Vékonyrétegek előállítása és alkalmazásai

2010. szeptember 6.

Dr. Geretovszky Zsolt

Követelmények

Az előadások látogatása *ajánlott*, a gyakorlatoké ***kötelező***.

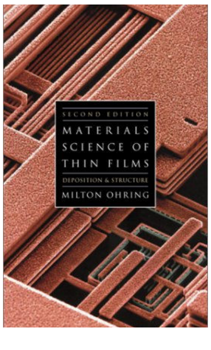
A kurzus segédanyagai a *http://opt.physx.u-szeged.hu/indexh.html* internet-címen az Oktatás/Kurzusok link alatt lesznek elérhetőek.

A *gyakorlati jegy* házifeladat megoldások és 1 db zárthelyi dolgozat alapján kerül megállapításra. A Zh javasolt időpontja: 2010. novermber 29.

A *kollokvium érdemjegye* a következő részteljesítések alapján alakul ki:

1) 10 perces kiselőadás (előre kiadott témában a félév 13. hetének óráján, 2010. november 30.) 30%
2) Írásbeli vizsgadolgozat a vizsgaidőszak elején egyeztetett időpontban:
    2a) elemző kérdések 40%
    2b) tételszerű kérdés 30%

Igény esetén szóbeli vizsgával a 2b) rész javítható.



Forrás:

döntő mértékben Milton Ohring: *Materials Science of Thin Films, Deposition and Structure*, Academic Press 2002, 2nd ed.

Formation of thin films

Deposition (leválasztás)

Material is deposited on the surface of the substrate.

see next slides

Transformation

The topmost part/layer of the substrate is transformed (chemically or structurally).

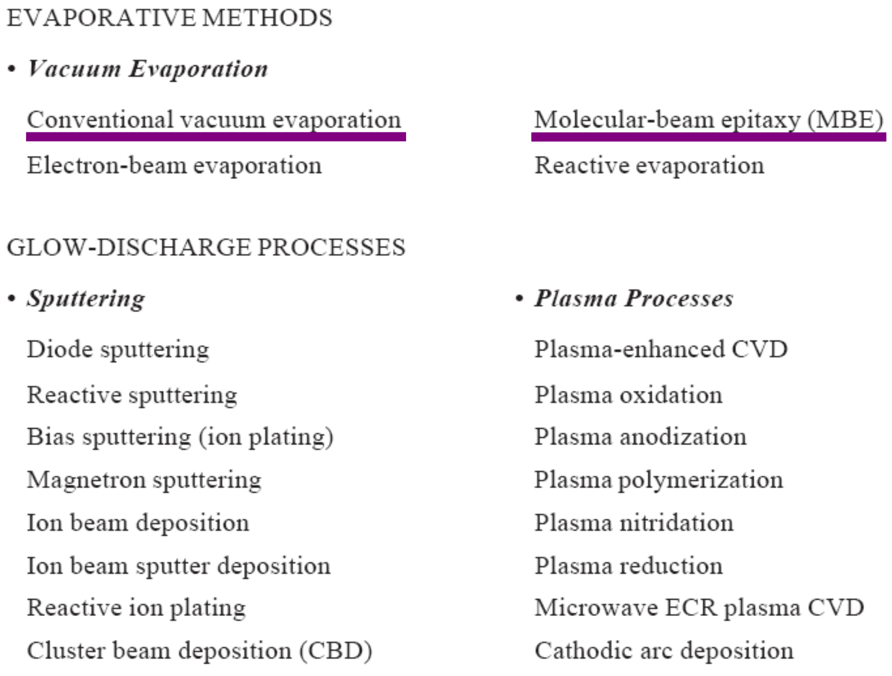
e.g. thermal oxidation, nitridation, silicide formation, ion implantation

Thin films:

are having thickness between few nanometers and about ten micrometer.

beyond this range the layers are called *ultra thin* or ***thick***

Classification



EVAPORATIVE METHODS

- ***Vacuum Evaporation***

Conventional vacuum evaporation

Electron-beam evaporation

Molecular-beam epitaxy (MBE)

Reactive evaporation

GLOW-DISCHARGE PROCESSES

- ***Sputtering***

Diode sputtering

Reactive sputtering

Bias sputtering (ion plating)

Magnetron sputtering

Ion beam deposition

Ion beam sputter deposition

Reactive ion plating

Cluster beam deposition (CBD)

