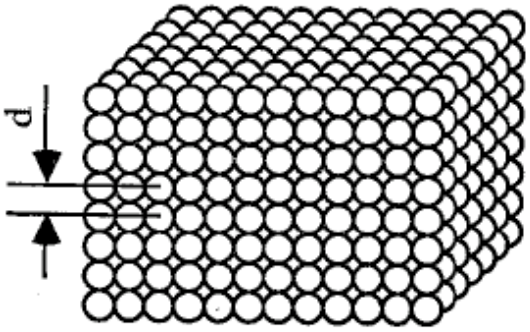
# Vacuum surface engineering

1. **Surface phenomena**
2. **Surface energetic ion interaction**

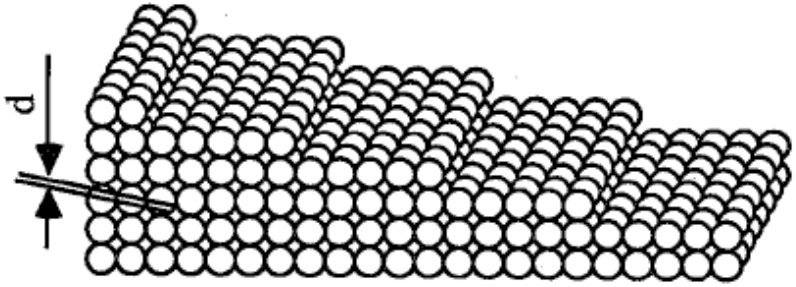


Aalto University
School of Chemical Technology

# Surface energy




Low-index surface




High-index surface consisting of low-index facets

$$\gamma(\mathbf{n}) = \frac{dW}{dA}$$

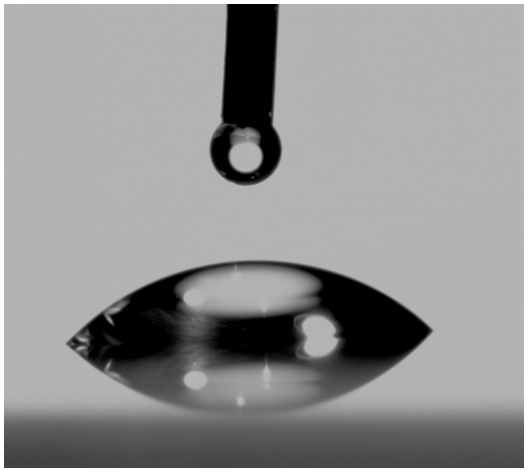
**γ surface tension = *dW* work needed to form surface *dA***

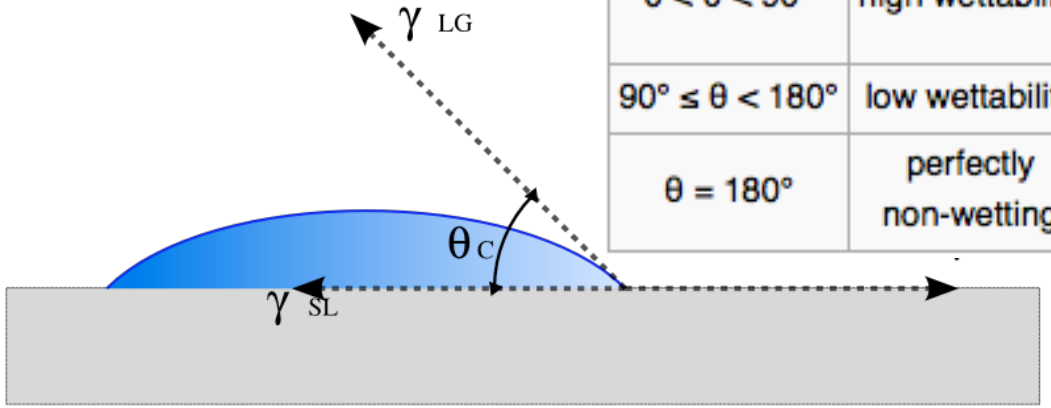
**In thermodynamic equilibrium:**

$$\int_A dA\, \gamma(\mathbf{n}) = \min.$$

# Contact angle

| Contact angle | Degree of wetting |
|---|---|
| θ = 0 | Perfect wetting |
| 0 < θ < 90° | high wettability |
| 90° ≤ θ < 180° | low wettability |
| θ = 180° | perfectly non-wetting |





