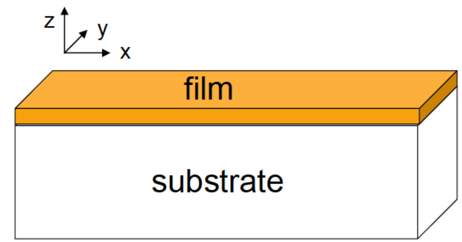
Surfaces and Films CHEM-E5150
Surface modification and coating

Jari Koskinen

Aalto-yliopisto
Kemian tekniikan korkeakoulu

Coatings and films terminology

- Film or coating is material which is restricted in one dimension
- Substrate is solid material supporting the film
- Distance from surface/Thickness
  - Surface atoms, thin film - Atomic level:
    - 2 – 5 atom layers on the surface (≈ 0.2 – 0.5 nm)
    - over 10 atomic layers (≈ 1 nm) is bulk
  - Thin films technically
    - 1nm – 10 μm
    - Needed layer thickness, which is needed to:
      - protect substrate
      - Wanted functionality of the coating
  - Coatings, thick films > 10 μm

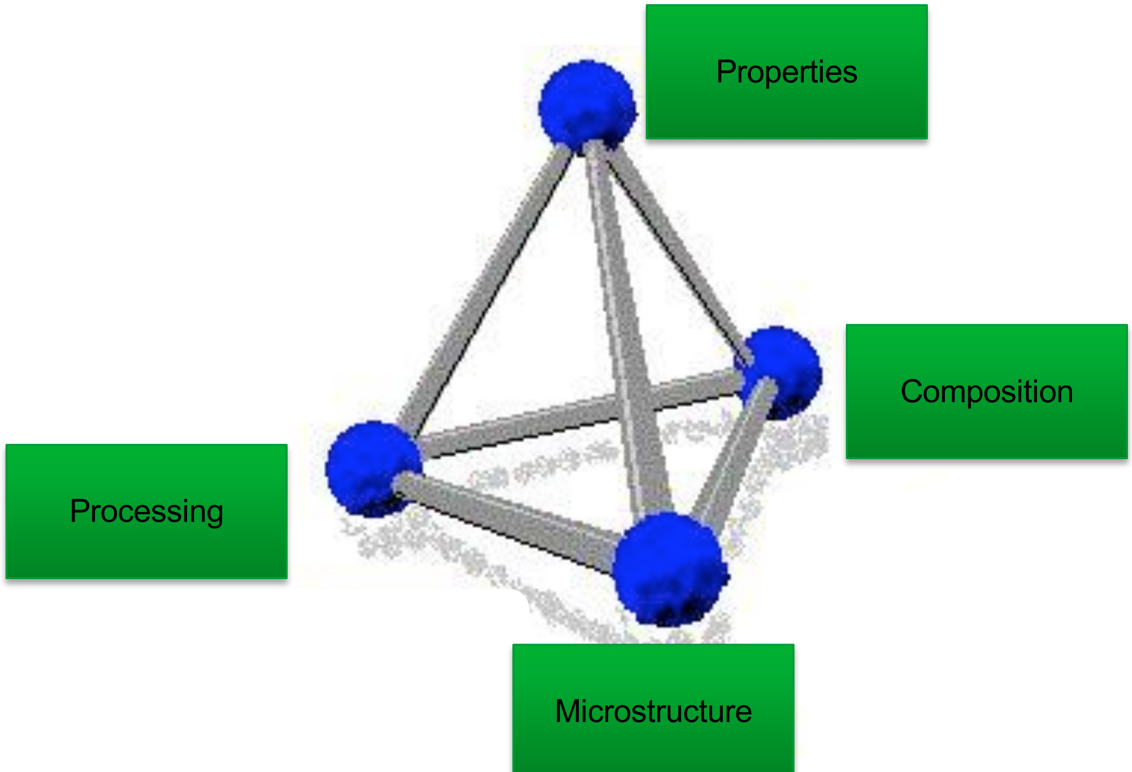


Mikko Ritala Thin Films

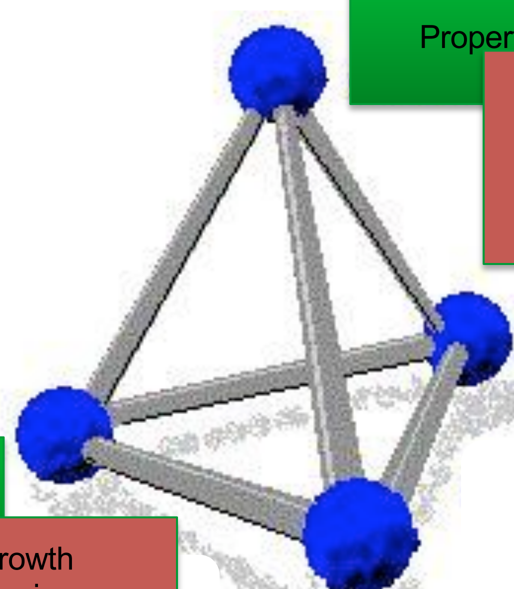
Motivations - why thin films?

- Interaction of solid material with surrounding often through surface
- Modification of surface ➡️ material properties
- Market of thin films and coatings
  - volume about 25 G€ in UK 2005
    - about 1% of GNP
  - common in all areas of industry
    - electronics
    - transport
    - energy
    - building

Materials Science tetra



Materials Science and Thin Films tetra



Properties

Protection
Transport
Stability
Functionallty

Composition

Depth distribution
Precipitation
Adsorption

Processing

Thin film growth
Post processing

Microstructure

Microstructure
Crystallinity/amorphous
Defects
interfaces

Processing for surface engineering

Handbook of
Physical Vapor
Deposition (PVD)
Processing – Mattox
2nd edition 2010

Table 1-1. Processes for Surface Engineering

Atomistic/Moleular Deposition

Electrolytic Environment
- Electroplating
- Electroless plating
- Displacement plating
- Electrophoretic deposition