- ***Plasma Processes***

Plasma-enhanced CVD

Plasma oxidation

Plasma anodization

Plasma polymerization

Plasma nitridation

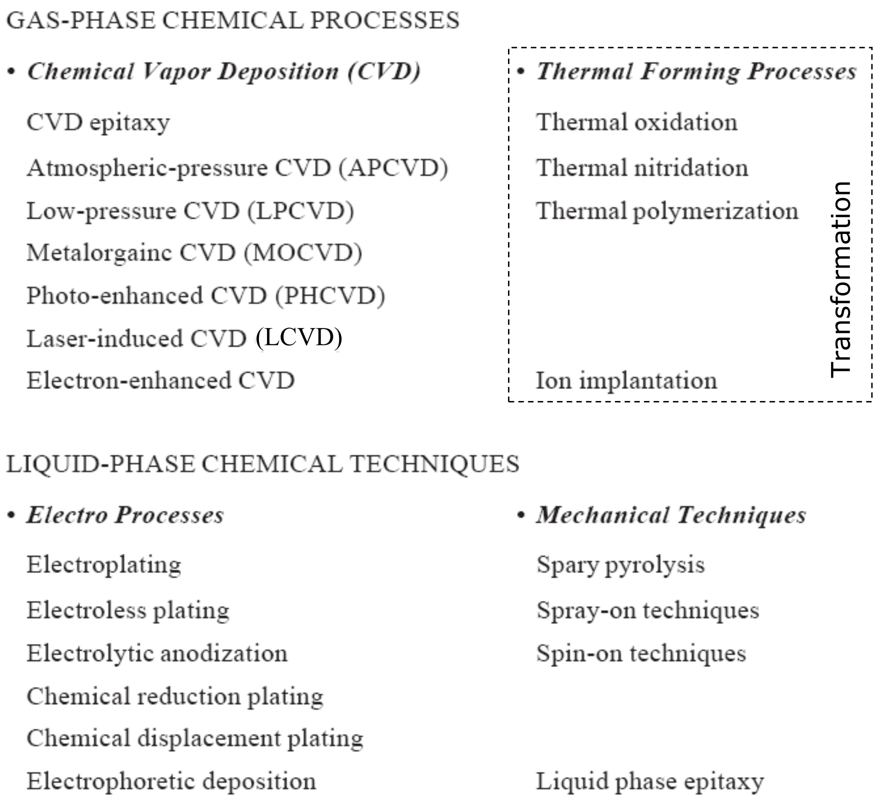
Plasma reduction

Microwave ECR plasma CVD

Cathodic arc deposition

Krishna Seshan: HANDBOOK OF THIN-FILM DEPOSITION PROCESSES AND TECHNIQUES
Principles, Methods, Equipment and Applications, 2nd ed., 2002 by Noyes Publications

… cont.



GAS-PHASE CHEMICAL PROCESSES

- ***Chemical Vapor Deposition (CVD)***

  CVD epitaxy
  Atmospheric-pressure CVD (APCVD)
  Low-pressure CVD (LPCVD)
  Metalorgainc CVD (MOCVD)
  Photo-enhanced CVD (PHCVD)
  Laser-induced CVD (LCVD)
  Electron-enhanced CVD

- ***Thermal Forming Processes***

  Thermal oxidation
  Thermal nitridation
  Thermal polymerization
  Ion implantation

Transformation

LIQUID-PHASE CHEMICAL TECHNIQUES

- ***Electro Processes***

  Electroplating
  Electroless plating
  Electrolytic anodization
  Chemical reduction plating
  Chemical displacement plating
  Electrophoretic deposition

- ***Mechanical Techniques***

  Spary pyrolysis
  Spray-on techniques
  Spin-on techniques
  Liquid phase epitaxy

Further techniques

ALD, Atomic Layer Deposition
LB, Langmuir-Blodgett film
etc.