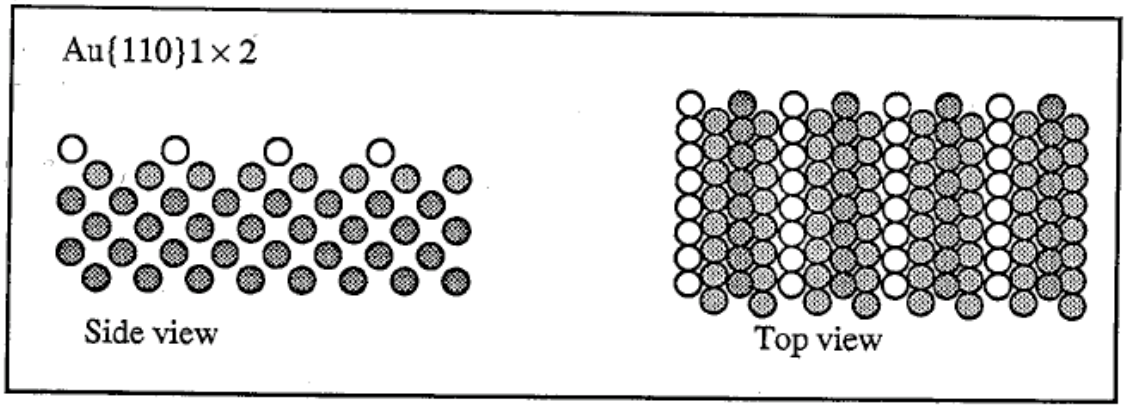

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$

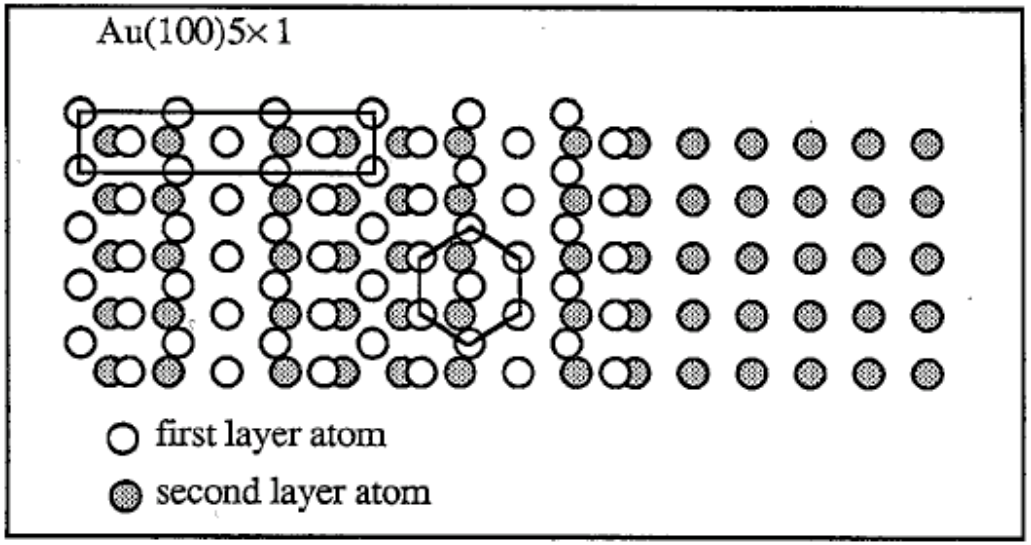
***Young equation***
**S solid**
**L liquid**
**G gas**

$$S = \gamma_{LG}(\cos\theta - 1)$$

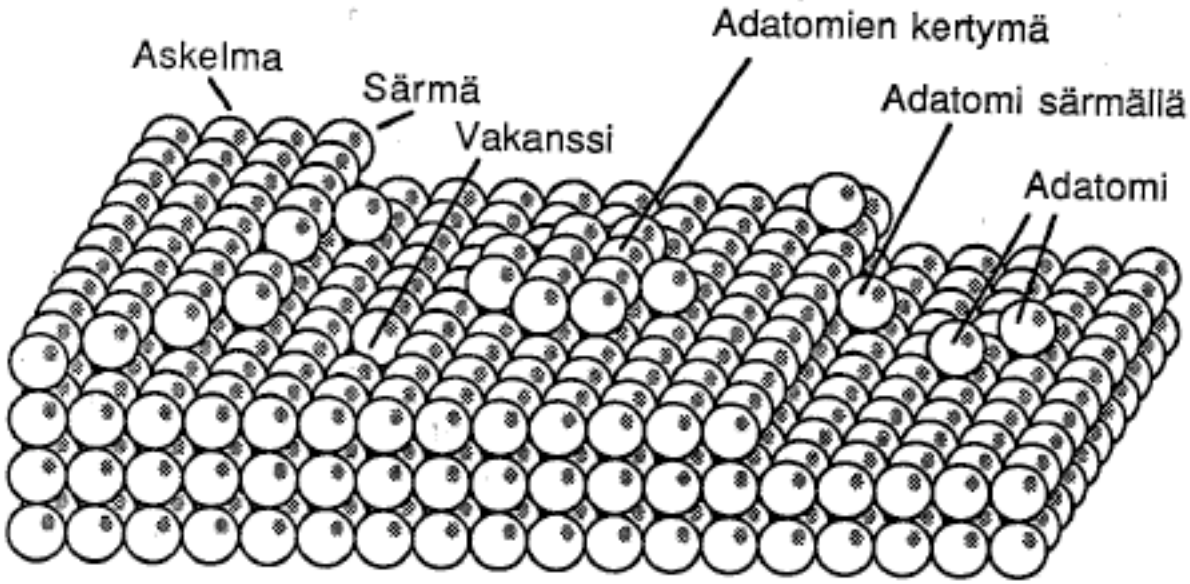
**Spreading parameter *S***
**Complete wetting when *S* ≈ 0**
**non-wetting when *S* ≈ -2 $Y_{LG}$**

# Surface reconstruction



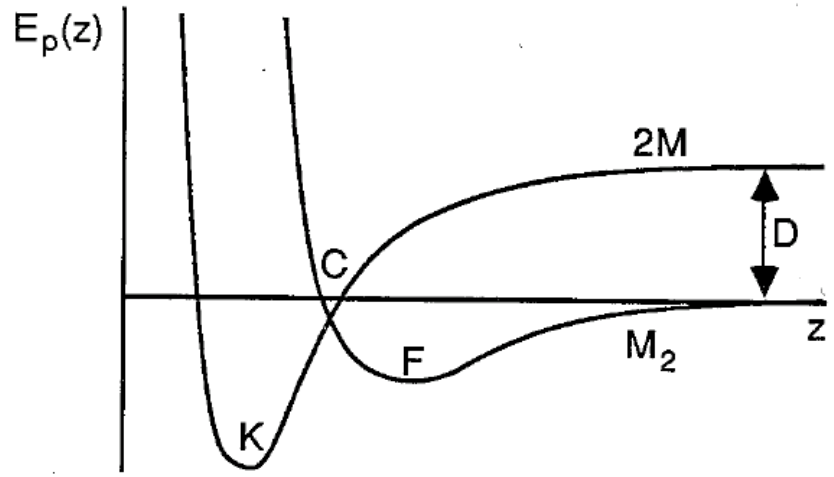



# Surface structure and defects



# Adsorption

- **Physisorption**
- **Chemisorption**

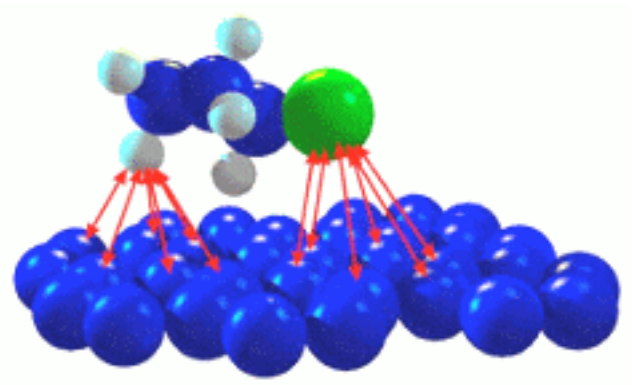


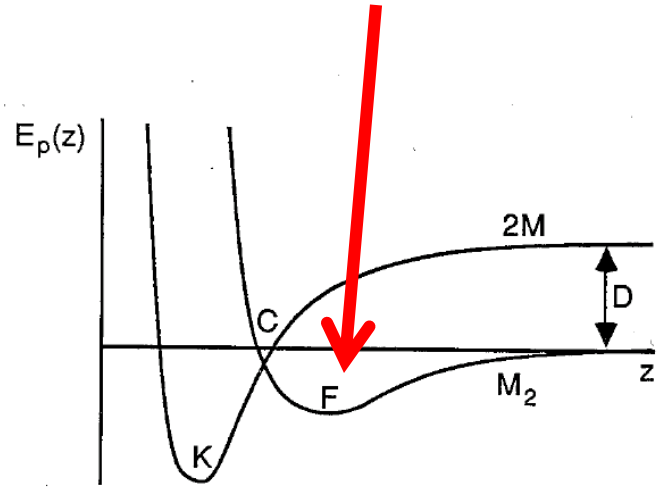

**Kuva 12.1.** *Lennard-Jones-diagrammi.*

# Adsorption

## Physisorption

- Chemical bonding:
  - polaroization (van der Waals)
- Bonding energy ≈ 0.001 – 0.5 eV
- Bond length ≈ 3 – 10 Å
- For example: nobel gas or molecules on materials
- Possibly precursion state before chemisorption



