NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
Sptember 19th, 2016

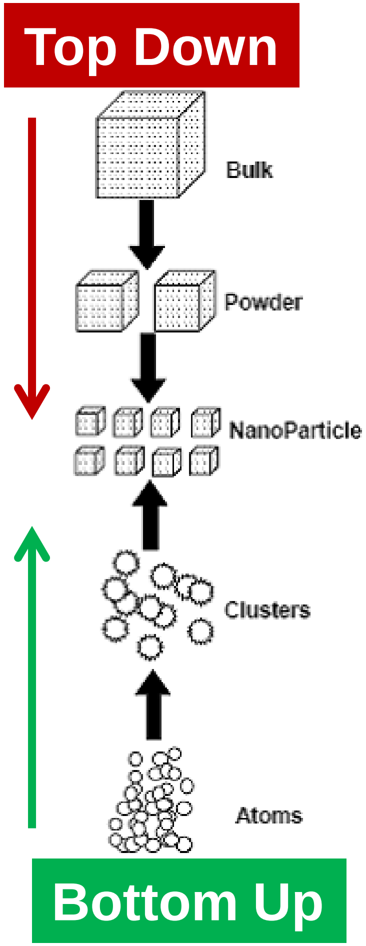
- Bottom-Up approches: Vapour phase methods

Outline

- Classification of *Bottom-Up* methods
- Vapour phase methods and growth mechanism
- Examples of vapour phase methods:
  - Flame Spray Pyrolysis (FSP)
  - Pulsed Laser deposition (PLD)
  - Magnetron-sputtering based Inert-gas-condensation

Synthesis of nanomaterials

- *"Top-down approach"* Refining or reducing bulk materials via Attrition / Milling
  - Involves mechanical and thermal cycles
  - Broad size distribution (10-1000 nm)
  - Varied particle shape or geometry
  - Impurities
- *"Bottom-up approach"* Scaling up from single groups of atoms
  - Building complex nanostructures from atoms to molecules under controlled conditions
  - Liquid phase methods (*previous lectures)* (sol-gel, wet chemical synthesis…)
  - Vapour Phase methods (pyrolysis, Inert gas condensation, Lased ablation…)



General classification of Bottom-Up methods

Bottom-Up methods

Chemical methods

Physical methods

- Wet chemistry
- Sol gel
- Colloids
- …..

Chemical Vapour Deposition (CVD) :
- Spray pyrolysis
- ALD
- ….

Physical Vapour Deposition (PVD)
- Sputtering
- PLD
- MBE
- ….

Today’s focus: Vapour phase synthesis!

Botom-up methods

TNN 67-75 pp

Vapour phase synthesis

Spray conversion processing

Atomization of chemical precursors into aerosol droplets that are dispersed in a gas medium

Example:
Flame spray pyrolysis

Chemical Vapour Deposition (CVD)

Gaseous species react or decompose on a hot surface to form a stable solid product

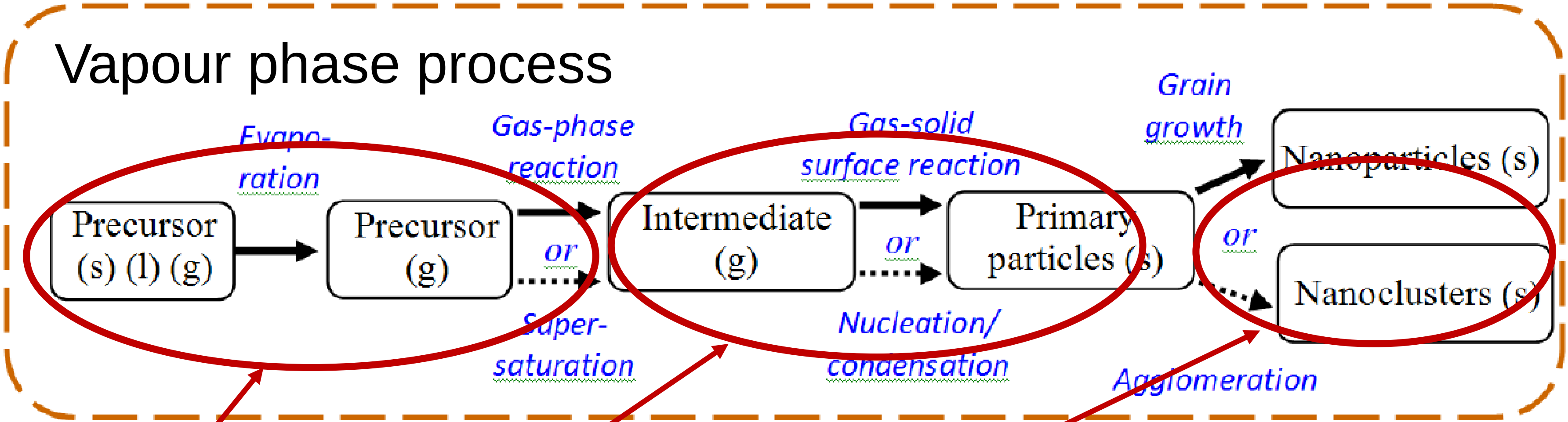
Example:
Plasma Enhanced CVD (PE-CVD)

Physical Vapour Deposition (PVD)

Generation of vapour phase from solid materials (sputtering, lased ablation, evaporation….)

Example:
PLD
Sputtering

Growth mechanism (3 main steps)



Step 1. Precursor evaporation (solid, liquid or gas)

Step 2. Nucleation (vapour to solid)

Step 3. Growth: collisions and or coalescence (solid)

Gas phase growth (equation)

Growth rate of vapor condensation:

Flux from gas kinetic theory

$$R = \xi A_{NP} \frac{\Delta p}{\sqrt{2\pi m k_B T}};$$

$$\Delta p = p_V - p_e$$

Spherical NP: $A_{NP} = 4\pi d_{NP}$

ξ... condensation coefficient (between 0 and 1)

A_{NP}... surface area of condensate (nanoparticle NP)

m .... mass of gas molecule

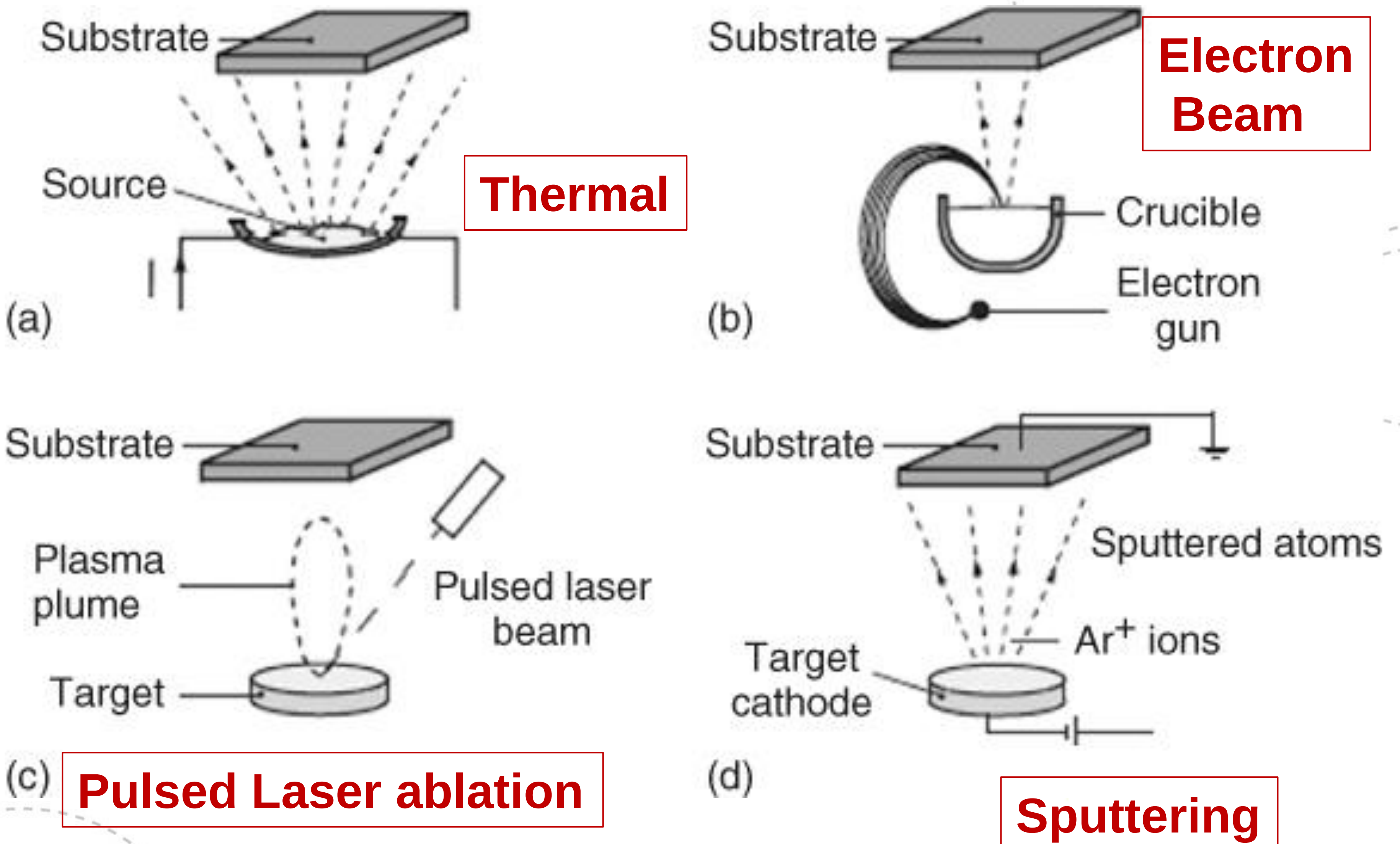
k_B .... Boltzmann constant, and T … absolute temperature