Application areas

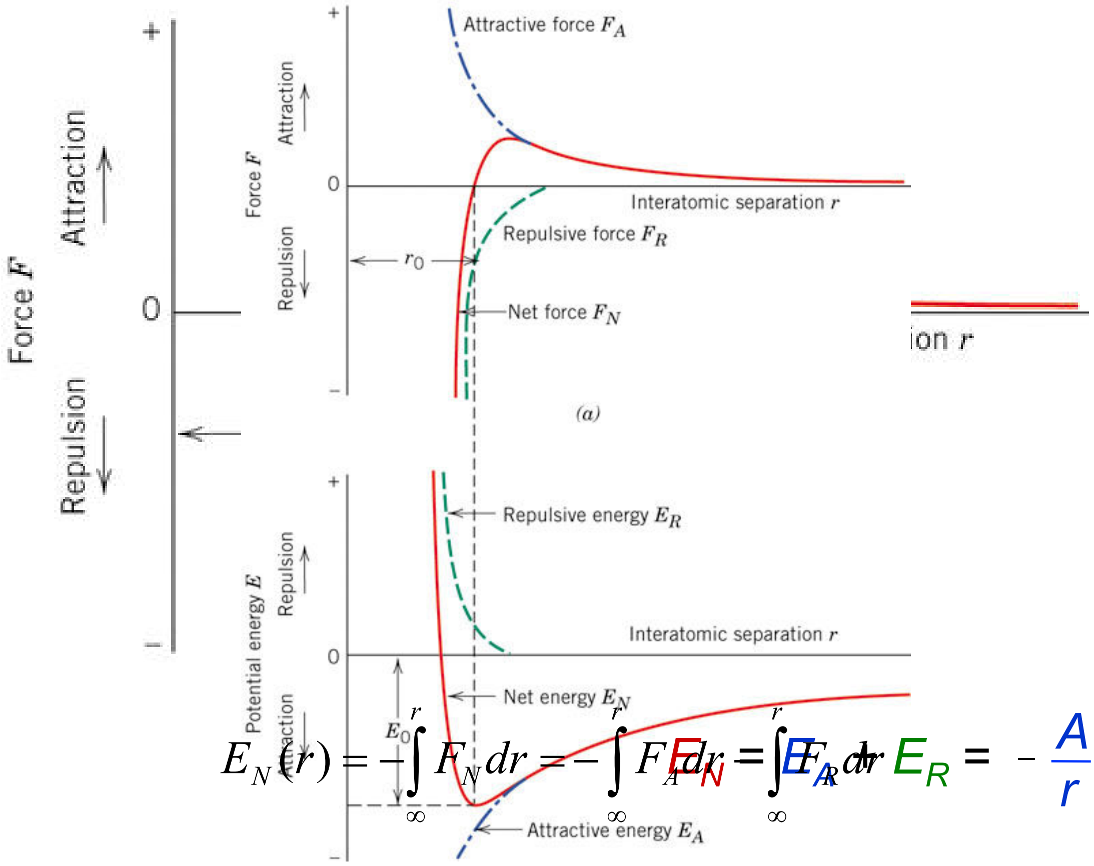
Solid-state electronics (ICs, VLSI, etc.)
Electronic displays
Optical coatings
Data storage (magnetic, optical)
Antistatic coatings
Hard surface coatings

Background in materials science

- ✓ *Bonds and bands* C2
  - Bonding in solids
  - The four classes of solids (metallic, ionic, covalent, van der Waals)
  - Energy band diagrams
- *Structure* C3-4, O1.1-1.3
  - Crystalline structure
  - Amorphous solids
  - Defects (vacancies, dislocations, grain boundaries)
- *Thermodynamics* O1.5, C9
  - Gibbs free energy, chemical reactions
  - ✓ Ellingham diagram
  - Phase diagrams
- *Kinetics*
  - ✓ Macroscopic transport
  - Diffusional transport (atomic movements) O1.6, C5
- ✓ *Nucleation* O1.7, C10.1-10.5

C = Callister: Materials science and engineering: an introduction, 7th ed.
O = Ohring: Materials science of thin films, 2nd ed.

1 atom – 2 atoms ...

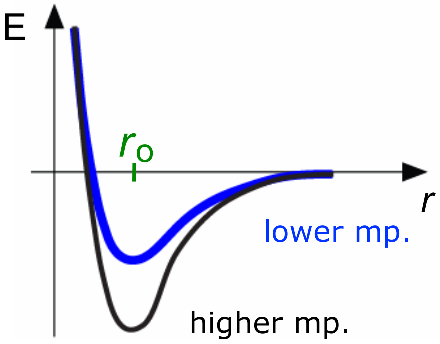


$$E_N(r) = -\int_\infty^r F_N\,dr = -\int_\infty^r F_A\,dr + \int_\infty^r F_R\,dr$$

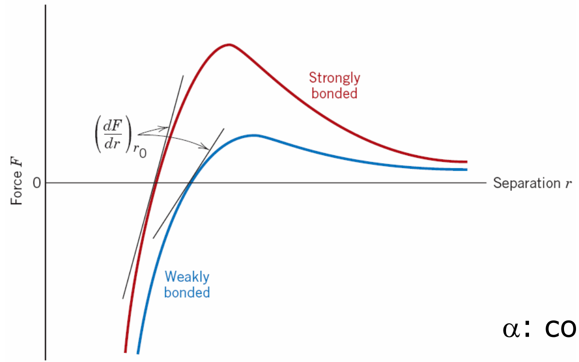
$$E_N = E_A + E_R = -\frac{A}{r} - \frac{B}{r^n}$$

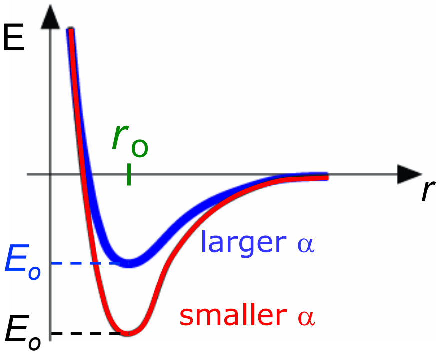
The type of bonding, bonding energy and the shape of the potential curve determines several physical properties.