Vacuum Environment
- Vacuum evaporation
- Ion beam sputter deposition
- Ion beam assisted deposition (IBAD)
- Laser vaporization
- Hot-wire and low pressure CVD
- Jet vapor deposition
- Ionized cluster beam deposition

Plasma Environment
- Sputter deposition
- Arc vaporization
- Ion Plating
- Plasma enhanced (PE)CVD
- Plasma polymerization

Chemical Vapor Environment
- Chemical vapor deposition (CVD)
- Pack cementation

Chemical Solution
- Spray pyrolysis
- Chemical reduction

Particulate Deposition

Thermal Spray
- Flame Spray
- Arc-wire spray
- Plasma spraying
- D-gun
- High-vel-oxygen-fuel (HVOF)

Impact Plating

Bulk Coatings

Wetting Processes
- Dip coating
- Spin coating
- Painting

Fusion Coatings
- Thick films
- Enameling
- Sol-gel coatings
- Weld overlay

Solid Coating
- Cladding
- Gilding

Surface Modification

Chemical Conversion
- Wet chemical solution (dispersion & layered)
- Gaseous (thermal)
- Plasma (thermal)

Electrolytic Environment
- Anodizing
- Ion substitution

Mechanical
- Shot peening
- Work hardening

Thermal Treatment
- Thermal stressing

Ion Implantation
- Ion beam
- Plasma immersion ion implantation

Roughening and Smoothing
- Chemical
- Mechanical
- Chemical-mechanical polishing
- Sputter texturing

Enrichment and Depletion
- Thermal
- Chemical

Atomistic/Moleular Deposition

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Handbook of Physical Vapor Deposition (PVD) Processing – Mattox 2nd edition 2010

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Chemical

Coating methods in the next slides

- Physical Vapor Deposition including evaporation and sputtering.
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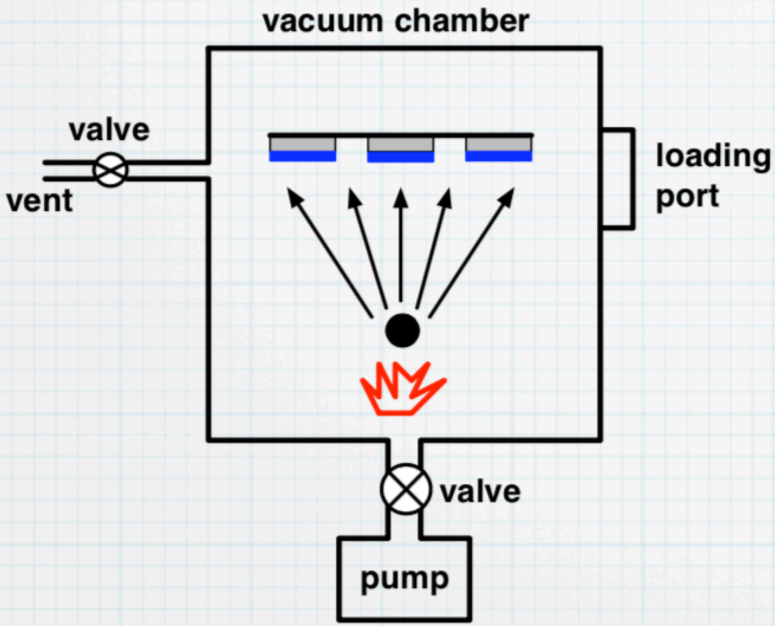
PVD_Vacuum evaporation



http://tuttle.merc.iastate.edu/ee432/topics/thin_films/evaporation.pdf

Basic vacuum chamber ($P \approx 10^{-6}$ Torr; $\lambda >>$ chamber dimensions.)

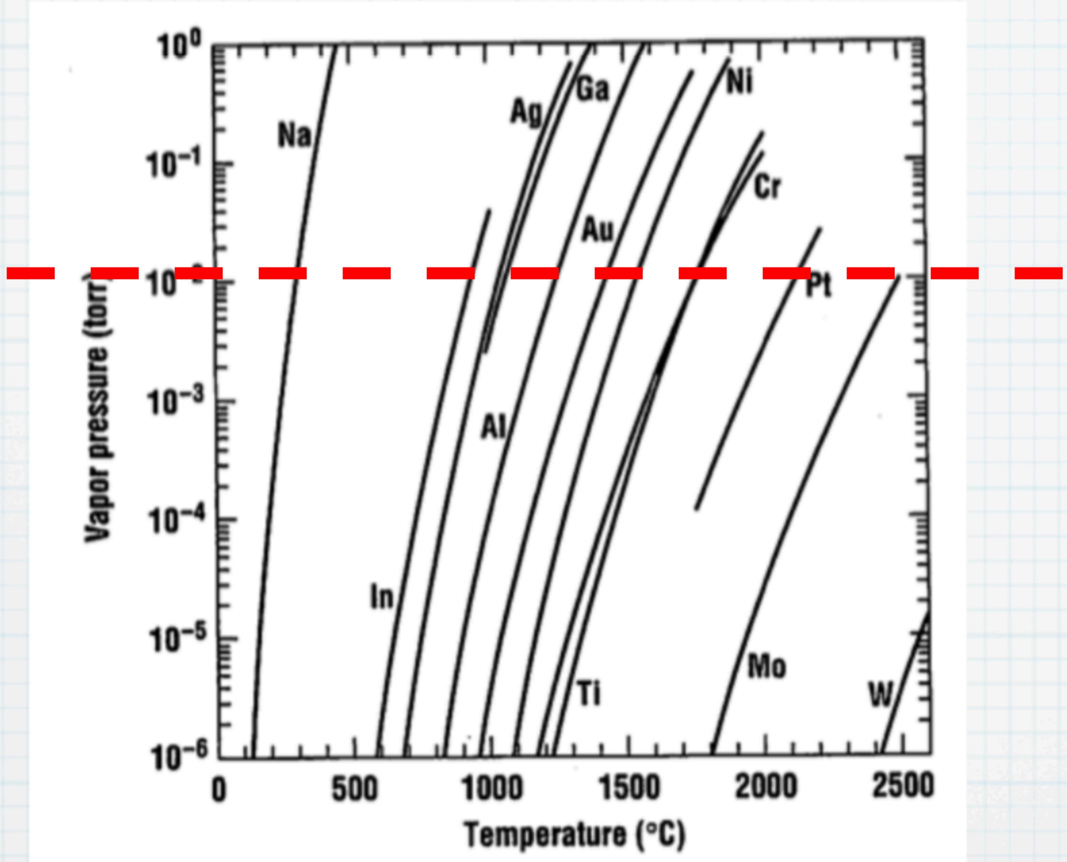
Substrates are loaded, facing down.