Driving force: pressure difference Δp

p_V ….instantaneous vapor pressure

P_e …. local equilibrium pressure at the growing cluster

Examples of evaporation techniques

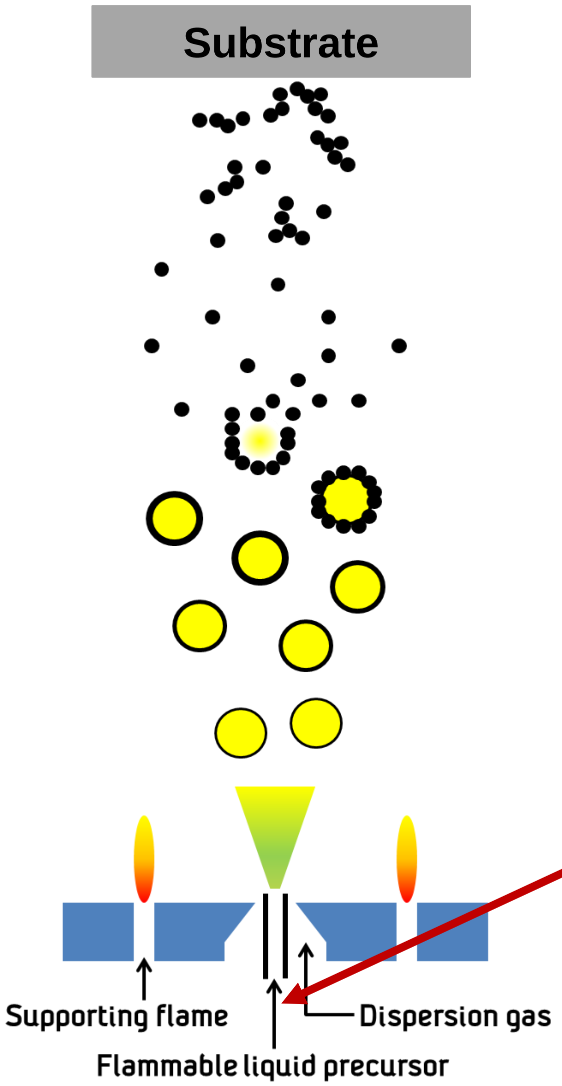


Examples of vapour phase methods for nanomaterial synthesis

- Flame spray pyrolysis (*Spray conversion processing*)
- PLD *(PVD for thin film deposition)*
- Inert gas condensation based on sputtering

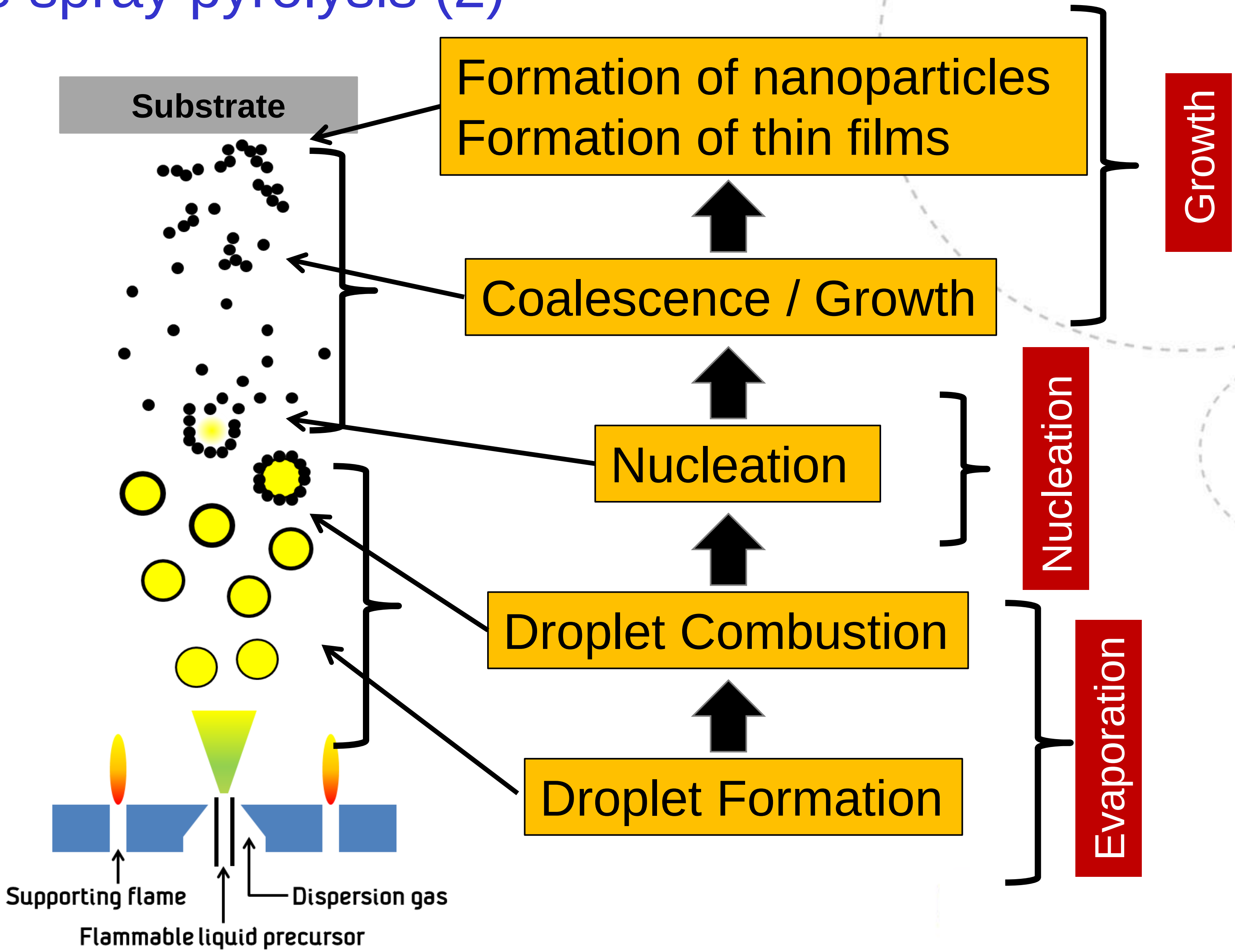
  (PVD for multicomponent nanoparticles)

Flame spray pyrolysis (FSP) (1)



- FSP is a high temperature flame process for synthesis of metal-oxide nanoparticles.
- Liquid or solid precursors are dissolved in or diluted with an appropiate organic solvent and sprayed into the flame

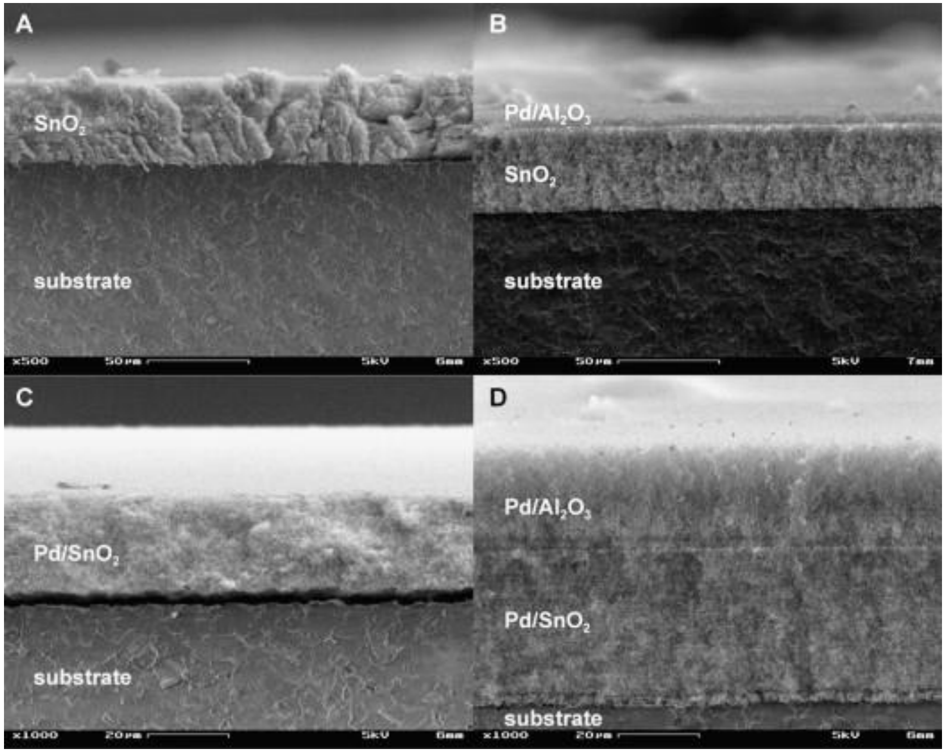
Flame spray pyrolysis (2)



Flame spray pyrolysis at NTNU-campus (SINTEF)

Flame spray pyrolysis (FSP)
Example of thin film

Cross-section SEM images of thin films deposited by FSP on ceramic substrates

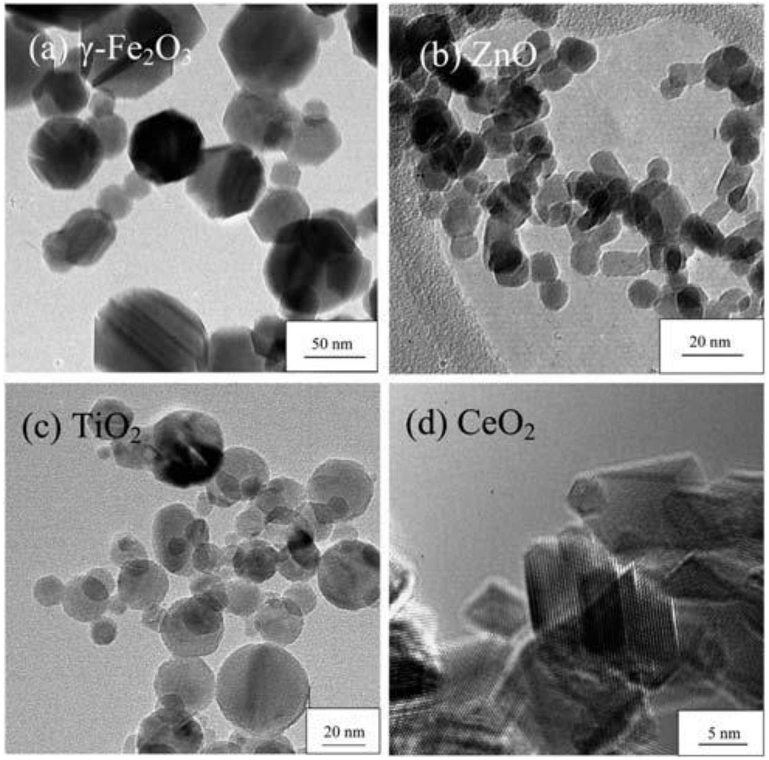


- (A) SnO_2 *(Tin dioxide*) thin film
- (B) Pd/Al_2O_3 layer on top of a SnO_2 film (A)
- (C) Pd/SnO_2 thin film
- (D) Pd/Al_2O_3 layer on top of a Pd/SnO_2 layer (C)

