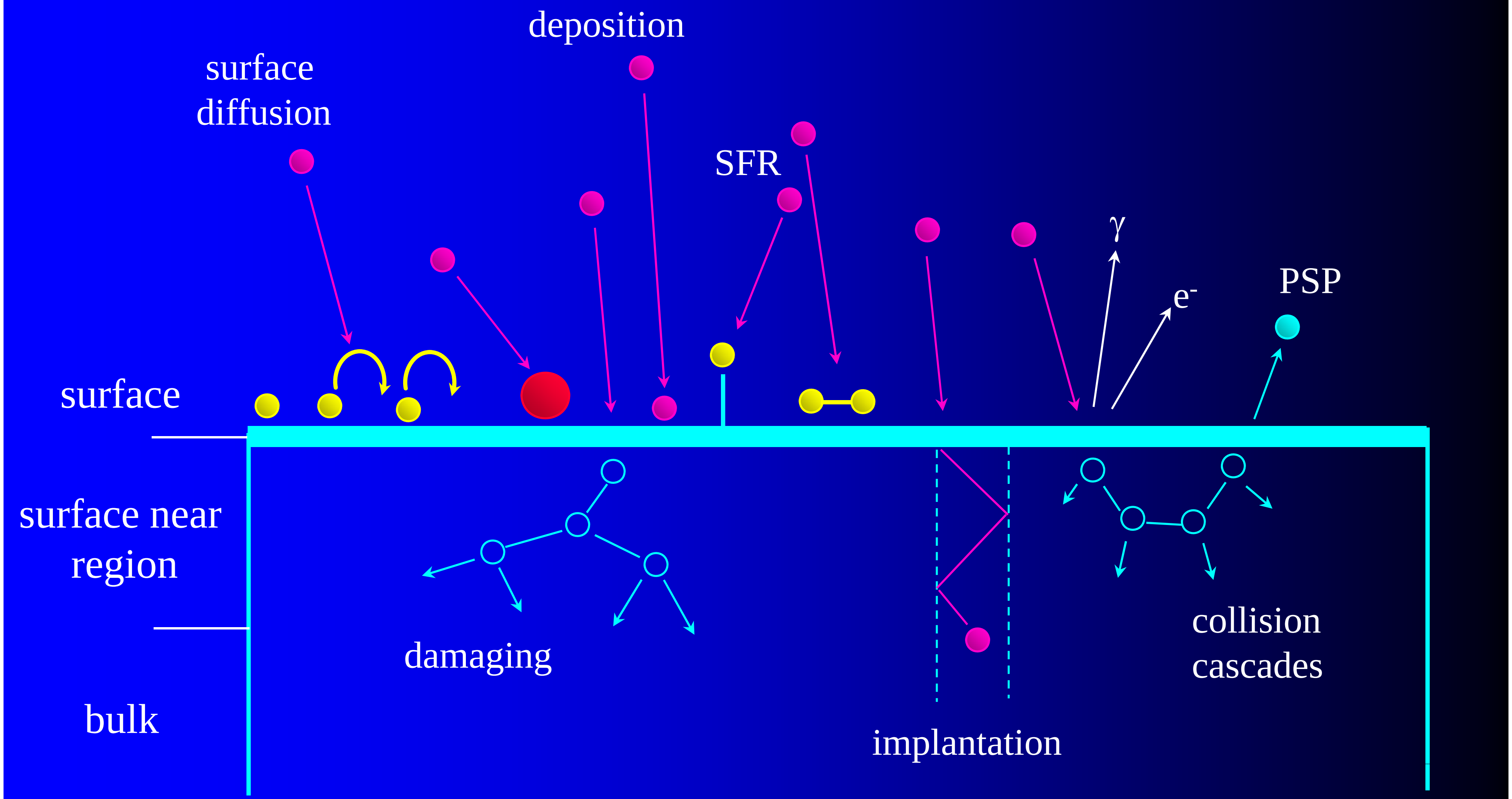


SFR recombination

$$k_{SFR} = k_{SFR}^0 \exp\{-E_{SFR}/kT_S\}$$


CSP
(abstraction)
SFR
SFR
(recombination)
substrate (T_S)
example :
silicon (dangling bonds)
hydrogen passivation
SiH_4 or Si_2H_6