- melting point:



- thermal expansion:

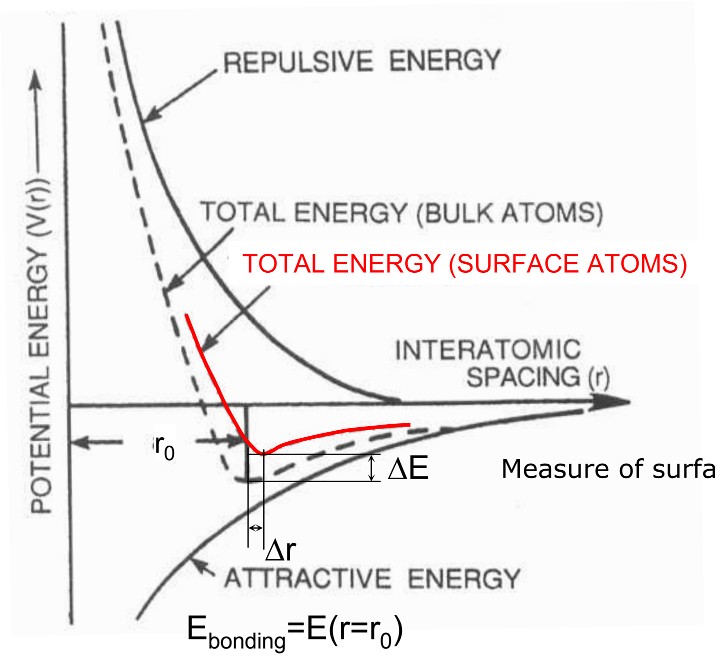




α: coefficient of thermal expansion

/The asymmetry in E(r) is a prerequisite of thermal expansion!/

Thin film *contra* bulk

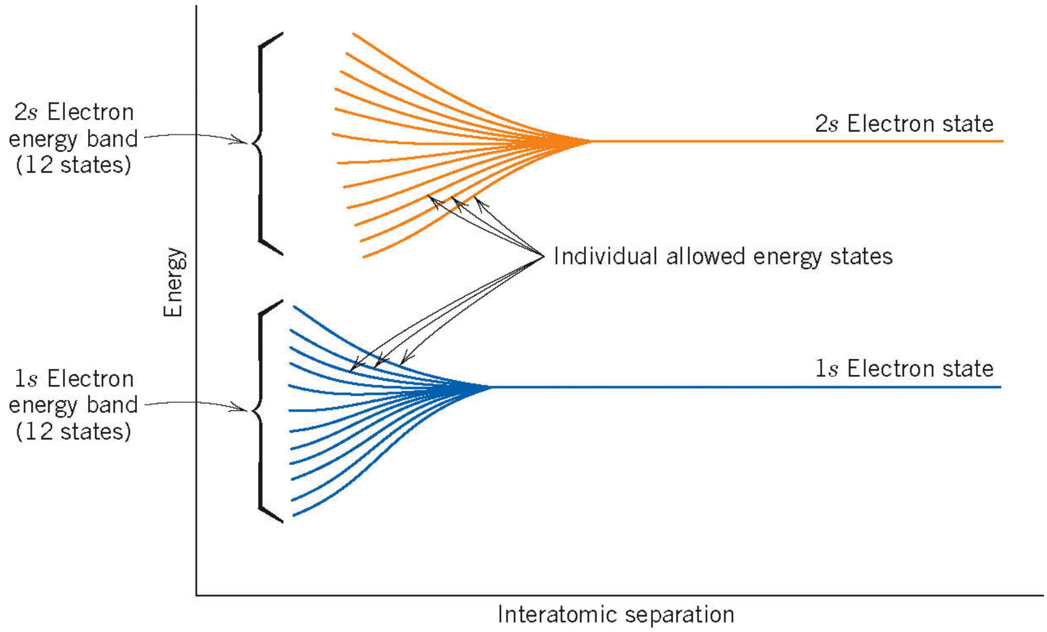


Measure of surface energy!