Ref. T. Sahm et al. Sensors and Actuators B 127 (2007) 63–68

Flame spray pyrolysis (FSP) Example of nanoparticles (NPs)

TEM images of metal-oxide NPs of different morphologies made by FSP



- (a) Hexagonal/octagonal NPs of Fe_2O_3
- (b) Slightly elongated ZnO NPs
- (c) Spherical TiO_2 NPs
- (d) Rhomboid-shaped CeO_2 (*Cerium dioxide)* NPs with sharp edges

Ref. W. Y. Teoh et al. Nanoscale, 2010, 2, 1324–1347

Flame spray pyrolysis (FSP)
Main Advantages and disadvantages

- FSP is a versatile technique for the rapid and scalable synthesis of nanostructured materials with engineered Functionalities.
- Due to the high temperature environment of the flame (up to 2500ºC), product nanoparticles are fully oxidized and crystalline *(No post-synthesis heat treatments are required).*
- FSP is limited by the polydispersity of the nanoparticle size distribution. (*There is an increasing demand, especially for bioapplications, for particles with narrow size distribution.)*

Pulsed Laser Deposition (PLD)
Nanofilm deposition

Definitions

Laser

A device that generates an intense beam of coherent radiation

Laser is acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation

Pulsed Laser Deposition (PLD)

PLD is a physical vapour deposition technique where a high power pulsed laser beam is focused to strike a target of the desired material. Material is then vaporised and deposited as a film on a substrate facing the target. This process can be performed in ultra high vacuum or in the presence of background gas, such as oxygen when depositing thin films of oxides

Concept of PLD (1)

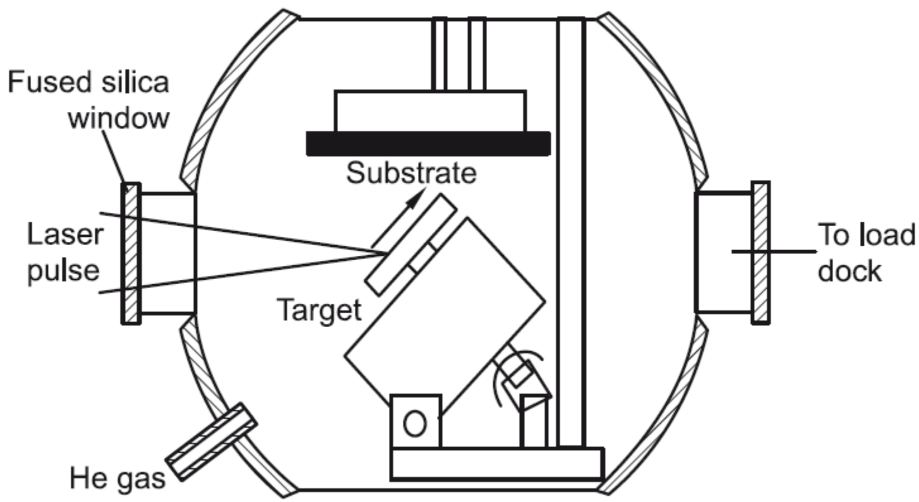


Fig. 3.3 Schematic of a laser ablation chamber equipped with a rotating target holder.

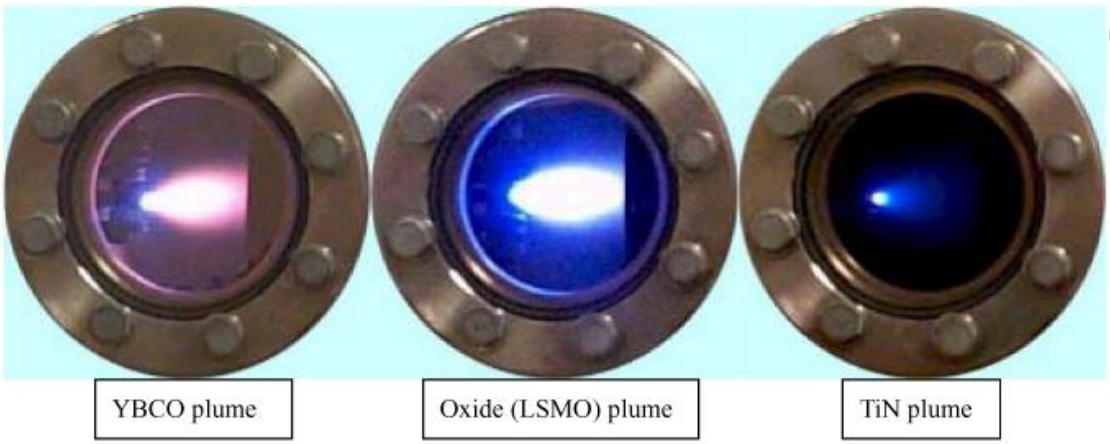
PLD stages

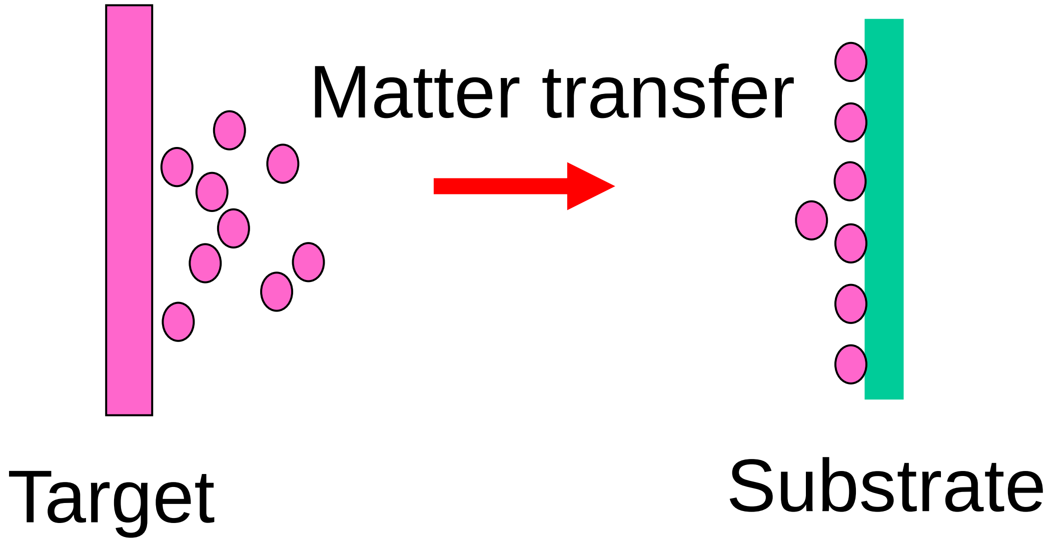
- Laser ablation of target
- Plasma genetation
- Film nucleation and growth

- The laser-target interaction: electromagnetic energy is converted into electronic excitation and then into thermal/mechanical energy to cause ablation
- A plume: atoms, molecules, e^-, ions, clusters, particles, molten globules
- The plume expands with hydrodynamic flow characteristics

Concept of PLD (2)

www.researchgate.net

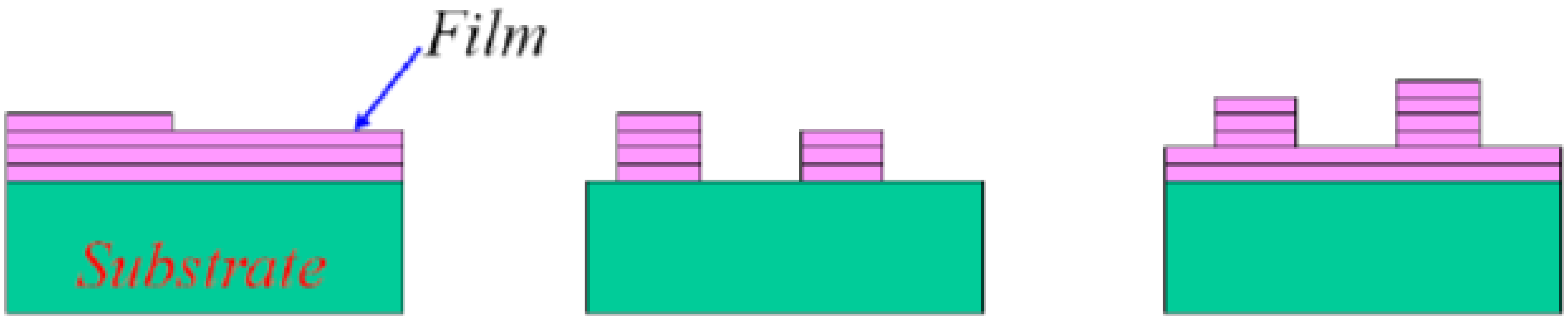




If $\gamma_s \geq \gamma_f + \gamma_{sf}$

$\gamma_s < \gamma_f + \gamma_{sf}$

$\gamma_s > \gamma_f + \gamma_{sf}$
With misfit



Layer-by-layer
(Frank-Van der Merwe)

3D islanding
(Volmer-Weber)

Layer-by-layer
followed by 3D islanding
(Stranski-Krastanov)

γ_s: surface energy of substrate
γ_f: surface energy of film
γ_{sf}: interface energy of substrate-film

by Dietrich R. T. Zahn

- Layer-by-layer – potentially high quality epitaxial films
- 3D islanding – potentially polycrystalline films.