A source of the metal to be evaporated is located below the wafers.

The source is heated to the point where it will evaporate.

The vapor condenses on the cool substrates (and chamber walls).

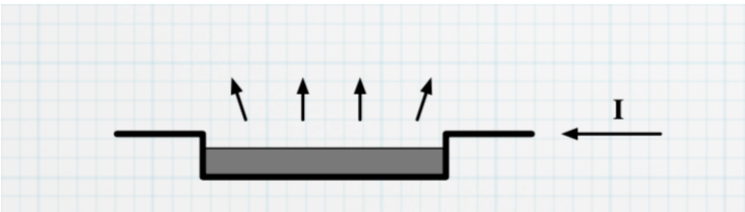
Vapor pressure curves



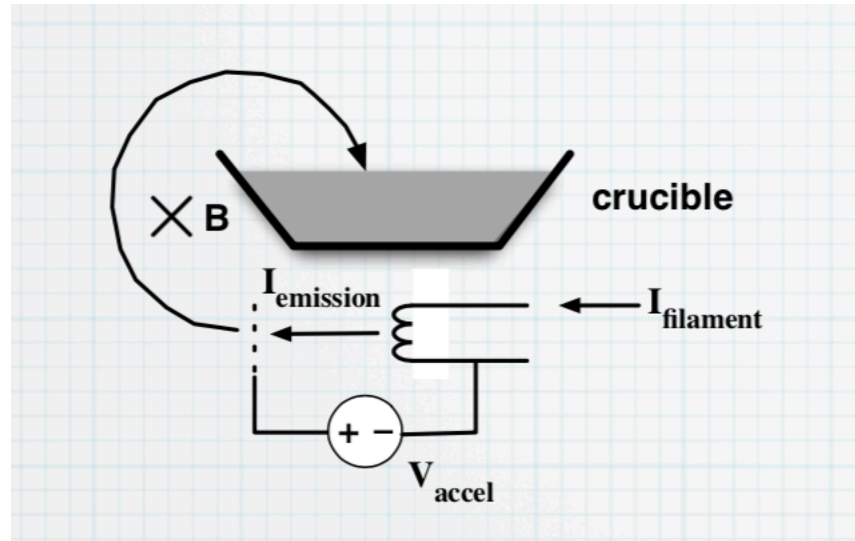
School of Chemical Technology

http://tuttle.merc.iastate.edu/ee432/topics/thin_films/evaporation.pdf

PVD_Vacuum evaporation
Vapous source



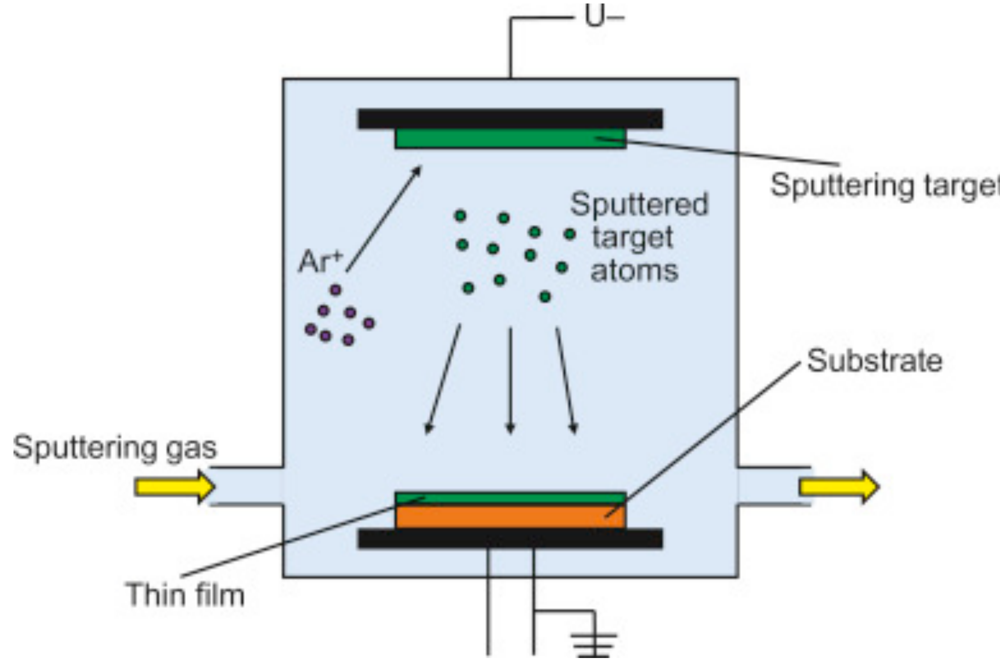
Resistive heating

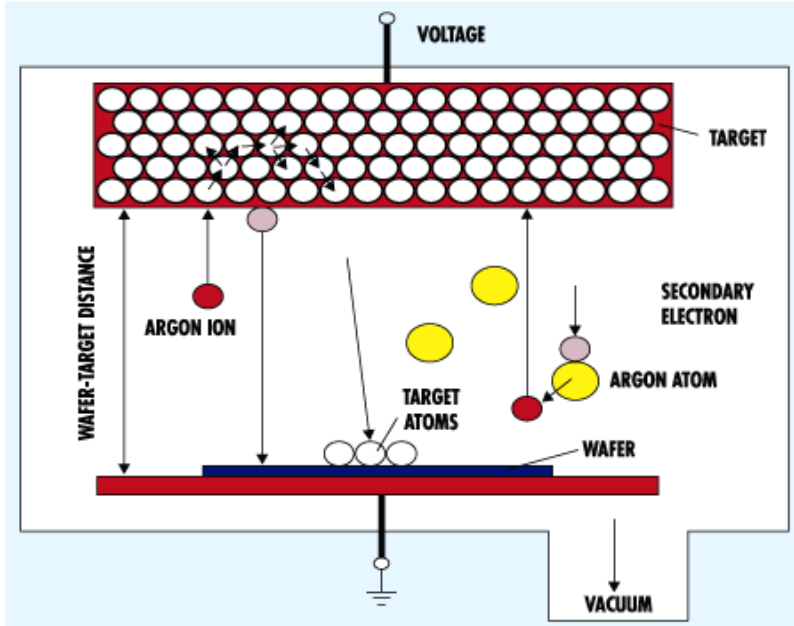


Electron beam heating

http://tuttle.merc.iastate.edu/ee432/topics/thin_films/evaporation.pdf

Physical Vapor Deposition PVD. Sputtering





- Plasma is needed to make the gas conductive, and generated ions can then be accelerated to strike the target.
- Higher pressures than evaporation: 1-100 mTorr.
- Better at depositing alloys and compounds than evaporation.
- The plasma contains ≈ equal numbers of positive argon ions and electrons as well as neutral argon atoms. Typically only <0.01% atoms are ionized!

Sputtering process

- Sputtering process can be run in DC or RF mode (insulator must be run in RF mode)
- Major process parameters:
  - Operation pressure (~1-100mTorr)
  - Power (few 100W)
  - For DC sputtering, voltage -2 to -5kV.
  - Additional substrate bias voltage.
  - Substrate temperature (20-700°C)

In addition to IC industry, a wide range of industrial products use sputtering: LCD, computer hard drives, hard coatings for tools, metals on plastics.

It is more widely used for industry than evaporator, partly because that, for evaporation:

- There are very few things (rate and substrate temperature) one can do to tailor film property.
- The step coverage is poor.
- It is not suitable for compound or alloy deposition.
- Considerable materials are deposited on chamber walls and wasted.