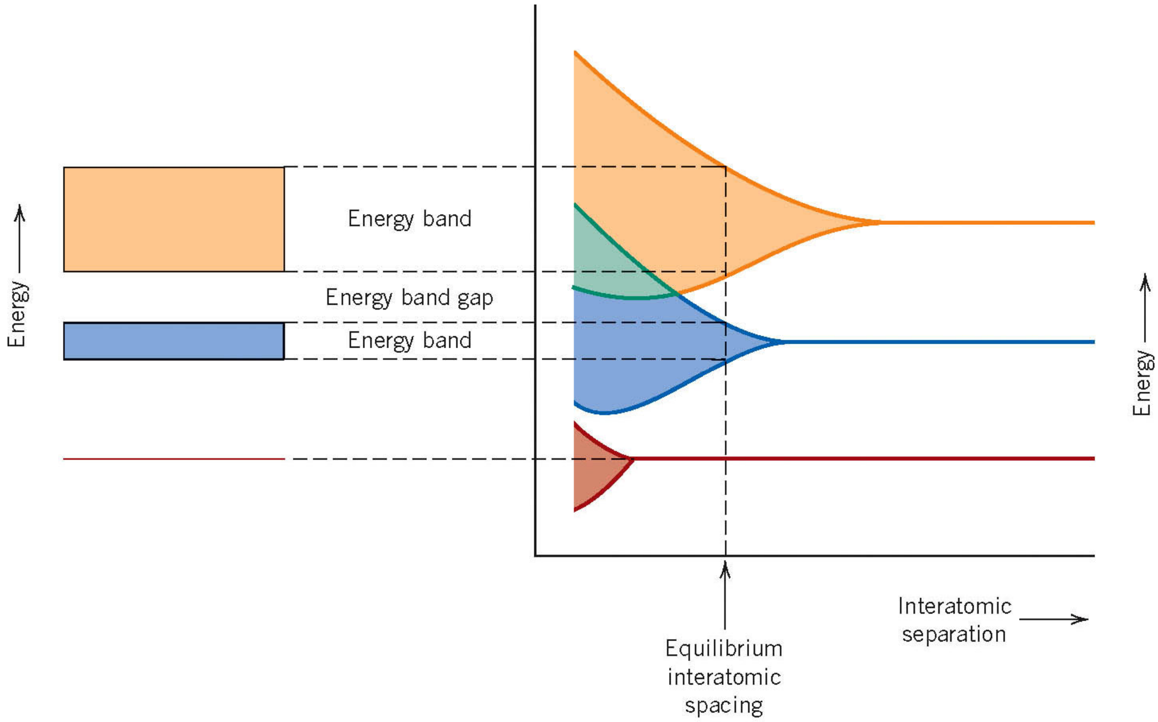
The concept is important in thin film adhesion.

… many atoms

The energy release is accompanied by the splitting of energy levels
(← Pauli exclusion principle).



From levels to bands



Mind-boggling 10^{23} levels in one mol of material!

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Four classes of solids

Despite many similarities, there are numerous distinctions between the four types of solid-state bonding and the properties they induce.

Metallic bond: **METALS**

delocalised electrons readily respond to applied electric field, thermal gradient and incident light (→ high thermal and electrical conductivity (resistivity $\approx 10^{-5}$-10^{-6} $\Omega\cdot$cm) and high optical reflectivity)

The temperature coefficient of resistivity is positive + conductivity of pure metals is always reduced with low levels of impurity (alloying).

The electric behavior of metals differs only slightly in bulk and thin film forms!

as opposed to ionic and covalently bonded materials

e.g. Au, Al, Cu, Cr, W …

Ionic bond: **INSULATORS**

Strong electrostatic bonds → high binding energy and melting point electron transfer → cations and anions → in solid state poor conductors of electricity (resistivity $\approx 10^{6}$-10^{15} $\Omega\cdot$cm)

e.g. SiO_2, MgF_2, ZnS, $YBa_2Cu_3O_7$, In_2O_3-SnO_2

Four classes of solids, cont.

Covalent bond: **SEMICONDUCTORS (, INSULATORS)**

Strong directional bonds → high melting point, hard materials their electrical conductivity is smaller than that of metals (resistivity $\approx 10^{-3}$-10^{6} $\Omega\cdot$cm)

The temperature coefficient of resistivity is negative + conductivity is significantly influenced via doping (i.e. impurity).

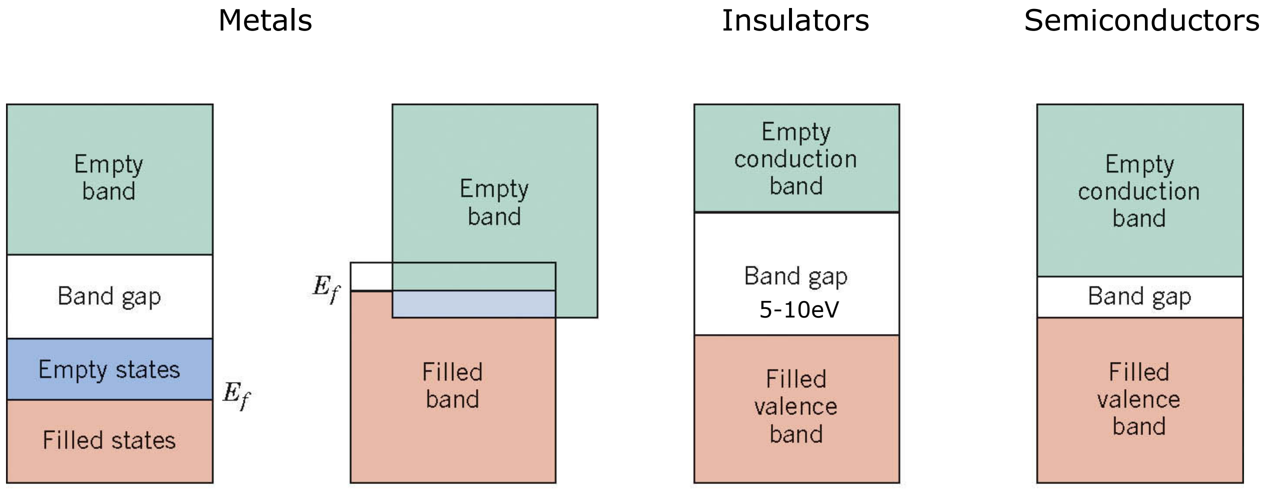
e.g. Si, Ge, GaAs, InP, SiC, TiC, TiN, etc.