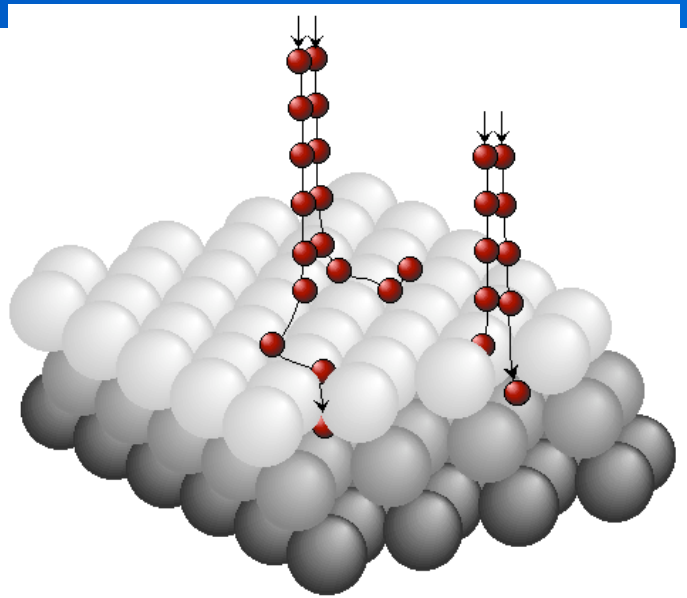


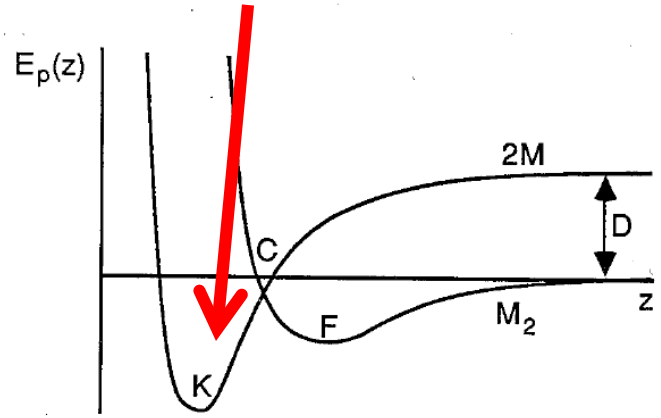

**Kuva 12.1.** *Lennard-Jones-diagrammi.*

# Adsorption

## Chemisorption

- Chemical bonding:
  - charge exchange
- Bonding energy ≈ 0.5 – 5 eV
- Bond length ≈ 1 – 3 Å
- For example: H, O, N, CO on metals
- Dissociation of molecule
- Final absorption



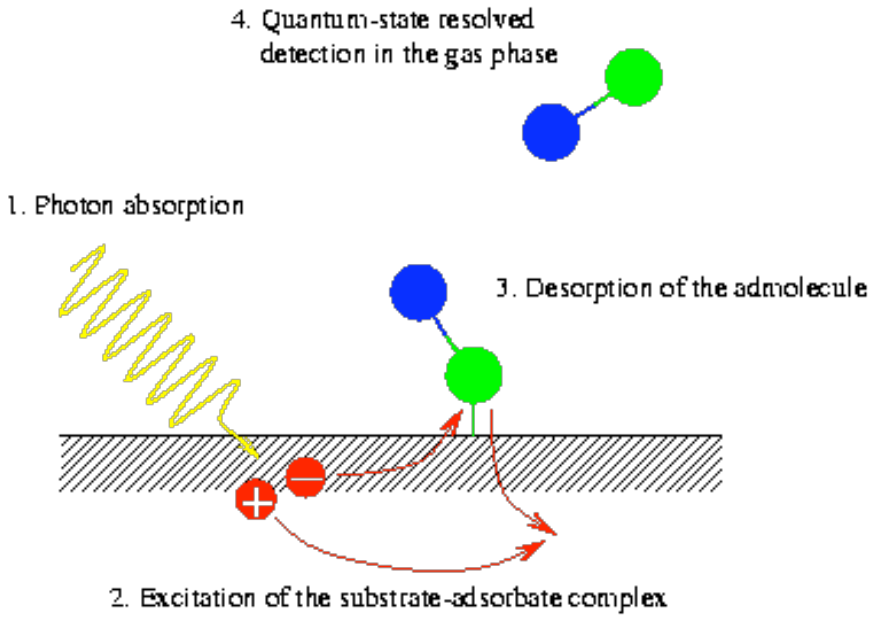



**Kuva 12.1.** *Lennard-Jones-diagrammi.*

# Desorption

**Adsorbed molecule receives energy $E_D$ in order to leave surface**

- **thermal**
- **radiation**
  - **photons**
  - **electrons**
  - **ions**
  - **electric field**



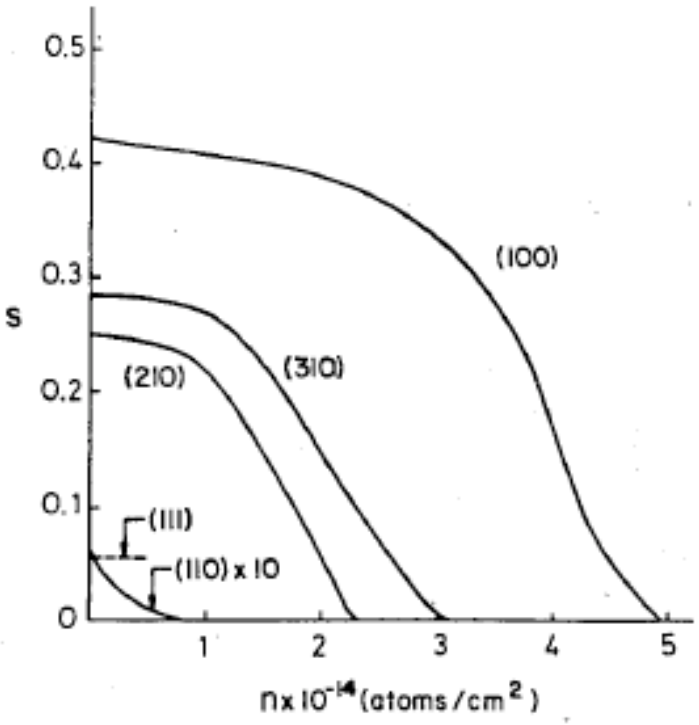
# Balance of absorption - desorption

- collisions of molecules (gas)
- S sticking coefficient
- $E_D$ energy for desorption
- P pressure

