PVD DEPOSITION METHODS AND APPLICATIONS

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Outline

I

- Physical vapor deposition
- Combinatorial PVD techniques
- DCA 2173 Combinatorial PVD machine
- PVD process parameters ... thin film properties
- Thin film growth:

PVD Parameters ⇨ Structure ⇨ Properties

⇨ Structure

⇨ Annealed structure

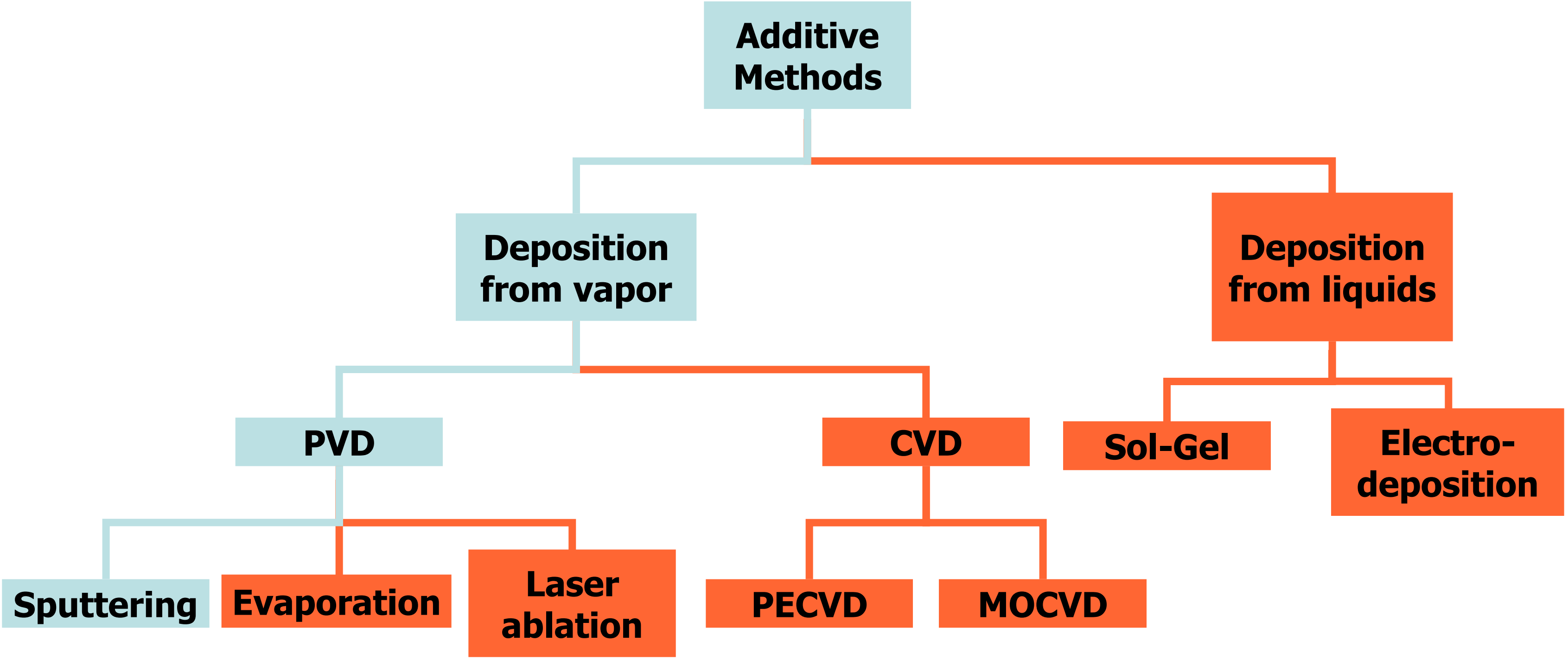
⇨ Properties

II

Pure and mixed films preparation using thermionic vacuum arc method

Thin Film Deposition

(a compilation from literature)



Additive Methods

Deposition from vapor

Deposition from liquids

PVD

CVD

Sol-Gel

Electro-deposition

Sputtering

Evaporation

Laser ablation

PECVD

MOCVD

PVD: Physical Vapor Deposition
IBAD: Ion Beam Assisted Dep.

CVD: Chemical Vapor Deposition
PE: Plasma Enhanced
MO: Metal-Organic

Sputtering (magnetron)

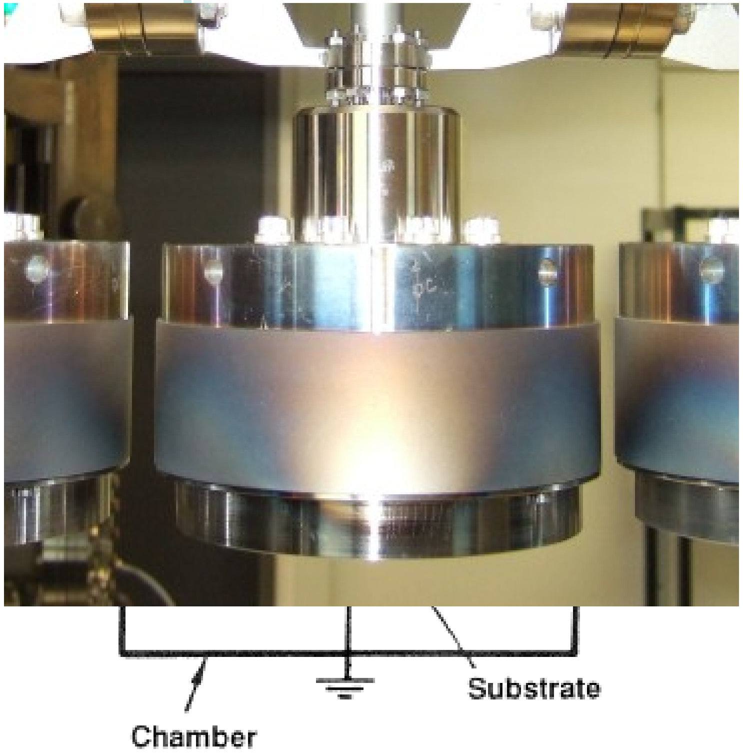
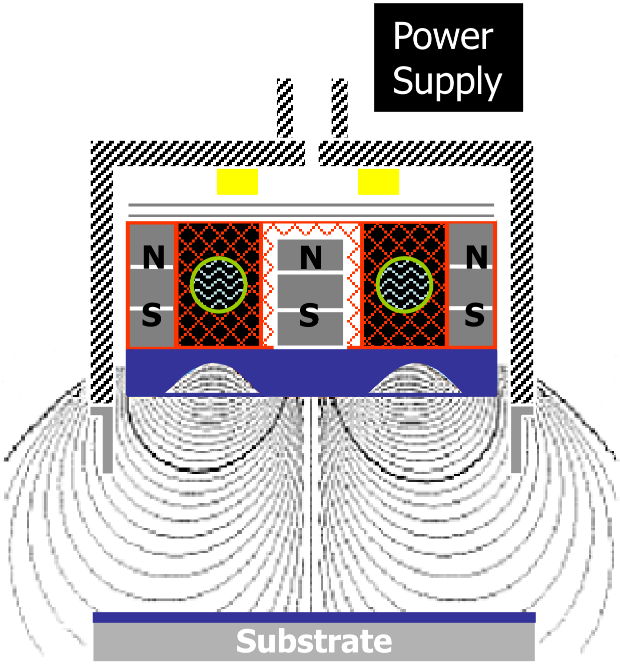


Figure A3.0.1. Schematic of a dc glow discharge sputtering system.

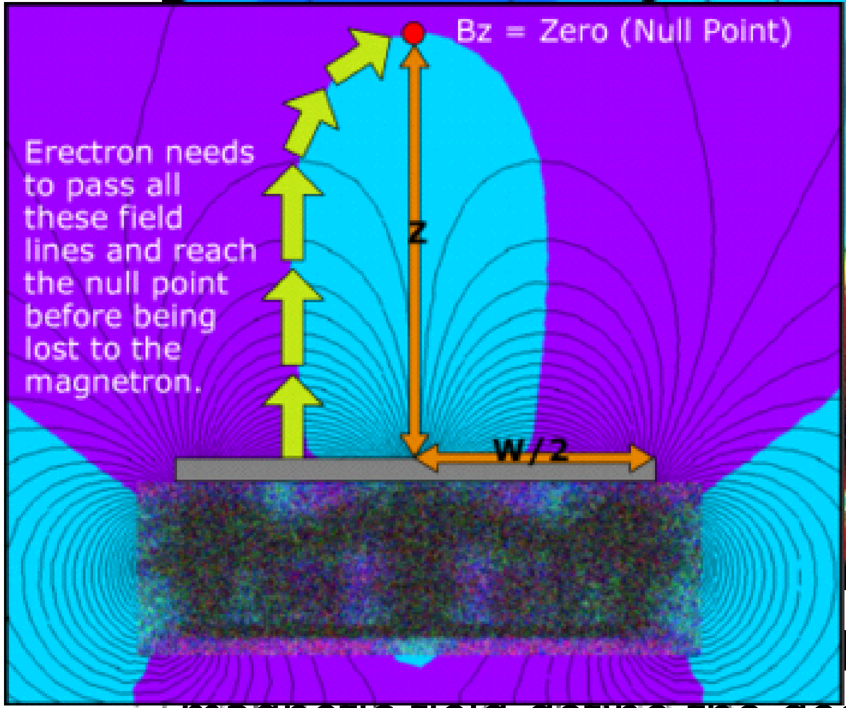


lotion

lotions)

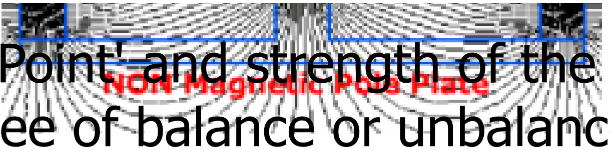
Sputter-down configuration

Magnetron Design



The "ease" of electron release from the magnetic trap is determined mainly by the geometrical position of the null point of the magnetic field.

If Z is large (i.e. ≥W) then the chance of an electron escaping is low and hence the magnetron is well balanced.

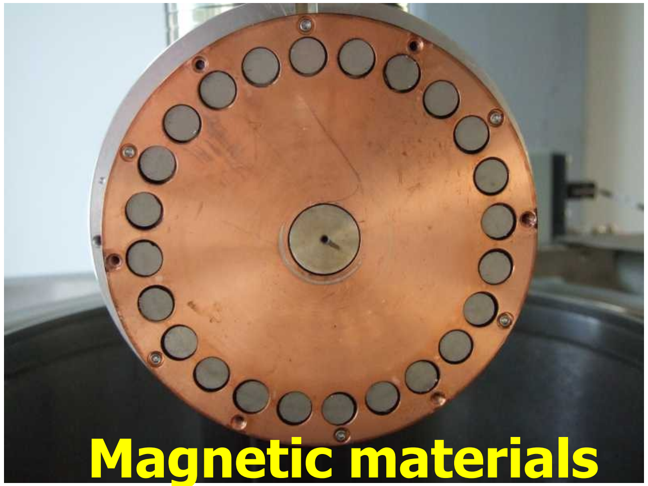


ll Point' and strength of the magnetic field define the degree of balance or unbalance of a magnetic system.

reduced field strength

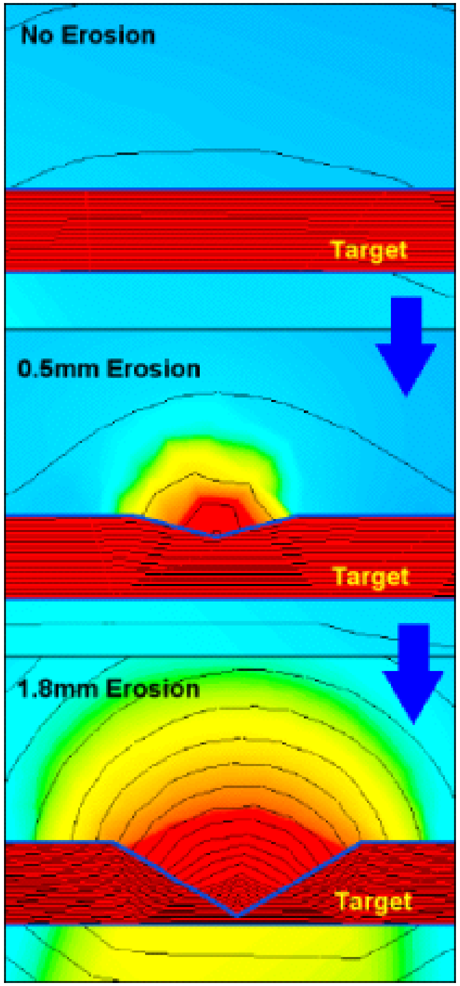
less balanced

Magnetron Sputtering Cathode


Magnetic materials

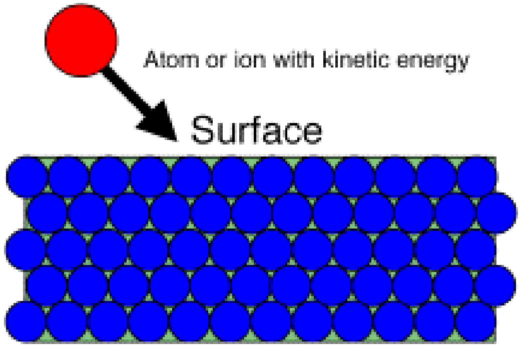

Max. rate (balanced)