Advantages-Disadvantages PLD

- Advantages
  - **Versatile method (any material)**
  - **Homogeneous evaporation**
  - **High deposition rates (10s nm/min)**
  - **Plume at high energy**
  - **Reactive gases (oxygen)**
  - **Broad range of gas pressures**

- Main disadvantage
  - **Improvements based on theory require extremely complex models**

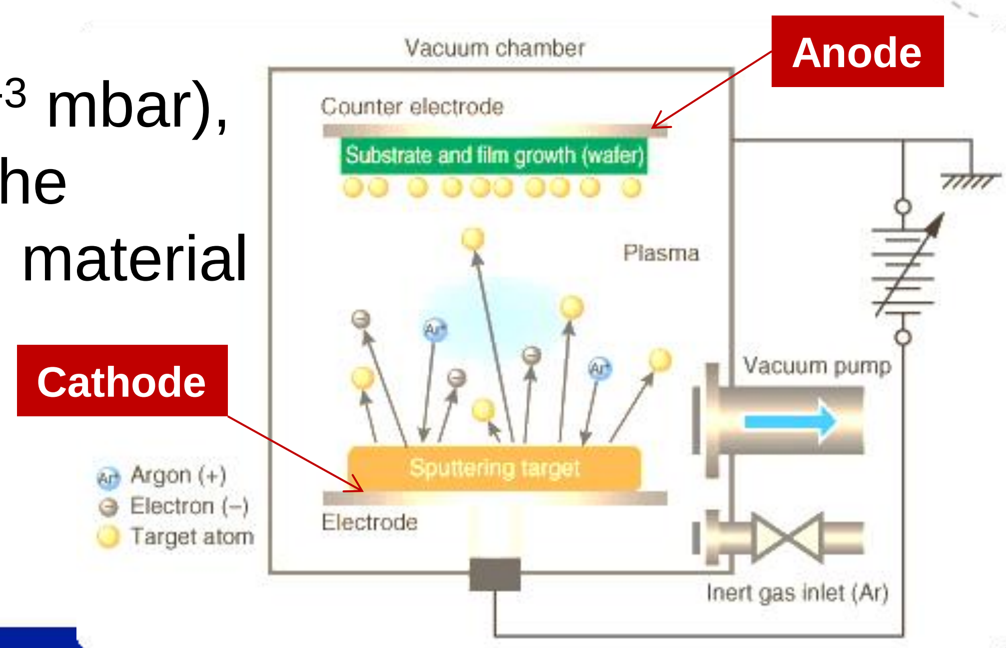
Advantage to highlight is the homogeneous evaporation, in comparison with other PVD techniques

Sputtering-Based methods

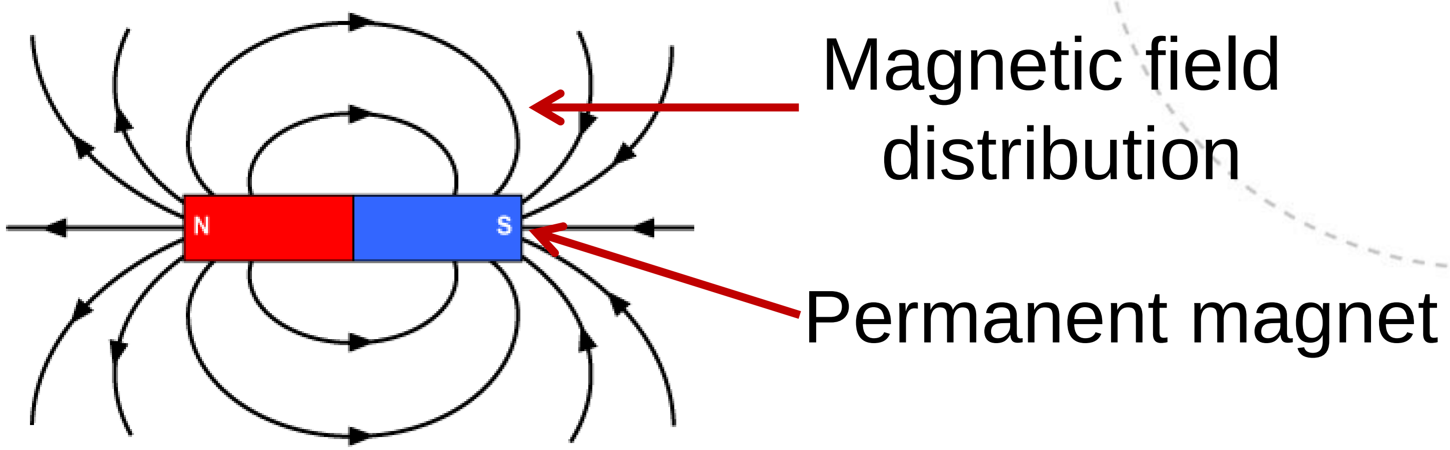
Concept of Sputtering (thin film deposition)

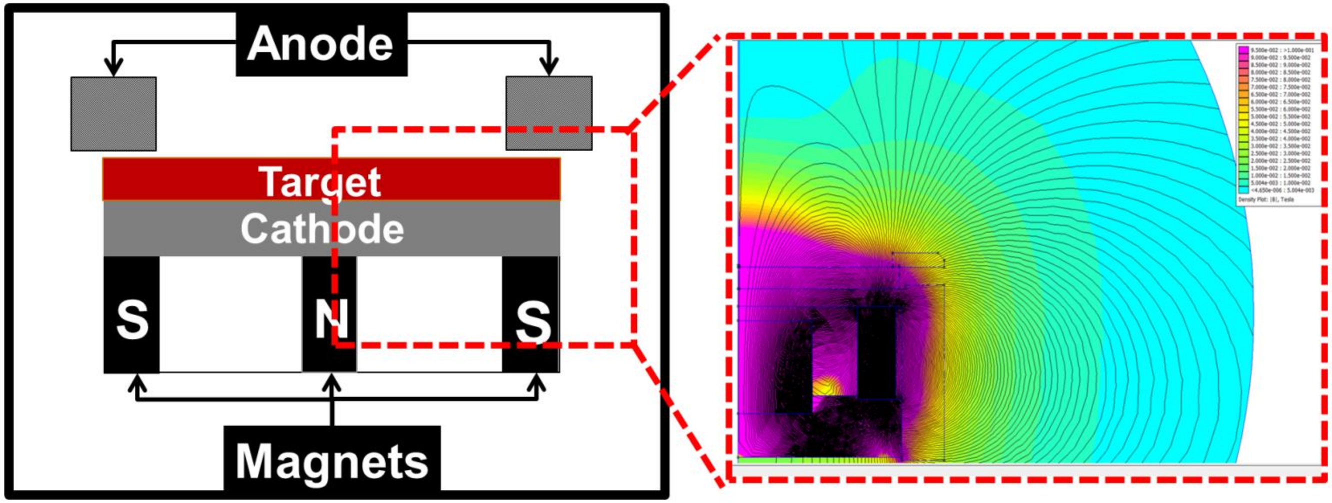
- Sputtering is a method of vaporization of materials from a solid surface by bombardment with high-velocity ions of an inert gas
- The target material and the substrate are placed in a vacuum chamber. A voltage is applied between them.
- Atoms and clusters are ejected from the surface of the target, and transported/deposited on the surface of the substrate.

- The process is performed under low pressure (below 10^{-3} mbar), as a higher pressure hinders the transportation of the sputtered material



Concept of “magnetron sputtering”: Density of plasma

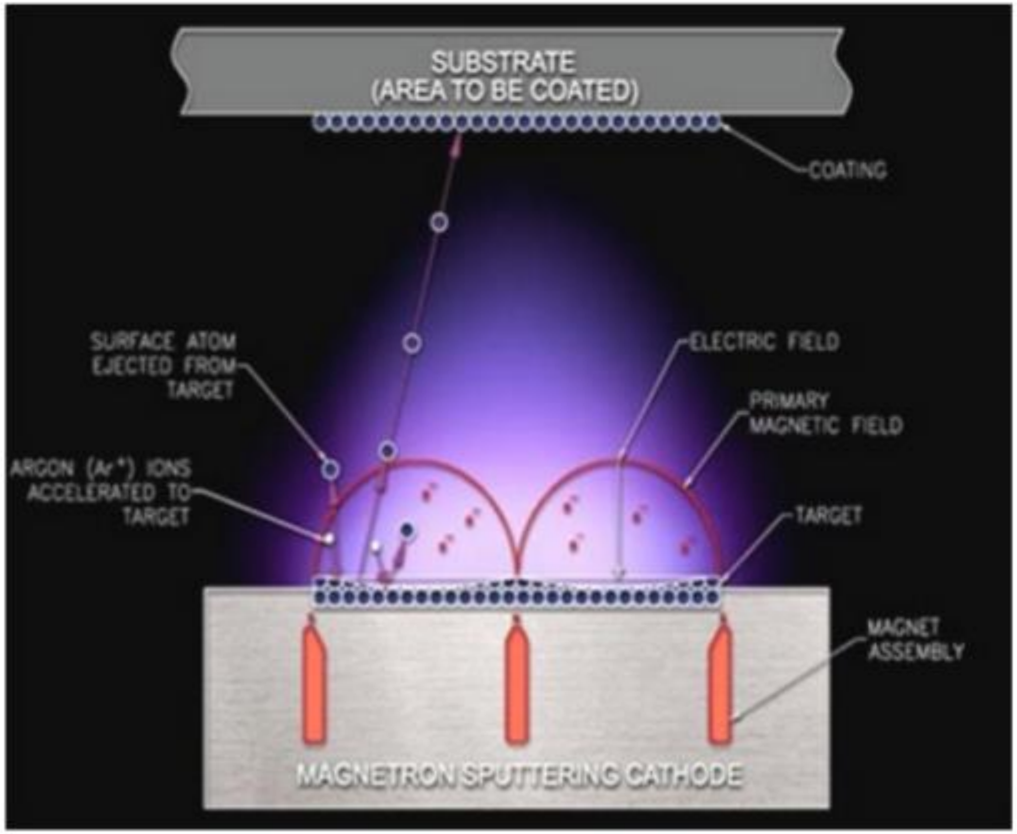




High density plasma

Magnetron Sputtering Principle

This technology uses powerful magnets to confine the "glow discharge" plasma to the region closest to the target plate. That vastly improves the deposition rate by maintaining a higher density of ions, which makes the electron/gas molecule collision process much more efficient.



