Aalto University
School of Chemical
Engineering

Surfaces and Films
CHEM E5150
Lecture 2B

J Koskinen

Items

- Low pressure – vacuum
- Thin film growth from incoming molecules
- Surface characterization

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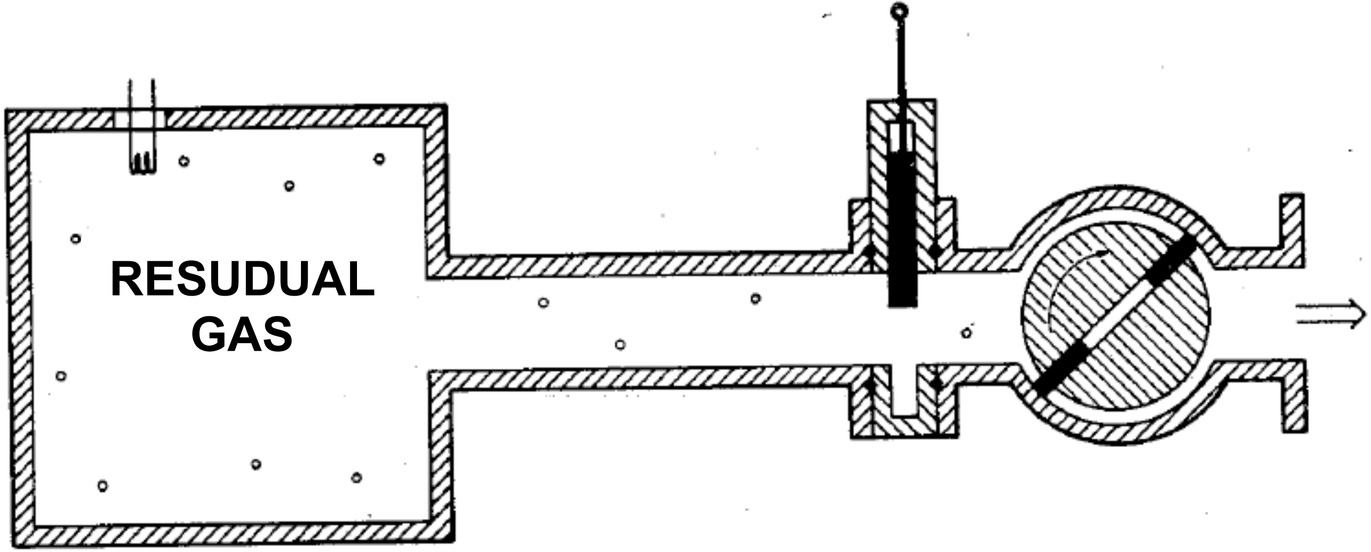
Vacuum system



VACUUM GAUGE

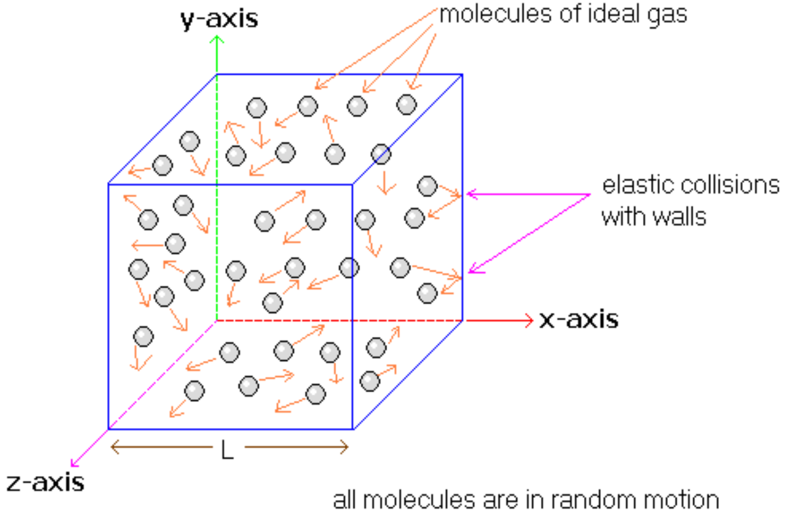
PUMP

RESUDUAL GAS

FLANCE

VACUUM CHAMBER

Idea gas collision



Video

https://simplexitysolutions.blogspot.com/2015/09/interpretation-of-pressure-on-kinetic.html

Vacuum – low pressure

Assume ideal gas: $PV = nRT = NkT$

P(atm), V(liter), n(moles), R(L-atm/mole-K), T(K)

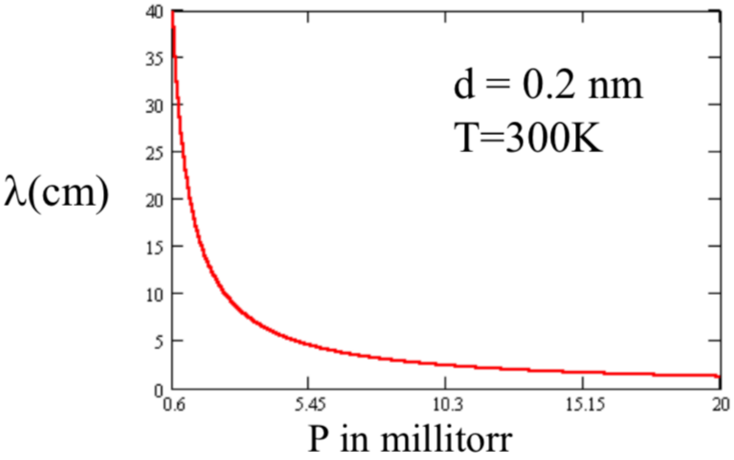
P(Pa), V(m^3), N(molecules), k(J/molecule-K), T(K)

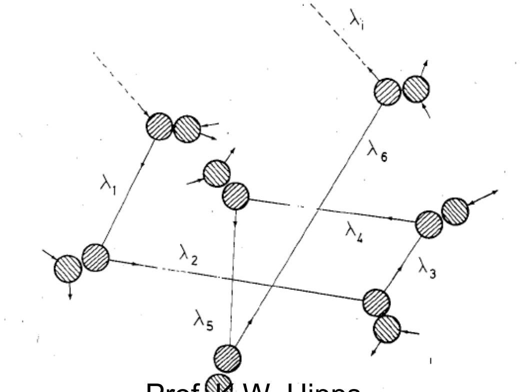
1 atm = 1,013 mbar = 1.013×10^5 Pa = 760 torr

The 'Mean Free Path' (λ) is given by:

$\lambda(P) = kT/[P\pi d^2]$ where all quantities are in mks units

$\lambda c(p) = 100kT/[0.133\, p\pi d^2]$: p in millitorr and λc in cm

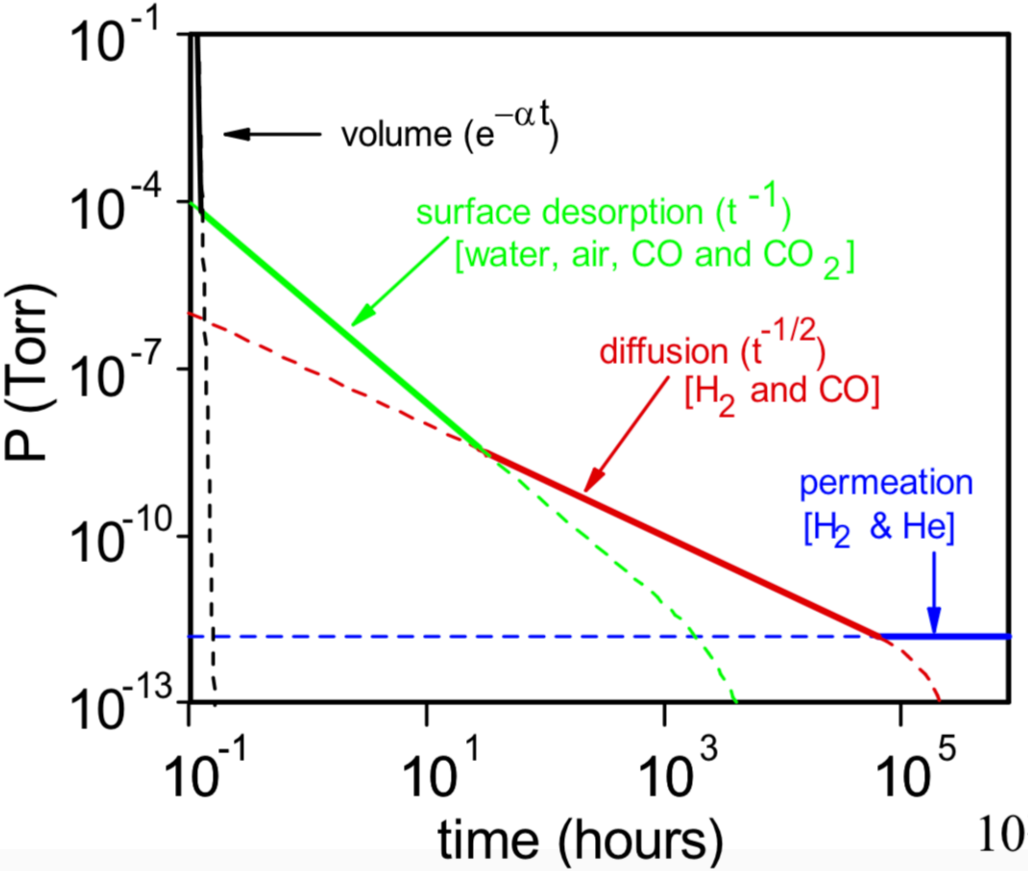




Prof. K.W. Hipps
www.wsu.edu/~hipps/M571.htm

Pump-down Pressure vs Time

Typical Unbaked Stainless Steel Chamber



- The ultimate pressure of a particular system is achieved when the pumping rate just equals the rate of gas evolution.