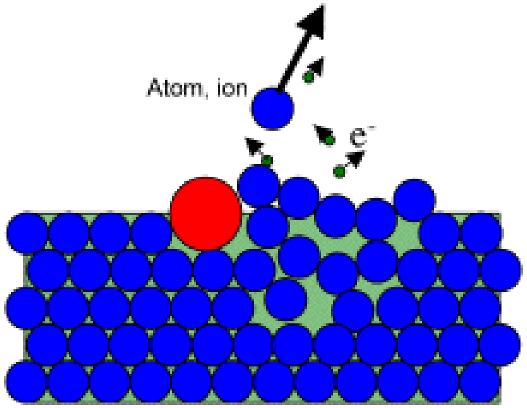
Sputtering of Magnetic Materials



Sputtering process

- momentum transfer process
    - o involves top 10 Å
    - o model as hard sphere collisions for energies < 50 keV



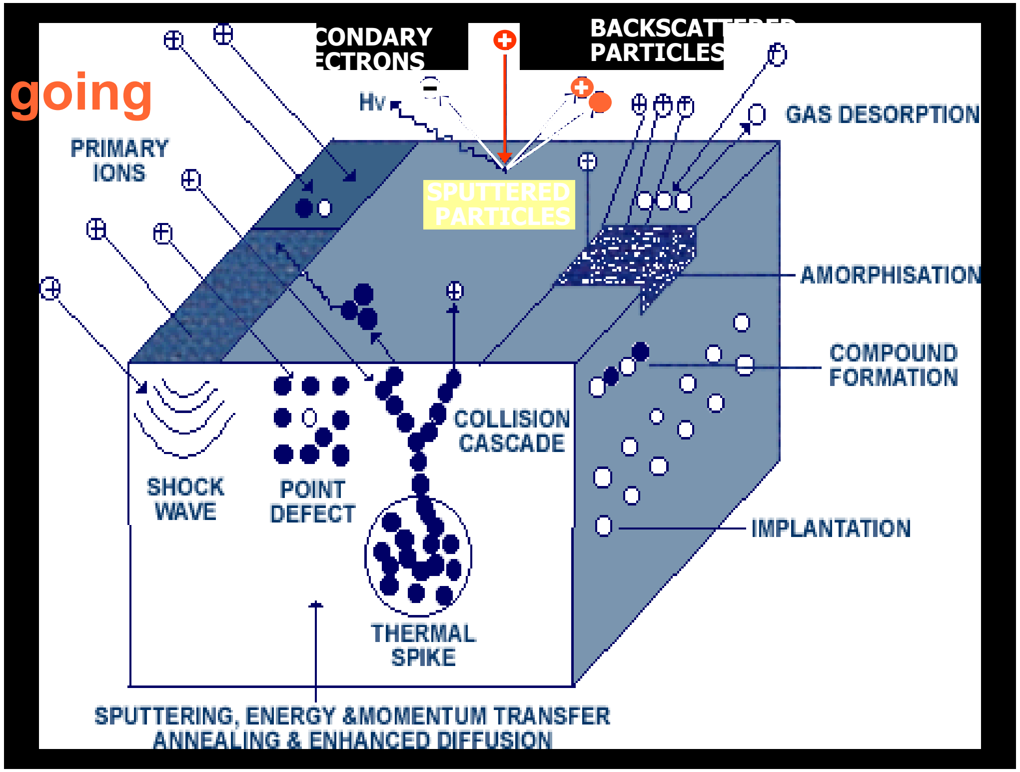


- 95 y goes ir
    - t (RF: avoi n
- 5 is carrie s
    - of 5-100 e
- target atoms eject with a non-uniform distribution
    - o cosine distribution (like a surface source)

Sputter processes (at the target)

- target atoms ejected
- target ions ejected (1 - 2 %)
- electrons emitted
  - helps keep plasma **going**

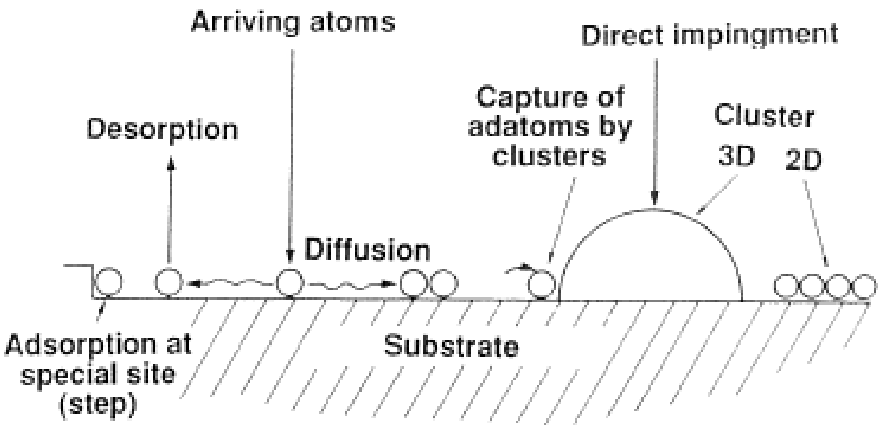
- Ar^+ ions reflected
  as Ar neutrals
- Ar buried in target
- photons emitted



Target – Substrate Transport

- Target atoms pass through Ar gas and plasma environment
  - one Ar^+ ion for every 10,000 Ar neutrals
  - electrons in plasma collide with Ar neutrals to form ions and more electrons
- Target atoms collide with Ar atoms, Ar^+ ions and electrons
  - treat as random walk "diffusion" through gas
  - target atoms lose energy (down to 1-10 eV)
  - chemical reactions may occur in gas
  - not a line of sight process (unless pressure reduced)
  - can coat around corners

Arrival at the substrate



Adding to film:

- impingement (deposition) on surface
  sticking coefficient typically not 1

Removing from film:

- reflection of impinging atoms
- desorption (evaporation, resputtering) from surface

Outline

- Physical vapor deposition
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- DCA 2173 Combinatorial PVD machine
- PVD process parameters
- Thin film growth

Combinatorial technique

- Method based on the creation of sets of materials (“materials libraries”) processed under identical, controlled conditions having regularly varying compositions.

Wang et al., Science, Vol 279, 1712, 1998

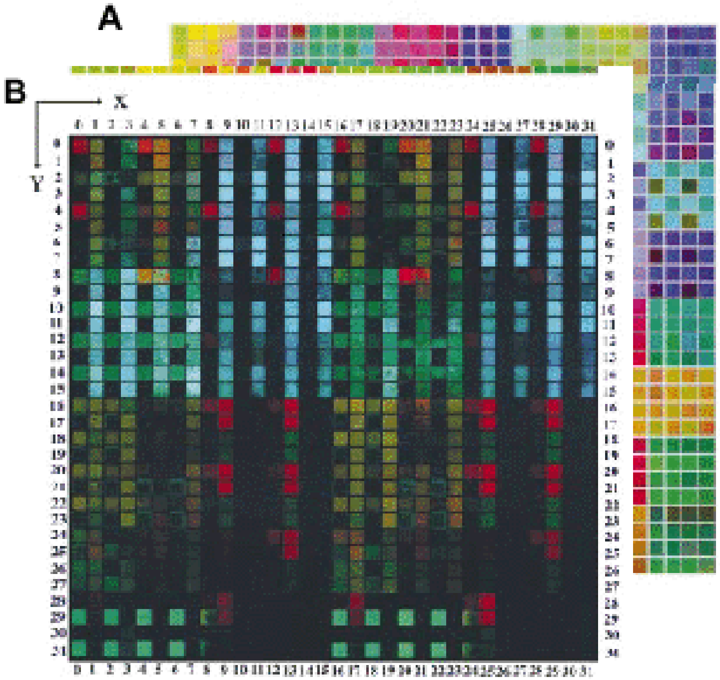
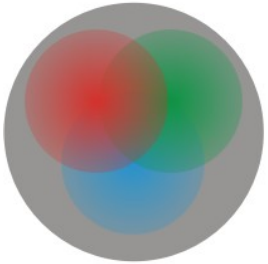
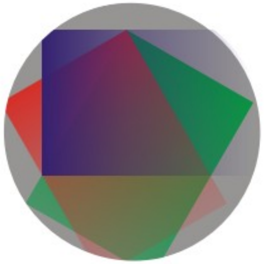


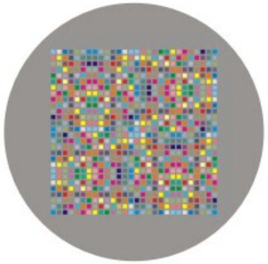
Fig. 2. (**A**) Photograph of the as-deposited quaternary library under ambient light. The diversity of colors in the different sites stems from variations in film thicknesses and the optical indices of refraction. (**B**) Luminescent photograph of the processed quaternary library under irradiation from a multiband emission UV lamp at short wavelength (centered around 254 nm).



Co-deposition



Wedges



In-situ masking

Combinatorial methods

- Precursor deposition using shadow masks
- Controlled thermal diffusion ⇨ stoichiometric compounds

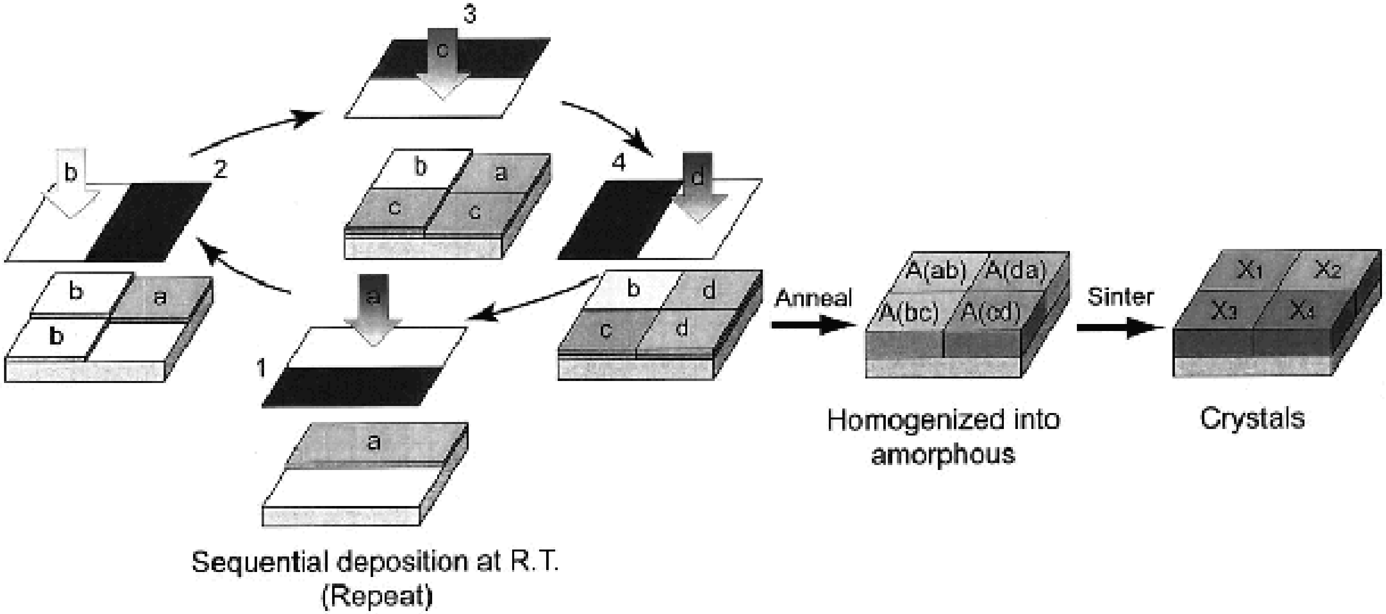
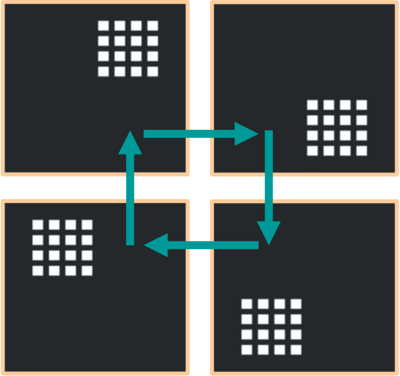


Fig. 2. Combinatorial synthesis of thin film library: precursor method. By increasing the number of masks (and sources), the number of products (pixels) in a library can be increased.