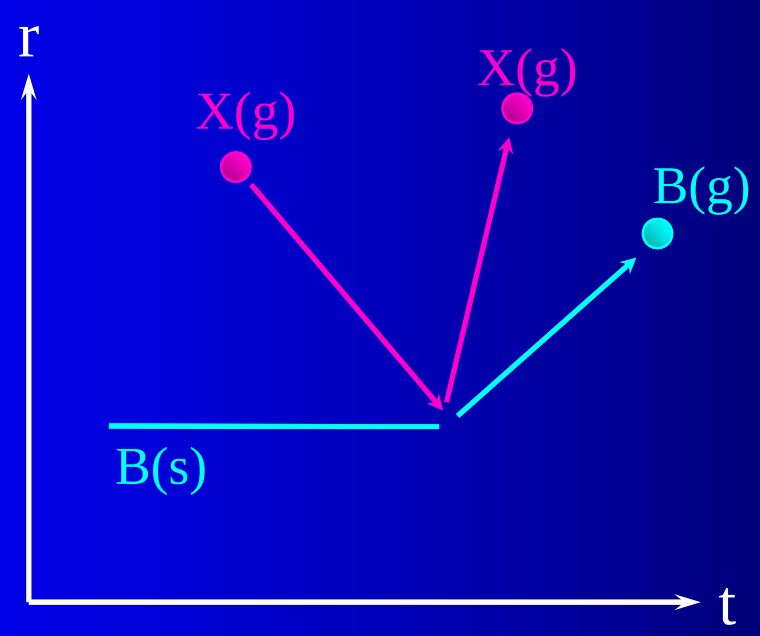
some effects of energetic particle bombardment



physical sputtering (PSP) :

$$B(s) + X(g) \xrightarrow{\sigma_{PSP}} B(g) + X(g)$$

$$R_{PSP} = \frac{dn_B}{dt} = -\, n_B \langle \sigma_{PSP} \rangle j_X = -\langle Y_B \rangle j_X$$