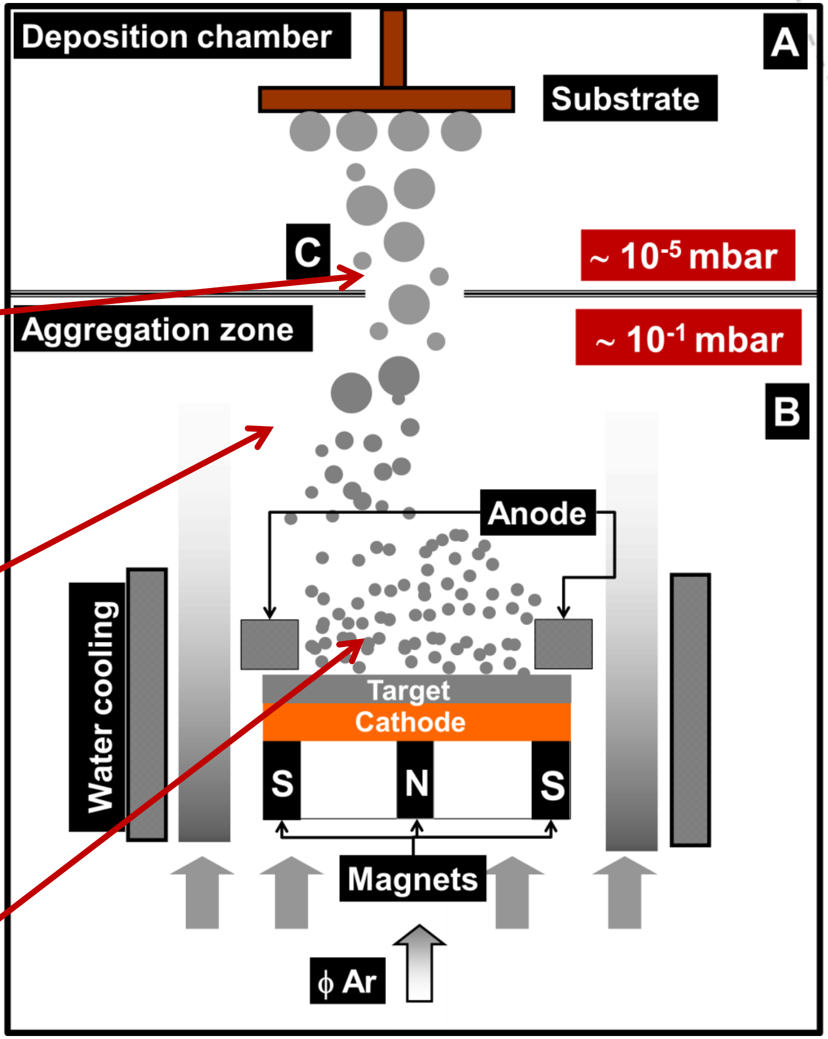
http://www.angstromsciences.com/technology/sputtering.htm

Concept of Sputtering (Nanoparticle deposition)

Aperture

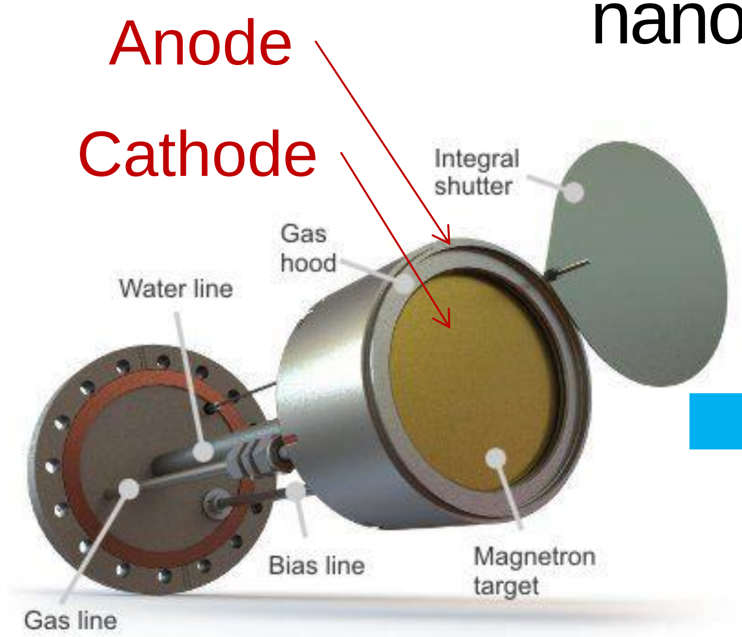
Aggregation zone: Nucleation and growth of NPs

Plasma zone

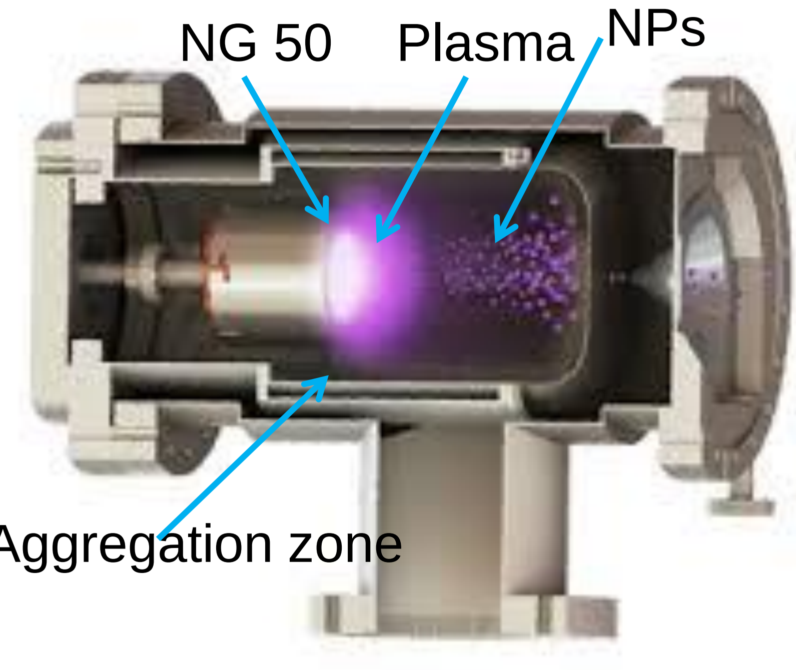


Particle pathway towards deposition chamber

Magnetron-sputtering cathode for nanoparticle generation



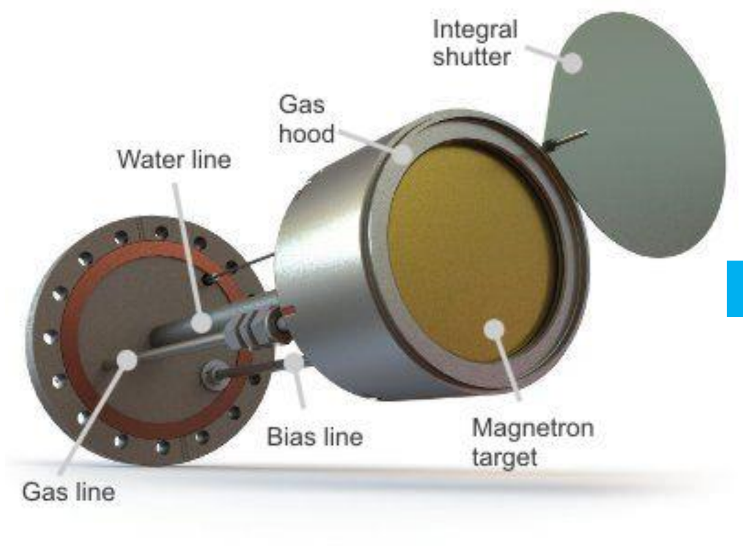
Conventional cathode (NG50)

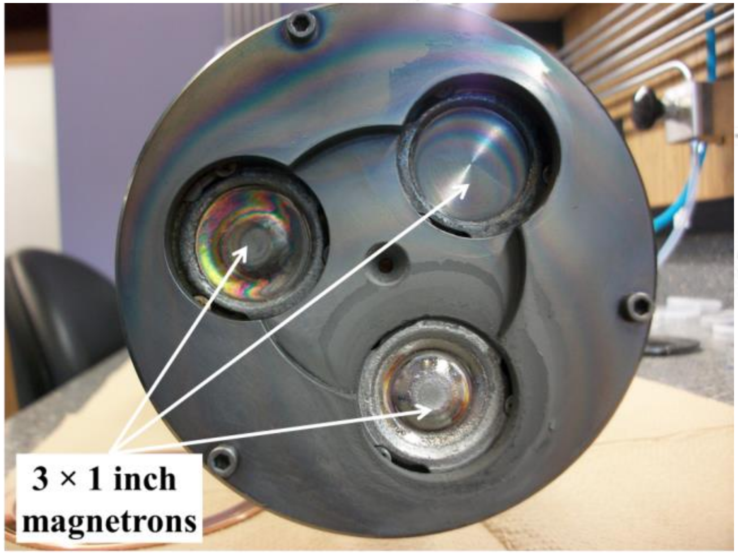


- Alloyed targets are needed to obtain multicomponent NPs,
- The composition of the target change with time:
  - The sputtering rate of the material is different
  - Segregation of materials can occur at the surface of the target during sputtering

What's new in the field?

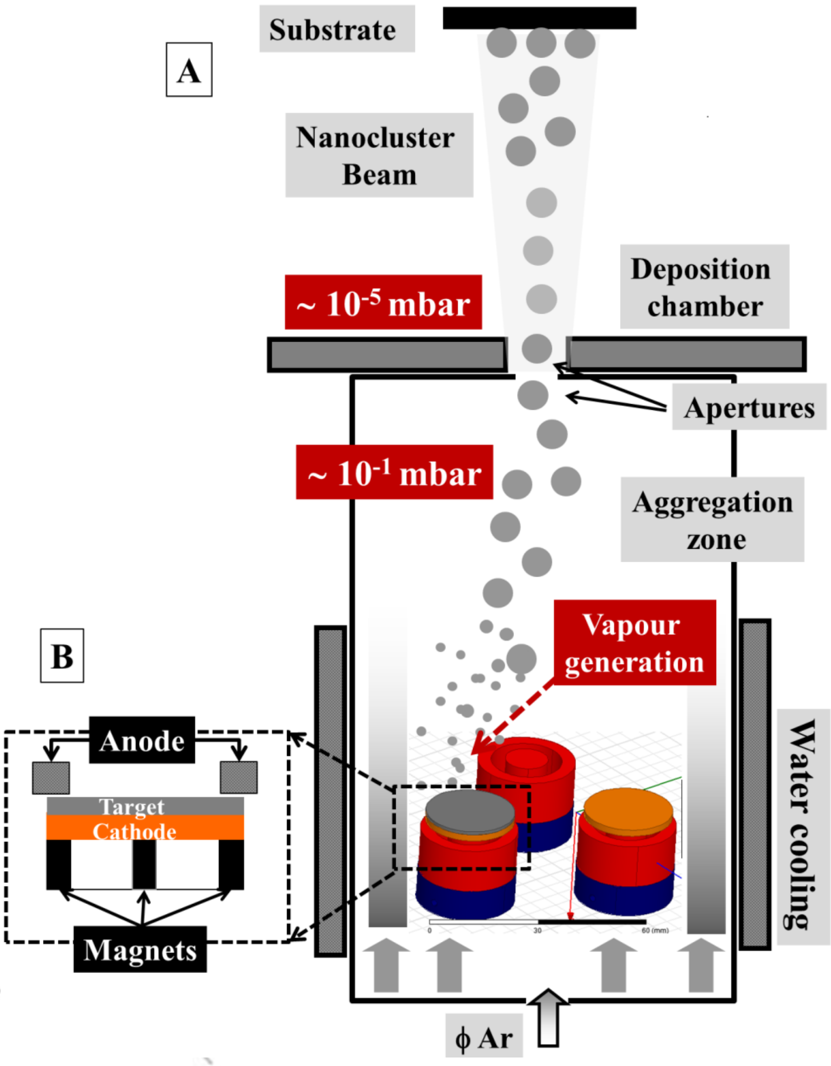
Modified magnetron-sputtering inert-gas-condensation system (*NG Trio Mantis*)