Targets for sputter deposition.

Advantages/disadvantages

Advantages:

- Able to deposit a wide variety of metals, insulators, alloys and composites.
- Replication of target composition in the deposited films.
- Capable of in-situ cleaning prior to film deposition by reversing the potential on the electrodes .
- Better film quality and step coverage than evaporation.
- This is partly because adatoms are more energetic, and film is 'densified' by in-situ ion bombardment, and it is easier to heat up to high T than evaporation that is in vacuum.
- More reproducible deposition control – same deposition rate for same process parameters (not true for evaporation), so easy film thickness control via time.
- Can use large area targets for uniform thickness over large substrates.
- Sufficient target material for many depositions.
- No x-ray damage.

Disadvantages:

- Substrate damage due to ion bombardment or UV generated by plasma.
- Higher pressures 1 –100 mtorr ($< 10^{-5}$ torr in evaporation), more contaminations unless using ultra clean gasses and ultra clean targets.
- Deposition rate of some materials quite low.
- Some materials (e.g., organics) degrade due to ionic bombardment.
- Most of the energy incident on the target becomes heat, which must be removed.

Comparison Sputtering/evaporation

EVAPORATION	SPUTTERING
low energy atoms	higher energy atoms
high vacuum path • few collisions • line of sight deposition • little gas in film	low vacuum, plasma path • many collisions • less line of sight deposition • gas in film
larger grain size	smaller grain size
fewer grain orientations	many grain orientations
poorer adhesion	better adhesion

Coating methods in the next slides

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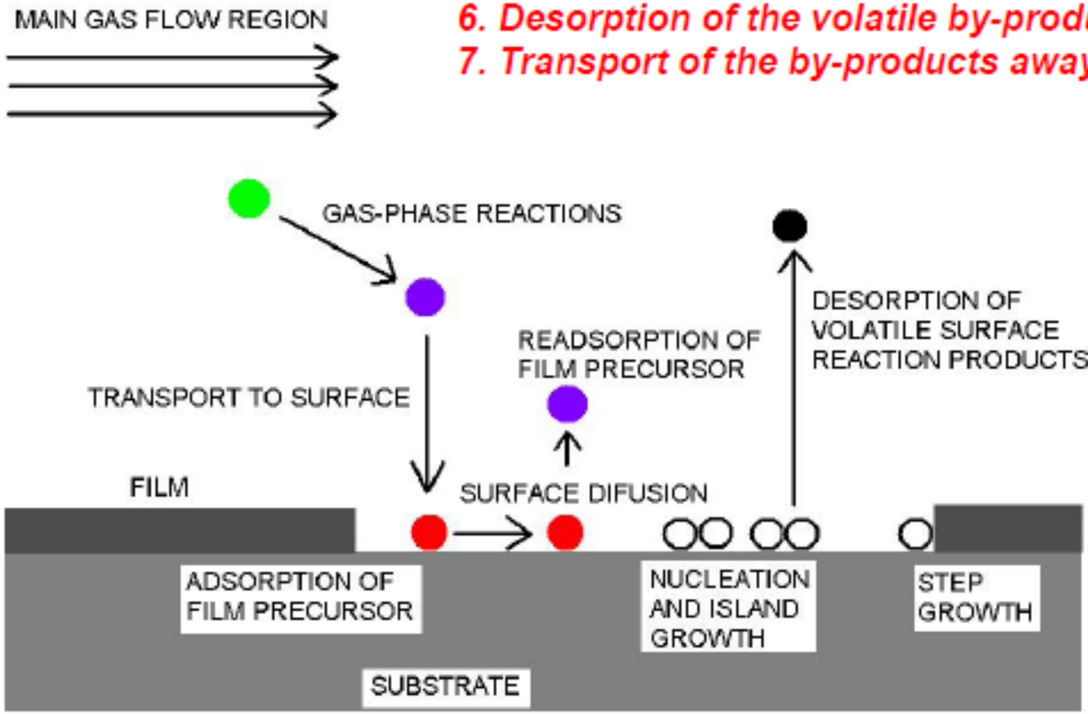
CVD – Chemical Vapor Deposition