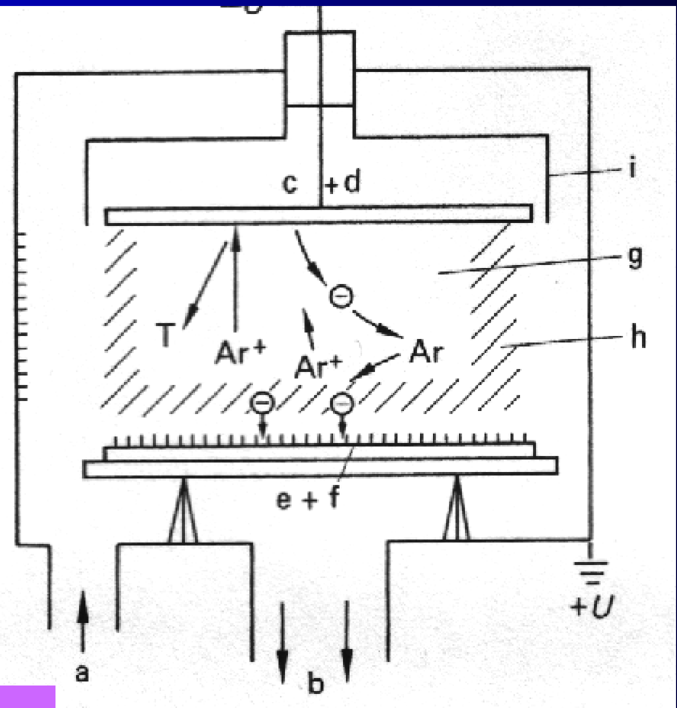


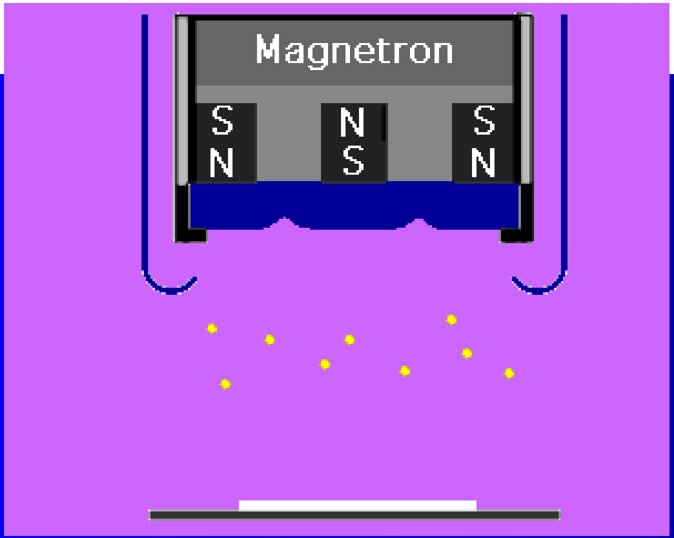
$$Y = Y(U, E_B, Z_P, Z_T, \ldots..)$$

Sputtering (PSP) for thin film deposition / coating

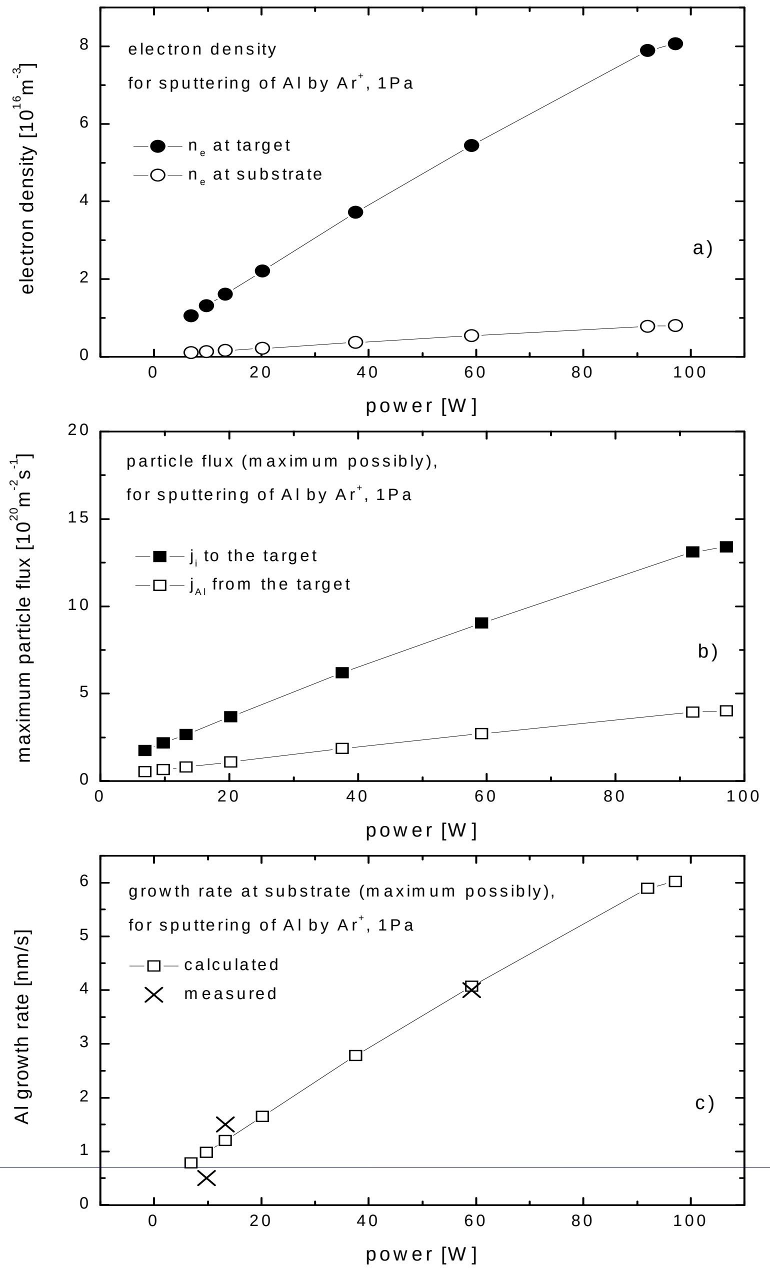
principle of dc cathode sputtering,
diode system

a gas flow
b pump
c cathode
d target
e anode
f deposited layer
g cathode fall
h positive column
I screening, shield





magnetron system (E X B)