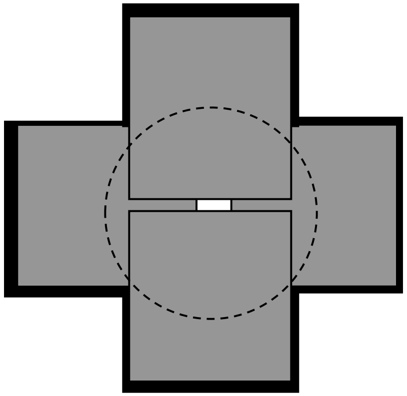
In-situ Masking

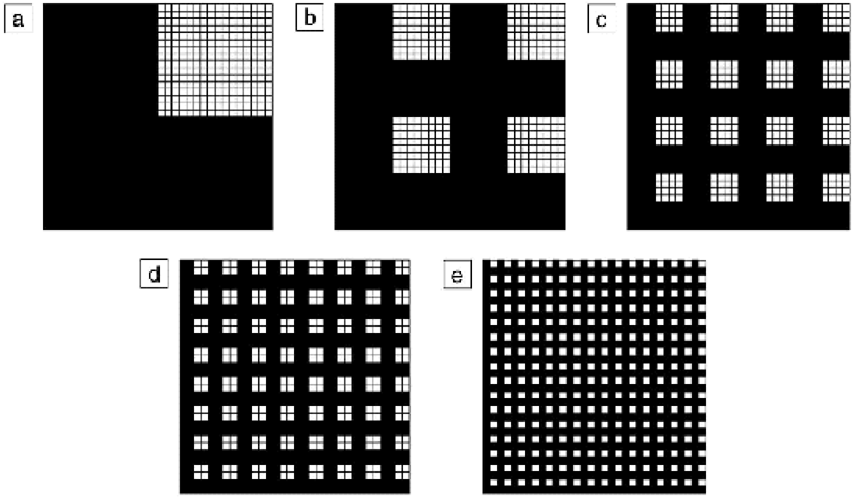
In-situ mask handling:

- mask rotation
- mask removal
- replace / change



4-D shutter movements





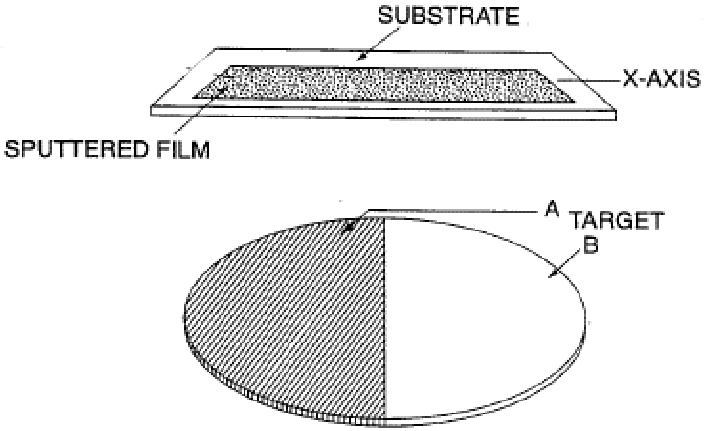
Precursor/Mask Technique

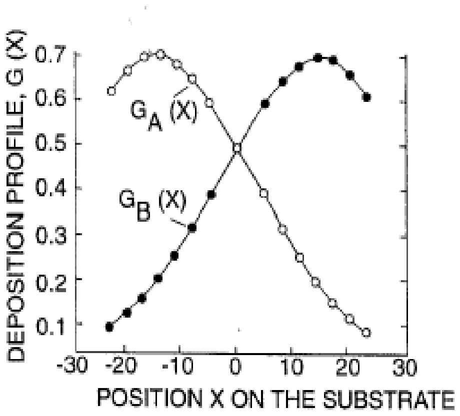
- ✓ Good for studies of dopants
- ✓ Large variety of different materials on a single wafer

- ✗ Method very complex for gradients
- ✗ Complex mask handling
- ✗ Mixing of the elements has to be performed in an additional process step
  - ⇨ adds problems of uniformity and reproducibility

Combinatorial methods

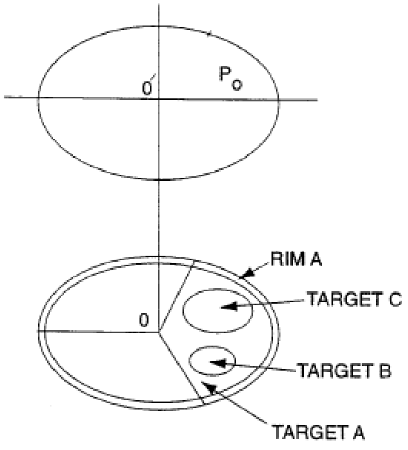
- Composite targets (Hanak, RCA)





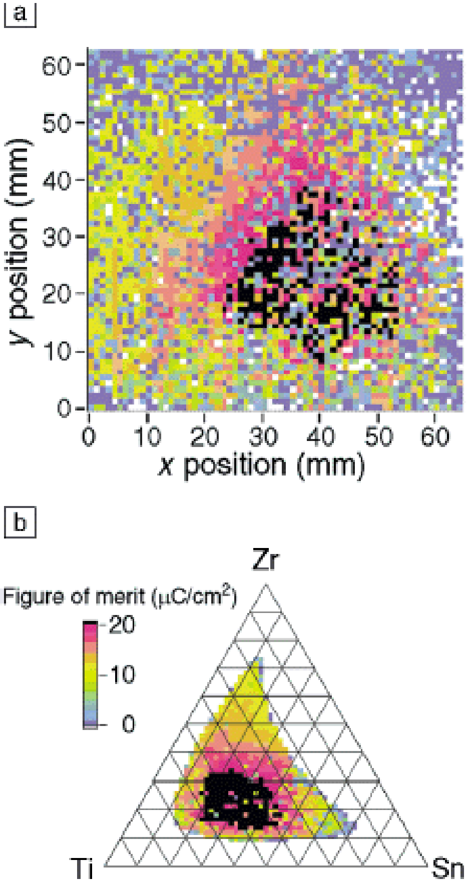
- ✓ Direct mixing
- ✗ Composition variation fixed by target geometry
- ✗ Different sputter rates of different materials

× ⇨ Difficult control of stoichiometry



Combinatorial methods

- Co-deposition



Co-deposition Technique

- ✓ Direct mixing of the elements

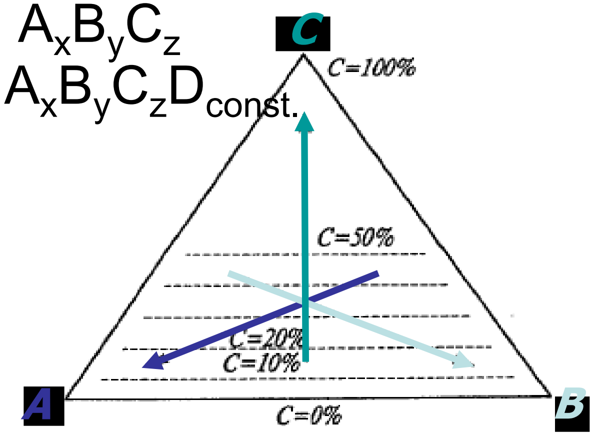
- ✕ Large substrates needed
- ✕ Large-area uniformity required
- ✕ Precision control of stoichiometry is difficult

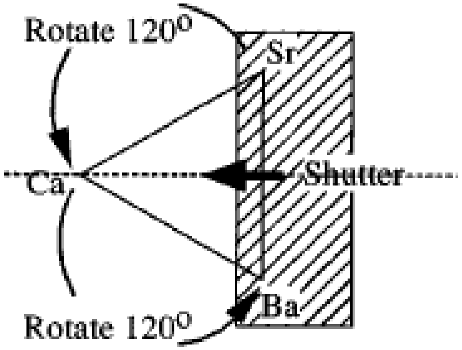
Combinatorial methods

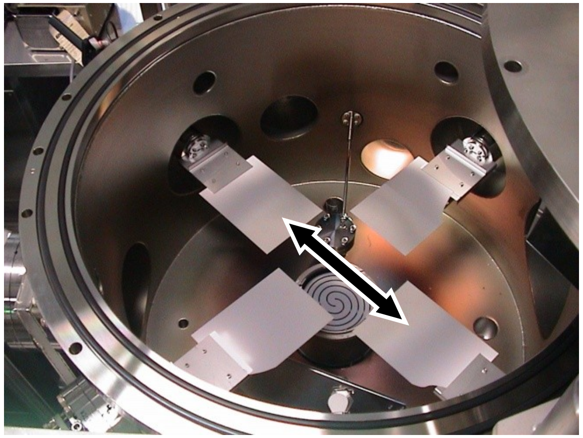
- Layered wedge deposition

$A_xB_yC_z$

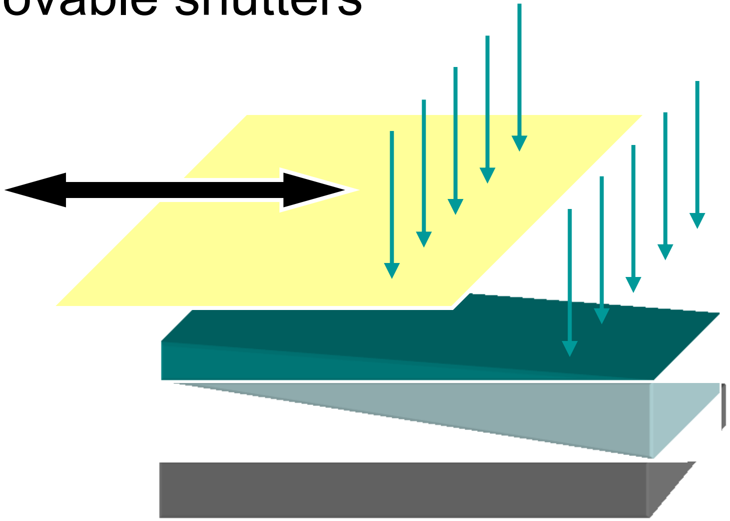
$A_xB_yC_zD_{const.}$







Deposition of wedge-type films with movable shutters



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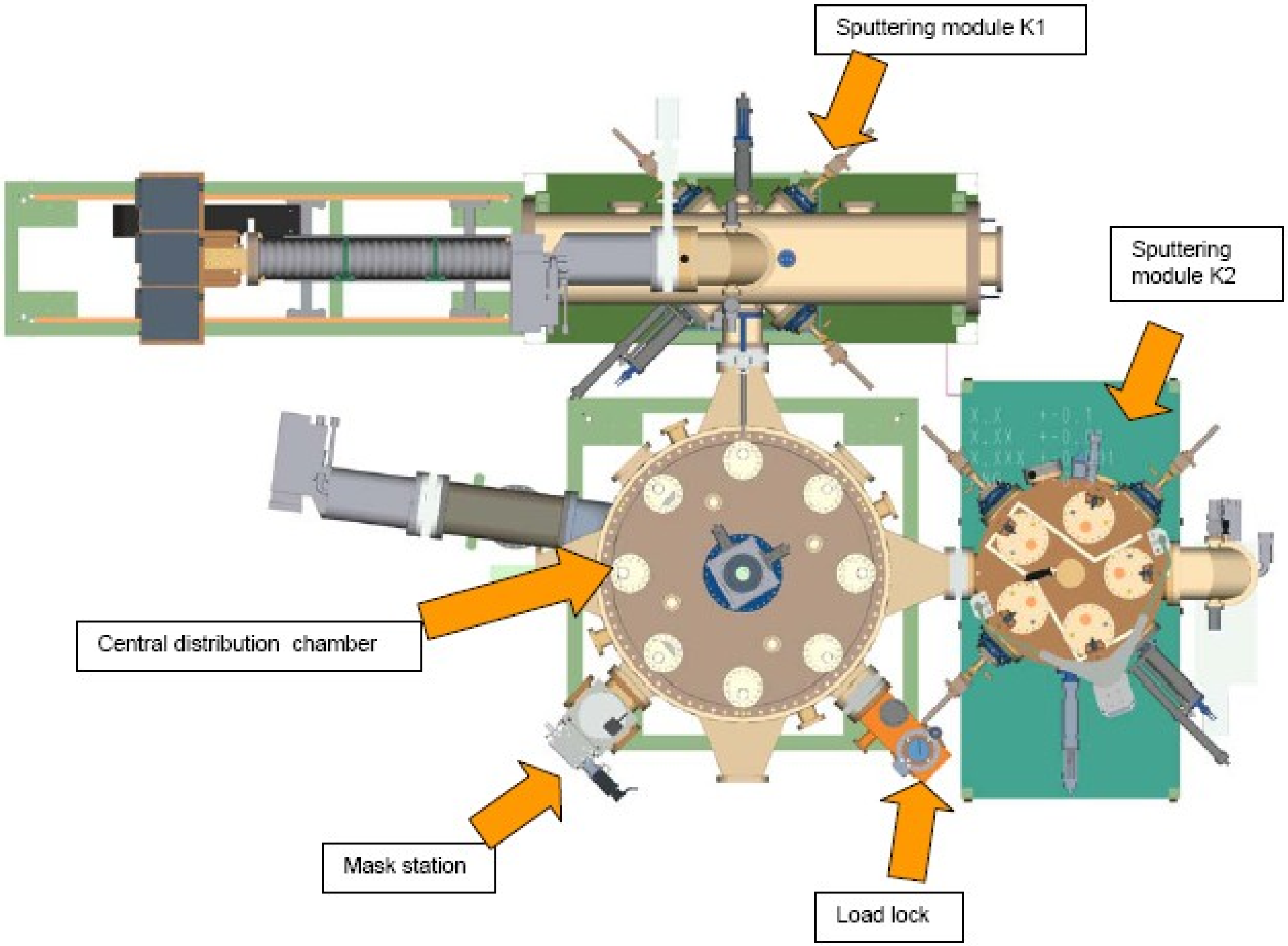
DCA 2173 for Combinatorial PVD



Sputtering module K1

Sputtering module K2

Central distribution chamber

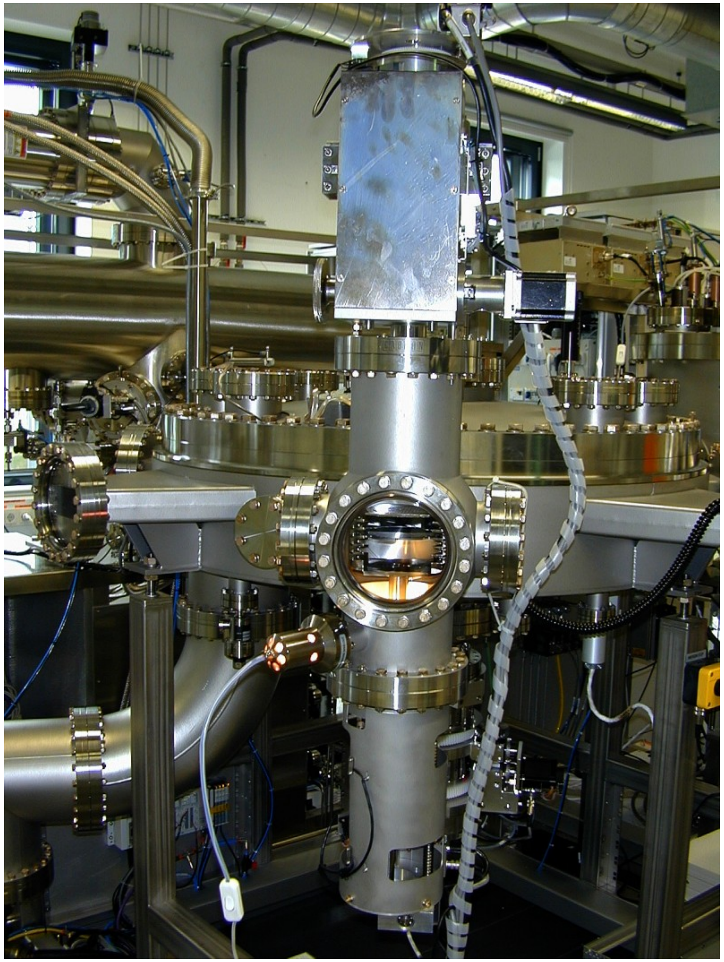
Mask station

Load lock

Loadlock

- keeps the other chambers clean
- designed for 4“ Si wafers
- can also use 4“ diameter carriers
  - must keep small samples from sliding or blowing away!
- sample thickness < 2 cm