van der Waals: **INSULATORS**

Weak molecular forces → low melting point, soft materials

e.g. polymer layers, photoresists

Energy band diagrams at 0 K



Metals

Empty band

Band gap

Empty states

Filled states

E_f

Empty band

E_f

Filled band

Insulators

Empty conduction band

Band gap 5-10eV

Filled valence band

Semiconductors

Empty conduction band

Band gap

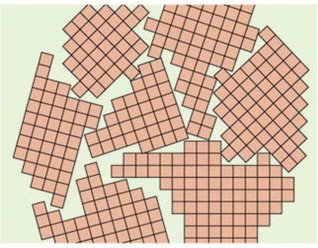
Filled valence band

Cu: unpaired 4s valance electron
Cu: [Ar]$3d^{10}4s^1$

Mg: filled 3s orbit
Overlapping 3s, 3p states.
Mg: [Ne]$3s^2$

Grain boundaries

Grain boundaries are area/surface defects that constitute the interface between two single-crystal grains of different crystallographic orientation.



Like atoms on surfaces, *atoms on grain boundaries are more energetic* than those within the grain. -> processes (like solid state diffusion, phase transformation, precipitation, corrosion, impurity segregation) are favoured/accelerated on grain boundaries

Typical *grain sizes in films* are 0.01-1.0 μm,

i.e. at least a factor of 100 smaller than grain sizes in bulk materials.
(Assuming a 0.1μm diameter spherical grain it means that every 100th atom resides on the grain boundary.)
-> thin films tend to be more reactive than their bulk counterparts.

How the surface-to-volume ratio depends on the grain size and the size of the atom?

Controlling grain morphology, orientation and size are quite important in thin-film technology.

e.g. microelectronic applications aim to eliminate grain boundaries (epitaxial growth)

Chemical thermodynamics

$$aA + bB \rightarrow cC$$

The free energy change of this reaction:

$$\Delta G = cG_C - aG_A - bG_B$$

Since the free energy of an individual reactant or product species is:

$$G_i = G_i^0 + RT\ln a_i$$

G_i^0: free energy of the species in its reference state (1atm, 25°C)
a_i: activity/thermodynamic concentration

$$\Delta G = \Delta G^0 + RT\ln\frac{a_C^c}{a_A^a a_B^b} \qquad \Delta G^0 = cG_C^0 - aG_A^0 - bG_B^0$$

If the system is in equilibrium

$$0 = \Delta G^0 + RT\ln\frac{a_{C(eq)}^c}{a_{A(eq)}^a a_{B(eq)}^b}$$

or

$$-\Delta G^0 = RT\ln K$$

The combination of $\Delta G = \Delta G^0 + RT\ln\frac{a_C^c}{a_A^a a_B^b}$ and $0 = \Delta G^0 + RT\ln\frac{a_{C(eq)}^c}{a_{A(eq)}^a a_{B(eq)}^b}$

$$\Delta G = -RT\ln\frac{a_{C(eq)}^c}{a_{A(eq)}^a a_{B(eq)}^b} + RT\ln\frac{a_C^c}{a_A^a a_B^b} = RT\ln\frac{a_C^c / a_{C(eq)}^c}{a_A^a / a_{A(eq)}^a a_B^b / a_{B(eq)}^b} =$$
$$= RT\ln\frac{\left(a_C / a_{C(eq)}\right)^c}{\left(a_A / a_{A(eq)}\right)^a \left(a_B / a_{B(eq)}\right)^b}$$

It is said that if
$$\begin{cases} \dfrac{a_C}{a_{C(eq)}} < 1 & \\ \dfrac{a_C}{a_{C(eq)}} = 1 & \text{the } i^{\text{th}} \text{ component is} \\ \dfrac{a_C}{a_{C(eq)}} > 1 & \end{cases}$$

subsaturated (unsaturated)

saturated

supersaturated

For many practical cases the thermodynamic activity of the species differs only little from unity, i.e.

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c}{a_A^a a_B^b} \approx \Delta G^0$$

so the standard free energy of the reaction tells a lot about the process.

