Thin Film Review

Beijing 2007

Plating Vacuum Techniques Atmospheric Plasmas **More >>**

薄膜製程技術

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Advanced Researc
Preferences
Language tools

Fundamentals ○ Plasma engineering ● Techniques ○

The XIII Workshop on RF Superconductivity

@ Peking University

Deposition Techniques already applied in the past to Superconducting Resonator Prototyping:

- Pb and Pb-Sn plating - (Caltech, Karlsruhe, Weizmann, Argonne, ANU Stony Brook, Seattle, INFN-LNL)
- Nb Anodic oxidation - (Karlsruhe, Weizmann, Cornell, Jlab …)
- Cu Plating onto S-Steel cavities or cryogenic components
- Sputtering of Nb, NbN, NbTiN - (CERN, INFN-LNL, Saclay, ANU, CIAE)
- Vapour Diffusion of Sn into Nb - (Wuppertal)
- Thermal diffusion of N into Nb (CERN, Genoa)
- Cladding of Nb and Cu - (Argonne, KEK, Cornell, INFN-LNL, DESY)

and:

- Plasma Spray of Cu onto Nb resonators - (Orsay)
- Electroforming of Cu cavities onto mandrels (Protvino, CERN)
- ECR Plasmas - (Jlab)
- Cathodic Arc Deposition of Nb - (Soltan Institute, UniRoma2)
- TiN coatings on Ceramic Windows - (DESY, KEK, Orsay, INFN-LNL)
- Hot-dip of Nb into liquid Sn - (INFN-LNL)
- Silanization of Vanadium - (INFN-LNL)
- Lead Deposition on photocathodes – (DESY, Soltan)

We need to establish a *Surface Finishing System*

since, the more time passes, the more

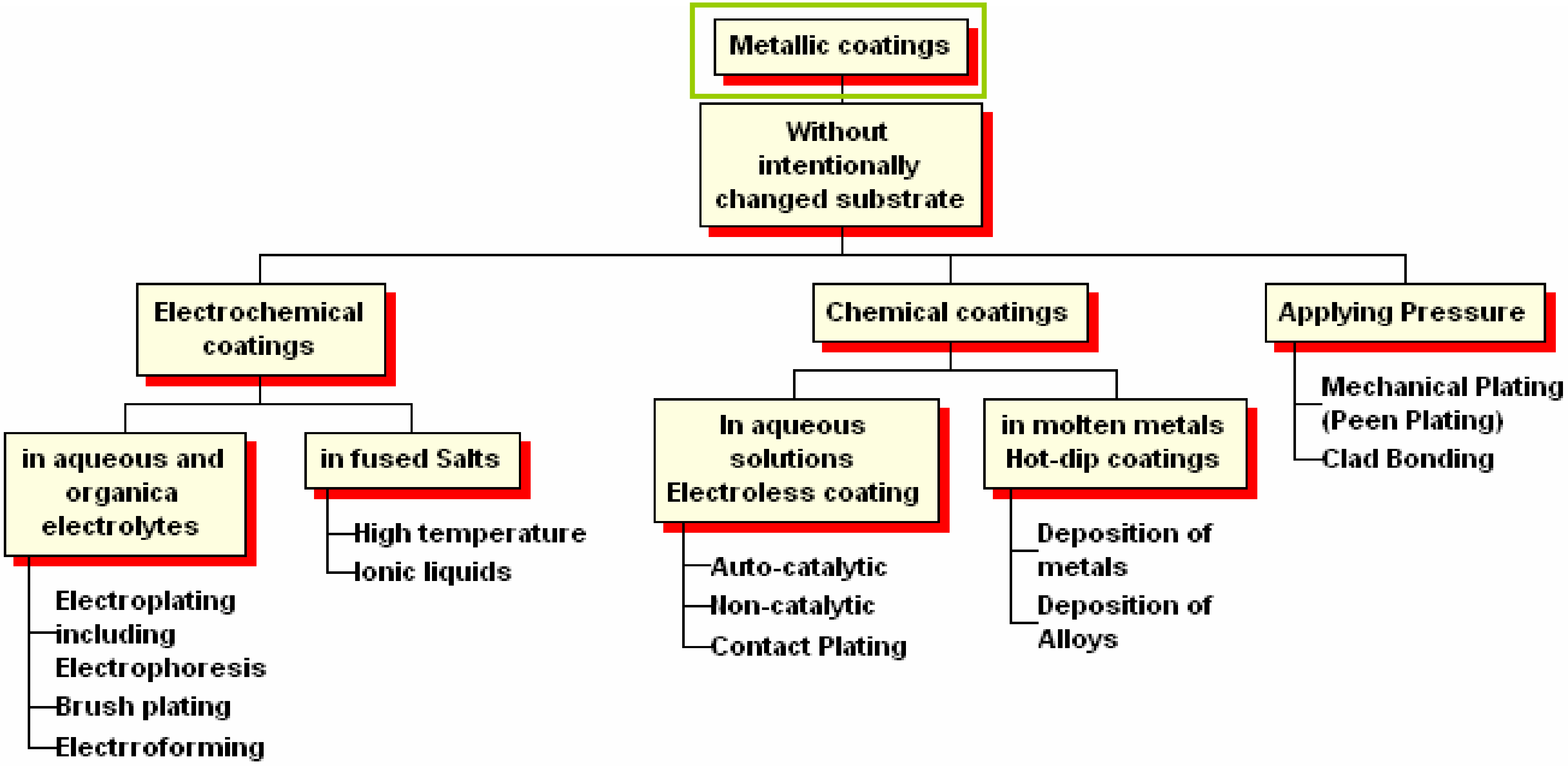
- Technology improves,
- Number of new results tends to diverge
- Acronyms do not help (e.g. Tancralization, Ihrgising, Metallizing, Metallising)
- More and more problems are solved by Hybrid techniques
- Without a clear classification system would be impossible to monitor the rapid flow of updating informations
- It would be even more difficult to develop new creative combinations of the presently known technologies