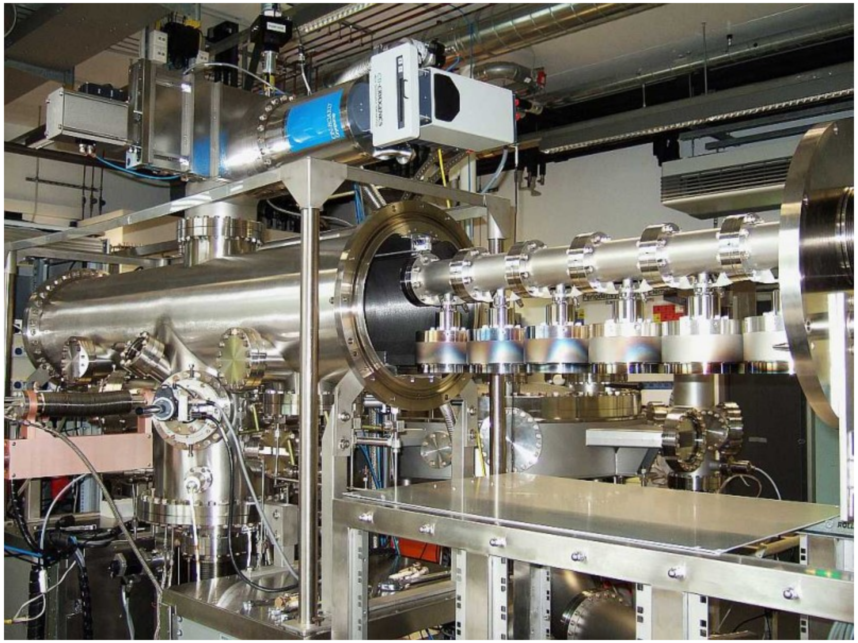
Mask Chamber



- < 2x 10^{-9} mTorr
- 6 storage slots:
  masks or wafers
- Place or remove masks
- Rotation of masks:
  90° increments
- Tolerances very close.
  Use with caution!

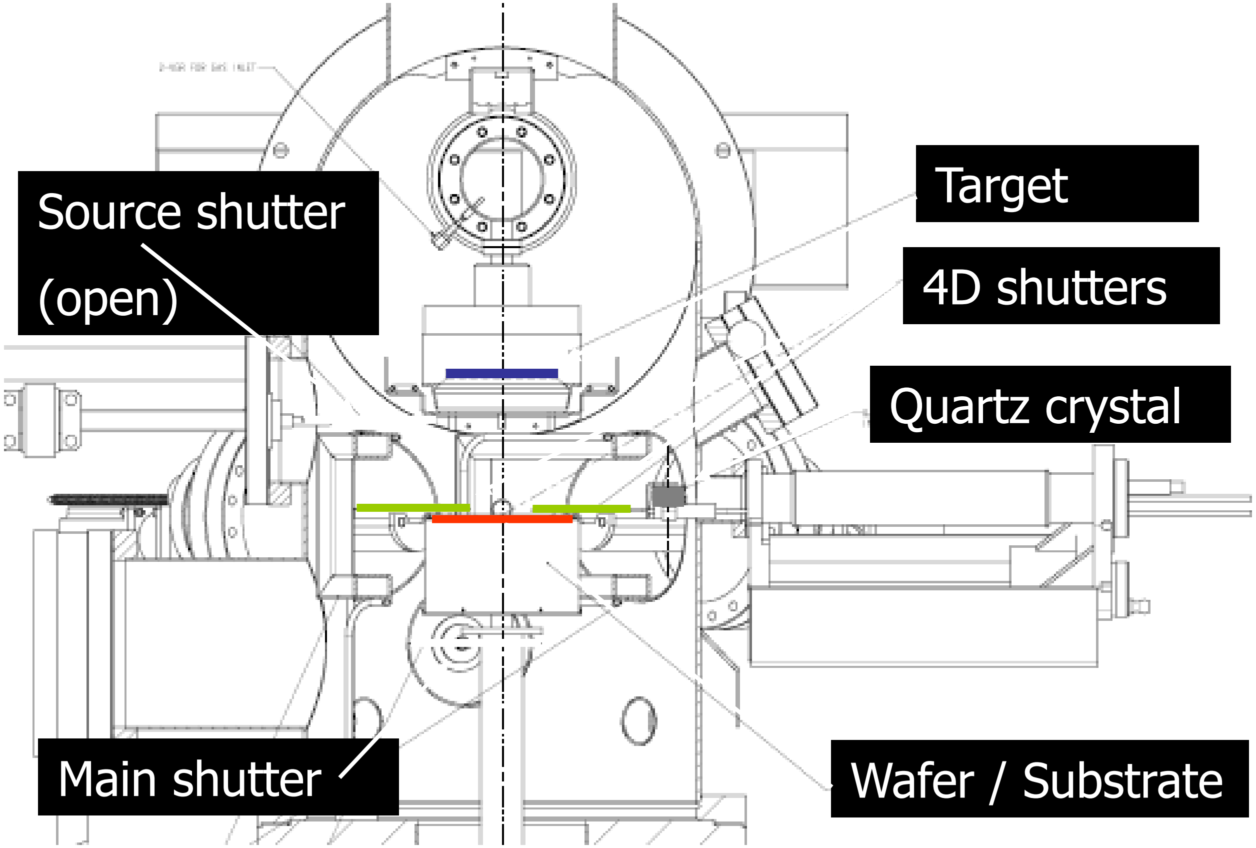
Linear chamber K1

K1



- Magnetically configurable cathodes
  - 3x DC, pulsed, 5 kW
  - 3x RF, 300 W, 13.56 MHz
- Target-to-Substrate:
  8.1 – 26.6 cm (13.8 cm)
- Pressure: 1–28 mT (5 mT)
- Gas: Ar, N_2, O_2, Xx
- RT – 1000°C (25° C)
- 4-D shutters
- ±178° oscillation (static)
- Bias: 0 – 50* W RF
- Magnetic field: 0.7 T
- Quartz crystal monitor

Linear chamber K1



Source shutter (open)

Target

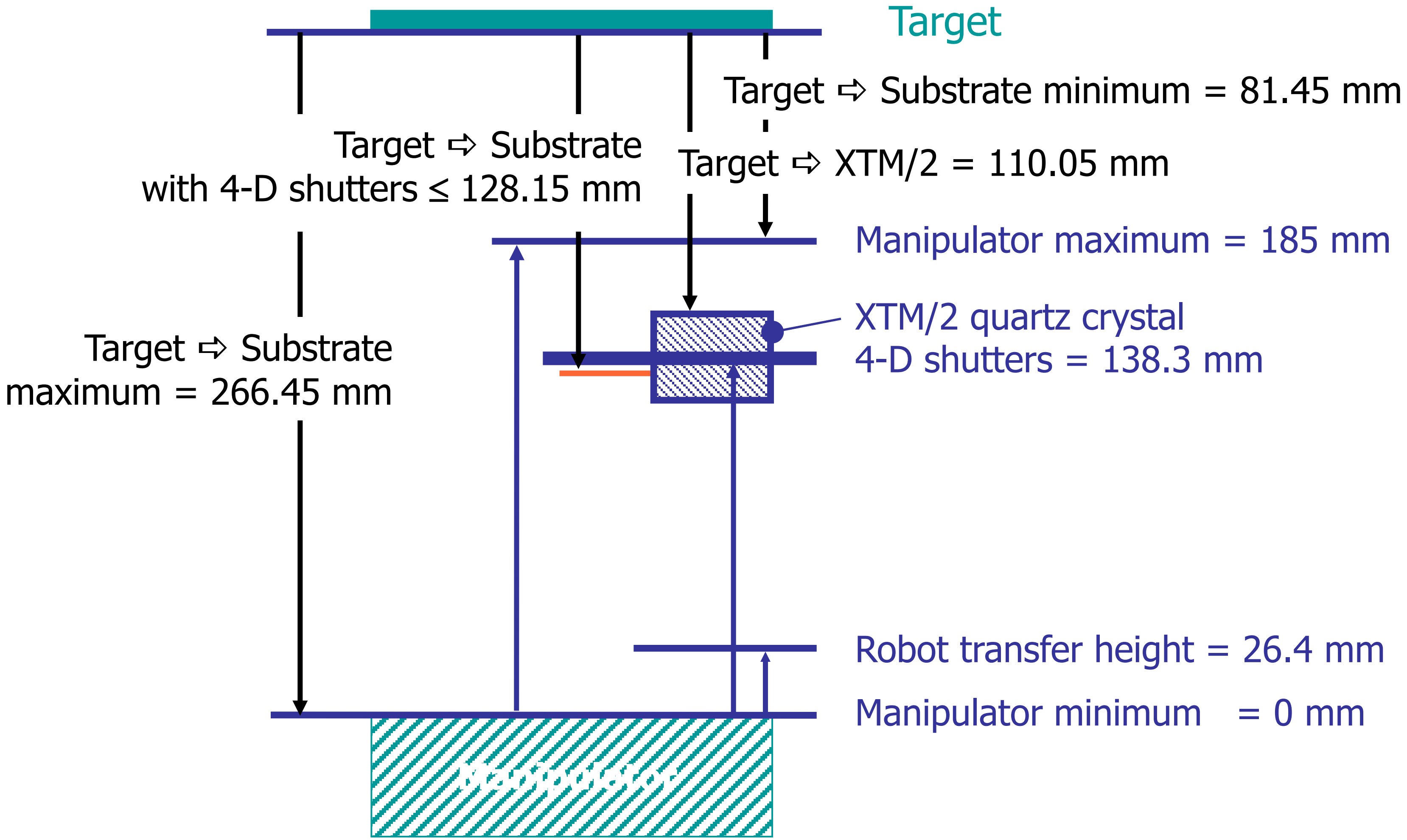
4D shutters

Quartz crystal

Main shutter

Wafer / Substrate

K1 critical distances



Target

Target ⇨ Substrate minimum = 81.45 mm

Target ⇨ Substrate
with 4-D shutters ≤ 128.15 mm

Target ⇨ XTM/2 = 110.05 mm

Manipulator maximum = 185 mm

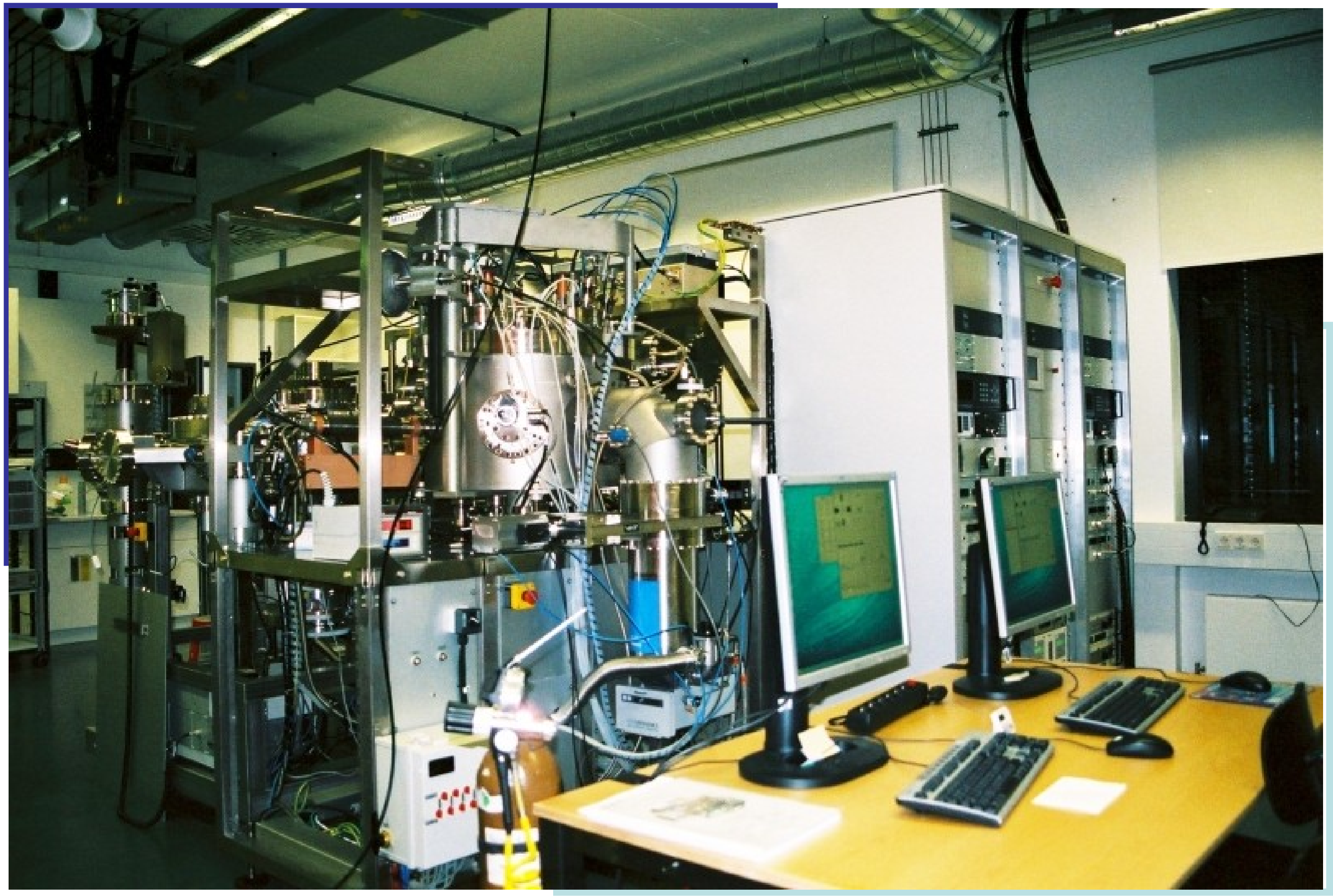
XTM/2 quartz crystal
4-D shutters = 138.3 mm