- A recently opened system requires a very long time (or a very large pump) to achieve reasonable vacuum levels.

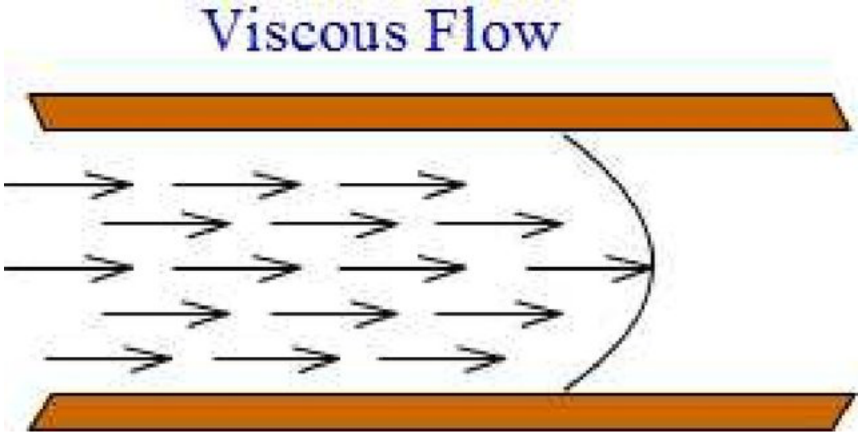
10^3 hrs is 42 days!!

Viscose flow

Viscous flow: $\lambda \ll D$

Water in a pipe. The intermolecular interactions are much more important than the interactions with the container.

$P \geq 50$ milliTorr = 7 Pa = 5×10^{-2} Torr



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Knudsen flow

Viscous flow: $\lambda \approx D$

Intermediate state. About as many intermolecular collisions as collisons with the wall

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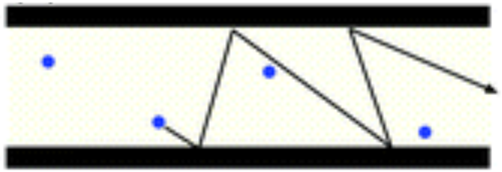
Ballistic flow

Viscous flow: $\lambda \gg D$

Bullets bouncing off walls. Negligible intermolecular interactions. Primary interactions are with the container

$P \leq 0.5$ milliTorr = 0.07 Pa = 5×10^{-4} Torr



ballistic atom motion

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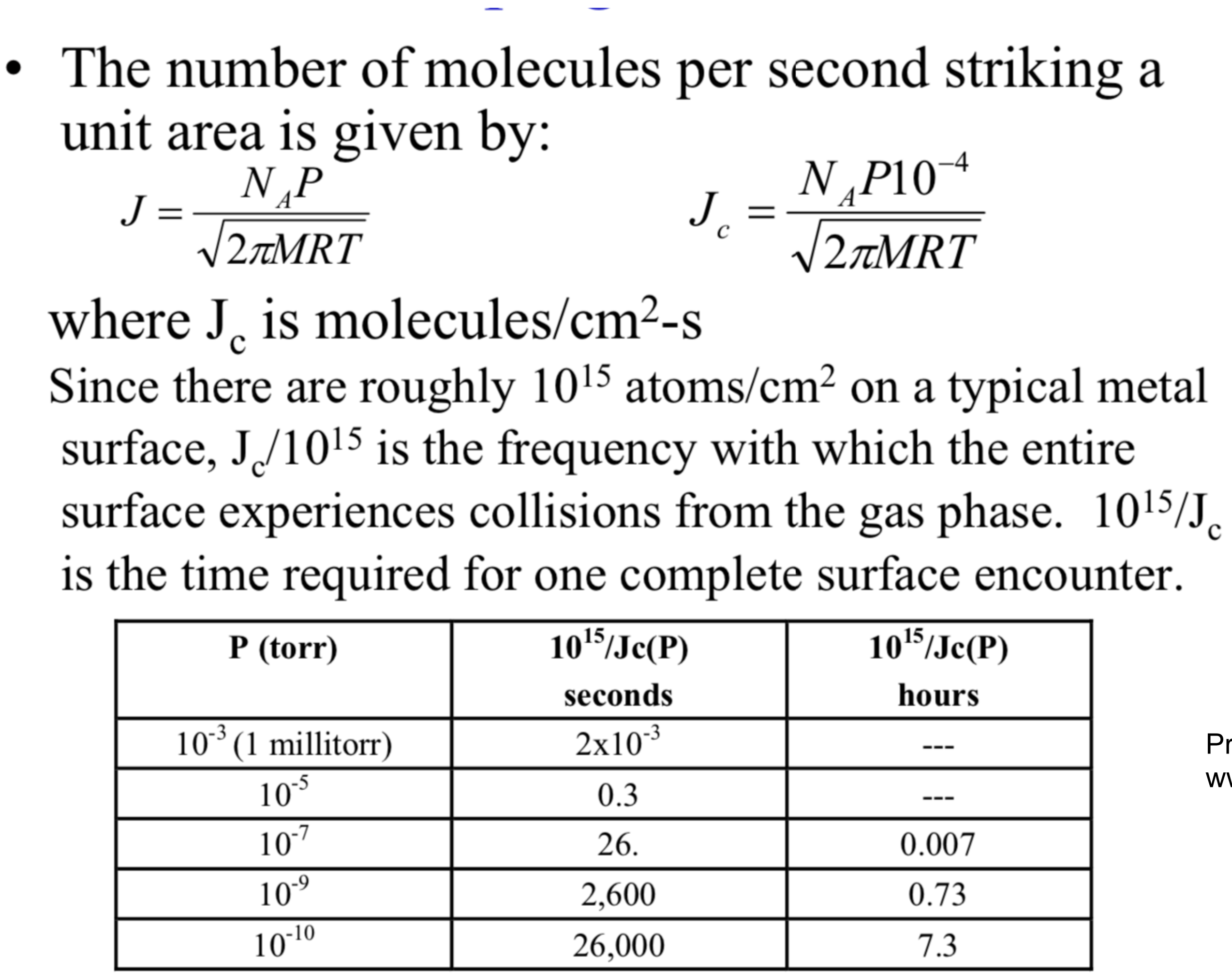
Impingement Rate



- The number of molecules per second striking a unit area is given by:

$$J = \frac{N_A P}{\sqrt{2\pi MRT}} \qquad J_c = \frac{N_A P 10^{-4}}{\sqrt{2\pi MRT}}$$

where J_c is molecules/cm^2-s

Since there are roughly 10^{15} atoms/cm^2 on a typical metal surface, $J_c/10^{15}$ is the frequency with which the entire surface experiences collisions from the gas phase. $10^{15}/J_c$ is the time required for one complete surface encounter.

P (torr)	**10^{15}/Jc(P) seconds**	**10^{15}/Jc(P) hours**
10^{-3} (1 millitorr)	$2\text{x}10^{-3}$	---
10^{-5}	0.3	---
10^{-7}	26.	0.007
10^{-9}	2,600	0.73
10^{-10}	26,000	7.3