The Ellingham diagram plots the standard free energy of a reaction (oxidation, sulfidation, carbidation, nitridation) as a function of temperature. Originally, values were plotted for the oxidation and sulfidation reaction of different metals, which reactions generally involve the reaction of a gaseous phase (the oxidising gas) with almost pure condensed phases (metal and oxide).

The diagram allows to calculate

- the standard enthalpy and entropy of the reaction (intercept and inverse of the slope, respectively) (remember: $\Delta G = \Delta H - T\Delta S$)
- the equilibrium composition of the system and its variation with temperature
- the feasibility of a reaction between a metal and the oxide of another metal can be estimated

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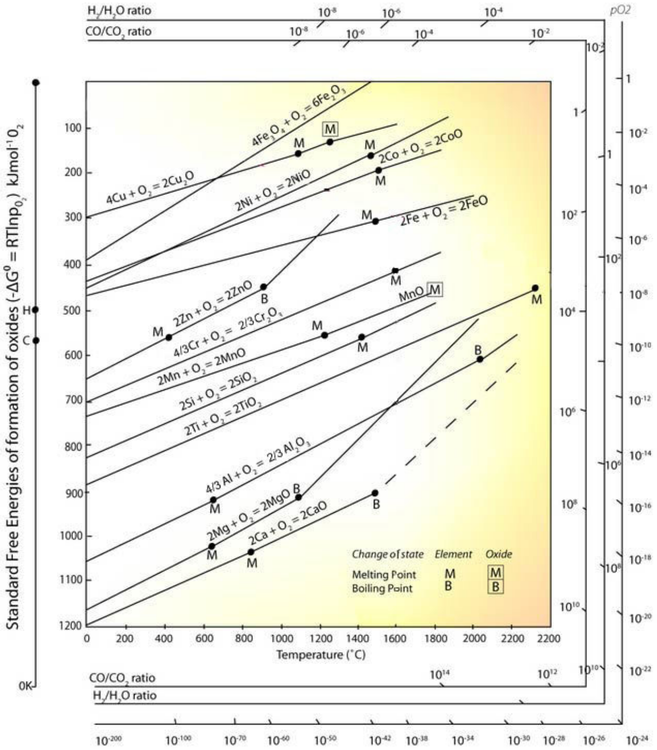
Thermodynamics

Ellingham diagram



Will be treated during the practical.

Kinetics

In solids, mass transport is accomplished by diffusion (≡ the migration of atomic or molecular species within a given matrix under the influence of a concentration gradient)

Fick's first law:

$$J = -D\frac{dC}{dx}$$

mass flux

concentration gradient

diffusion coefficient
$[D]=cm^2/s$

Fick's second law:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

$$D = D_0 e^{-\frac{E_D}{kT}}$$

E_D: activation energy for diffusion

The atomic movement should be read in Ohring's book. O1.6

The early stages of film growth

Nucleation:
sufficient number of vapour atoms/molecules condense and establish a permanent residence on the substrate

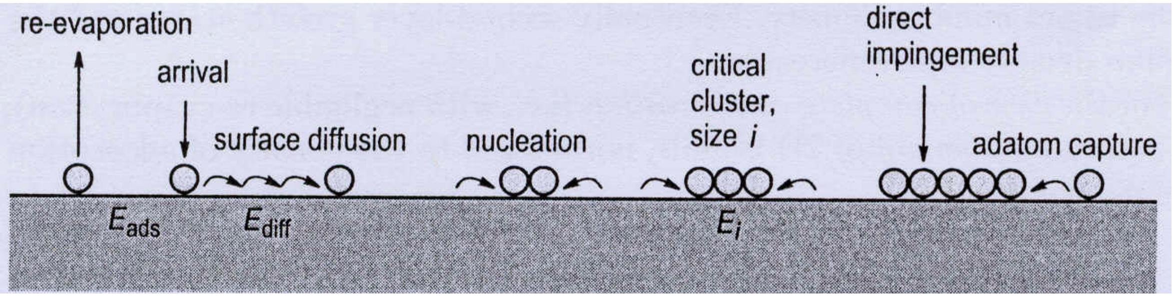
Nucleus growth:
prior nuclei incorporate impinging atoms and subcritical clusters and grow in size while the island density rapidly saturates

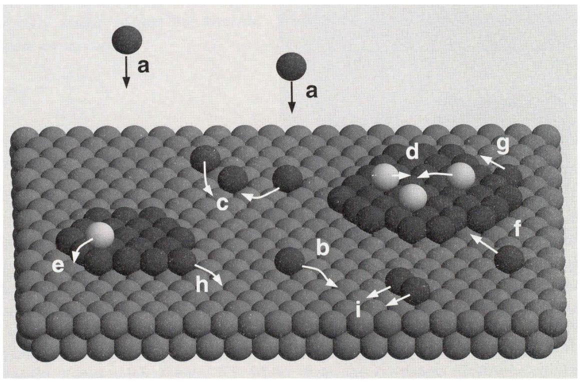
Coalescence:
this stage involves merging of islands by the coalescence phenomenon which decreases the island density, resulting in local denuding of the substrate where further nucleation can then occur; crystallographic facets and orientations are frequently preserved; continued deposition results in the filling of channels and finally the voids in between the islands and leads to a so called continuous film.