Different classification systems can be built depending on the application, but … some are more useful than others:

1. One can order on the basis of the coating purpose (e.g. Superconductive, Decorative, Corrosion protective, functional), but ….what about NbTiN ?
2. Traditionally it is also used the distinction in chemical, electrochemical, thermochemical and thermomechanical coating technology, but .. again NbTiN?
3. It is possible to classify as a function of the energy applied to the source producing the coating, or as a function of the coating - substrate type of bond.

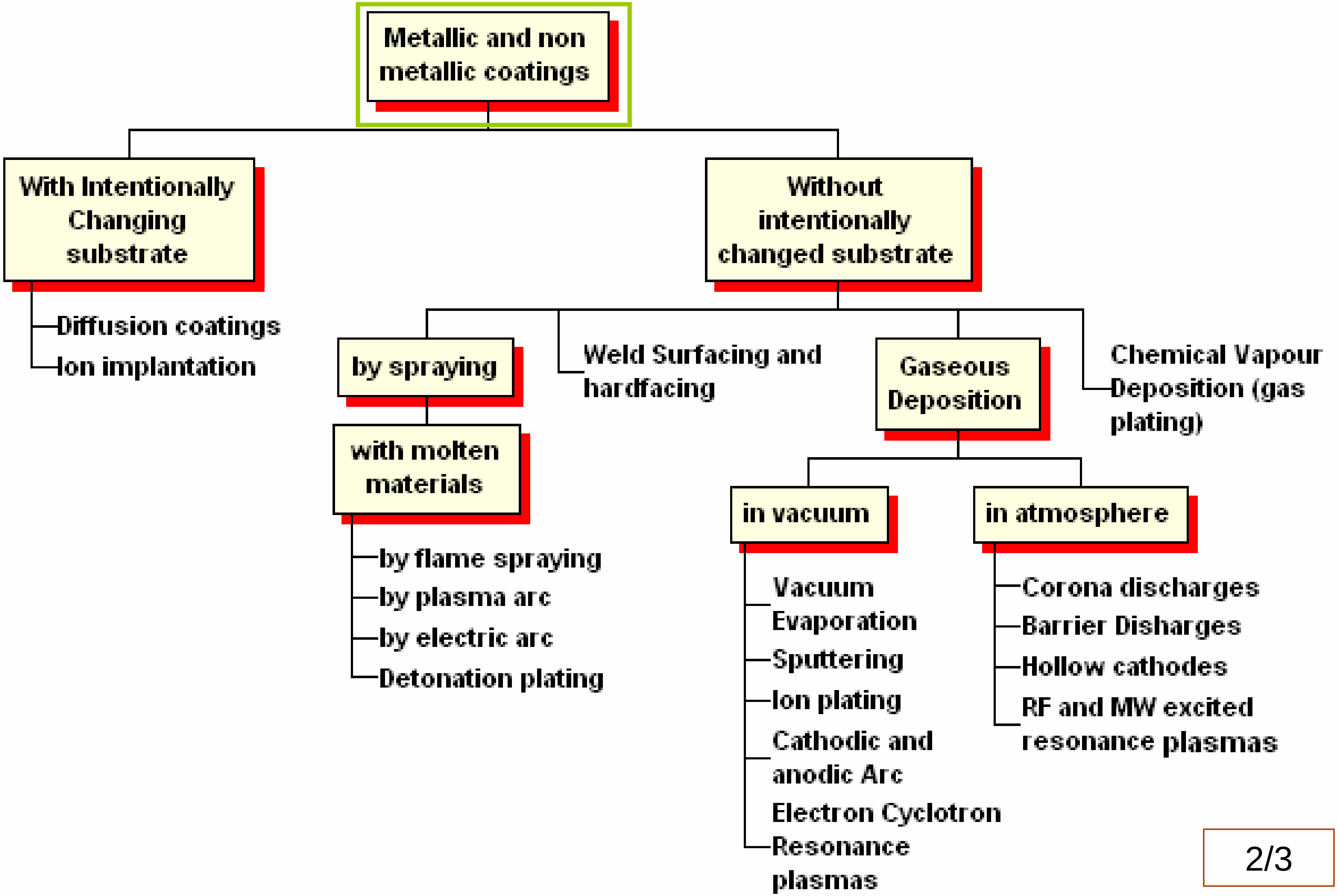
We will adopt the ASM system proposed by Rudski, based on the distinction between processes "with" or "without intentional change of the substrate", emphasizing so the difference between the diffusion and the autodiffusion that takes place spontaneously at room temperature.

Deposition Technologies in the Surface Finishing System



- Metallic coatings
  - Without intentionally changed substrate
    - Electrochemical coatings
      - in aqueous and organica electrolytes
        - Electroplating including Electrophoresis
        - Brush plating
        - Electrroforming
      - in fused Salts
        - High temperature
        - Ionic liquids
    - Chemical coatings
      - In aqueous solutions Electroless coating
        - Auto-catalytic
        - Non-catalytic
        - Contact Plating
      - in molten metals Hot-dip coatings
        - Deposition of metals
        - Deposition of Alloys
    - Applying Pressure
      - Mechanical Plating (Peen Plating)
      - Clad Bonding