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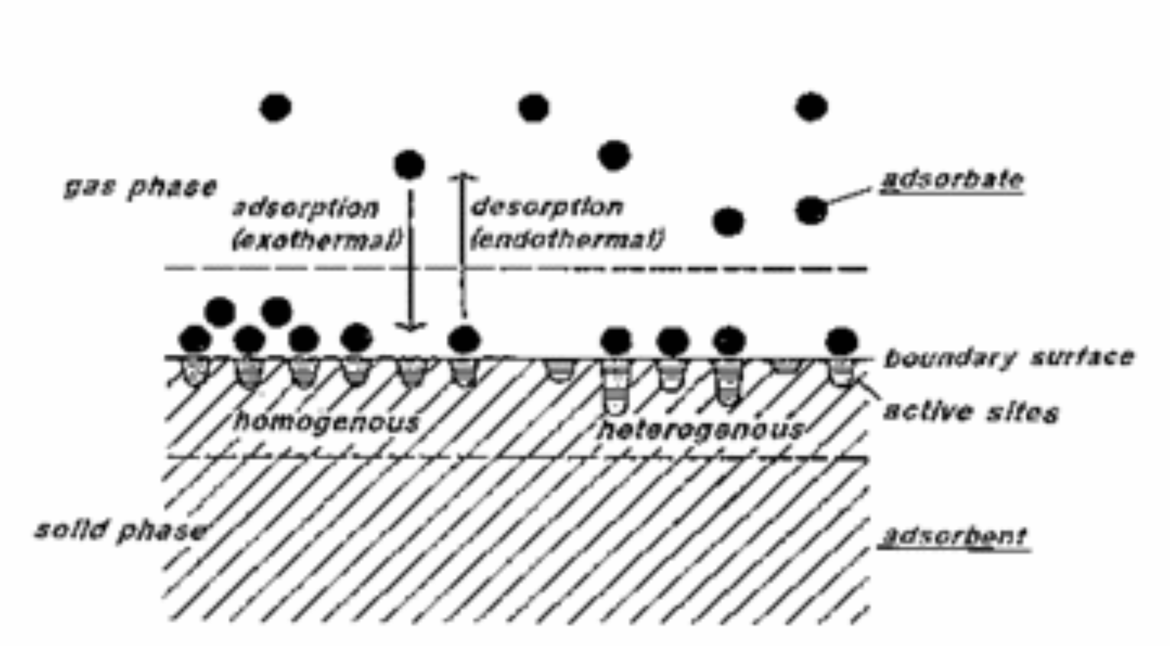
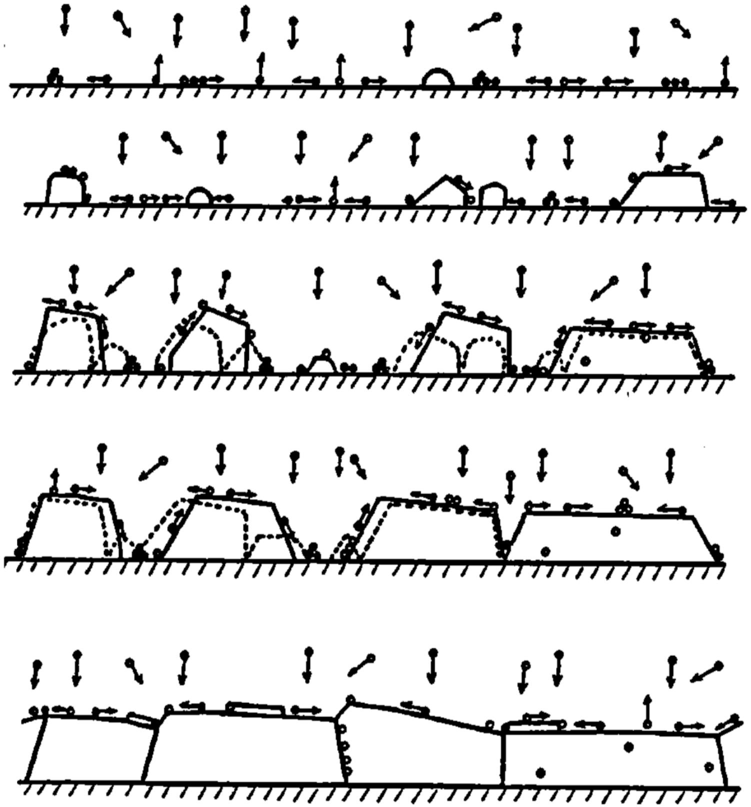
- **Thin film growth from incoming molecules**
- Surface characterization

Adsorption of atoms on surface



http://soft-matter.seas.harvard.edu/index.php/File:Fig6.gif

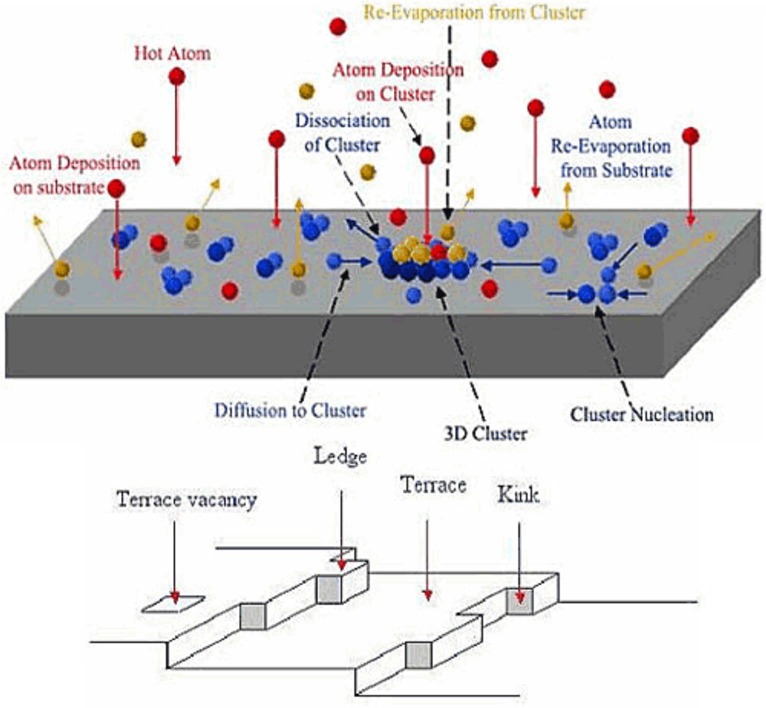
Thin films growth



J. Vac. Sci. Technol. A 21„5…, SepÕOct 2003

FIG. 1. Schematic diagram illustrating fundamental growth processes controlling microstructural evolution: nucleation, island growth, impingement and coalescence of islands, grain coarsening, formation of polycrystalline islands and channels, development of a continuous structure, and film growth (see Ref. 9).

Nucleation

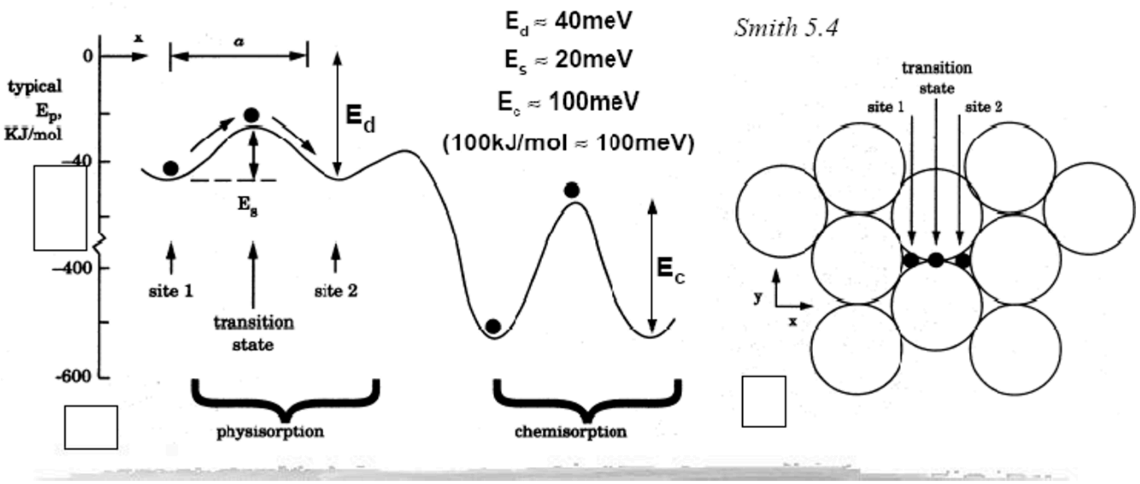

Re-Evaporation from Cluster
Hot Atom
Atom Deposition on Cluster
Dissociation of Cluster
Atom Re-Evaporation from Substrate
Atom Deposition on substrate
Diffusion to Cluster
3D Cluster
Cluster Nucleation
Ledge
Terrace vacancy
Terrace
Kink

Surface diffusion

extremely important for thin film formation

- allows adsorbed species to form clusters (homogeneous nucleation)
- allows adsorbed species to find heterogeneous nucleation sites (steps etc.)
- adsorbed atoms move in potential energy "landscape"

generated by substrate or thin film surface atoms: diffusion, hopping



$E_d \approx 40$meV

$E_s \approx 20$meV

$E_c \approx 100$meV

(100kJ/mol ≈ 100meV)

Wake Forest University NAN 242 Thin Film Fabrication 2010

M. Ohring, Materials Science of thin films, 2002

Surface diffusion

$E_S < E_d$, E_c: only partial breaking of bonds

Molecular hopping rate: $k_s = v_{0s} \cdot \exp\left(-\frac{E}{R \cdot T_s}\right)$ (influence of substrate temperature, T_S)

($v_{0s}=10^{13}\ldots10^{16}$ Hz: attempt frequency)

Diffusion: random walk, not directed.

Equal hopping probabilities for forward and backward motion

Diffusion length, $\Lambda : \Lambda = r \cdot \sqrt{N_0} \approx a \cdot \sqrt{N_0} = a \cdot \sqrt{k_s \cdot t}$

(r: rms change in distance per hopping event, N_0: number of hops, a: lattice constant, t: diffusion time)

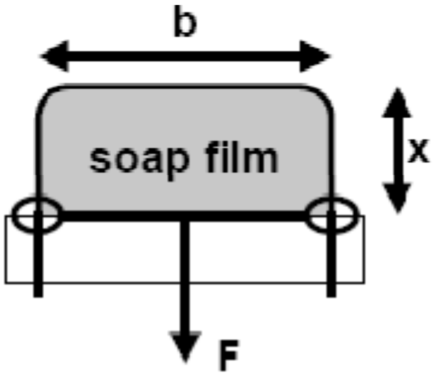
$$\left.\begin{array}{l} v_{0s} = 10^{13} S^{-1} \\ E_s = 20meV \\ E_s = 200meV \\ T = 1000K \\ t = 1s \\ a = 0.3nm \end{array}\right\}$$

$\Lambda = 300\mu m$ (physisorbed)

$\Lambda = 5nm$ (chemisorbed)

Strong influence of bonding conditions!