Target ⇨ Substrate
maximum = 266.45 mm

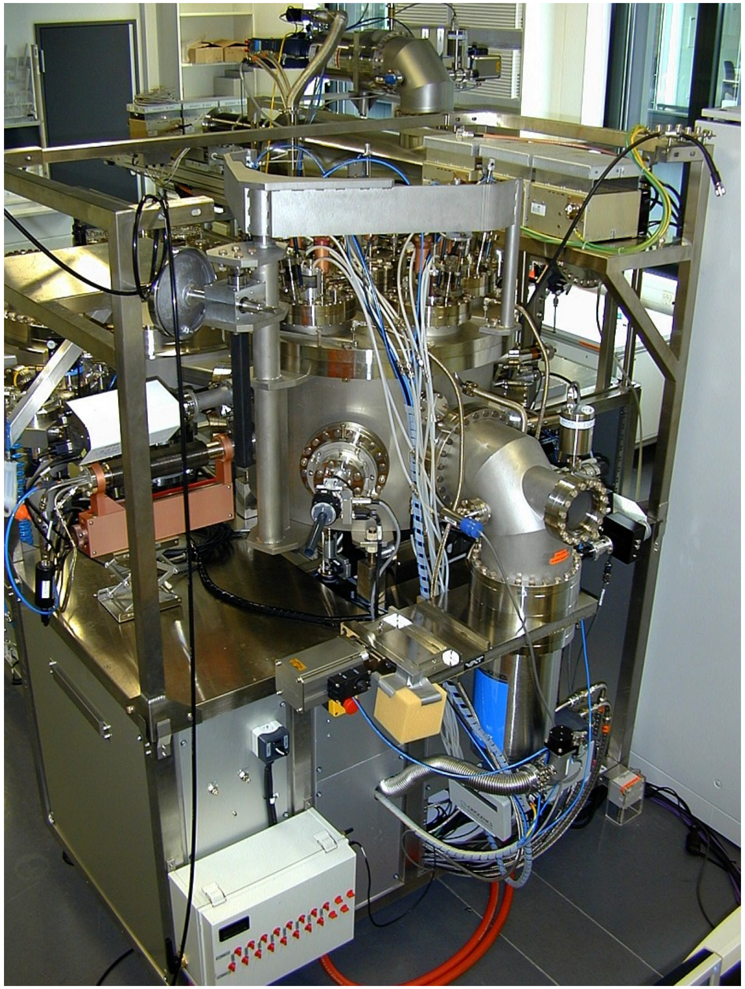
Robot transfer height = 26.4 mm

Manipulator minimum = 0 mm

Co-sputter chamber K2



K2

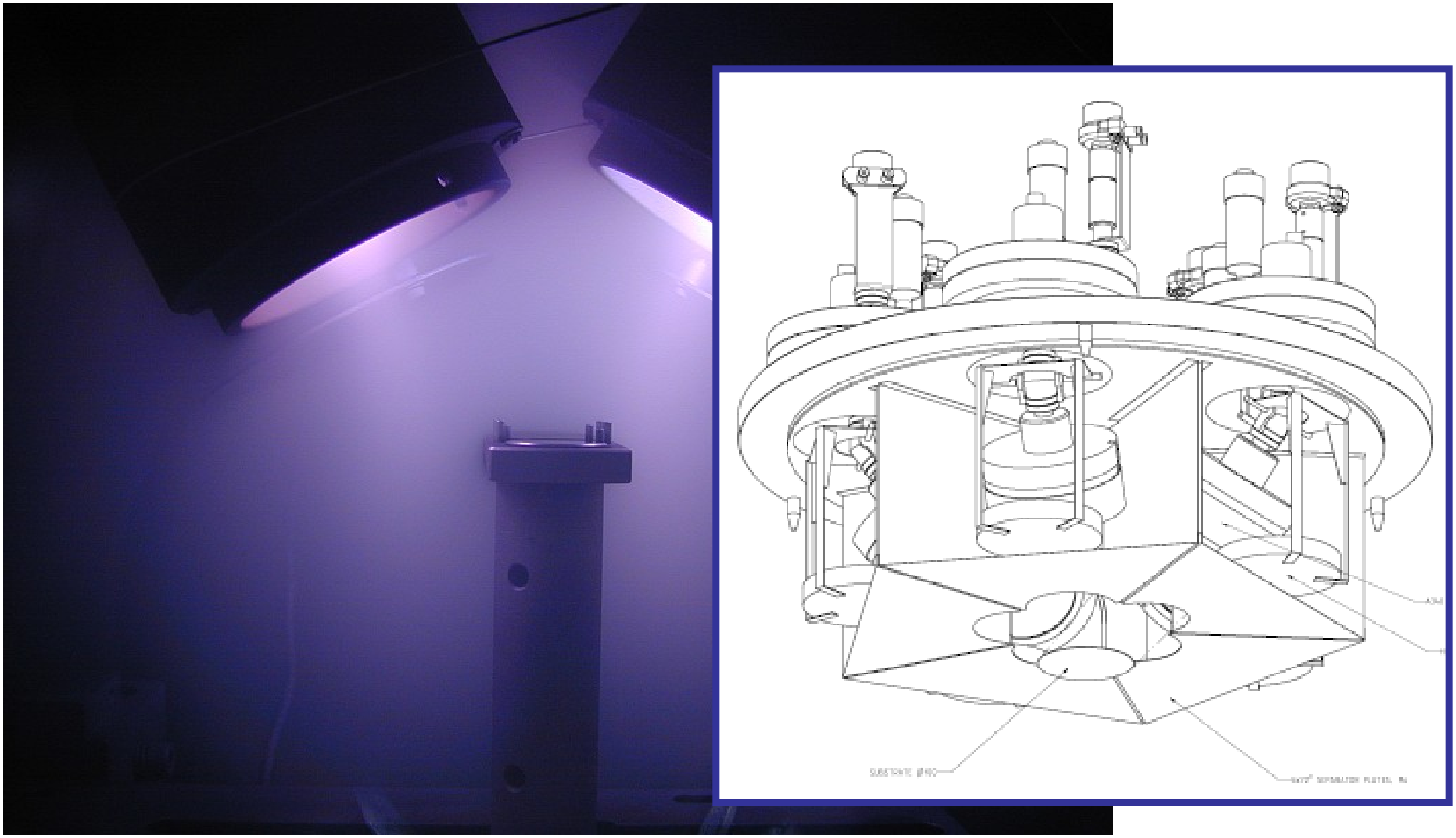


- Magnetically configurable cathodes
  - 2x DC, pulsed, 5 kW (1x)
  - 3x RF, 300 W, 13.56 MHz
- Target-to-Substrate:

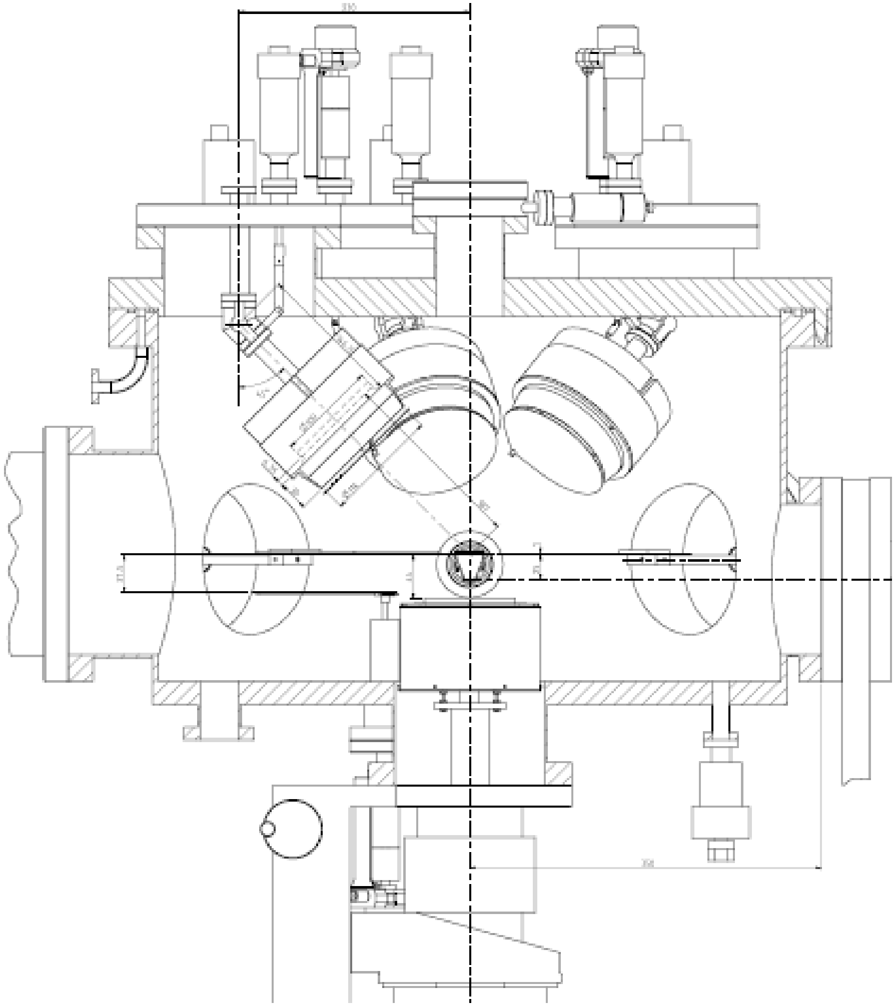
  19.5 cm to focal point
- Pressure: 1–28 mT (5 mT)
- Gas: Ar, N_2, O_2, Xx
- RT – 1000°C (25° C)
- 4-D shutters
- 0 or 10 rpm rotation speed
- Bias: 0 – 50* W RF

  0 – 500 V DC (0–3 mA)
- Quartz crystal monitor

Co-sputtering



K2 critical distances



Co-sputtering:

(best mixing; best deposition rate)

5-cathodes aimed to the focal point
and
Substrate just below 4D shutters
then
Target ⇨ Wafer center = 195.3 mm

Single or Multilayers:

(best uniformity)

Each cathode aimed to wafer edge
then
Target ⇨ Substrate edge = 189 mm

Target ⇨ XTM/2 = 187 mm

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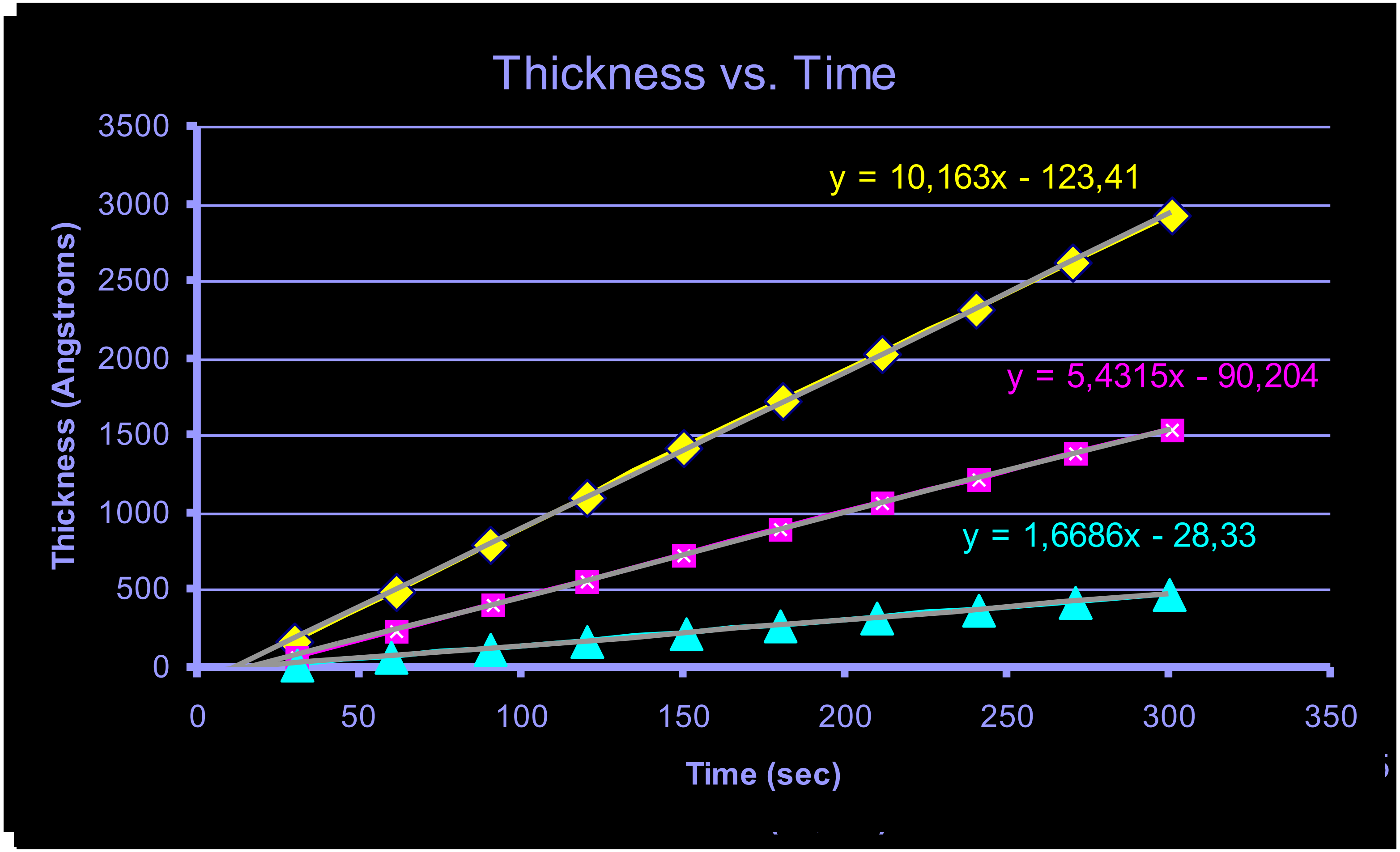
Process Parameters in PVD