Deposition Technologies in the Surface Finishing System



Metallic and non metallic coatings

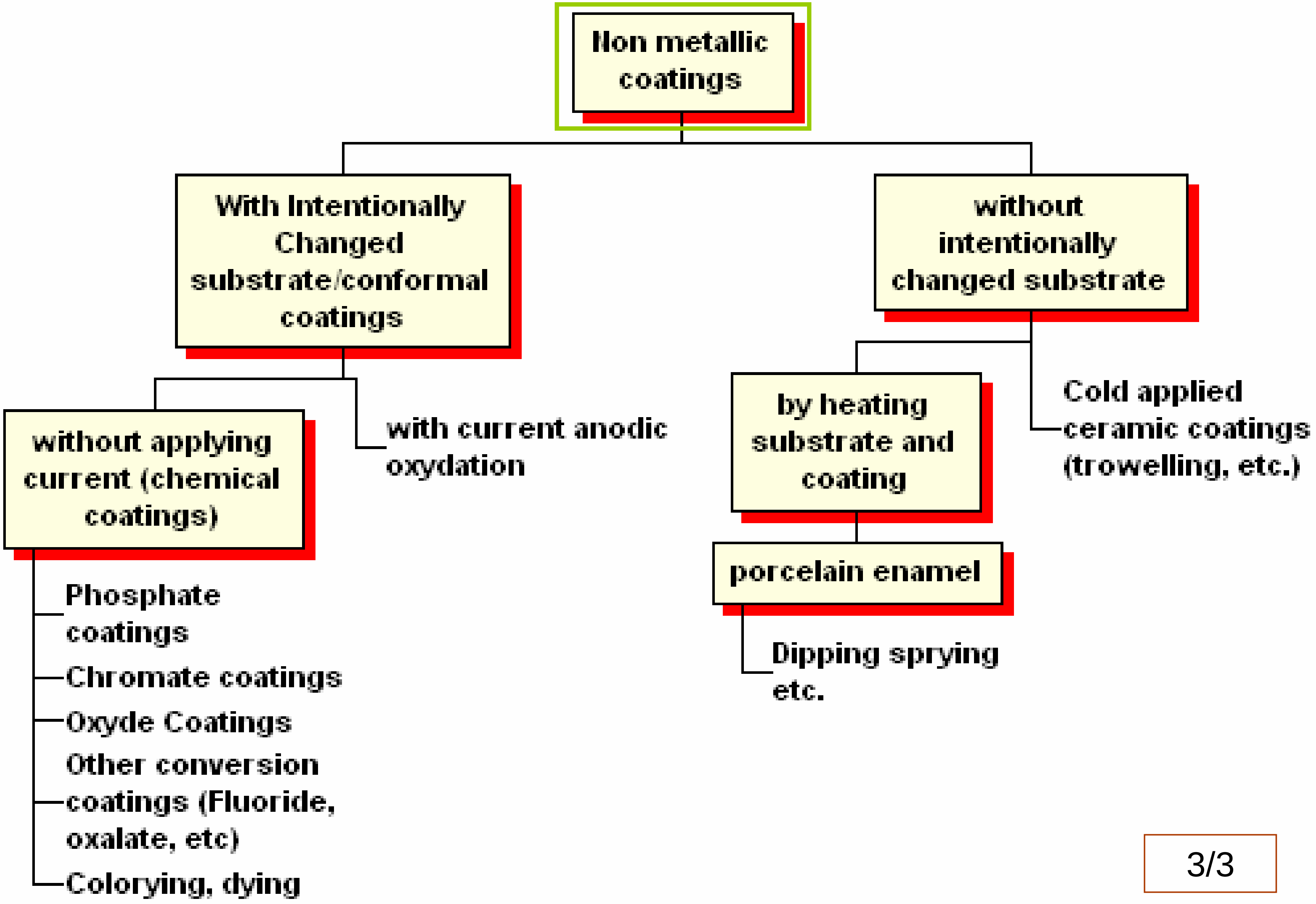
With Intentionally Changing substrate

- Diffusion coatings
- Ion implantation

Without intentionally changed substrate

- by spraying
  - with molten materials
    - by flame spraying
    - by plasma arc
    - by electric arc
    - Detonation plating
- Weld Surfacing and hardfacing
- Gaseous Deposition
  - in vacuum
    - Vacuum Evaporation
    - Sputtering
    - Ion plating
    - Cathodic and anodic Arc
    - Electron Cyclotron Resonance plasmas
  - in atmosphere
    - Corona discharges
    - Barrier Disharges
    - Hollow cathodes
    - RF and MW excited resonance plasmas
- Chemical Vapour Deposition (gas plating)

Deposition Technologies in the Surface Finishing System



Non metallic coatings

With Intentionally Changed substrate/conformal coatings

without applying current (chemical coatings)

Phosphate coatings

Chromate coatings

Oxyde Coatings

Other conversion coatings (Fluoride, oxalate, etc)

Colorying, dying

with current anodic oxydation

without intentionally changed substrate

by heating substrate and coating

porcelain enamel

Dipping sprying etc.