Nucleation – minimizing surface energy



$$\Delta W = 2\,\gamma \cdot \Delta A = 2\,\gamma \cdot \Delta x \cdot b$$

$$\frac{F}{b} = \frac{\Delta W}{\Delta x \cdot b} = 2\,\gamma$$

Force acts tangentially

Tends to decrease surface area

Fundamental to thin film growth:

Surface energy can be minimized by surface diffusion

Chemical composition
crystallographic orientation
atomic reconstruction

$$\longrightarrow \quad \gamma \cdot A \rightarrow \min$$

Surface topgraphy

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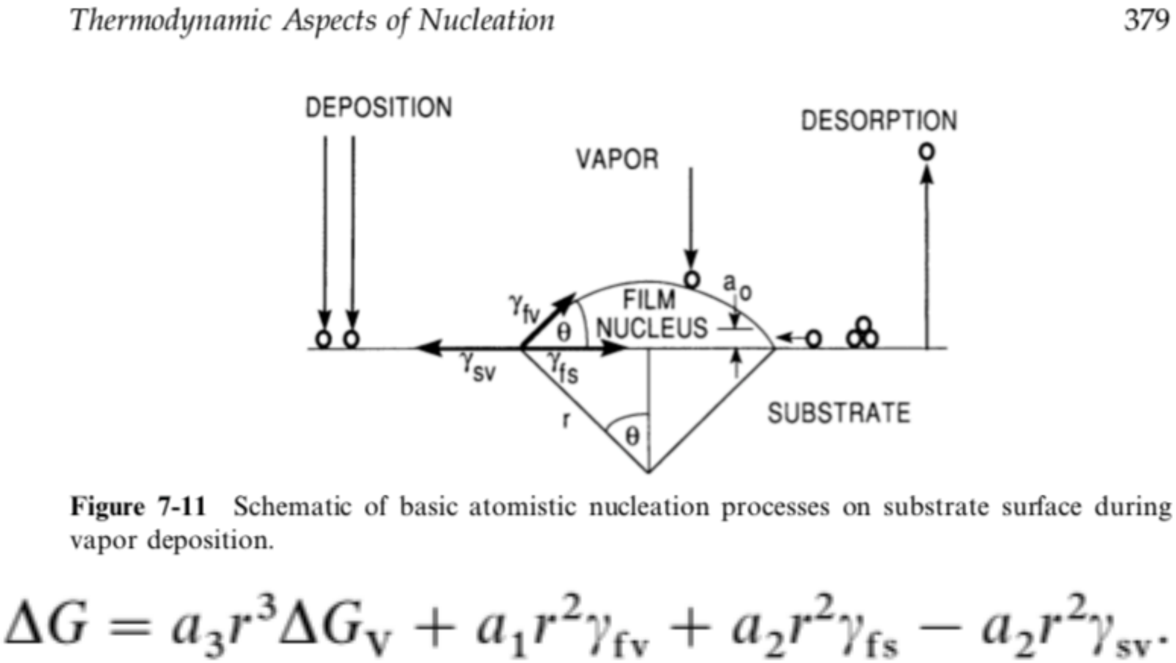
M. Ohring, Materials Science of thin films, 2002

Nucleation of a growing film



Thermodynamic Aspects of Nucleation 379

Figure 7-11 Schematic of basic atomistic nucleation processes on substrate surface during vapor deposition.

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}.$$

M. Ohring, Materials Science of thin films, 2002

Density of nuclei

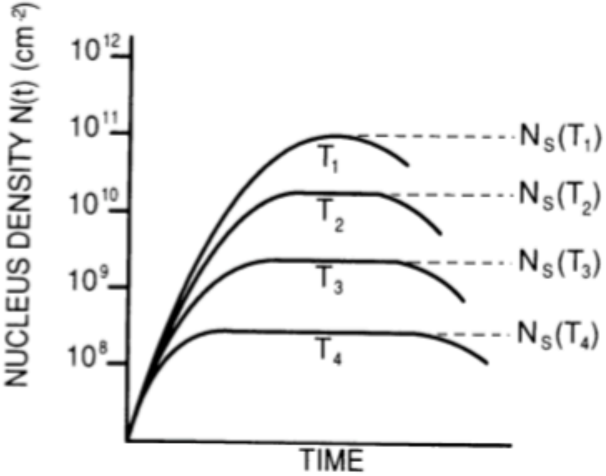


Figure 7-16 Schematic dependence of $N(t)$ with time and substrate temperature. $T_1 > T_2 > T_3 > T_4$. (From Ref. 19.)

M. Ohring, Materials Science of thin films, 2002

Coalescence - ripening

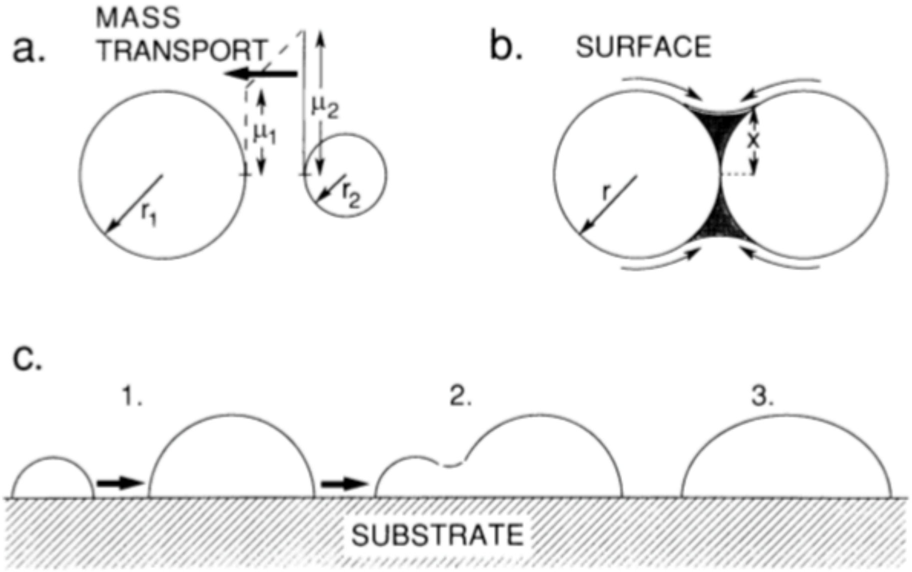


Figure 7-17 Coalescence of islands due to (a) Ostwald ripening, (b) sintering, (c) cluster migration.

M. Ohring, Materials Science of thin films, 2002

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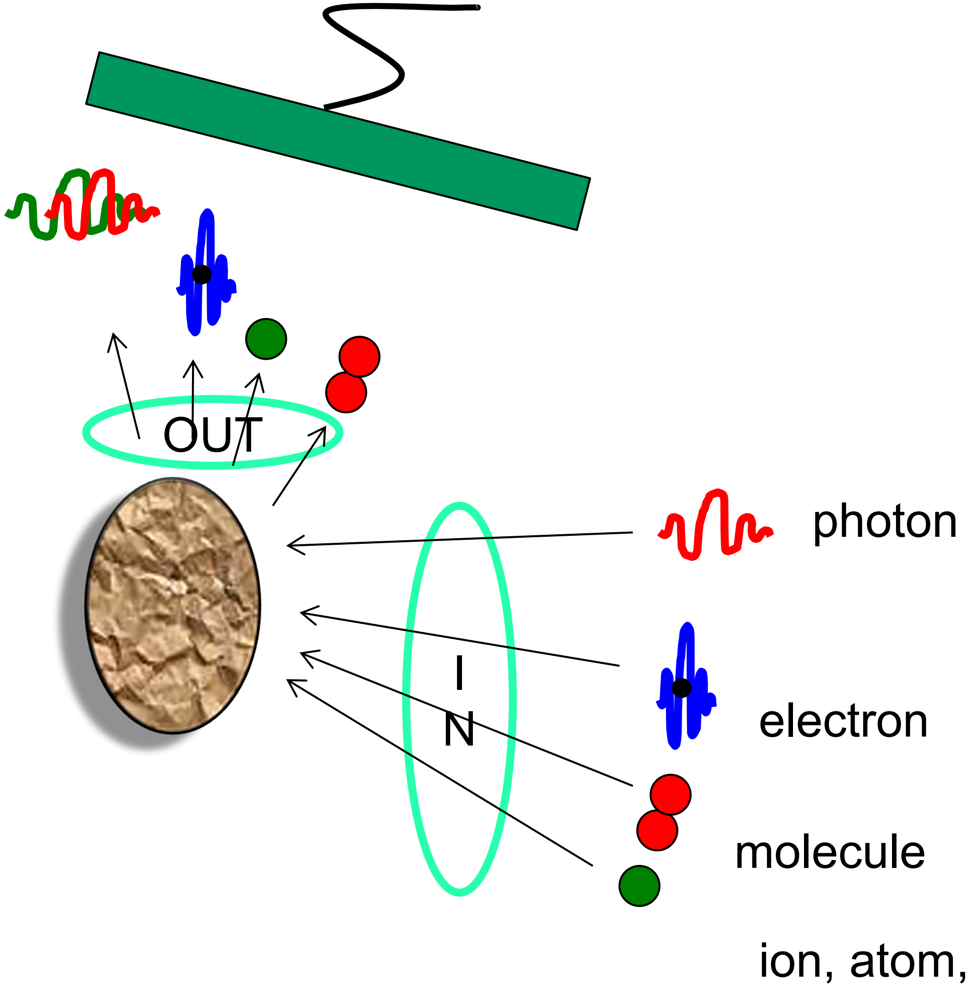
- **Surface characterization**