Coverage

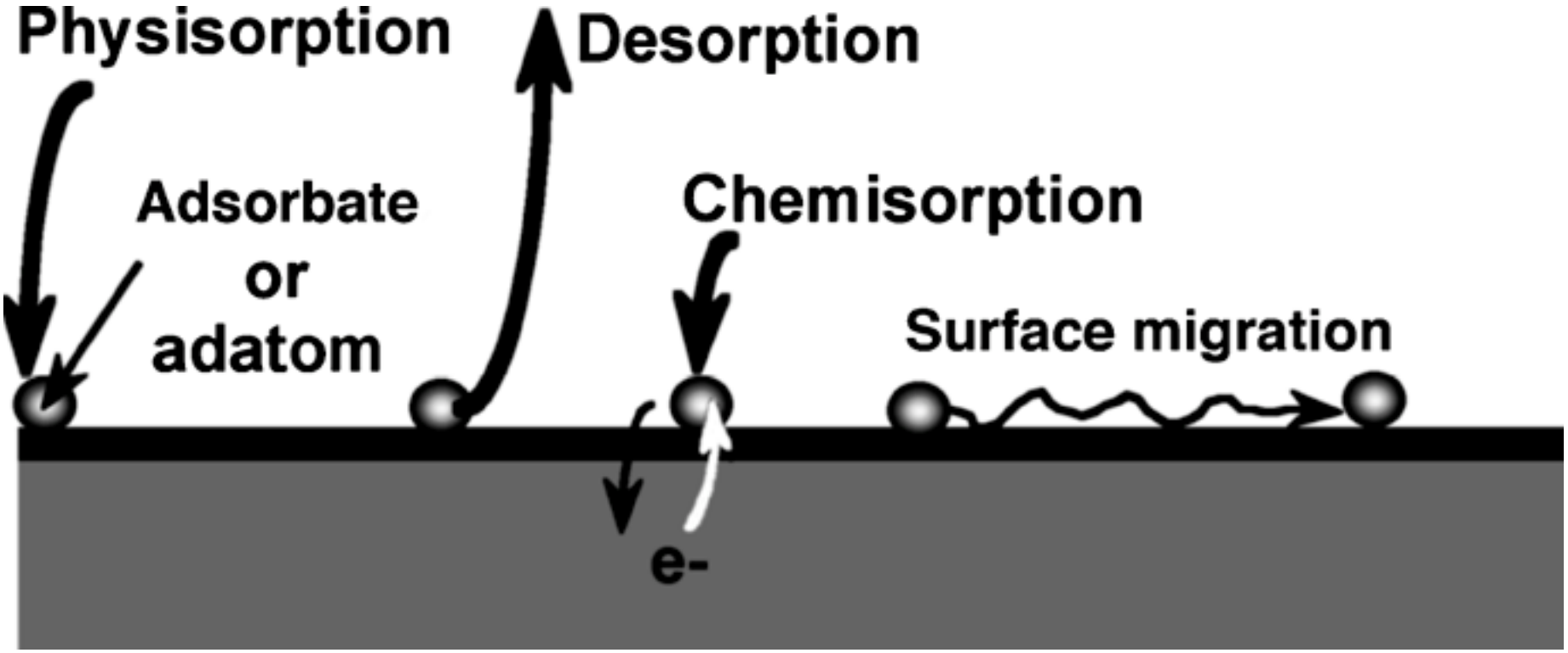
$$\approx = const. * \frac{S * P * e^{(E_D / kT)}}{\sqrt{(kT)}}$$

- High P, low T ⟶ more adsorption
- $E_D$ large, full coverage
- very little adsorption in UHV




*Kuva 9. Tarttumiskertoimen riippuvuus pinnalle adsorboituneiden atomien tiheydestä tapauksessa, jossa typpimolekyylit $N_2$ adsorboituvat volframin kidepinnoille.*

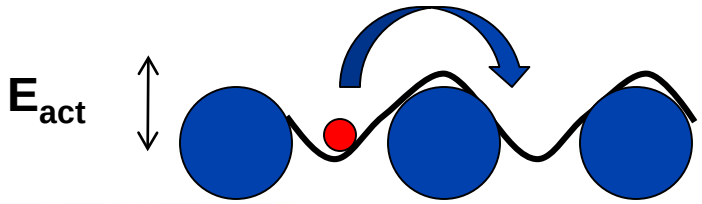
# Surface diffusion

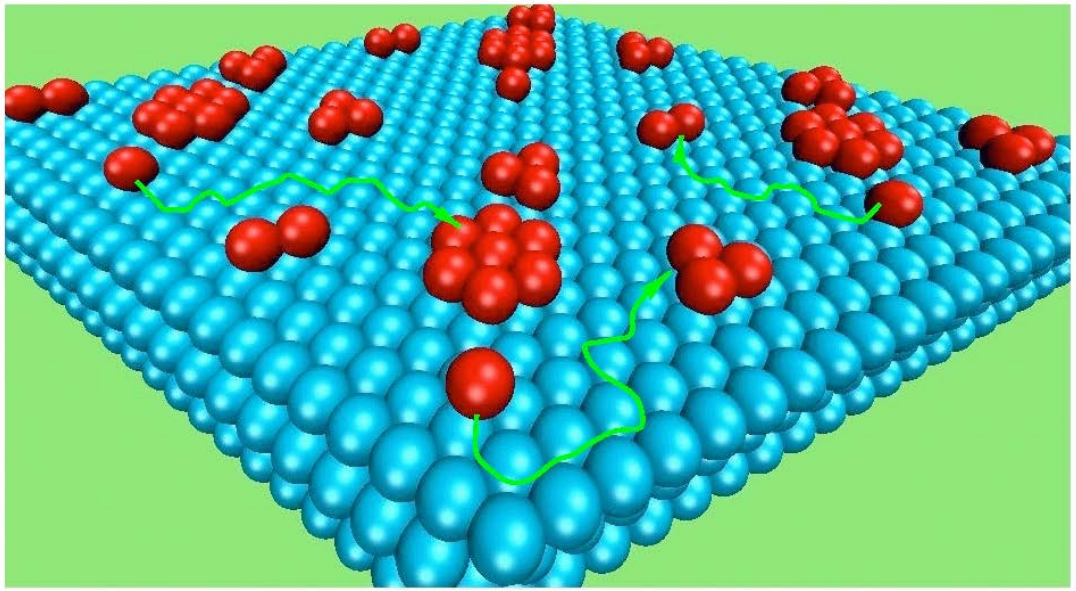



http://iramis.cea.fr/spcsi/Phocea/Vie_des_labos/Ast/astimg.php?voir=60&type=groupe