The fundamental sequential steps of CVD process:

1. *Transport of reactants to the reaction zone.*
2. *Chemical reactions in the gas phase.*
3. *Transport of reactants and their products to the substrate.*
4. *Adsorption and diffusion on the substrate surface.*
5. *Heterogeneous reactions catalyzed by the surface leading to film formation.*
6. *Desorption of the volatile by-products of surface reactions.*
7. *Transport of the by-products away from the reaction zone.*



www.ttu.ee › mtx9010 › Korgtehnoloogia_Deposition_methods

CVD – Chemical Vapor Deposition

CVD is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomically on a suitable placed substrate.

Thermal CVD – heat energy for activation of the required gas and gas-solid phase reactions.

Plasma-enhanced CVD – plasma activation of the chemical species

1. APCVD – atmospheric pressure CVD
2. LPCVD – low pressure CVD
3. MOCVD – metalorganic CVD
4. LECVD – laser-enhanced CVD
5. PECVD (PACVD) – plasma-enhanced (assisted) CVD

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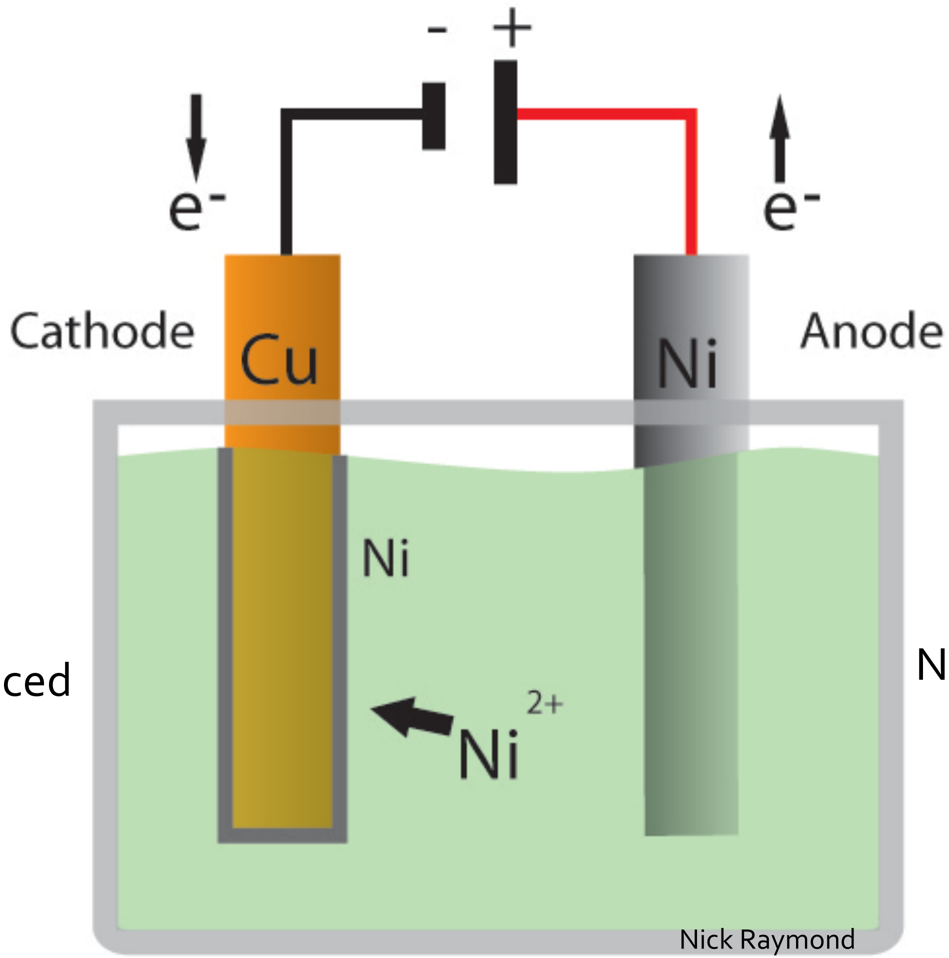
Electro plating

Copper Cathode is reduced (accepts electrons)



Nickel Anode is oxidized (gives us electrons)

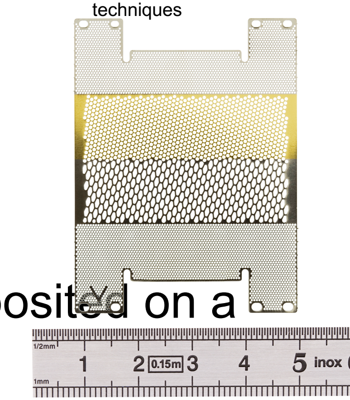
Ni^{2+} ions within solution become attracted to Copper cathode

www.santarosa.edu › PROJECTS › Electroplating Powerpoint

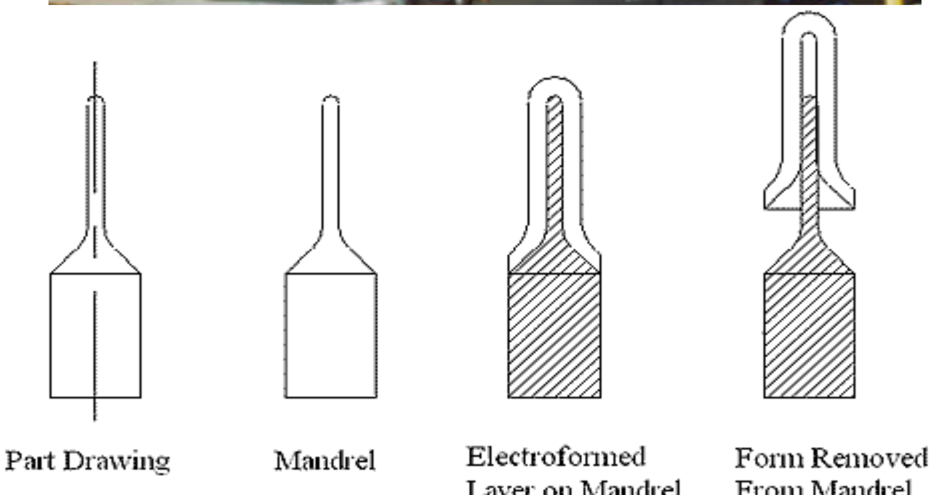
Electroless Plating and Electroforming

- Electroless Plating
  - Chemical Reaction
  - More Expensive $$
  - Uniform Thickness