$n_e = n_e(U,I,p)$

↓

$j_i = j_i(n_e, A_{eff})$

↓ sputter-Yield, TRIM

$j_{Al} = Y j_i$

↓ $\gamma = 1$, geometry

Al-film thickness

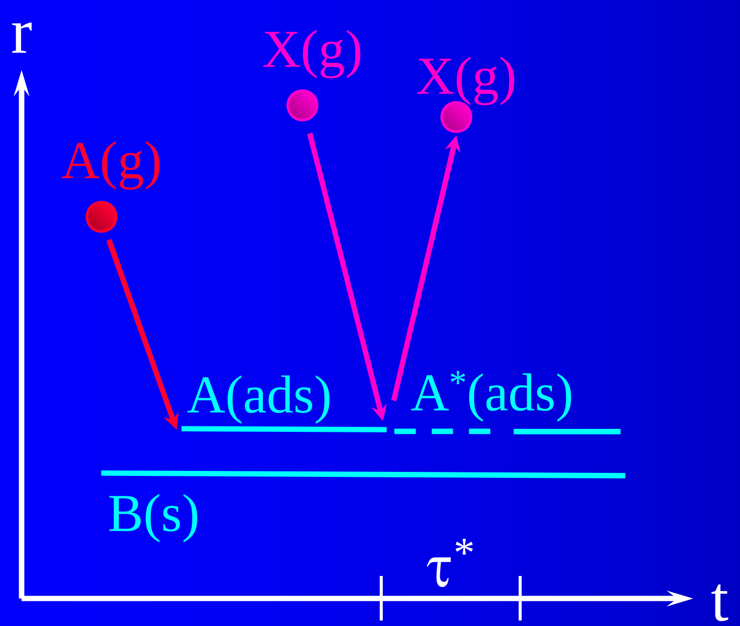
↓

deposition rate R_{dep}
(maximum estimation)

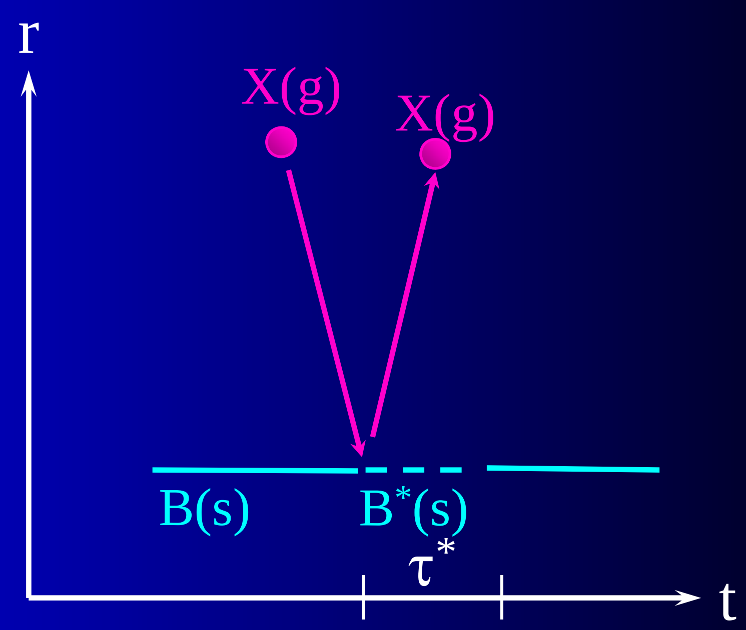
surface activation

$$A(ads) + X \xrightarrow{\sigma_*} A^*(ads) + X \qquad\qquad B(s) + X \xrightarrow{\sigma_*} B^*(s) + X$$