# Surface diffusion

- Diffusion is thermally activated random movement of adsorbed atoms
- $D = D_0 e^{-E_{act}/kT}$
- $E_{act}$ large -> slow diffusion
- T high – fast diffusion



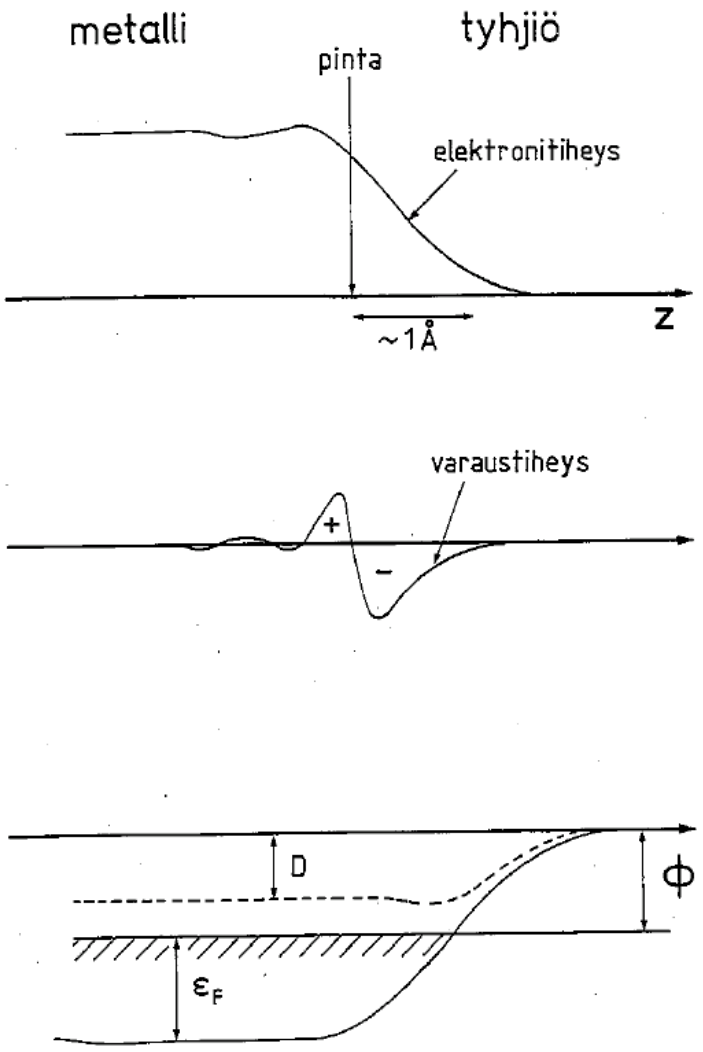



http://iramis.cea.fr/spcsi/Phocea/Vie_des_labos/Ast/astimg.php?voir=60&type=groupe

**Surface diffusion of Cu on Cu(111)**

# Work function

- Work function $\phi$
- $E_F$ Fermi energy
- D dipole potential



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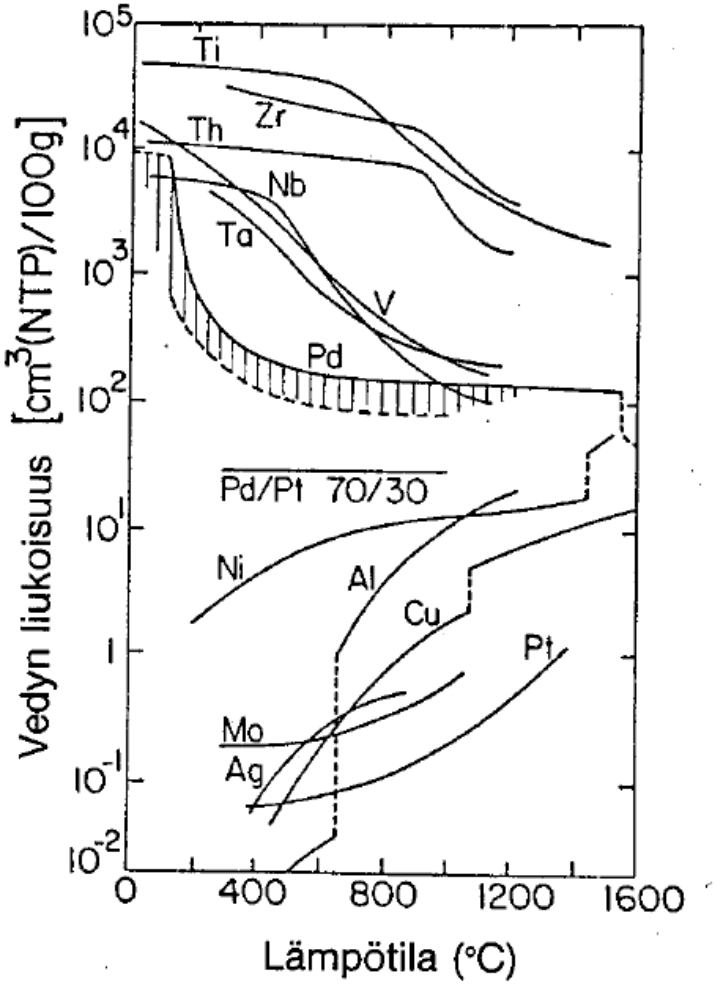
# Work function of some metals

| Element | eV | Element | eV | Element | eV | Element | eV | Element | eV |
|---|---|---|---|---|---|---|---|---|---|
| Ag: | 4.52-4.74 | Al: | 4.06-4.26 | As: | 3.75 | Au: | 5.1-5.47 | B: | ~4.45 |
| Ba: | 2.52-2.7 | Be: | 4.98 | Bi: | 4.34 | C: | ~5 | Ca: | 2.87 |
| Cd: | 4.08 | Ce: | 2.9 | Co: | 5 | Cr: | 4.5 | Cs: | 2.14 |
| Cu: | 4.53-5.10 | Eu: | 2.5 | Fe: | 4.67-4.81 | Ga: | 4.32 | Gd: | 2.90 |
| Hf: | 3.9 | Hg: | 4.475 | In: | 4.09 | Ir: | 5.00-5.67 | K: | 2.29 |
| La: | 3.5 | Li: | 2.93 | Lu: | ~3.3 | Mg: | 3.66 | Mn: | 4.1 |
| Mo: | 4.36-4.95 | Na: | 2.36 | Nb: | 3.95-4.87 | Nd: | 3.2 | Ni: | 5.04-5.35 |
| Os: | 5.93 | Pb: | 4.25 | Pd: | 5.22-5.6 | Pt: | 5.12-5.93 | Rb: | 2.261 |
| Re: | 4.72 | Rh: | 4.98 | Ru: | 4.71 | Sb: | 4.55-4.7 | Sc: | 3.5 |
| Se: | 5.9 | Si: | 4.60-4.85 | Sm: | 2.7 | Sn: | 4.42 | Sr: | ~2.59 |
| Ta: | 4.00-4.80 | Tb: | 3.00 | Te: | 4.95 | Th: | 3.4 | Ti: | 4.33 |
| Tl: | ~3.84 | U: | 3.63-3.90 | V: | 4.3 | W: | 4.32-5.22 | Y: | 3.1 |
| Yb: | 2.60 [2] | Zn: | 3.63-4.9 | Zr: | 4.05 | | | | |