Thin films characterization

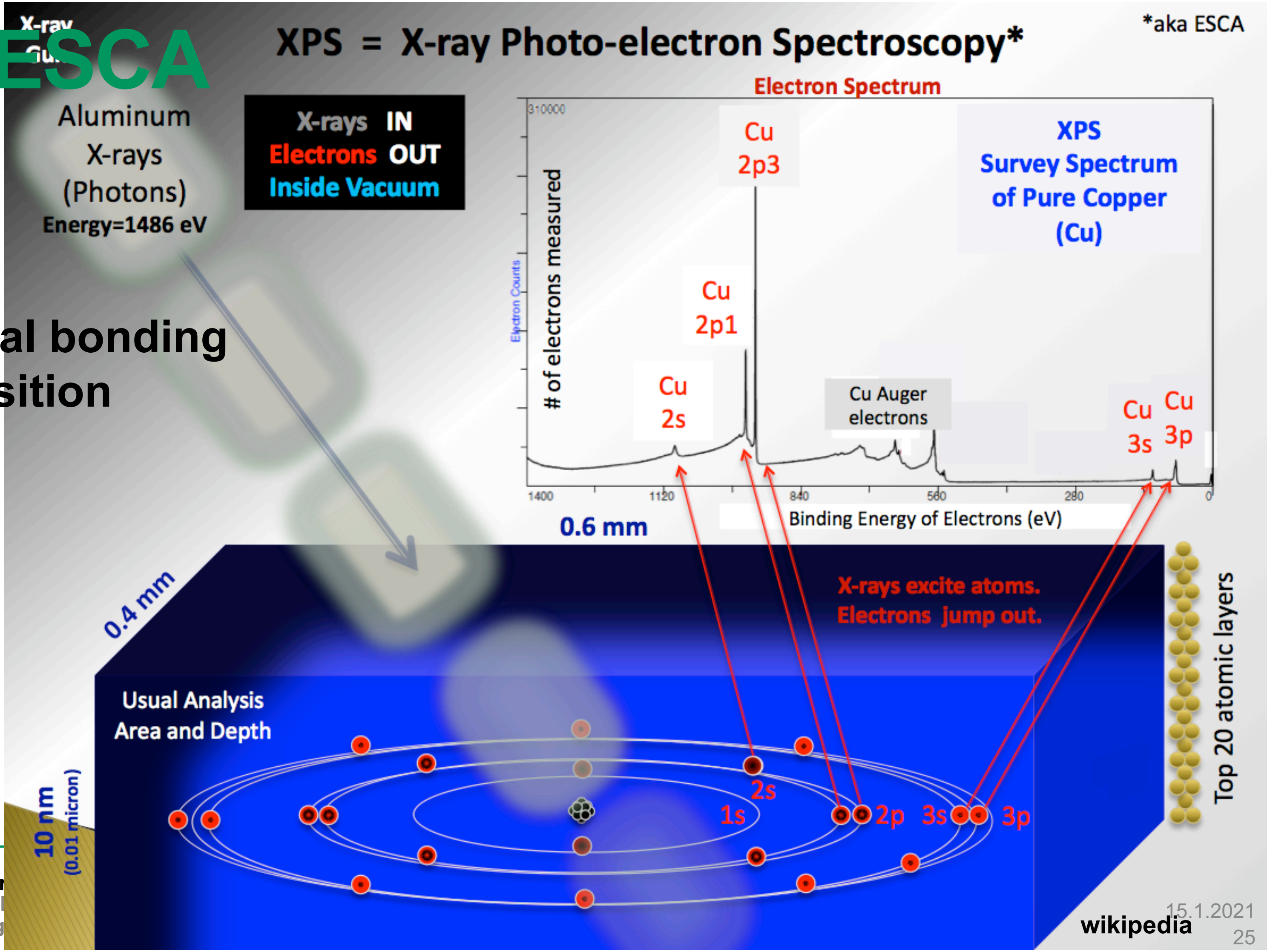
- **Why vacuum for cahracterization of thins film and surfaces?**
  - Only in high vacuum surfaces are clean
  - Many characterization methods are scatter physics:
    - *Particle in or particle out (high mean free path λ needed)*



- particles ➔in vacuum !!
- elastic scattering
  - mass, density
  - diffraction
- inelastic scattering
  - information on material
    - DOS
    - bonding
    - identification of elements
    - …