- Seed layer

……

- Pressure
- Voltage (Power)
- Temperature
- Substrate bias
- Target-to-Substrate distance
- Target-to-Substrate angle (K2)
- Substrate rotation/oscillation
- Sputter gas
- Magnetic field (K1)

Target characterization



Fe: DC, K1

Substrate Bias

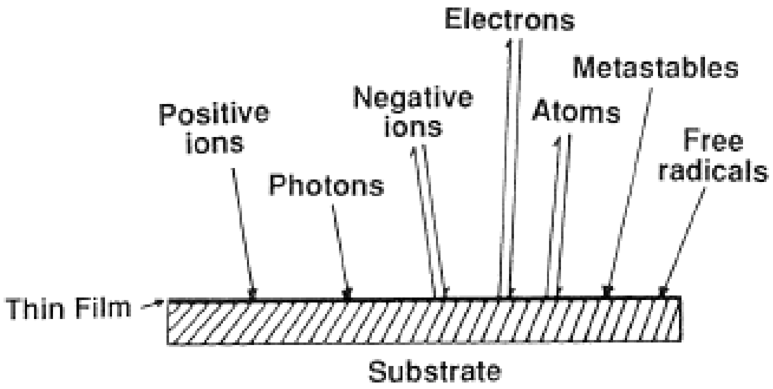


Figure A3.0.15. Particles impinging and ejecting from the surface of the substrate.

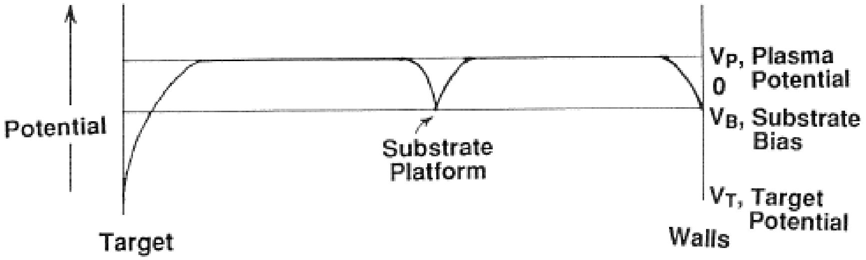


Figure A3.0.16. Distribution of the voltage during bias-sputtering in a dc diode system.


High negative bias


Positive bias

Parameters in PVD

- Seed layer

- Induce preferred orientation
- Adhesion to substrate

- Pressure
- Power
- Temperature
- Bias
- Target-to-Substrate
- Angle; rotation
- Sputter gas
- Magnetic field

- Deposition rate
- Particle energy
- Surface bombardment
- Mean free path
- Arrival angle
- Surface diffusion length
- Depth diffusion length

Thin Film Property Optimization

Gene
cond

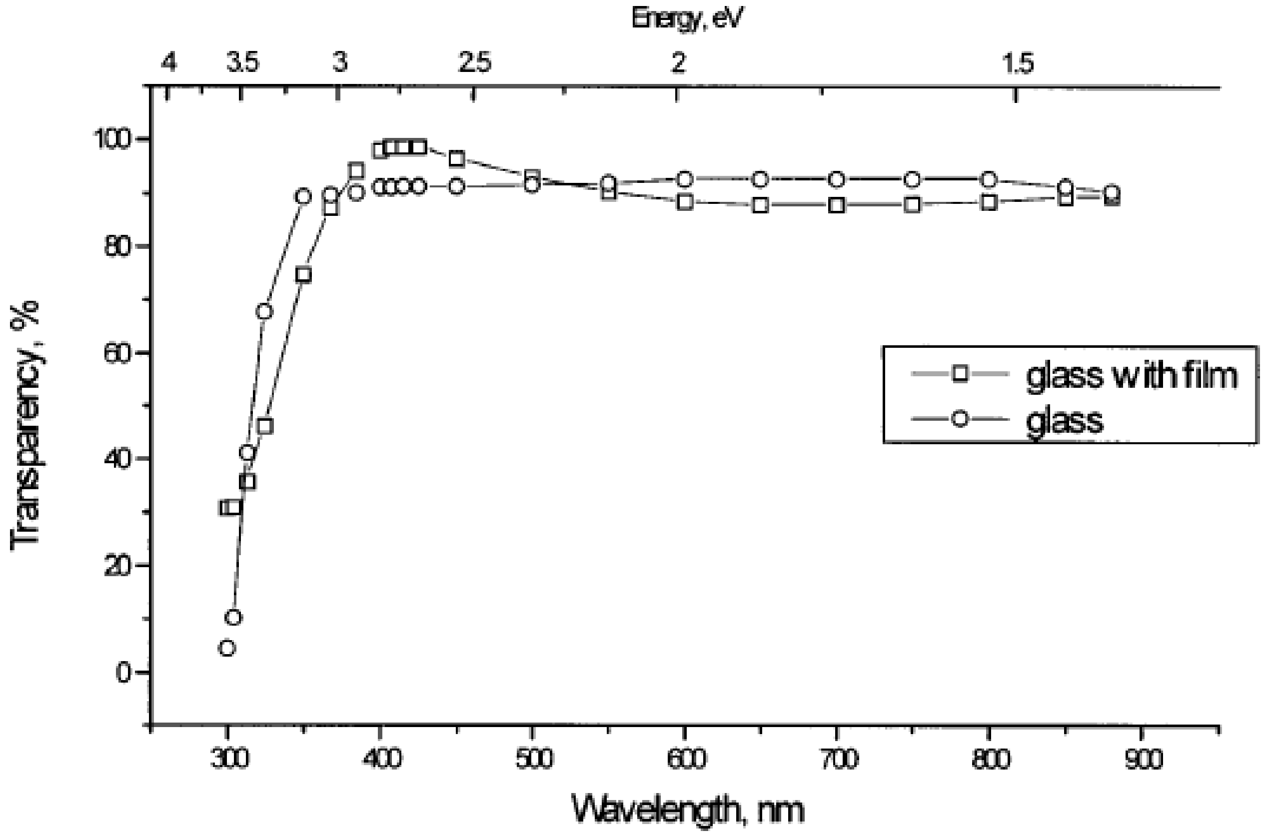
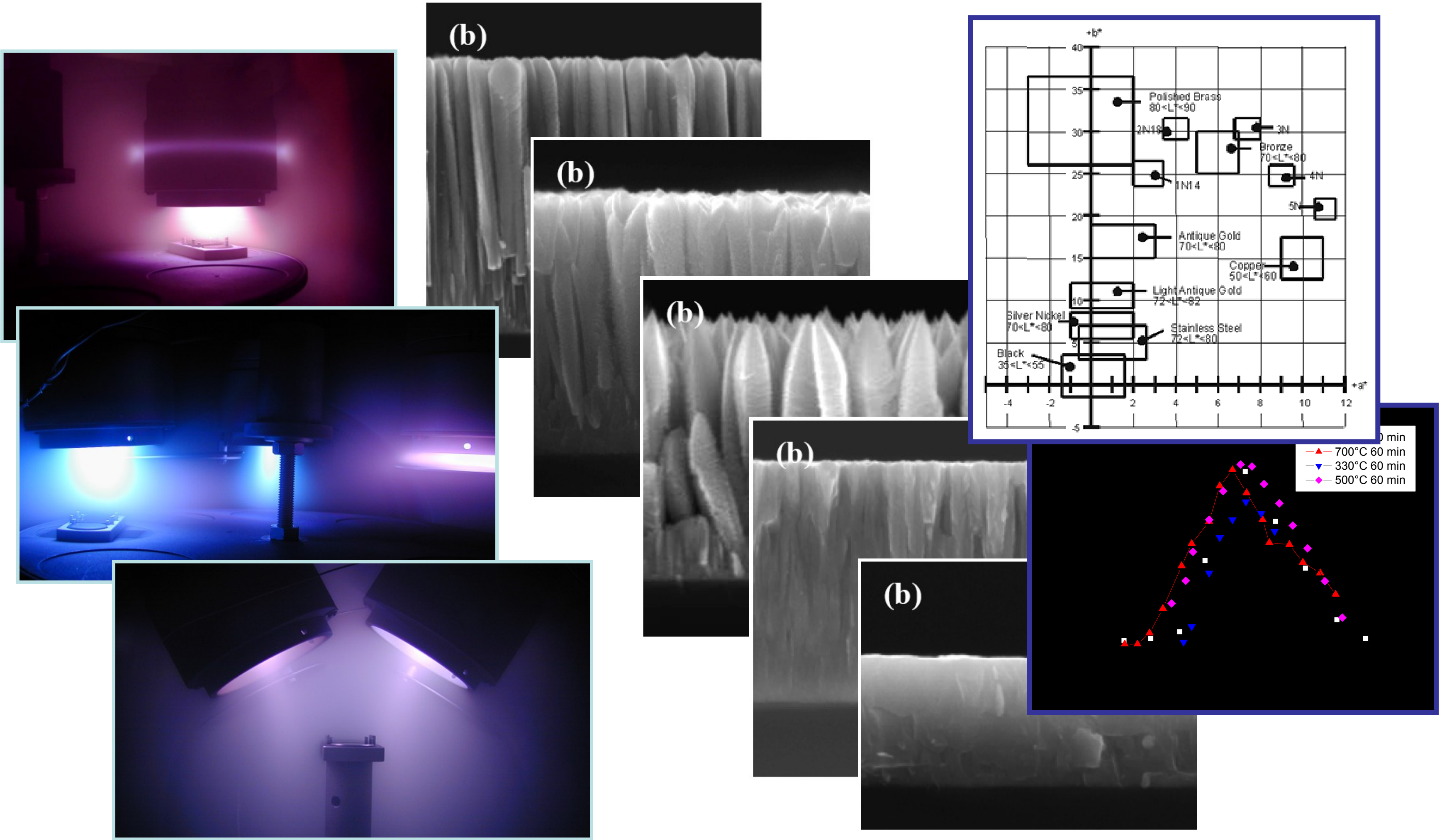


FIG. 2. Typical transparency characteristics of an In_2O_3 coating on glass.

nm]

Parameters – Structure – Properties



Microstructure effects for H-storage

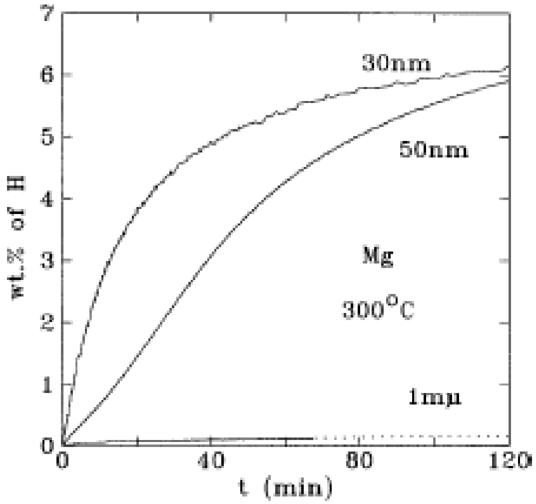


Fig. 1. Effect of grain size on hydrogen absorption of ball-milled magnesium powder: absorption at 300°C, first cycle, no activation

Appl. Phys. A 72, 157–165 (2001) /

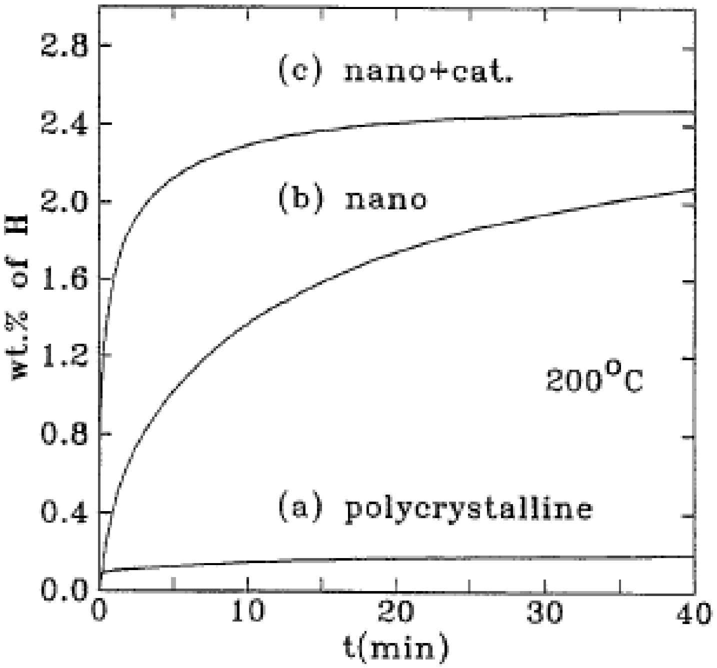


Fig. 10. Rate of hydrogen absorption by Mg_2Ni: polycrystalline (a), nanocrystalline (b) and nanocrystalline with catalyst (c); first cycle, no activation, temperature 200 °C, pressure 15 bar.