- ✓ Integration of 3 small cathodes in a single magnetron head
- ✓ Independent control
- ✓ Sputtering of up to 3 different materials at the same time

Sketch of the modified magnetron sputtering inert gas condensation system



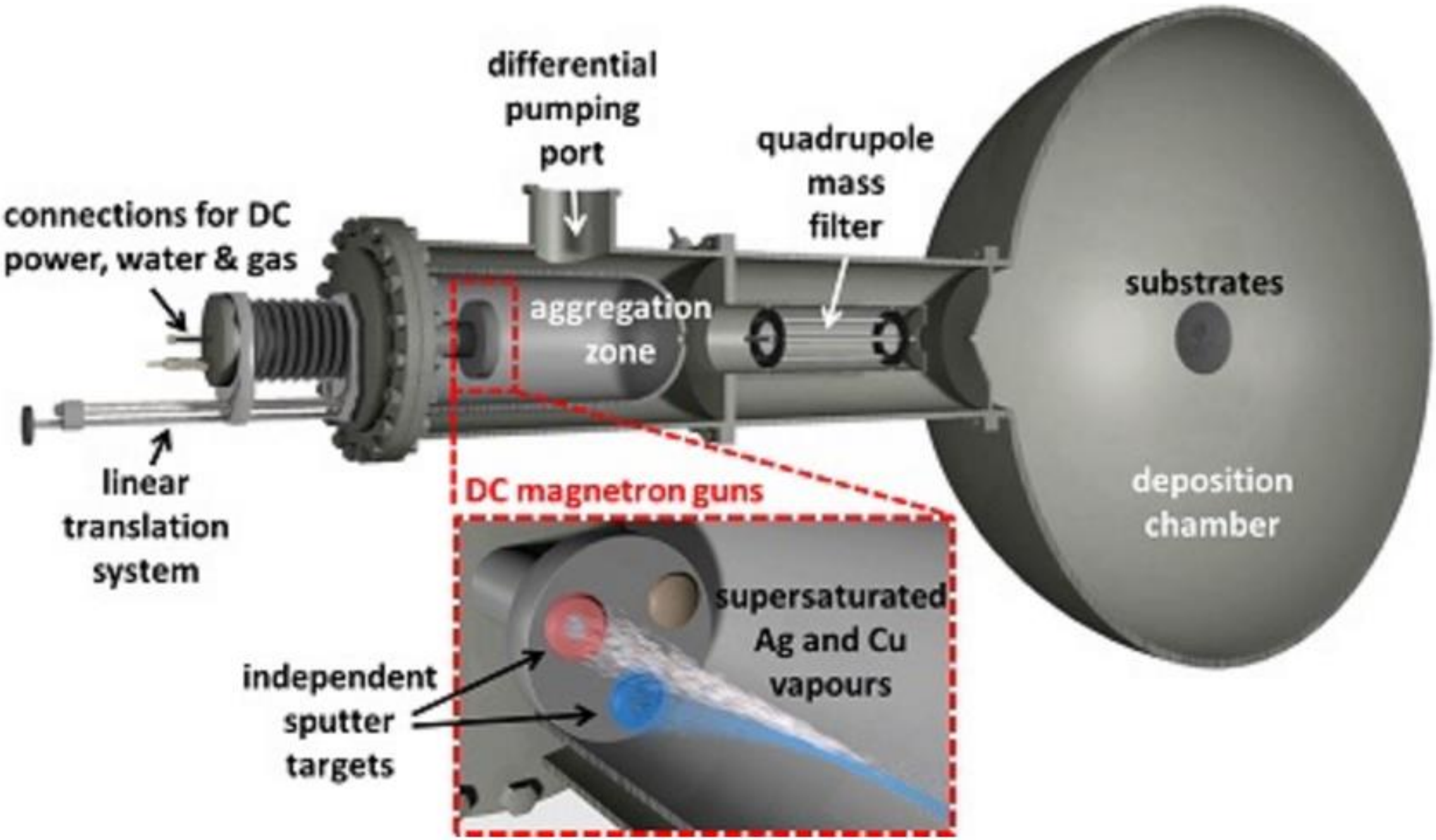
Controlled parameters:

- Independent power on the targets
- Aggregation zone length
- Working pressure

Main advantages:

- Multi-component nanoparticles
- Chemical composition control
- Reproducible processes

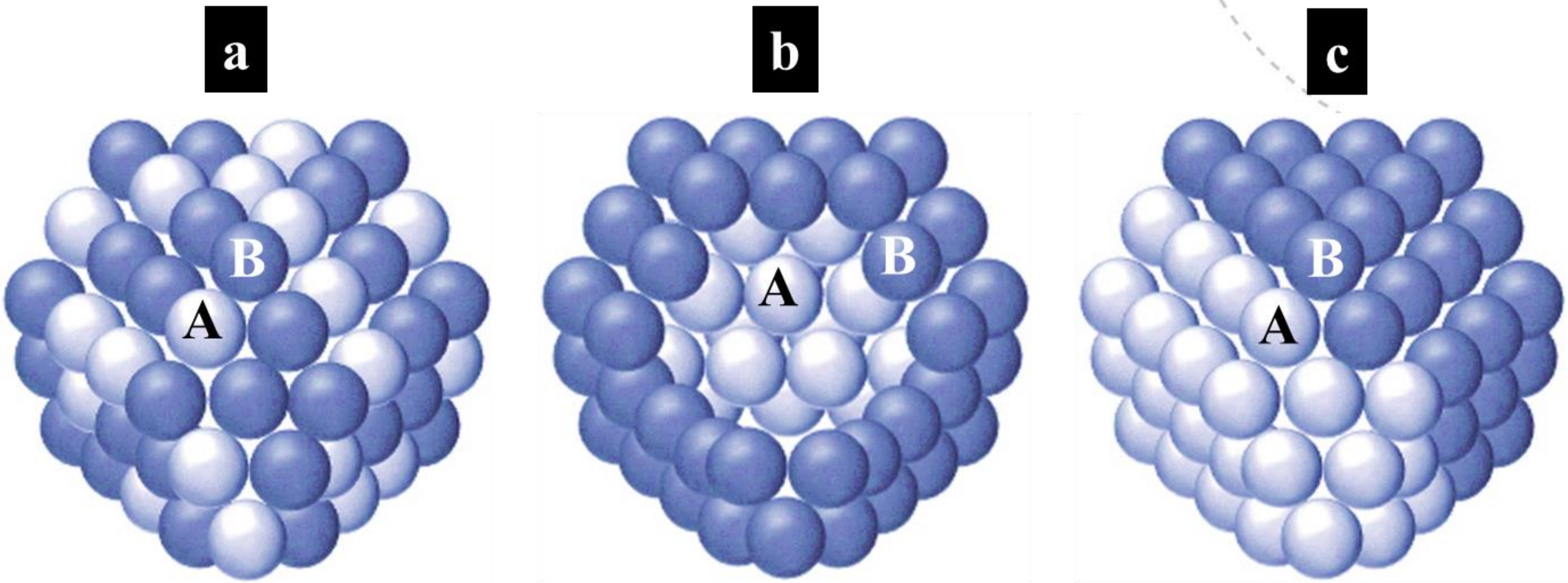
Simple configuration of the system (*NG Trio Mantis*)



Generating nanoparticles by magnetron sputtering based inert-gas-condensation

(Binary nanoparticles)

Schematic images of binary nanoparticles



Mixed structure **Core-shell structure** **Layered structure**

Factors influencing the formation of binary NPs by inert-gas-phase methods

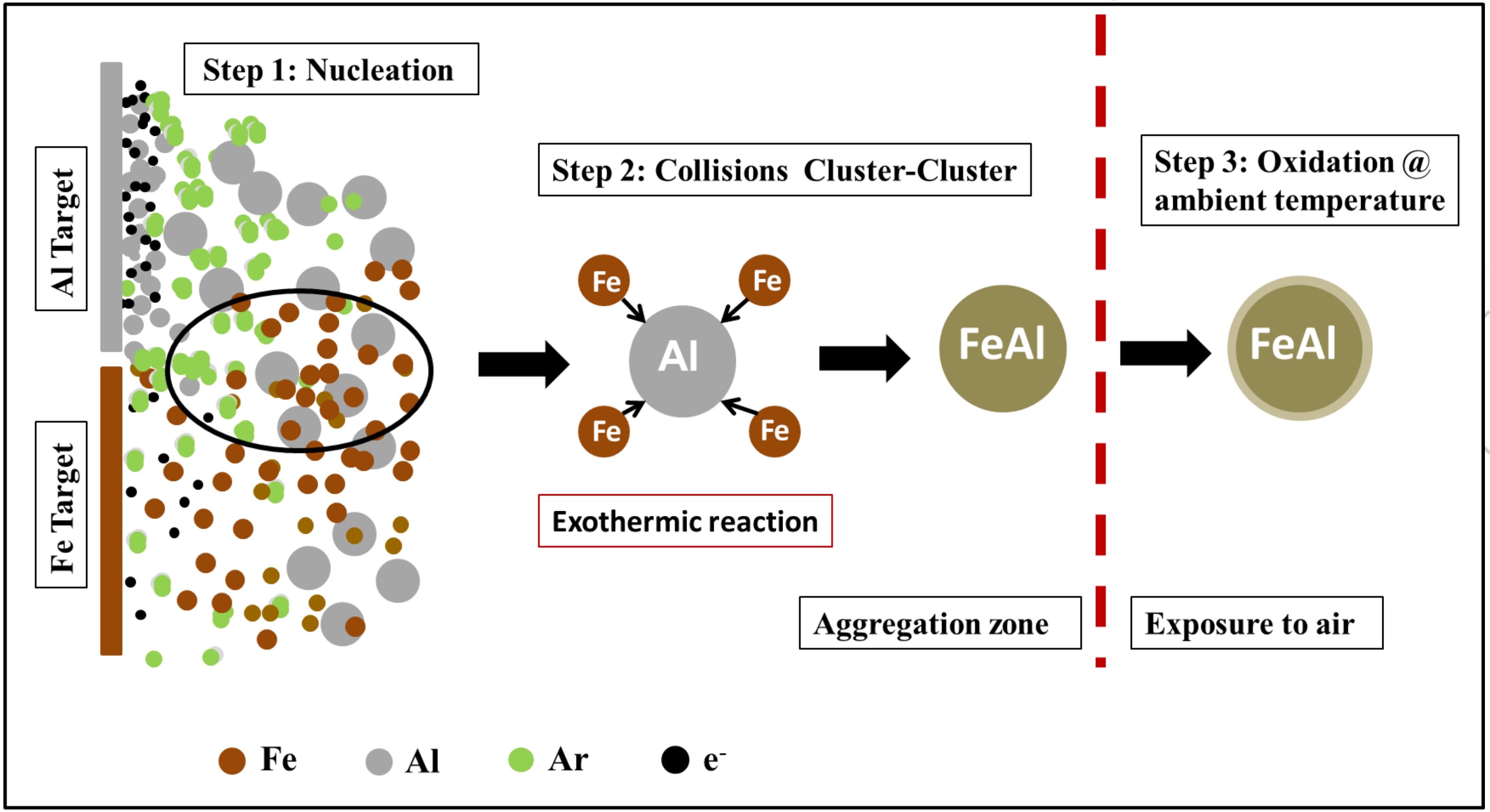
- **Bond strength:** For two different metals A and B, if the A-B bond is stronger than the A-A and B-B bonds, this will favour inter-mixing of elements.
- **Surface energies:** The material with the highest surface energy tends to occupy core positions.
- **Atomic radii**:
  - For immiscible materials, the element with the smallest atomic radius tends to occupy the core position.
  - For metals fully or partially miscible materials the formation of either a solid solution or a new phase can occur.
- **Electronegativity and charge transfer:** When the elements involved in a reaction have a large electronegative difference, the probability that they form an intermetallic compound instead of a solid solution is higher.