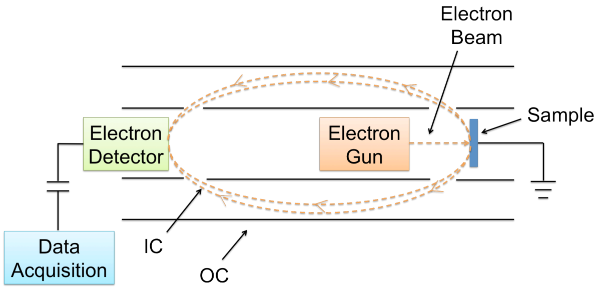
XPS -ESCA

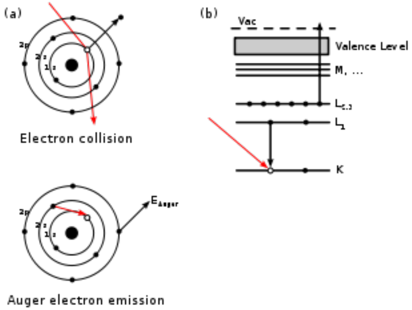
- Chemical bonding
- Composition

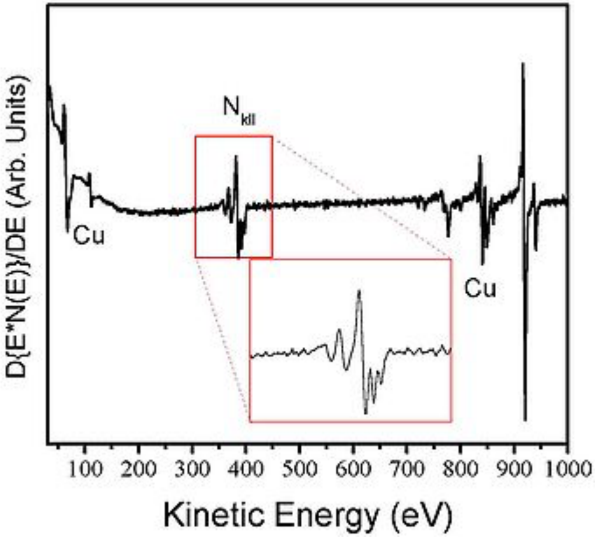


Auger electron spectroscopy

- Surface composition
- Chemical bond

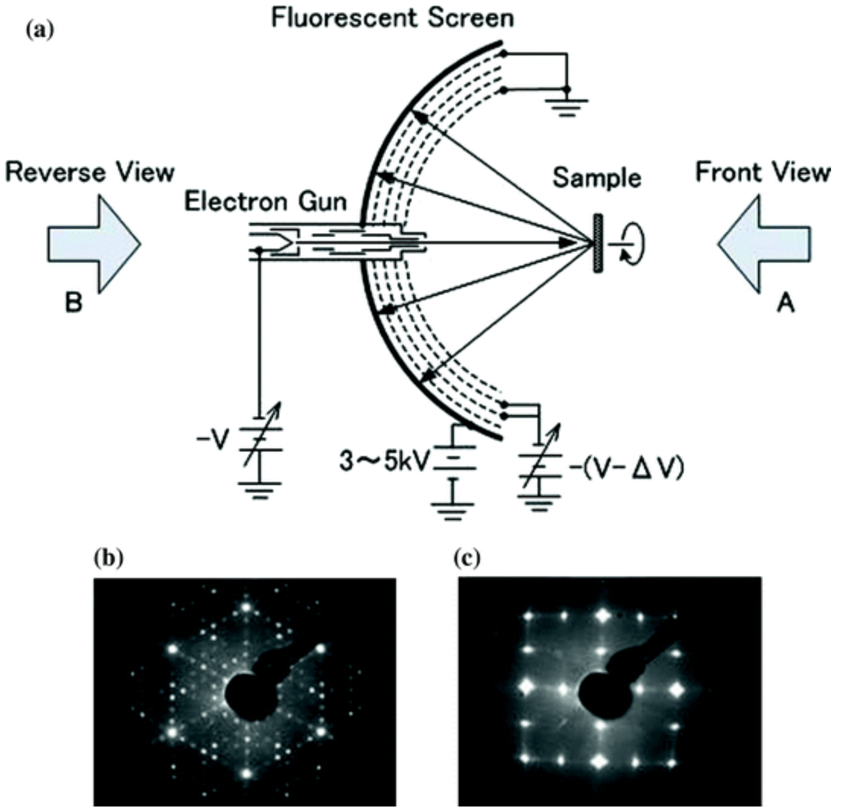




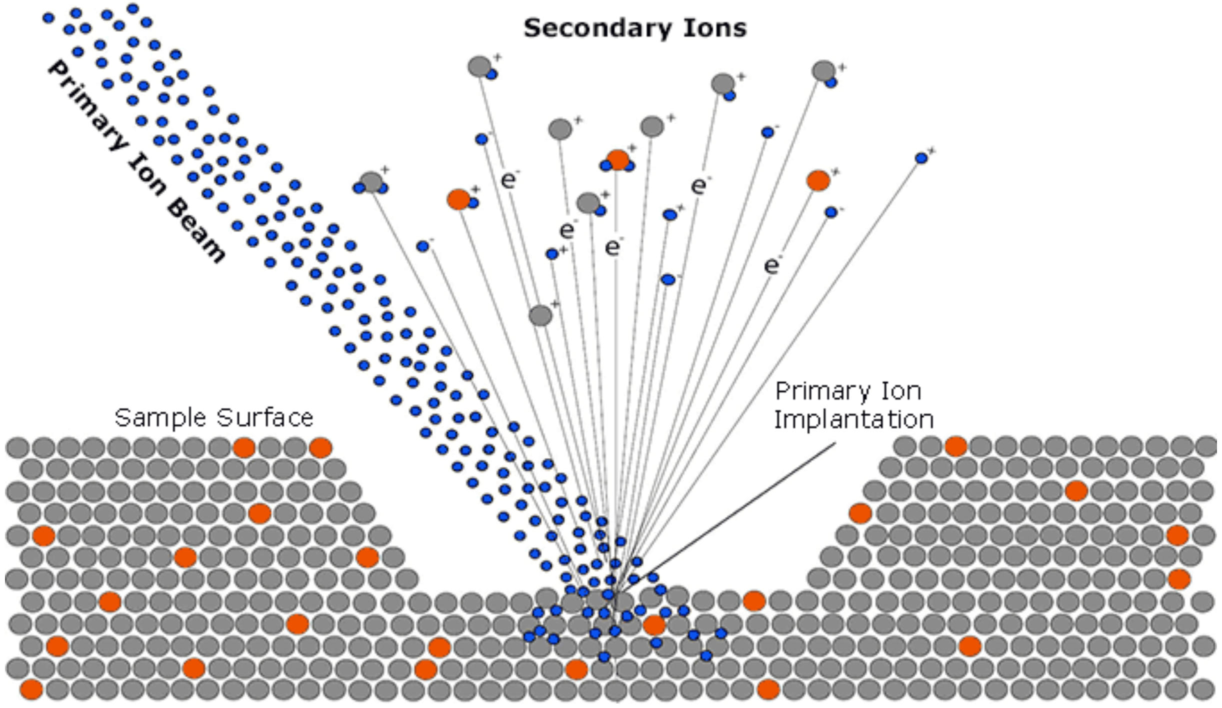


LEED Low Energy Electron Diffraction

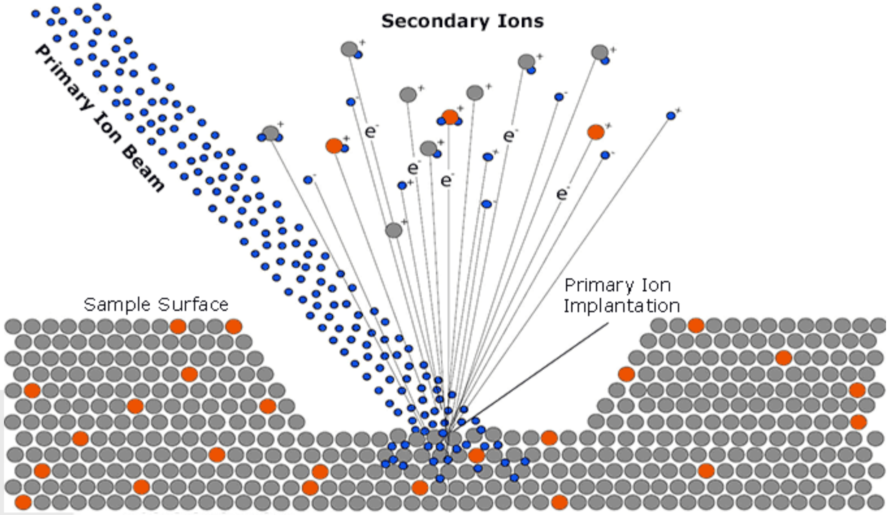
- **Crystalline structure**

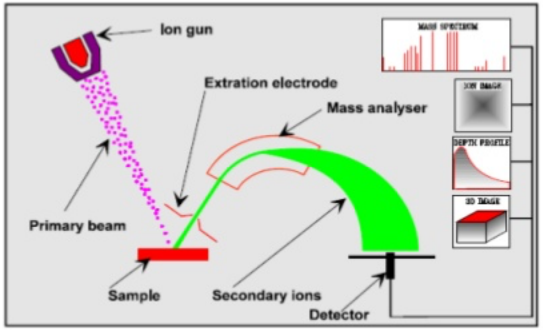


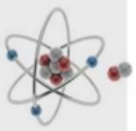
Seconday ion mass specroscopy



Seconday ion mass specroscopy

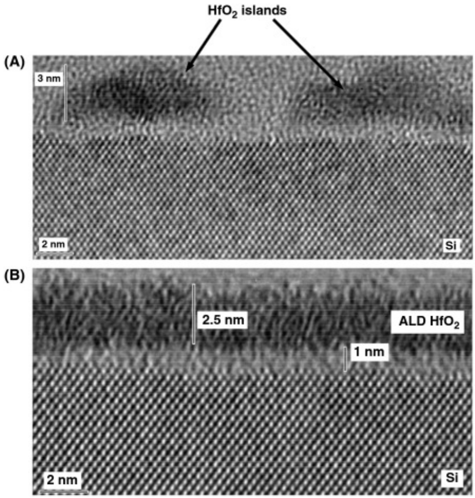


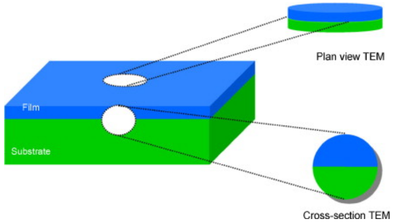




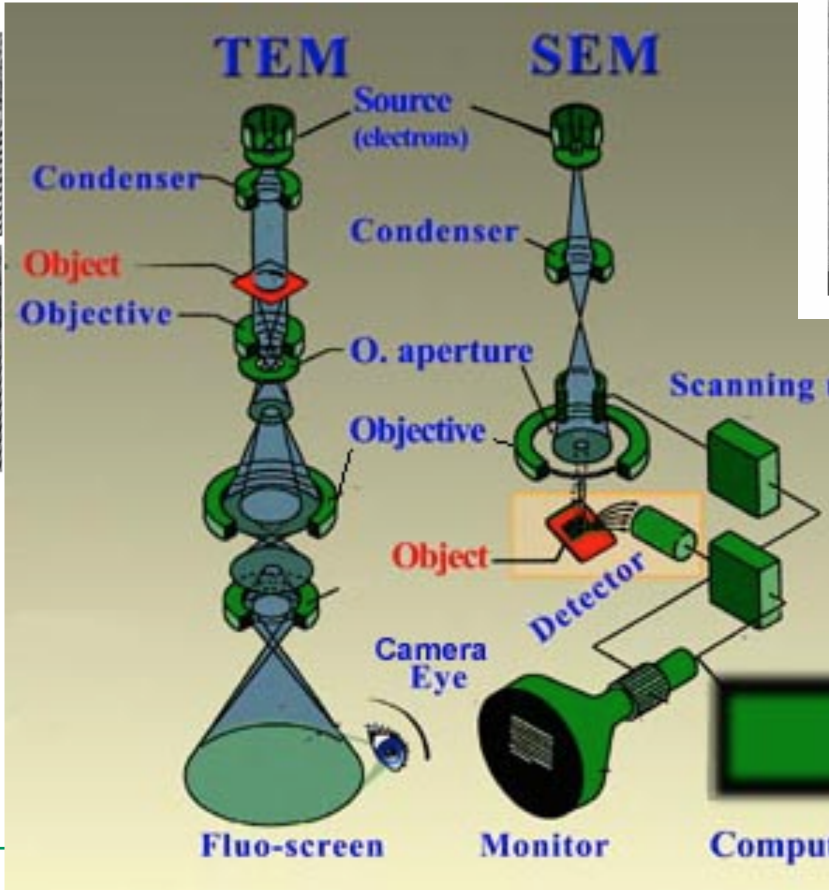
- Vacuum roughly 10^{-6} mbar
- Ions: Ar^+, O_2^+, Cs^+ (M 133) 1 – 30 keV
- sensitivity $10^{12} – 10^{16}$ atoms/cm^3
- beam focus down to 1 µm
- mapping of elements
- Depth profiling by sputter etching
- seconday ion yield depends on chemical composition of sample
  - reference samples with known composition necessary for quantitative analysis
- Sputtering - > mixing of composition
  - depth resolution decreases when sputtering deeper