$$R_* = \frac{dn_{ads^*}}{dt} = n_{ads}\,\sigma_*\,j_X \qquad\qquad R_* = \frac{dn_{B^*}}{dt} = n_B\,\sigma_*\,j_X$$



activation of adsorbate



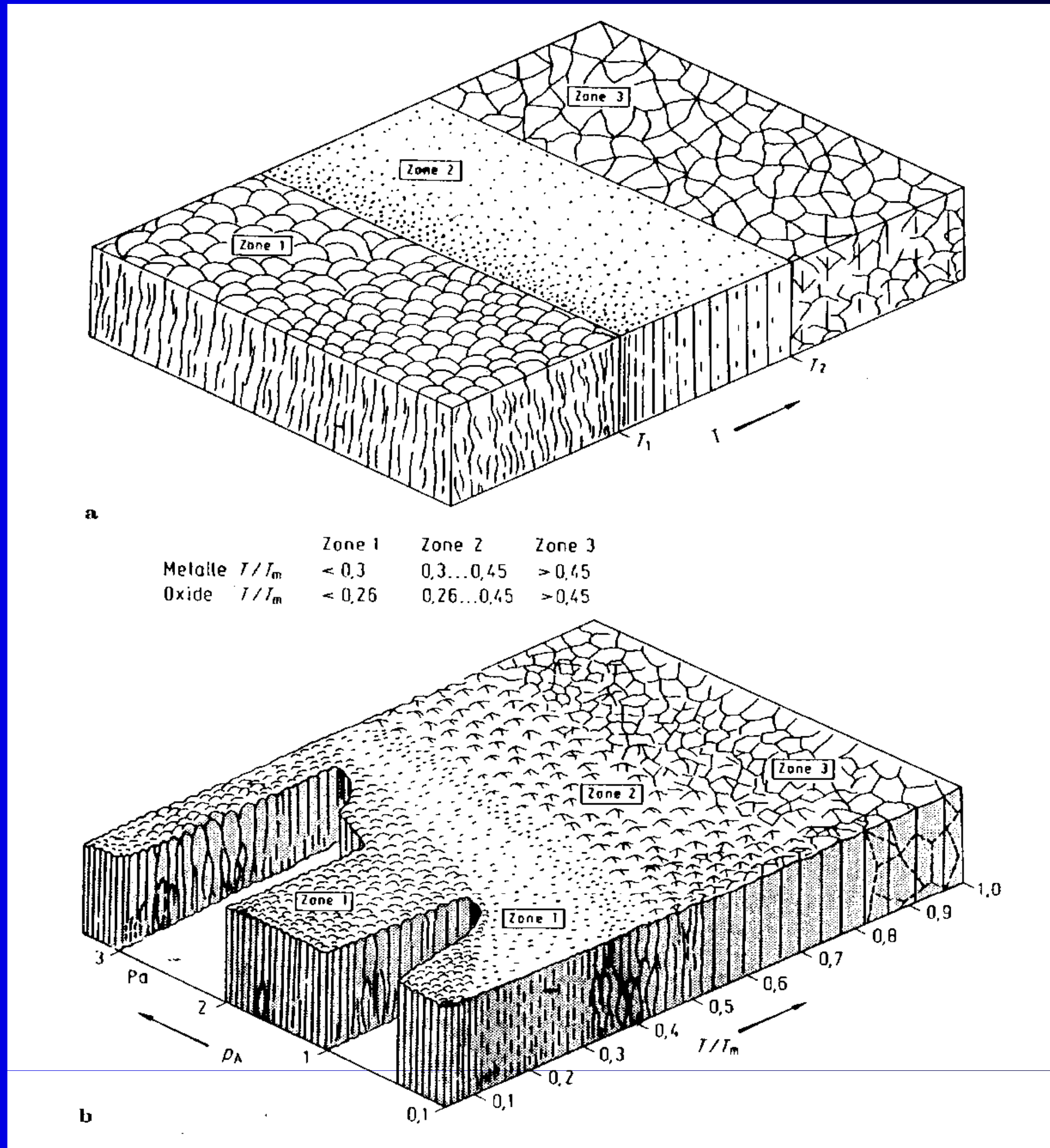
activation of surface

surface deactivation :

$$R = -\frac{dn_{ads^*}}{dt} = -\,n_{ads\,*} / \tau_* \qquad\qquad R = -\frac{dn_{B^*}}{dt} = -\,n_{B^*} / \tau_*$$

structure (morphology, crytal orientation ...)