Example 1. Iron aluminide (FeAl) nanoparticles (partially Bulk-miscible materials)

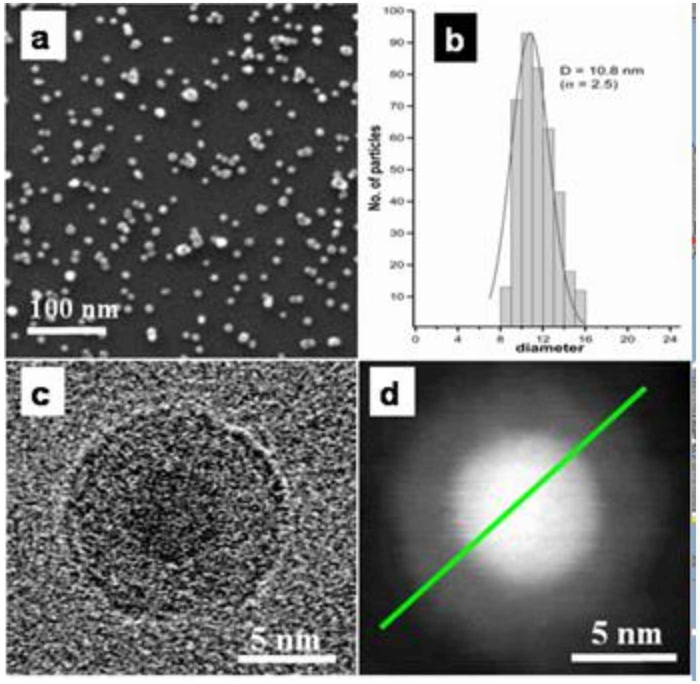
Materials and deposition parameters

- ✓ One inch Fe (99.9%) target
- ✓ One inch Al (99.9995%) target
- ✓ Ar flow rate in aggregation zone 80 sccm
- ✓ Working pressure at Aggregation zone 3.10^{-1} mbar
- ✓ Pressure at deposition chamber $8.4.10^{-4}$ mbar
- ✓ The aggregation zone length is set to 90 mm
- ✓ The substrate is rotated during deposition (Si (100))
- ✓ Al power (16W) > Fe power (11W)

Mechanism of formation of NPs



Results (1): Morphology of the NPs



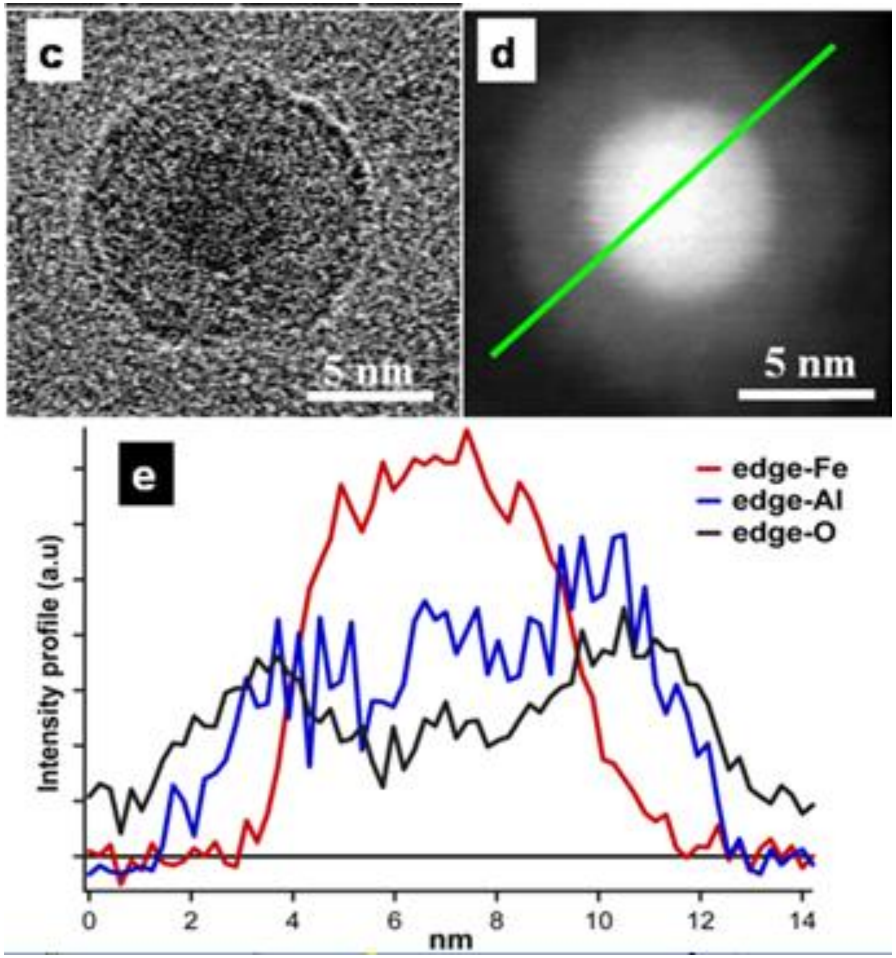
(a) SEM image of the as deposited NPs . The NPs are dispersed (no signs of aggregation)

(b) Size distribution of NPs showing an average diameter of 10.8 nm ± 2.5 nm.

(c) TEM micrograph and **(d)** STEM image of a representative NPs revealing a core-shell structure.

APL Mater. **2**, 116105 (2014); http://dx.doi.org/10.1063/1.4901345

Results (2): Chemical composition of the NPs



(e) EELS line profiles acquired along the representative NPs in **(d)** showing:

- Fe-$L_{2,3}$ edge at 707 eV
- Al-$L_{2,3}$ edge at 76 eV
- O-K edge at 532 eV

❖ The core shows high content of Fe

❖ The shell is composed mainly of Al and O.

APL Mater. **2**, 116105 (2014); http://dx.doi.org/10.1063/1.4901345

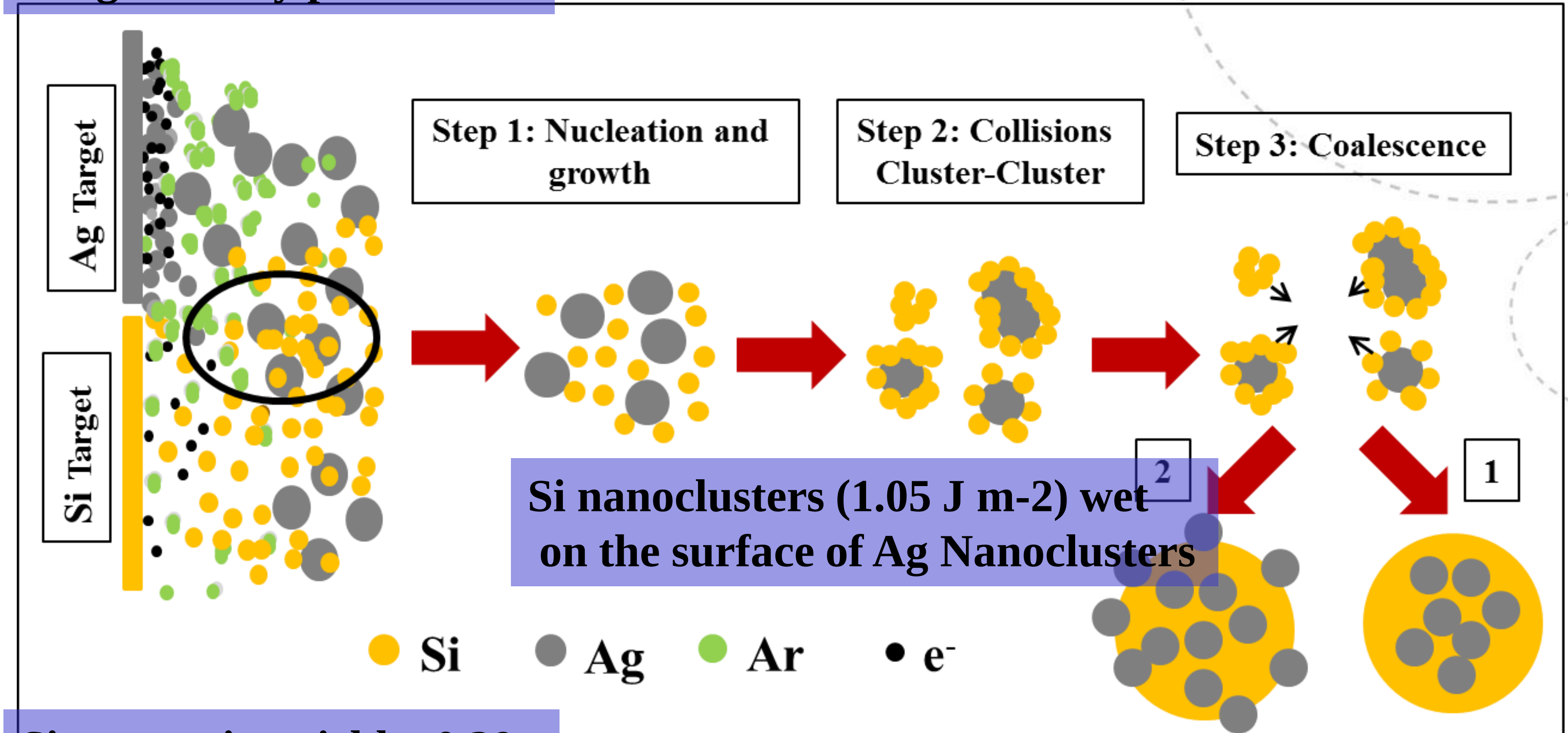
Example 2. Silicon-Silver (SiAg) nanoparticles (Bulk-immiscible materials)