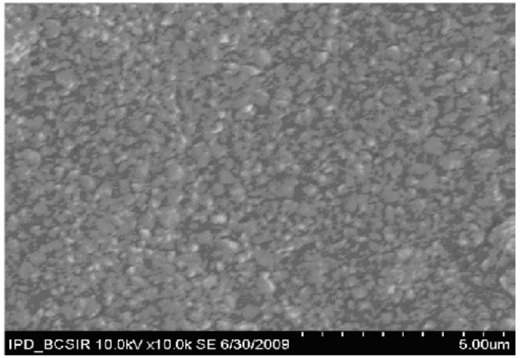
Electron microscopy





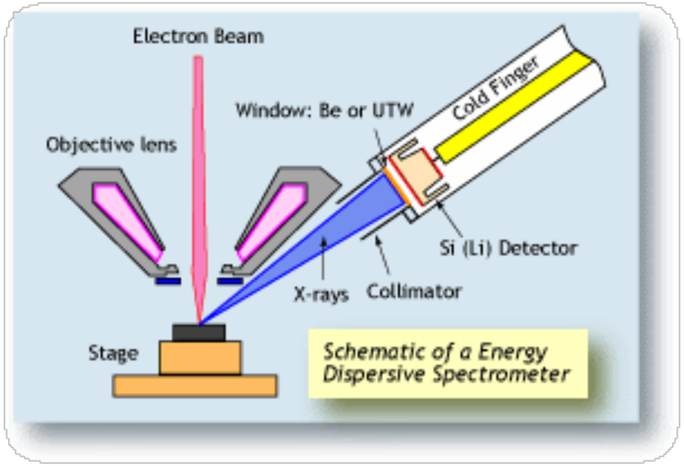
- Atomic structure
- Defects

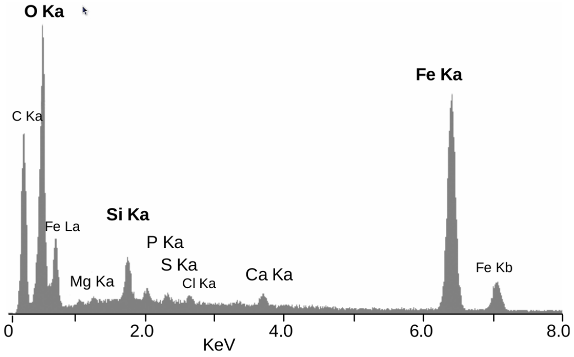


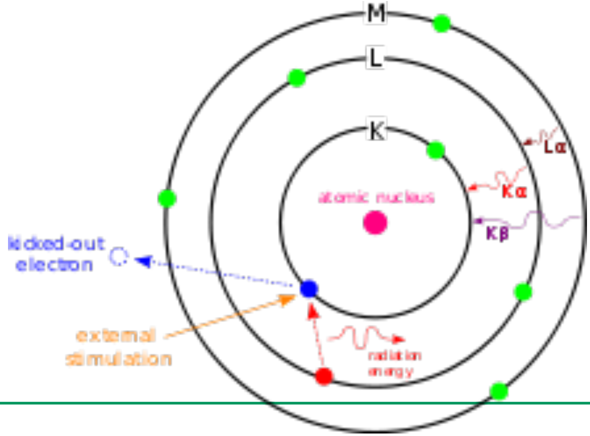


- Topography
- Defects
- Impuriteis
- Thickness

SEM - EDS Energy Dispersive Spectroscopy

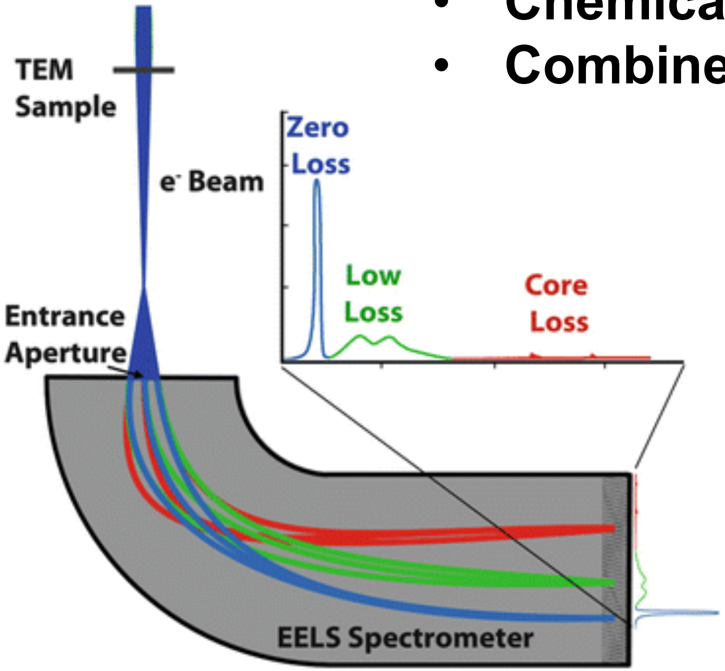






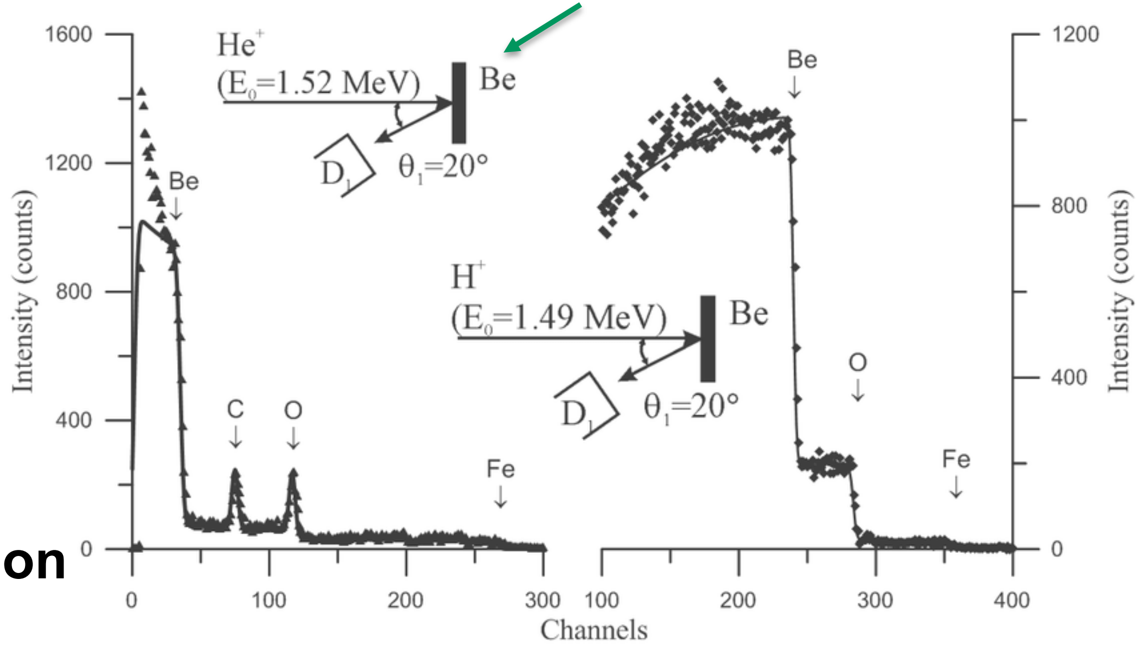
TEM EELS Electron Loss Spectroscopy

- **Chemical bonding**
- **Combined with atomic resolution**



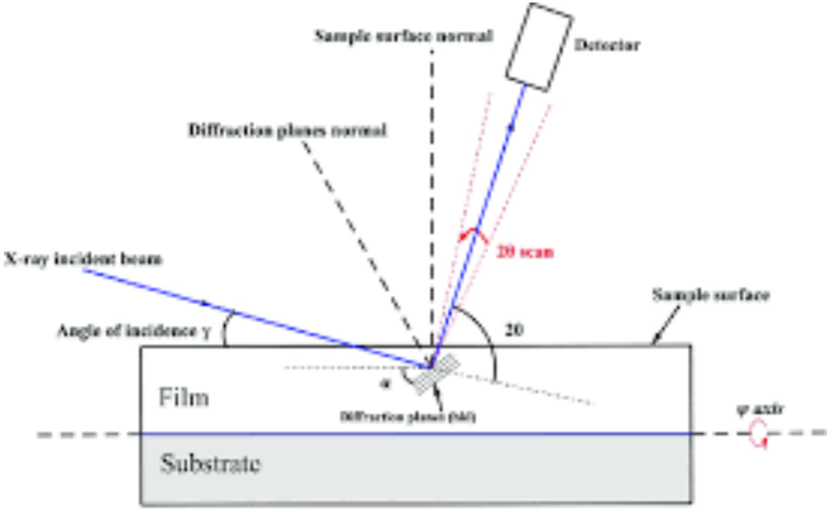
Ion beam scatter (Rutherford Back Scattering RBS)