## Adsorbed atoms alloying effect work function

# Solubility of gasses (hydrogen) into metals

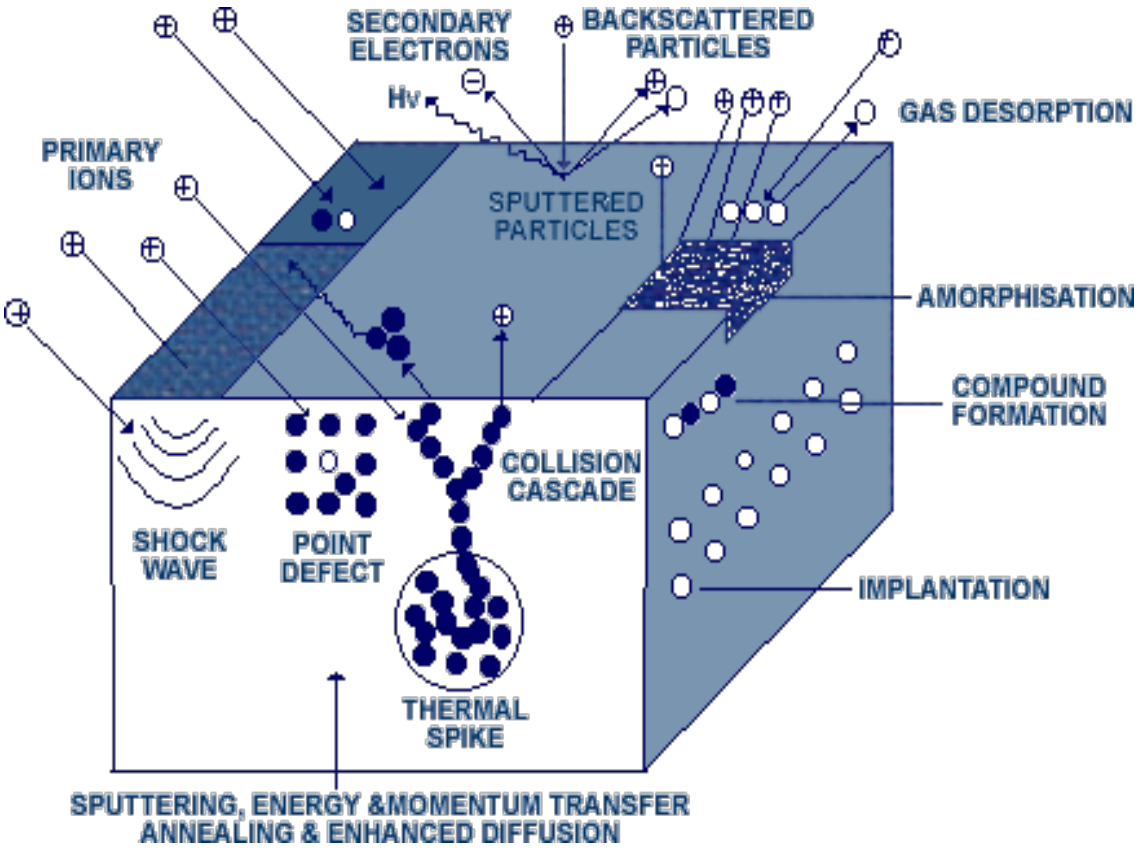



*Kuva 7. Vedyn liukoisuuden riippuvuus lämpötilasta eräillä metalleilla ($P_{H_2} = 10^5$ Pa)[3].*