Materials and deposition parameters

- ✓ One inch Si (99.9%) target
- ✓ One inch Ag (99.9995%) target
- ✓ Working pressure at Aggregation zone 3 10-1 mbar
- ✓ Pressure at deposition chamber 3.5 10-3 mbar
- ✓ The aggregation zone length is set to 90 mm
- ✓ The substrate is rotated during deposition (Si 100)
- ✓ Power on Si power 60 W
- ✓ Power on Ag power (4.7 W and 6.7W)

Mechanism of formation of NPs

Ag sputtering yield ~ 1.20 = high density plasma

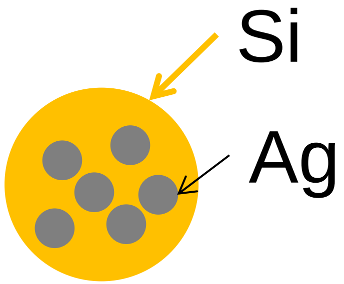


Si nanoclusters (1.05 J m-2) wet on the surface of Ag Nanoclusters

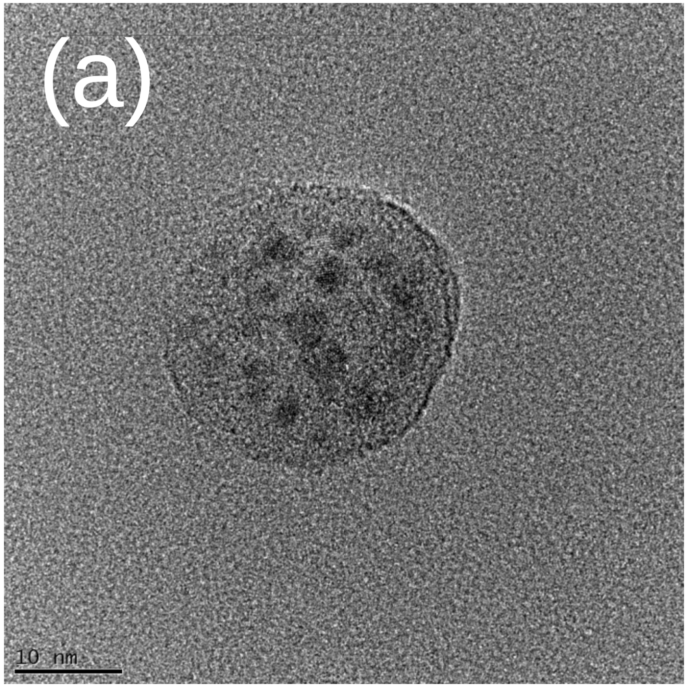
(6.7 W) **(4.7 W)**

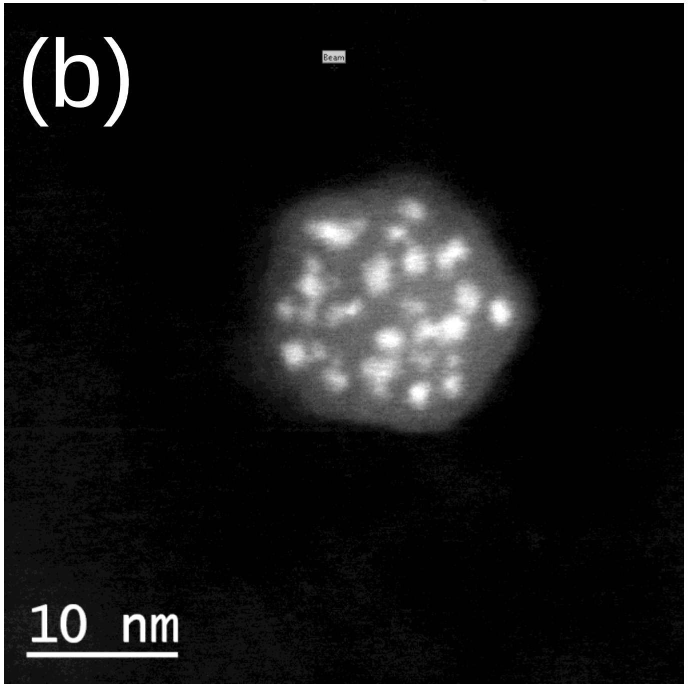
Si sputtering yield ~ 0.29 = Low density plasma

"Designing hybrid NPs" IOP Concise physics (2015)



Ag@Si

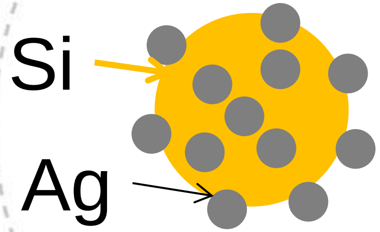


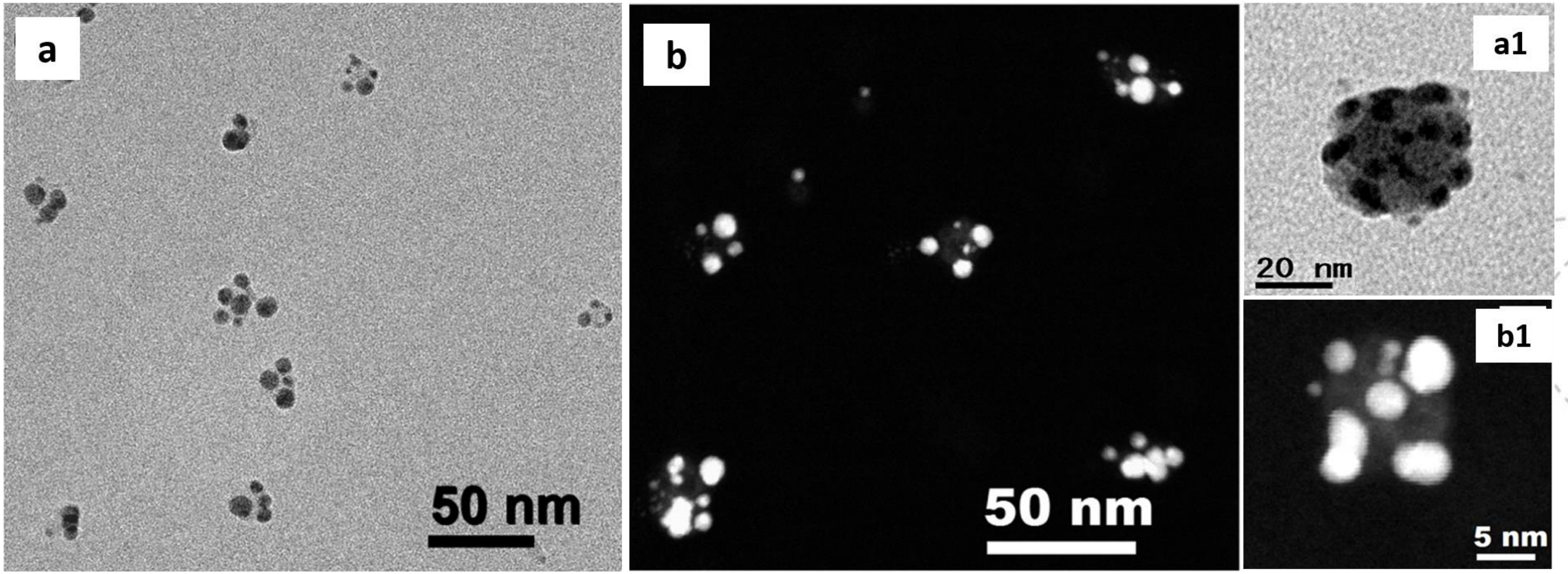


(a) High magnification TEM image

(b) High magnification STEM image

Ag@Si@Ag





(a) Low magnification TEM image
(a1) High magnification TEM image
(b) Low magnification STEM image
(b1) High magnification STEM image

Fundamental parameters controlling the size, morphology and yield of the nanoclusters in gas condensation method:

- Rate of atom supply to the region of supersaturation where condensation occurs (*plasma density*)
- Rate of energy removal from the hot atoms via the condensing gas medium (*flux of Ar gas*)
- Rate of removal of clusters once nucleated from the supersaturated region (*pressure differential*)

Technical acrynoms

NPs: Nanoparticles
TEM: Transmission Electron Microscope
HRTEM: High Resolution Transmission Electron Microscope
STEM: Scanning Transmission Electron Microscope
SEM: Scanning Electron Spectroscopy
EELS: Electron Energy Loss Spectroscopy
XPS; X-ray Photoelectron Spectroscopy
PE-CVD: Plasma Enhanced Chemical Vapour Deposition
PLD. Pulsed Laser Deposition
FSP: Flame Spray Pyrolysis
Sccm: standards cubic centimeters per minute
ALD: Atomic Layer Deposition
PVD: Physical Vapour Deposition
MBE: Molecular Beam Epitaxy

Recommended bibliography

Hao Zeng and Shouheng Sun, Adv. Funct. Mater. 2008, 18, 391–400 DOI: 10.1002/adfm.200701211
“Syntheses, Properties, and Potential Applications of Multicomponent Magnetic Nanoparticles”

Next lecture

Characterization of nanomaterials
TEM, SEM, XPS