https://www.vecofrance.fr/en/solutions-techniques



- Electroforming
  - Metal-fabrication
  - Metal electrodeposited on a mandrel



[Electroplating, Electroless Plating, and Electroforming - UNM ...](www.me.unm.edu › ME260_FALL2005 › Presentation_11_30_05)
www.me.unm.edu › ME260_FALL2005 › Presentation_11_30_05

Conversion Coatings

- Anodizing-
  - The workpiece is the anode in an electrolytic cell
- Coloring-
  - Alters color of metals, alloys, and ceramics
  - Conversion of surfaces into chemical compounds: oxides, chromates, and phosphates

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www.me.unm.edu › ME260_FALL2005 › Presentation_11_30_05

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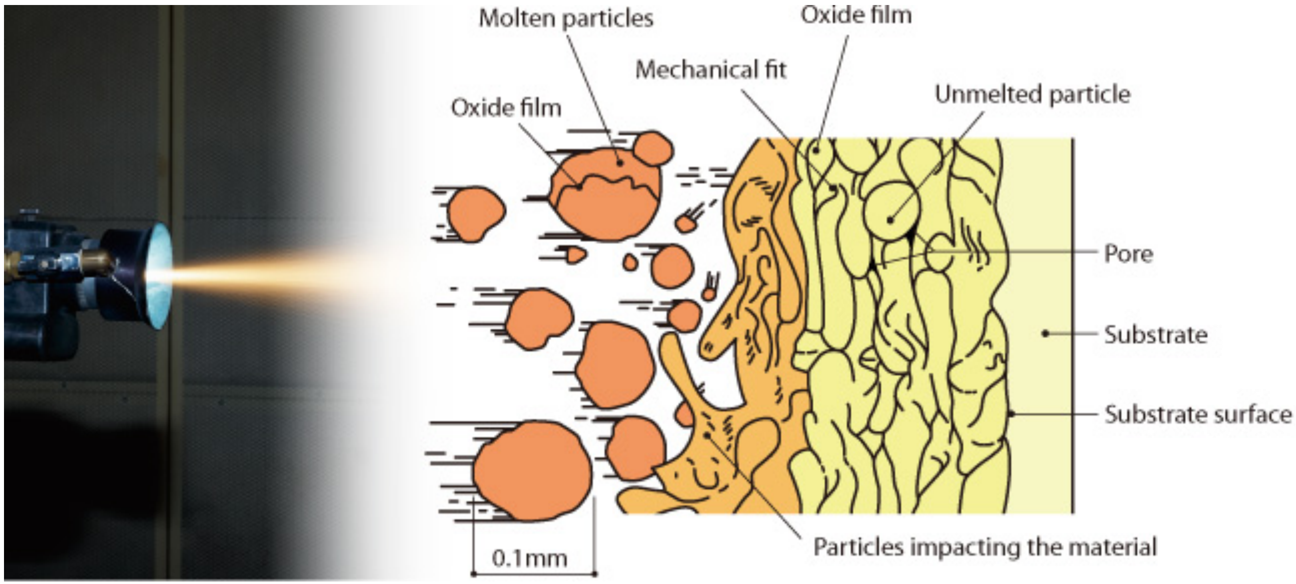
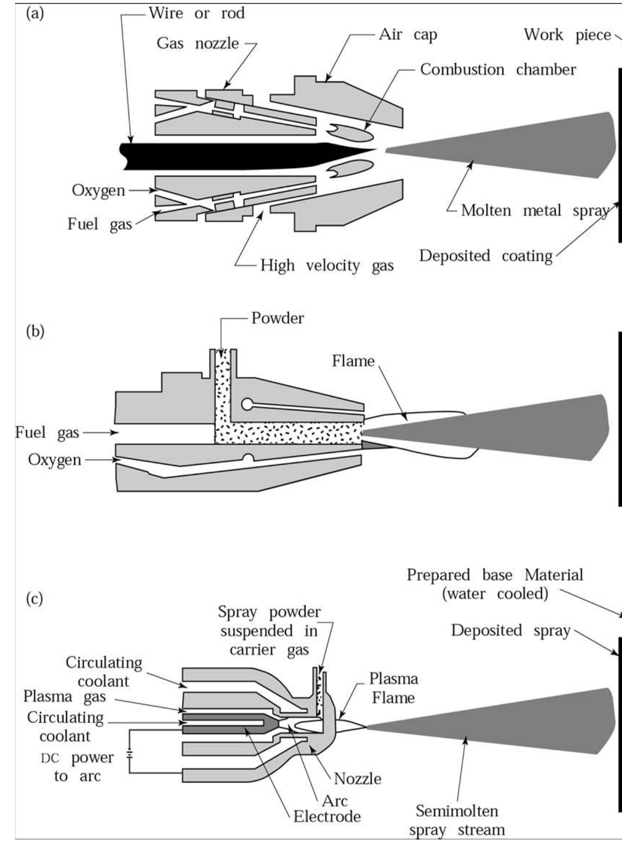
Thermal spray – coating growth from molten particles