Sample thin film



- **Surface composition**

Grazing angle x-ray spectroscopy



$$\alpha = \theta - \gamma$$

X-Ray Reflectivity XRR

- Thin Film
  - thickness
  - density
  - roughness
  - rougness of interface

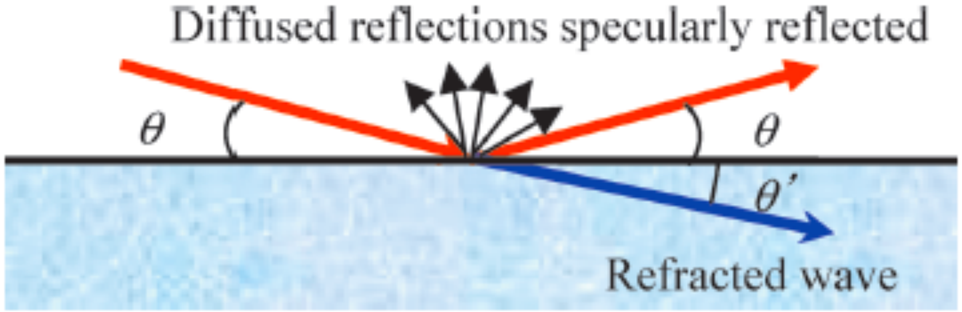


Fig. 1. Reflection and refraction of X-rays on material surface.

Miho Yasaka, The Rigaku Journal, 26(2), 2010

Thickness of film – contact profilometry

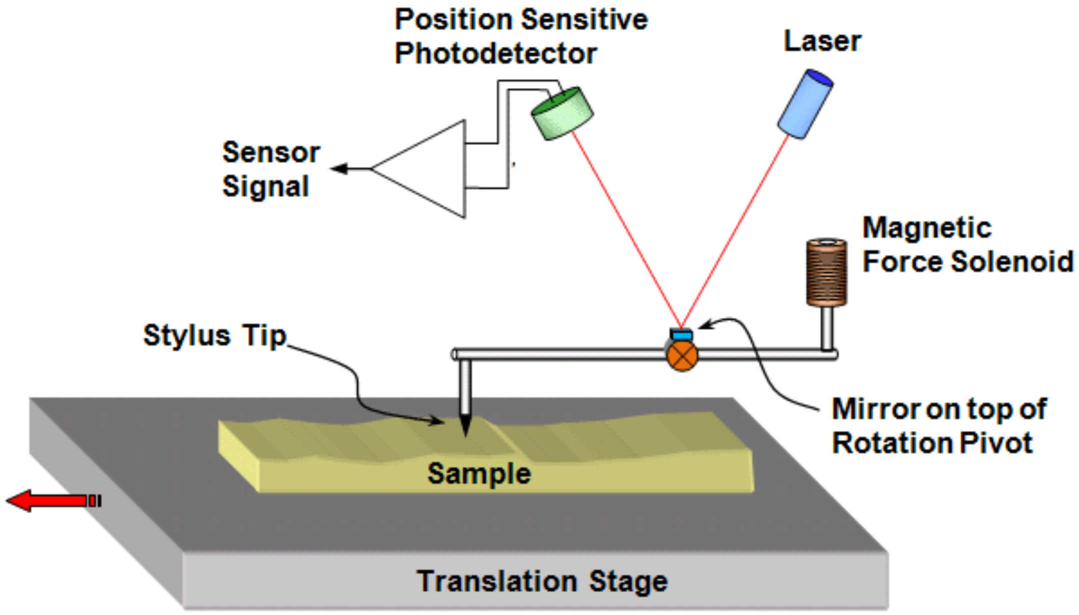
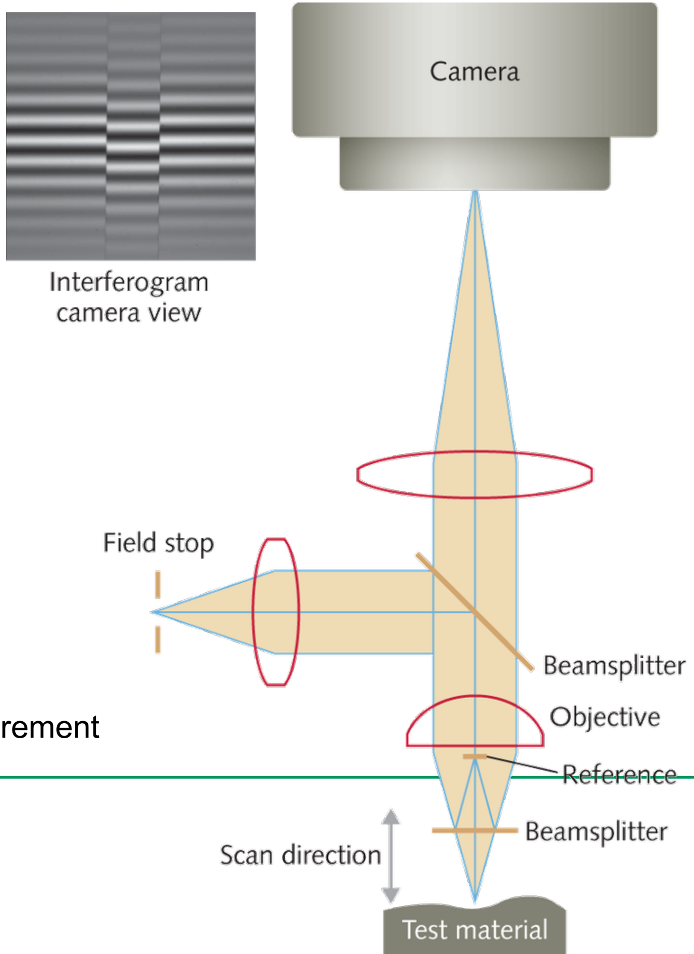


Figure 1 Basic elements of a stylus profilometer.

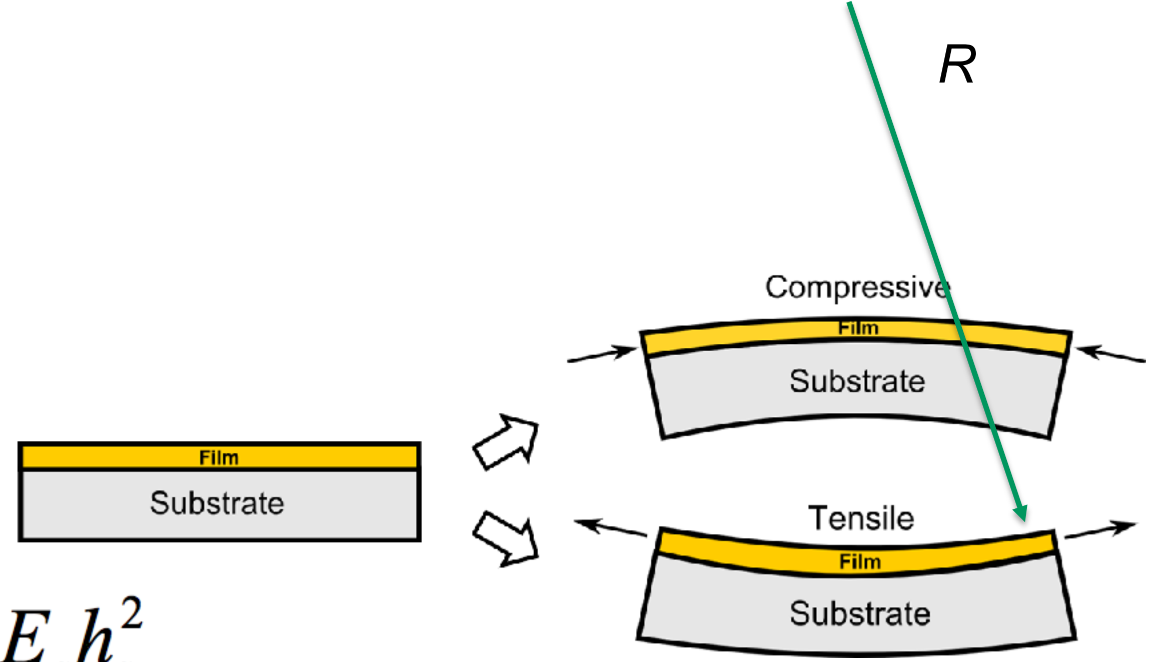
https://australiasurfacemetrologylab.org/new-page

Optical non-contact profilometry



https://www.laserfocusworld.com/test-measurement

Residual stress of thin films



$$\sigma_f = \frac{E_s h_s^2}{6h_f(1-\upsilon_s)R}$$