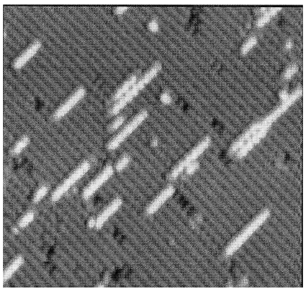
(typically up to few tens of nm thickness)

Atomic Processes in Nucleation & Growth

Adsorption, diffusion, incorporation, nucleation, desorption, coarsening



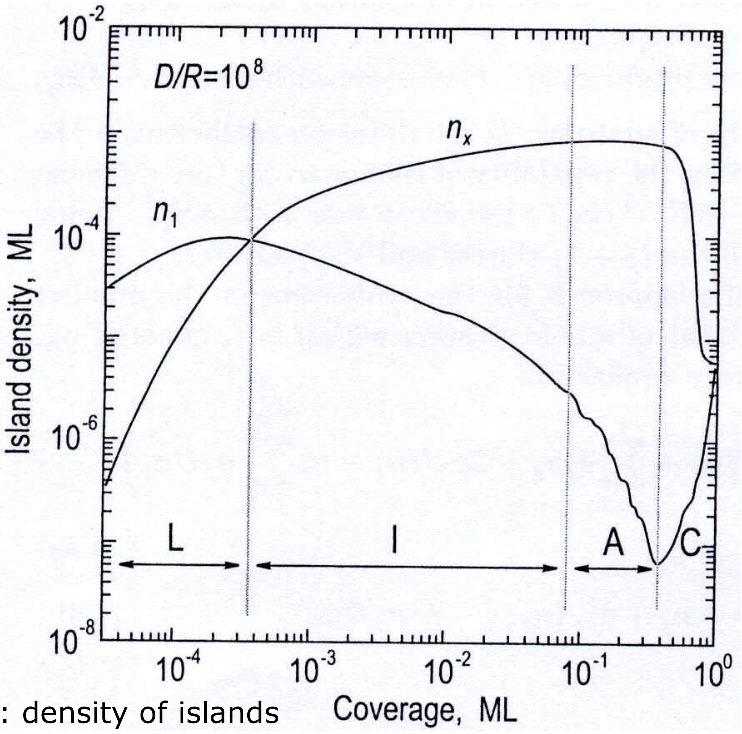




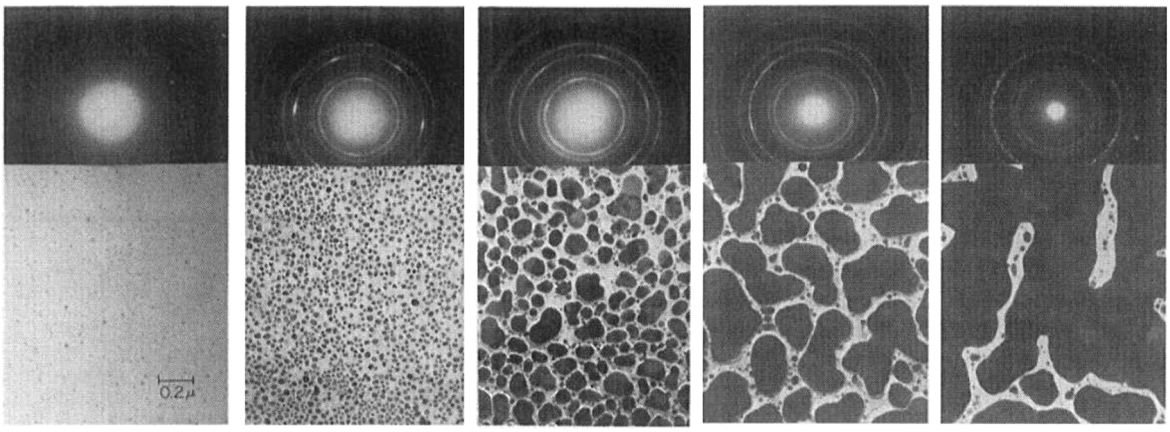
Si islands on Si(001)

Stages of sub-ML nucleation and growth

1. **Low coverage** (L), nucleation dominates
2. **Intermediate coverage** (I), island density approaches saturation
3. **Aggregation** (A), island density saturates
4. **Coalescence** (C), island density decreases



n_x: density of islands
n_1: adatoms



2.5nm 10nm 30nm 70nm 90nm

Figure 7-1 Transmission electron microscope images of nucleation, growth, and coalescence of Ag films on (111) NaCl substrates. Corresponding diffraction patterns are shown. (From Ref. 2, courtesy of R. W. Vook.)