effect of
$T_S,\ j_X,\ j_X/j_A$



THORNTON-
model

particle balances
in the interface

rate = deposition - etching : $R = dx/dt = R_D - R_E$

for species k : $R_k = \dfrac{M_k}{L\rho_k} \dfrac{d\,n_k}{d\,t}$

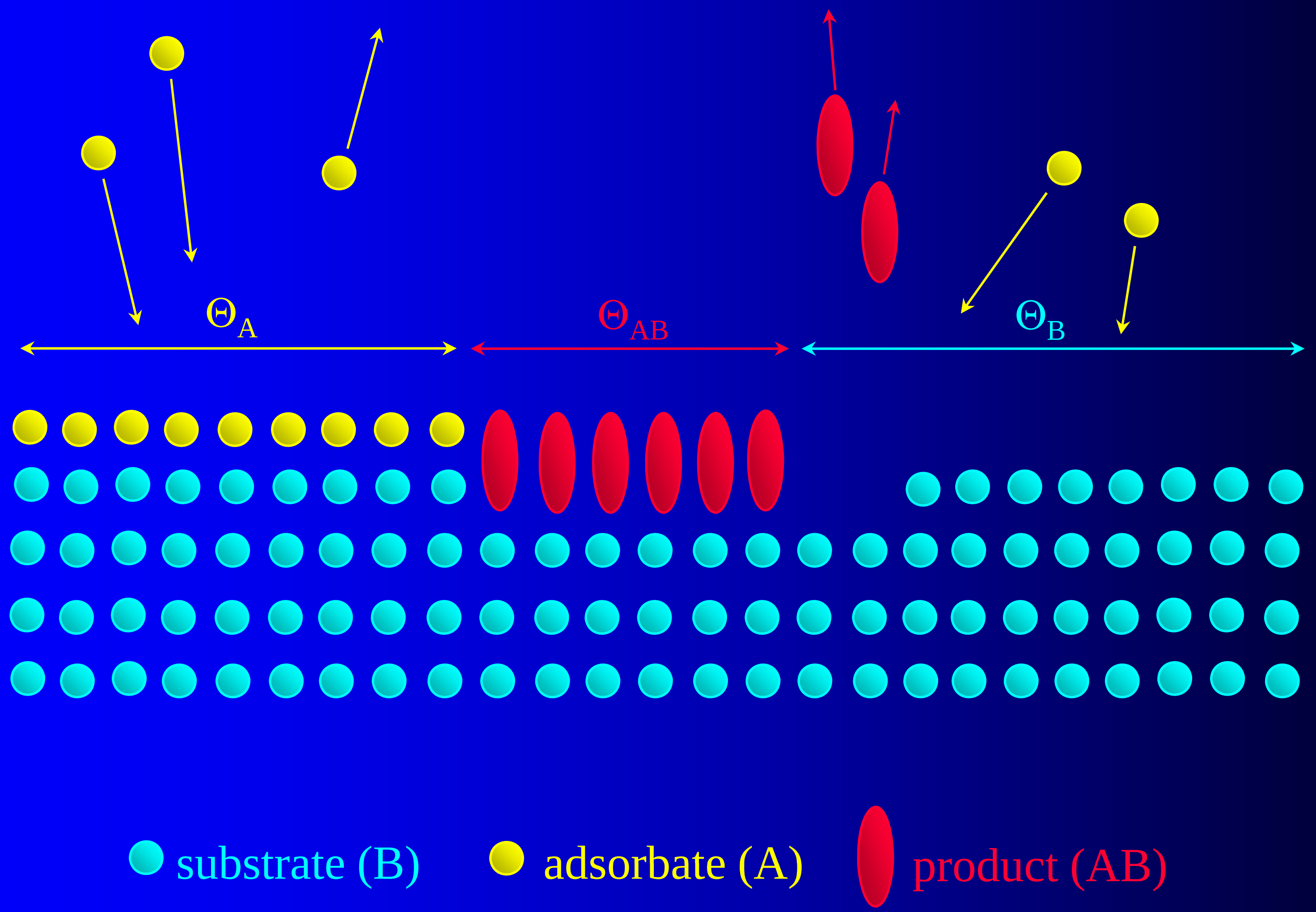
species at the surface :
(gain, loss)