Journal of Alloys and Compounds 253–254 (1997) 70–79

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- PVD process parameters ... ≠ Properties!
- Thin film growth

Reference reviews - books

W. Espe and M. Knoll: *Werkstoffkunde der Hochvakuumtechnik,(**1936**)*
S. Dushman: *Scientific Foundation of Vacuum Techique, (**1949**)*
H. Mayer*: Physik dünner Schichten, Teil I (**1950**) und II (**1955**)*
O. S. Heavens*: Optical Properties of Thin Films (**1955**)*
L. Holland: *Vacuum Deposition of Thin Films, (**1956)***
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K. L. Chopra: *Thin Film Phenomena, (**1969)***
L. I. Maissel, R. Glang*:* Handbook of Thin Film Technology, ***(1970)***
H. Mayer: *Physics of thin films Parts, I and II, (Complete bibliography), (**1972)***
B. Lewis, J.C. Anderson: *Nucleation and Growth of Thin Films (**1978**)*

Thin Film Growth

Steps in Film Formation

1. thermal accommodation
2. binding
3. surface diffusion
4. nucleation
5. island growth
6. coalescence
7. continued growth

Thin Film Growth

- target atoms and ions impinge
- electrons impinge
- Ar atoms and residual molecules impinge
    - Ar pressure typically 1 - 100 mTorr
    - Ar may be incorporated into film
    - 10^{-6} Torr: ~1 monolayer/s impinges a surface
- energetic particles may modify growth
- substrates heat up
    - 100° – 200°C is possible (heat of condensation can also be significant)
    - for a thermally isolated sample (no heat conduction)

Thin Film Growth

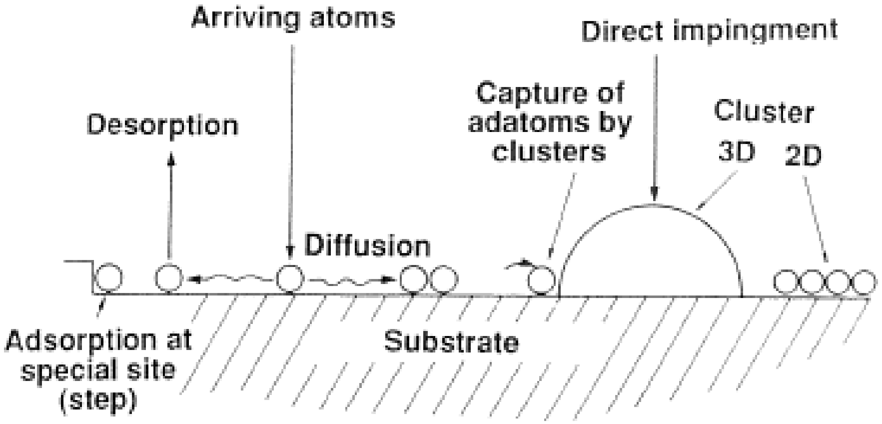


Figure A3.0.14. Processes at the substrate surface.

Adding to film:

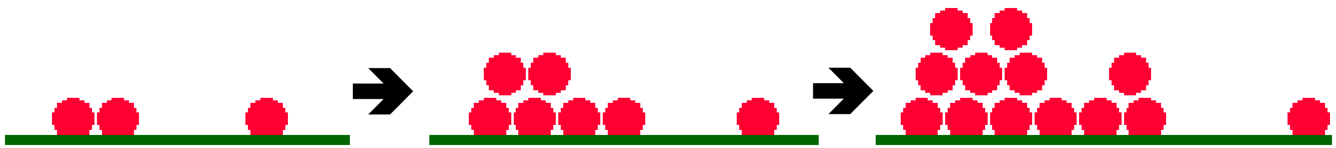
- impingement (deposition) on surface

Removing from film:

- reflection of impinging atoms
- desorption (evaporation, resputtering) from surface

Thin Film Growth Modes

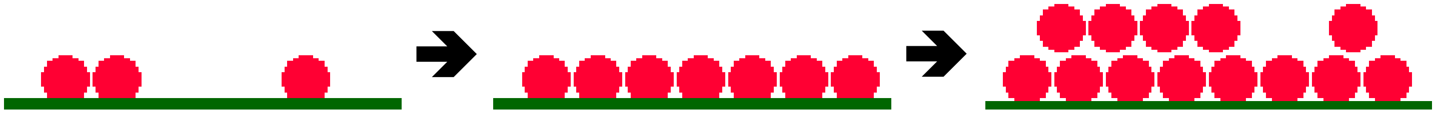
Island growth (Volmer - Weber)



- form three-dimensional islands
- conditions:
  - o film atoms more strongly bound to each other than to substrate
  - o and/or slow diffusion

Thin Film Growth Modes

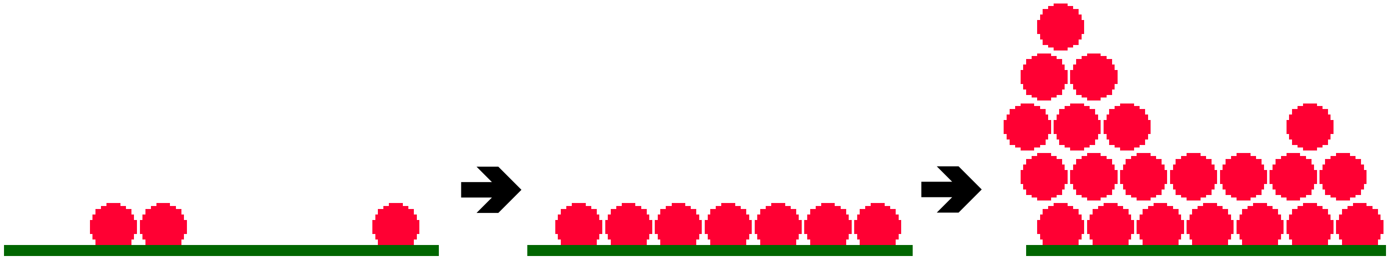
Layer by layer growth (Frank van der Merwe)



- generally highest crystalline quality
- conditions:
  - film atoms more strongly bound to substrate than to each other
  - and/or fast diffusion

Thin Film Growth Modes

Mixed growth (Stranski - Krastanov)



- initially layer-by-layer
- then forms three dimensional islands

  ➔ change in energetics

Microstructural Evolution

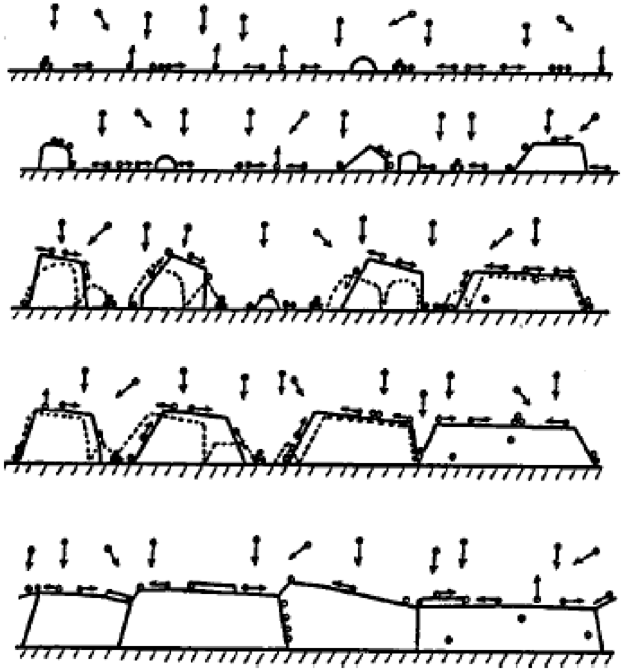


FIG. 1. Schematic diagram illustrating fundamental growth processes controlling microstructural evolution: nucleation, island growth, impingement and coalescence of islands, grain coarsening, formation of polycrystalline islands and channels, development of a continuous structure, and film growth (see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

Å ⇨ nm

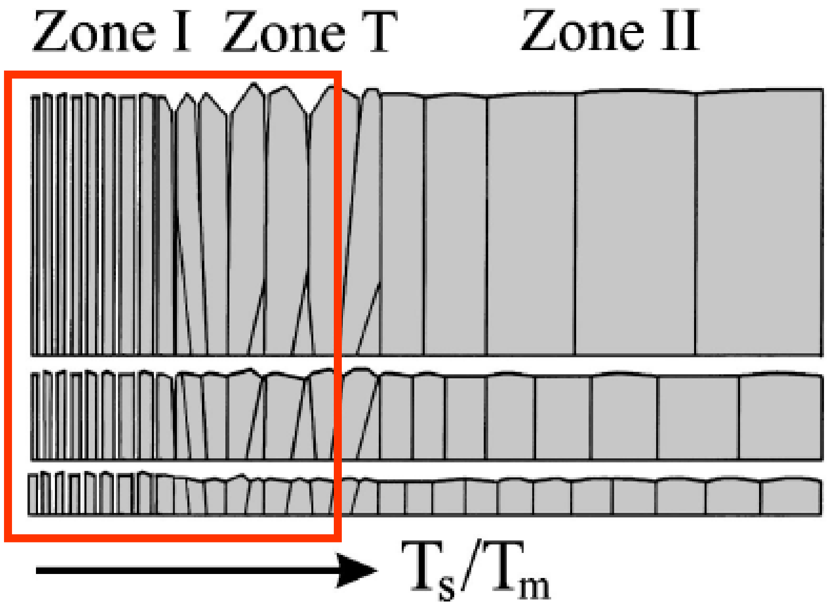


FIG. 3. SZM schematically representing microstructural evolution of pure elemental films as a function of the reduced temperature T_s/T_m, where T_s is the deposition temperature and T_m is the melting point of the material, both expressed in degrees K (see Ref. 9).

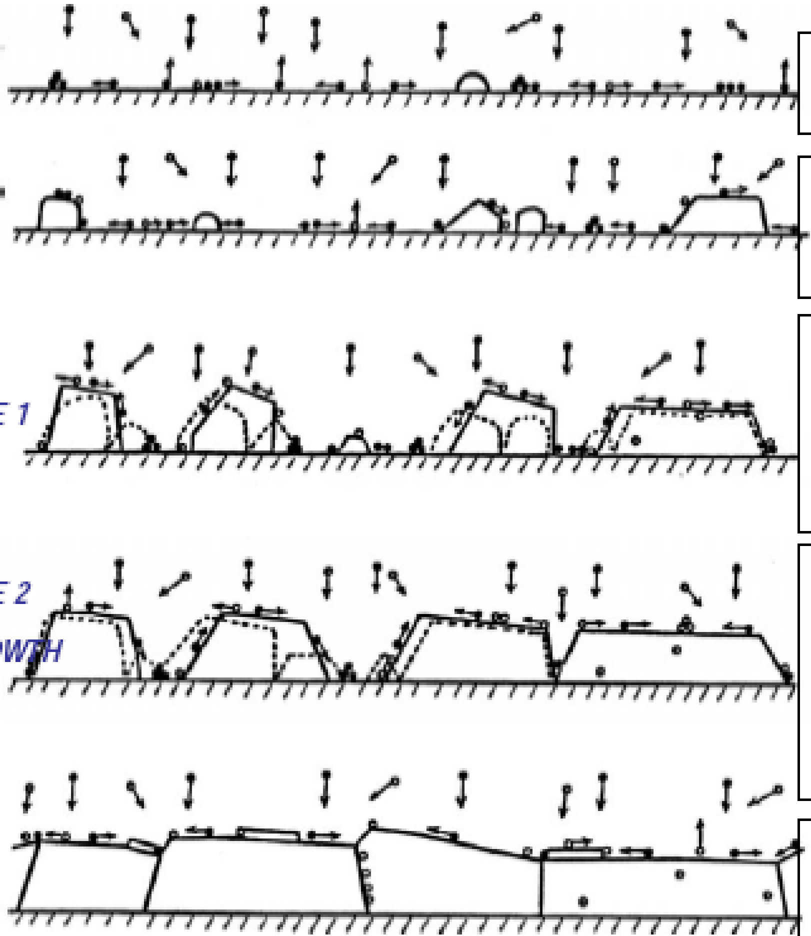
nm ⇨ μm

P. Barna, et al.

The elementary atomic processes and related fundamental phenomena of structure formation operating in various stages of film growth (elemental film, $T_s > 0{,}3T_m$)

GROWTH STAGES

atomic processes
FUNDAMENTAL PHENOMENA



NUCLEATION

migration of adatoms on substrate
CLUSTERING/NUCLEATION primary

ISLAND GROWTH

self surface diffusion
CRYSTAL GROWTH on substrate
NUCLEATION primary

COALESCENCE 1

self surface diffusion
CRYSTAL GROWTH
bulk diffusion
COALESCENCE TYPE I complete
NUCLEATION secondary