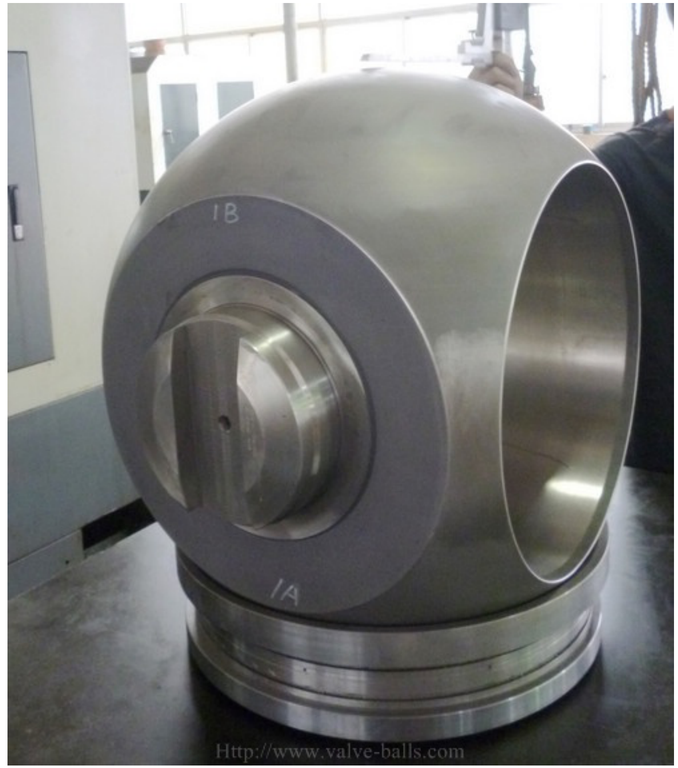


Thermal Spray

- Combustion Spraying
  - Thermal Wire Spray
  - Thermal Metal-Powder Spray
  - Plasma Spray