$$\frac{d\,n_k}{d\,t} = \sum_k G_k + \sum_k V_k \lesseqqgtr 0$$

$$\frac{d\,n_k}{d\,t} = \gamma_k j_k f(\Theta) + k_{SFR,k-1} n_{k-2} n_{k-1} + \sigma_{CSP,k-1} n_{k-1} j_{k-1} + n_{*,k}/\tau_{*,k} + \ldots$$

$$- n_k/\tau_{des,k} - k_{SFR,k} n_k n_{k-1} - \sigma_{CSP,k} n_k j_{k-1} - \sigma_{PSP,k} n_k j_x - \sigma_{*,k} n_k j_x - \ldots$$

example for particle balances
(schematic)



particle balances (example, schematic)

here only : B, A, AB

assumption : chemical etching of B

$$\frac{d\,n_A}{d\,t} = \gamma_A j_A \Theta_B - n_A / \tau_{des,A} - k_{SFR,B} n_A n_B = 0$$

$$\frac{d\,n_{AB}}{d\,t} = k_{SFR,B} n_A n_B + \sigma_{CSP,B} n_B\, j_A - n_{AB} / \tau_{des,AB} = 0$$

$$\frac{d\,n_B}{d\,t} = - k_{SFR,B} n_A n_B - \sigma_{CSP,B} n_B\, j_A = R_{Ä,B} L \rho_B / M_B$$

$$\Theta_A + \Theta_B + \Theta_{AB} = 1 \qquad \Theta_A = n_A / n_0, \quad \Theta_{AB} = n_{AB} / n_0, \quad \Theta_B = n_B / n_0,$$

$$\frac{R_{E,B}}{n_0} = \frac{1}{\tau_{des,AB} + \dfrac{(1/\tau_{des,A}\gamma_A j_A) + (n_0 k_{SFR,B}/\gamma_A j_A) + 1/n_0}{k_{SFR,B} + (\sigma_{CSP,B}/\gamma_A)(1/\tau_{des,A} + n_0 k_{SFR,B})}}$$

N. Hershkowitz et.al. (JVST A11(1993)4, 1283 and ISPC-12, 1995, 533.) :

"... plasma processing characteristics are similar ... when only a limited number of plasma parameters are identical at the plasma-wafer sheath boundary. Identical values of energy flux and particle concentration result in identical rates."

PSI at LPPP is affected by :

- *energy (E) of impinging particles (energy transfer)*
- *particle flux density (j) towards the substrate (momentum transfer)*

➡ *energy influx (J)*
temperature of the substrate surface (T_s)

thermal / energetic conditions at the substrate surface during plasma processing essentially determine

- *elementary processes (adsorption, diffusion, desorption ...)*
- *chemical reactions (CSP, SFR ...)*
- *composition (stoichiometry ...)*
- *structure (morphology, crystal orientation ...)*

contributions to energy influx at substrate surface :

- radiation (plasma, walls, sources)
- kinetic energy of charge carriers (electrons, ions)
- energy of neutrals (kinetic energy, excitation energy,
  heat of adsorption and condensation)
- exothermic chemical reactions
- external heating

energy losses at substrate surface :

- radiation (environment)
- heat conduction and convection (substrate holder, gas)
- desorption
- endothermic chemical reactions
- sputtering of particles and secondary electron emission
- external cooling