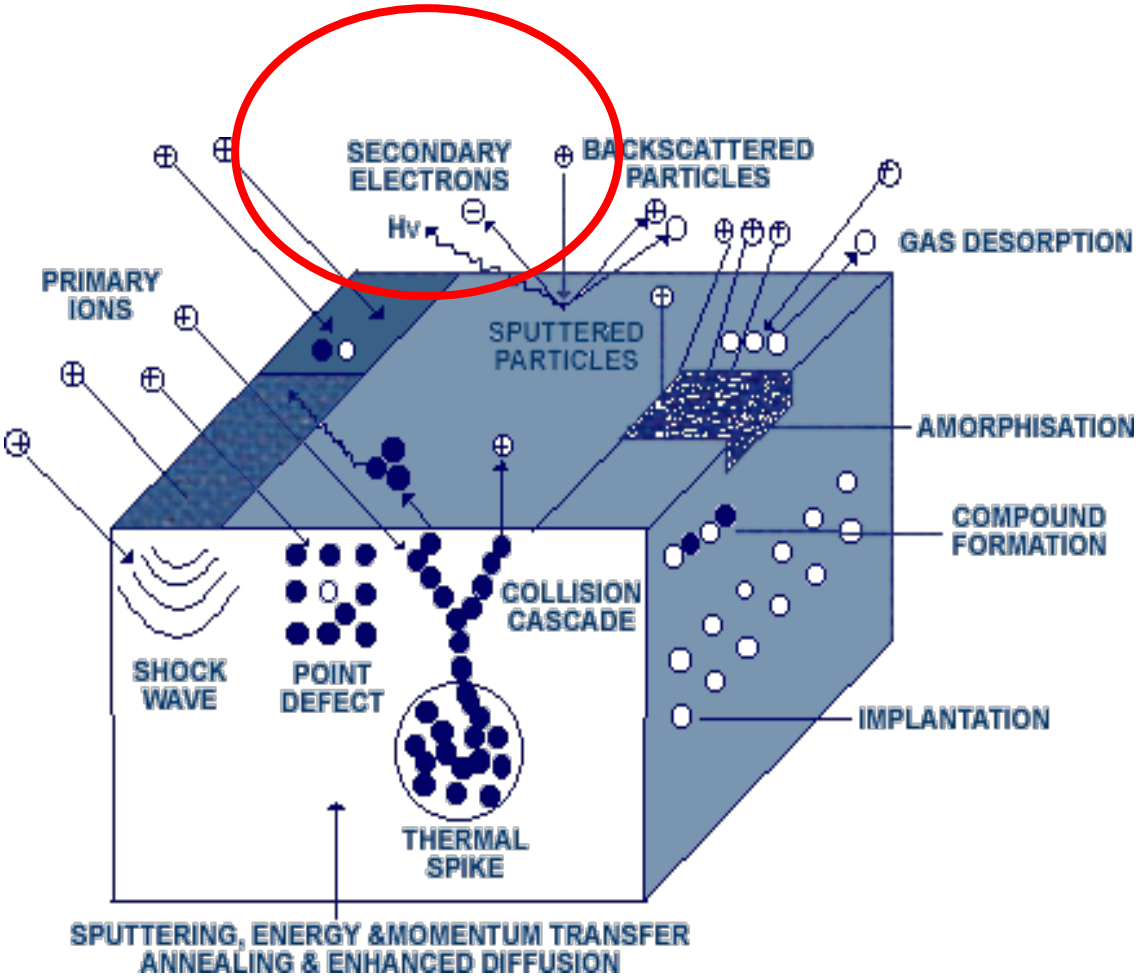
# Vacuum surface engineering

1. Vacuum technology
2. Surface phenomena
3. **Surface energetic ion interaction**

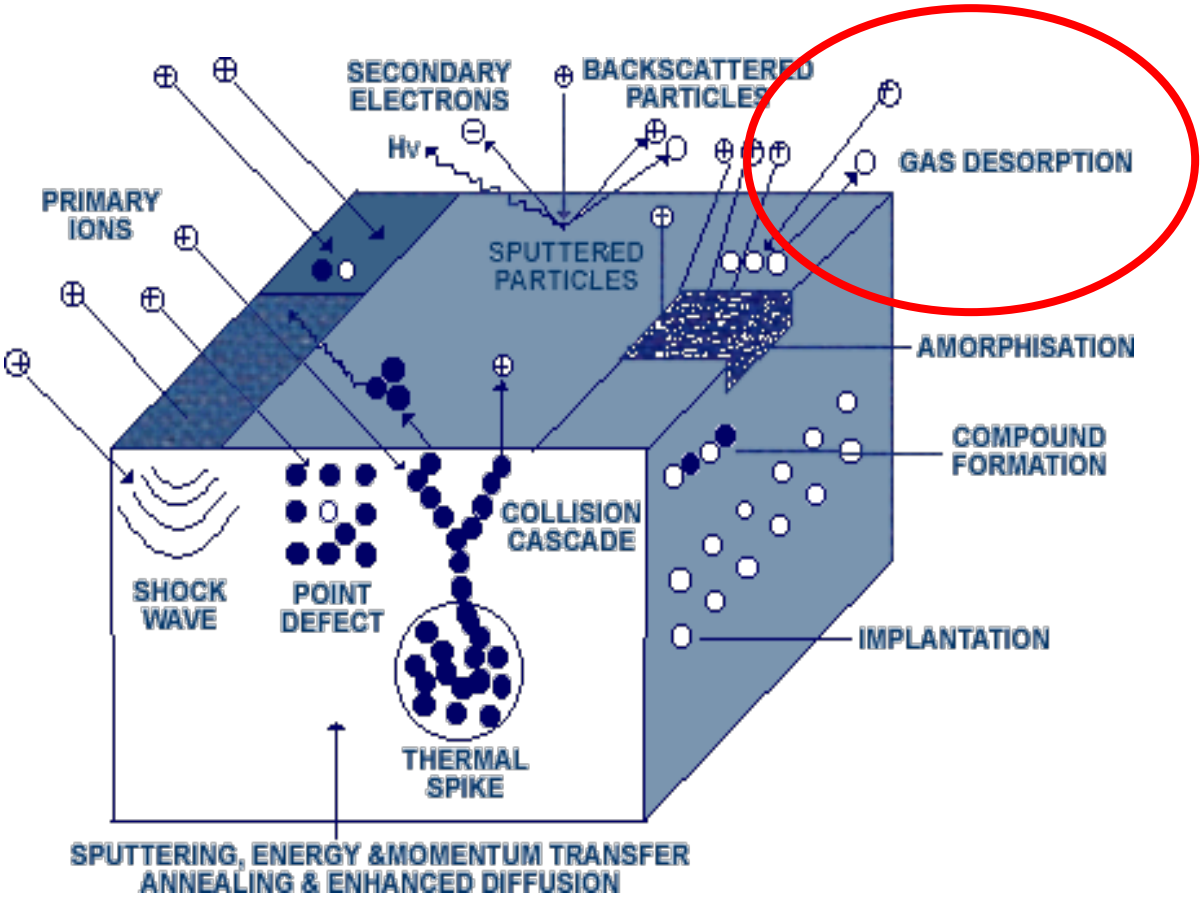
# Energetic ion surface interactions



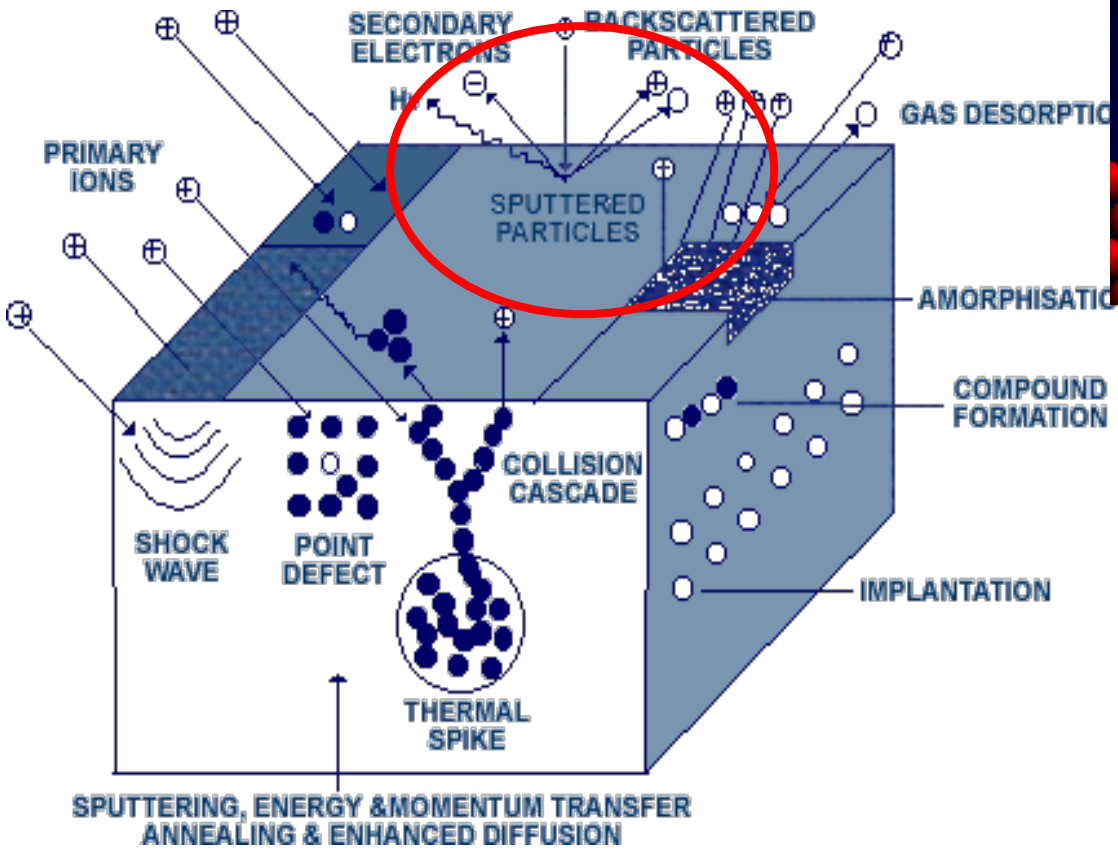
# Secondary electrons

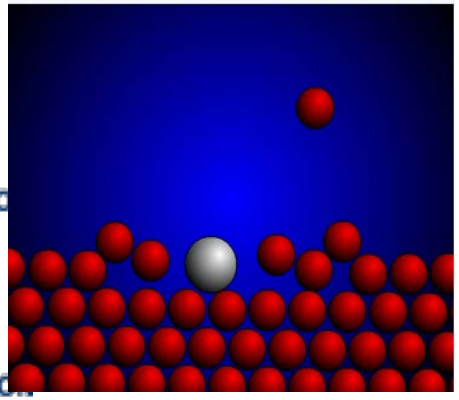


# Desorption, cleaning

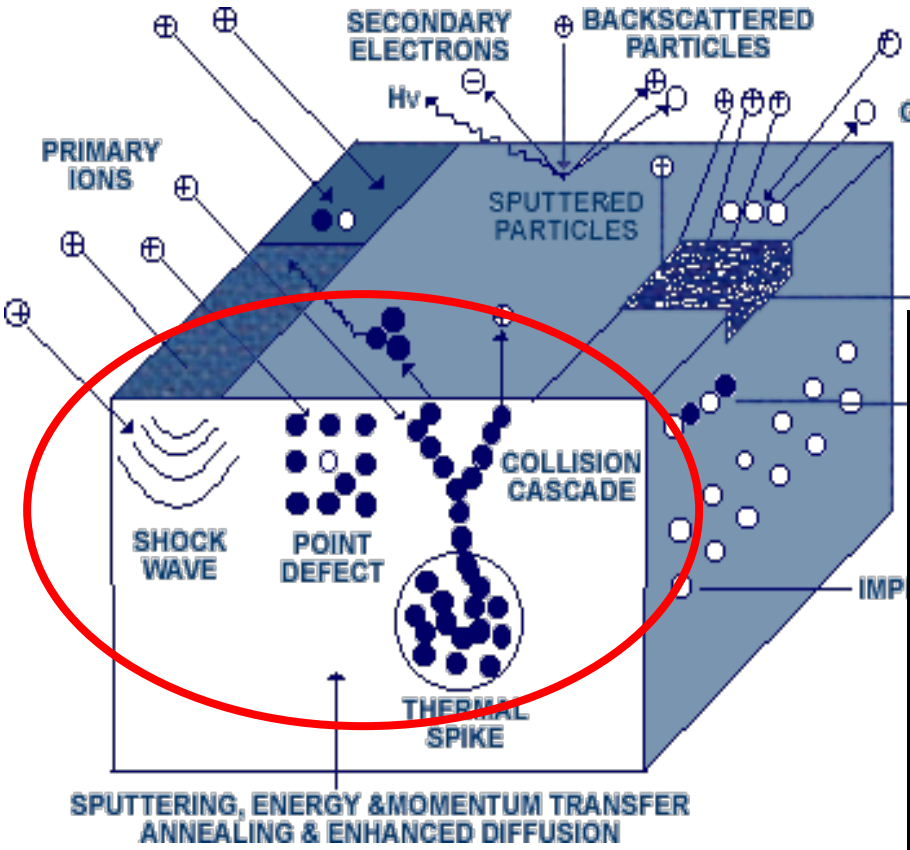


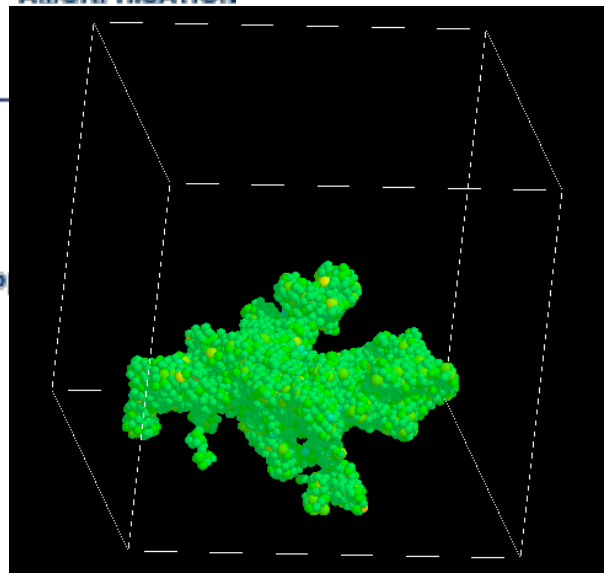
# Sputtering


SECONDARY ELECTRONS
BACKSCATTERED PARTICLES
PRIMARY IONS
SPUTTERED PARTICLES
GAS DESORPTIO
AMORPHISATIO
COMPOUND FORMATION
COLLISION CASCADE
SHOCK WAVE
POINT DEFECT
IMPLANTATION
THERMAL SPIKE
SPUTTERING, ENERGY &MOMENTUM TRANSFER
ANNEALING & ENHANCED DIFFUSION



# Collision cascade, thermal spike



K. Nordlund

# Thermal spike

**10 keV Au ion to Au surface**

http://en.wikipedia.org/wiki/File:10kevau_au.gif

**HY Nordlund simulations**

http://beam.acclab.helsinki.fi/~knordlun/anims.html

http://beam.acclab.helsinki.fi/~knordlun/gif/au500.avi

# doping, compounds