Thermal spray coating of ball valve

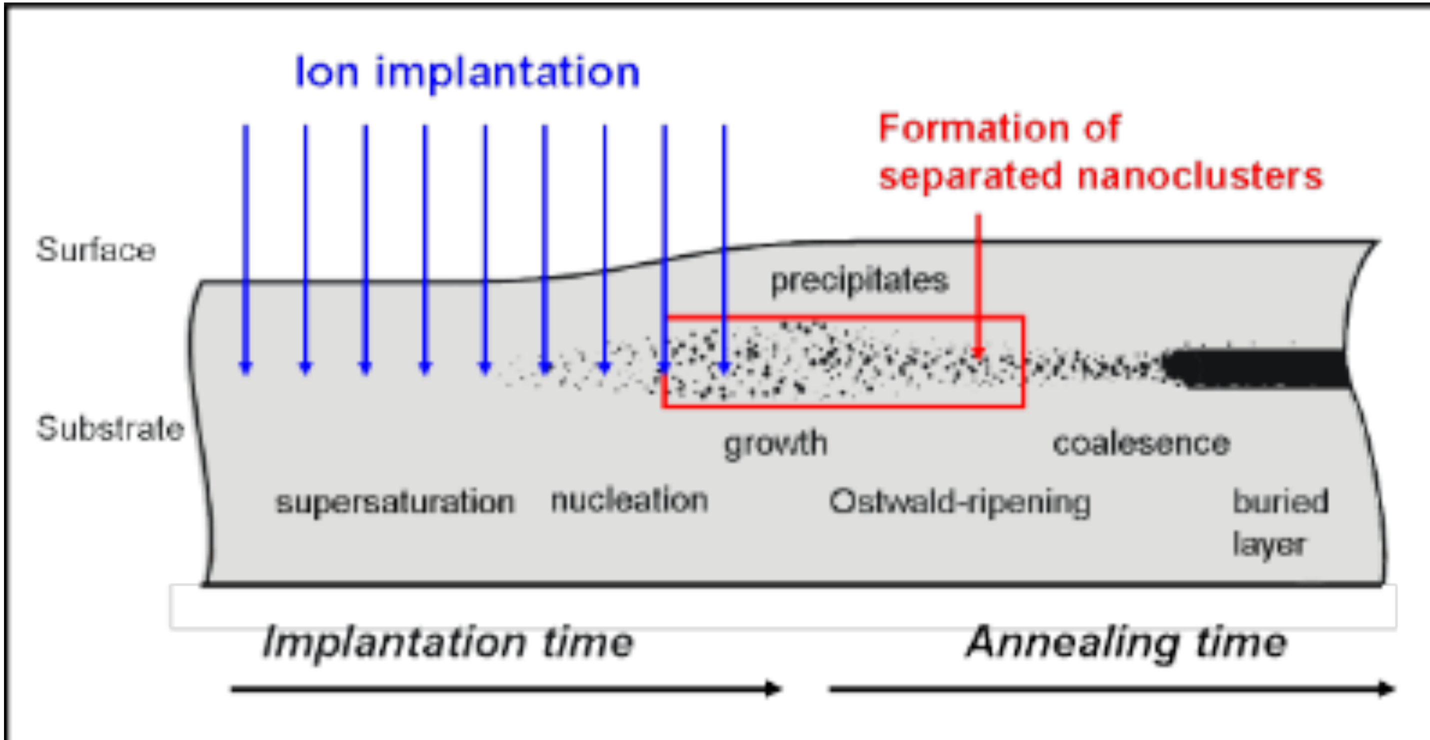


https://www.valve-balls.com/valve-balls/metal-seated-balls.html

Surface modification

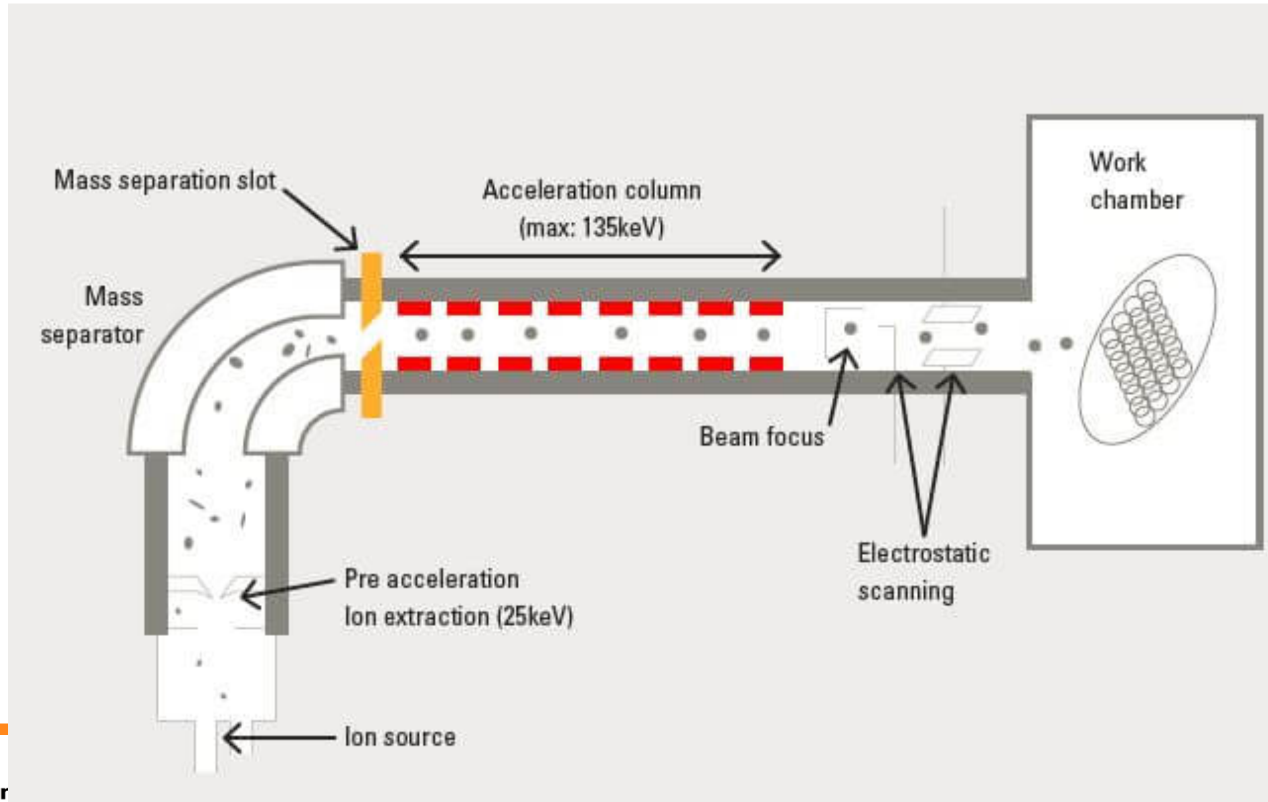
- Laser treatment
- Ion implantation

Ion implantation



https://www.hzdr.de/db/Cms?pOid=24316&pNid=0

Ion implanter



http://blog.bodycote.com/2017/08/02/what-is-ion-implantation/ion-implantation/

Ion implantation

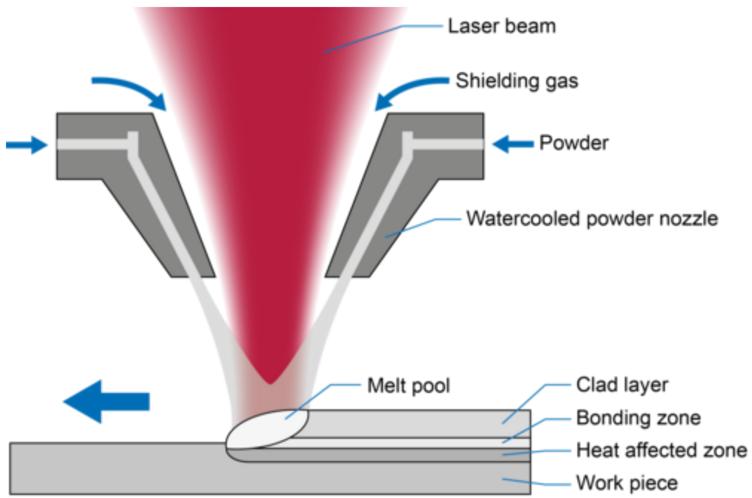
- Low process temperature
- Benefits from
  - controlled alloying (electrical properties)
  - Defects and intersitials (mechanical hardening)
- No (or minute) dimensional changes
- Expensive

Laser Treatments

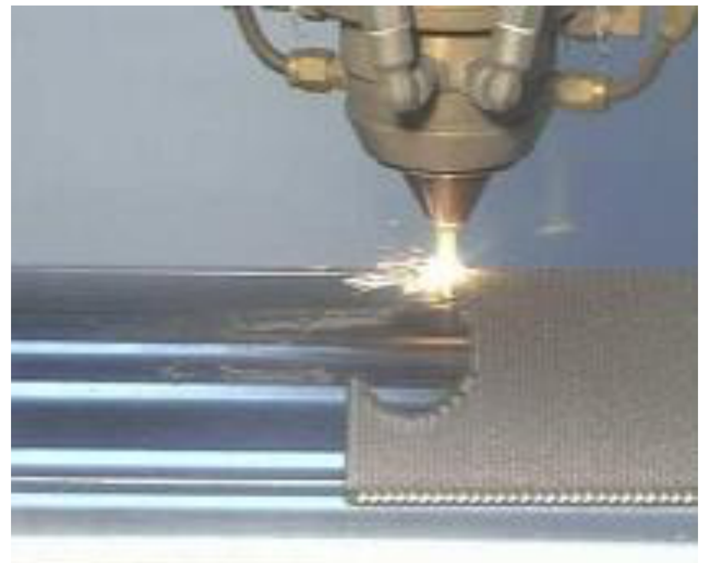
- Heating
- Melting
- Vaporization
- Peening

http://www.raymax.com.au/a/157.html

Laser gladding



https://www.laserline.com/en-int/laser-cladding/



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