COALESCENCE 2

CHANNEL GROWTH

self surfce diffusion
CRYSTAL GROWTH
bulk diffusion
COALESCENCE complete/incomplete
GRAIN GROWTH abnormal
NUCLEATION secondary

THICKNESS GROWTH

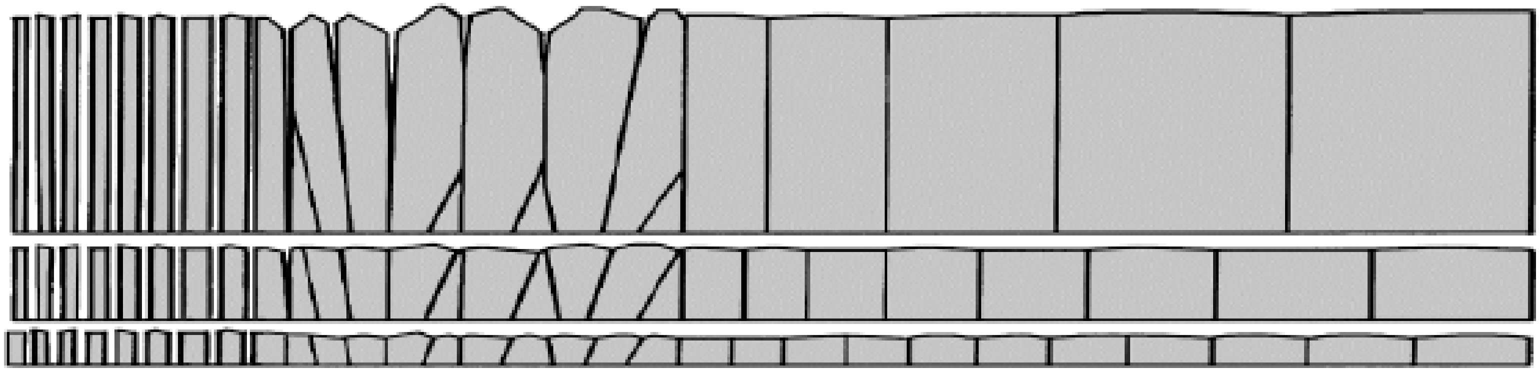
self surface diffusion
CRYSTAL GROWTH
bulk diffusion
GRAIN GROWTH abnormal/normal

(P.Barna, in Diagnostics and Application of thin films, Ed. L. Eckertova, I. Ruzicka, IOP, 1992, p.295)

DERIVATION of the STRUCTURE ZONE MODEL of elementary thin films growing on amorphous substrate

random | competitive growth texture | restructuring growth texture

Zone I **Zone T** **Zone II**



Zone I

(crystal growth)

nucleation

adatom migration on substrate (very limited)

self.surf.diff. (very limited)

Zone T

crystal growth (competitive)

nucleation

adatom migration on substrate

self.surf.diff.

Zone II

grain growth (abnormal)

crystal growth

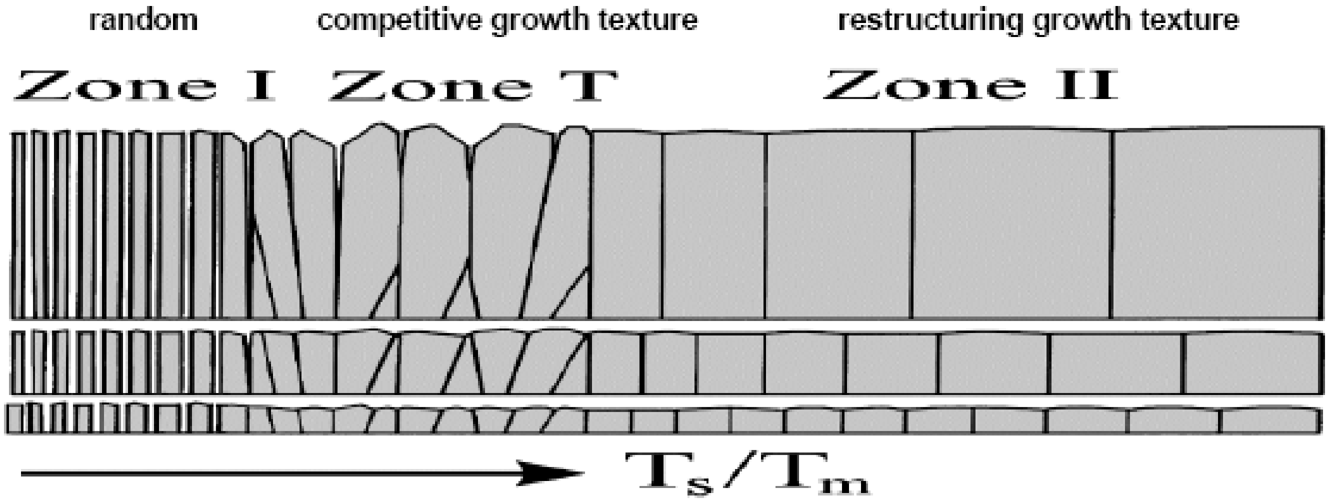
nucleation

adatom migration on substrate

self. surf. diff

bulk diffusion

GB migration



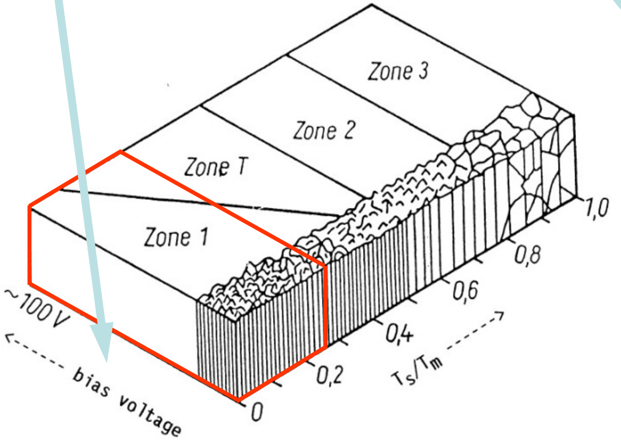
Ts is the deposition temperature and *Tm* is the melting point in K

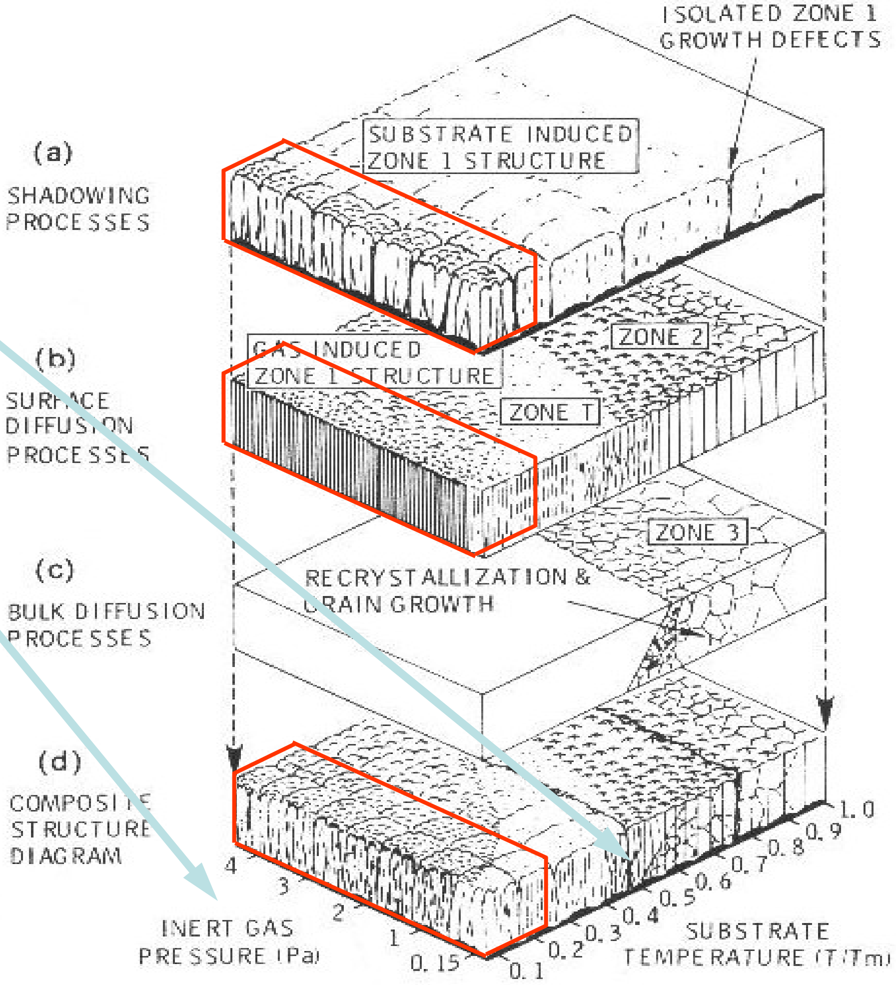
Conclusions on structure evolution in elemental thin films

*** correlation exists between grain size, grain morphology, surface topography and texture, these are developing together**
*** the in-plane size (column diameter) and the orientation of crystals can be controlled by the temperature**
*** the as-deposited structure has low thermal stability**
*** the possible zones are: Zone I, Zone T and Zone II**
*** in Zones I and II the structure and orientation are uniform along thickness, crystals penetrate through the film**
*** no grain boundaries parallel to the substrate, i.e. no equiaxed grain morphology (Zone III) can exist**

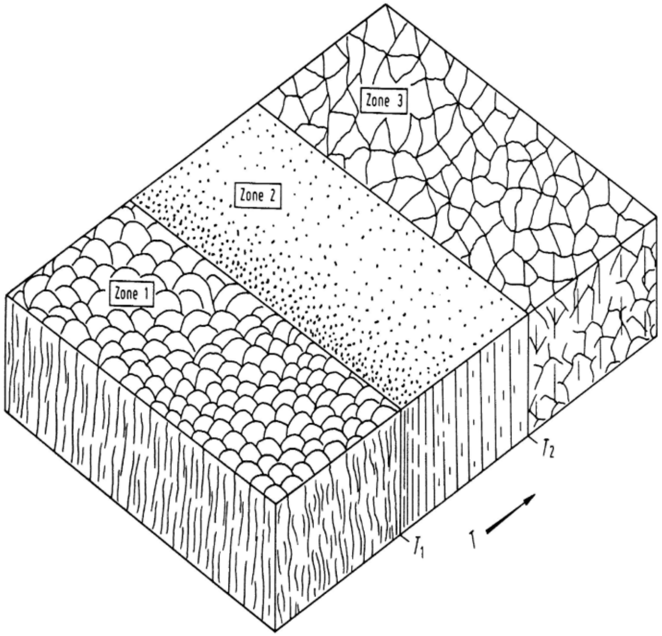
PVD Structure Zone Models

- Movchan – Demchishin
  T/T_m : grain structure
- Thornton
  Inert gas pressure
- Messier
  Particle energy

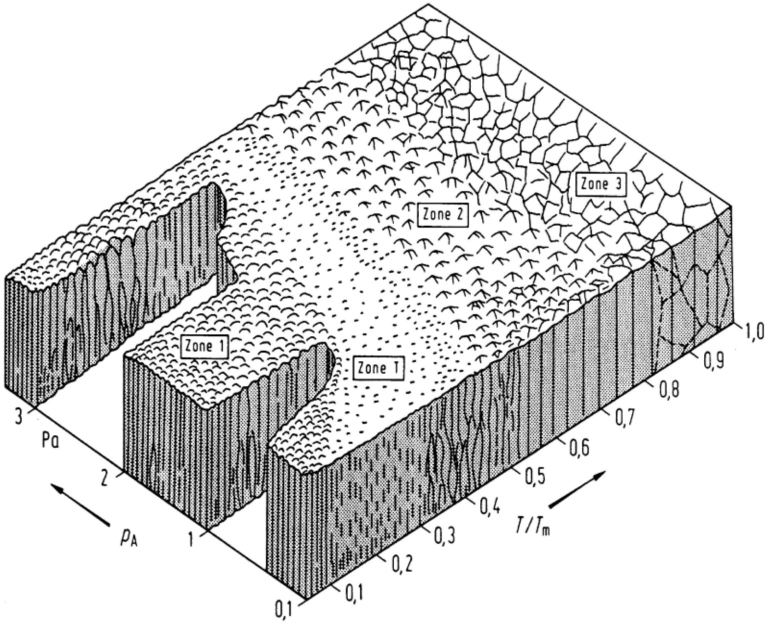




Movchan-Demchishin: Evaporation



Thornton: Sputtering



Conclusions

(P.B. Barna, M. Adamik, Thin Solid Films, 317(1998)27; I. Petrov, P.B. Barna, L. Hultman, J.E. Greene, J. Vac. Sci. Technol.,21(2003)S117)

- **The structure evolution in polycrystalline films (**both elemental and multicomponent**) can be described by a pathway (**characteristic for every materials system**) on the basis of the same fundamental phenomena of structure formation: nucleation, crystal growth, grain growth**
- **The operation of every single fundamental phenomenon is related to a thermally activated atomic process (temperature dependence of the pathway)**
- **The atomic processes are:**

adatom diffusion (Ts > ~ 0,05Tm) (nucleation)
self surface diffusion (Ts > ~ 0,1Tm) (crystal growth, coalescence)
bulk diffusion (Ts > ~ 0,3Tm) (grain growth)

in multicomponent films additionally:

chemical interaction among species
including
process induced segregation of excessive species
resulting in
delayed nucleation of secondary phase(s)

Acknowledgment

- Fully acknowledge the contribution of Alan Savan, CAESAR, Germany