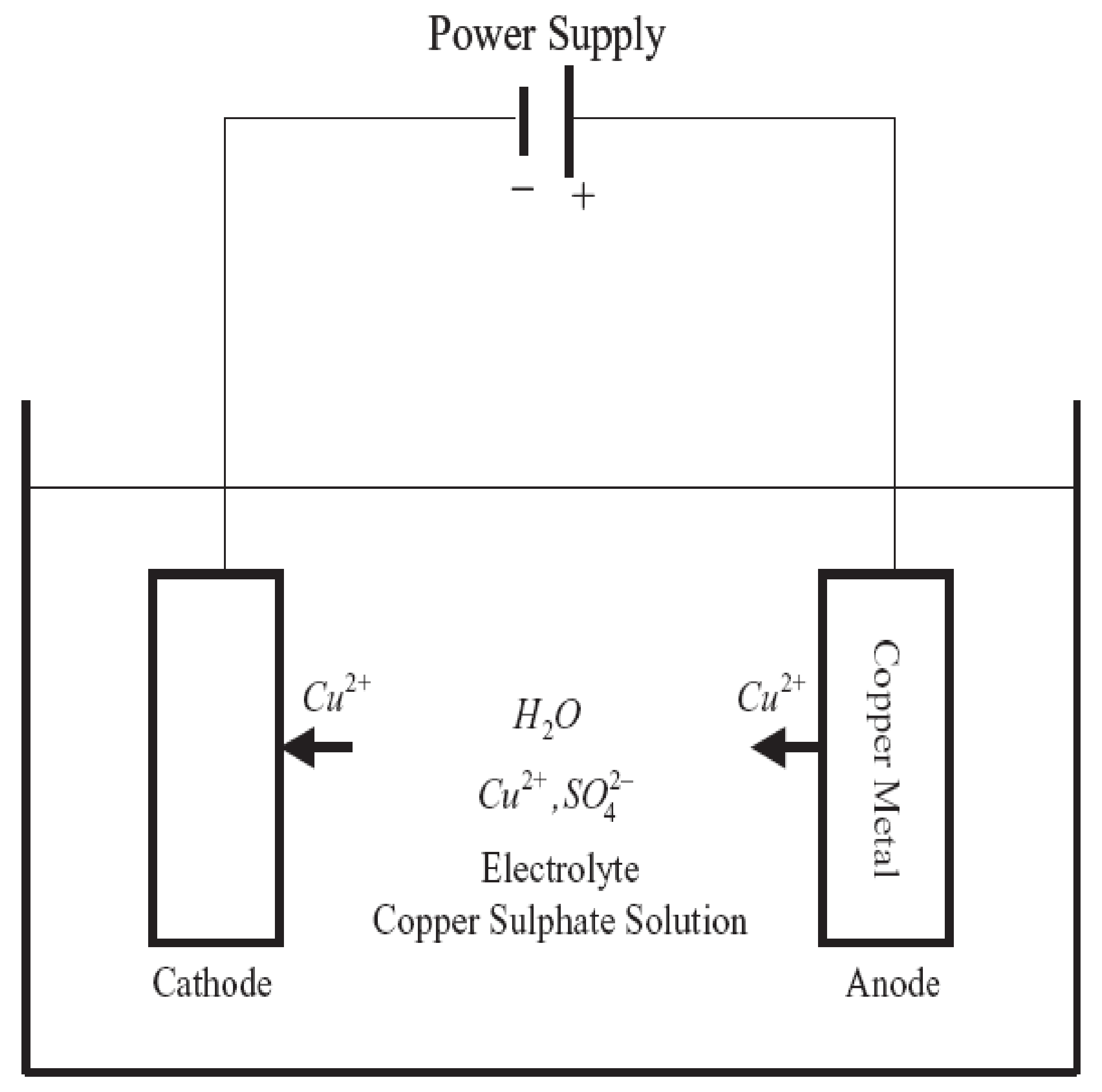
Cold applied ceramic coatings (trowelling, etc.)

Electrochemical plating 电化镀层,电化学镀法

- The substrate is the cathode and it is immersed in the electrolyte together with the anode.
- When the potential is applied, the metals ions are discharged at the cathode.
- Simultaneously either the anode is dissolving, or the metal ions are depleted by the electrolyte (to be buffered).
- Hydrogen can be codeposited

Required Tools:

i) a storage tank for the Electrolyte; ii) anode and substrate to be plated; iii) the electrolyte and the neutralization baths; iv) a Power supply that can be: D.C.; Periodic Reverse Current; Superimposed A.C.; Pulsed Current; v) bath stirring; vi) recirculation and filters


Power Supply
−
+
Cu²⁺
H₂O
Cu²⁺, SO₄²⁻
Electrolyte
Copper Sulphate Solution
Cu²⁺
Copper Metal
Cathode
Anode

Electrolyte: Aqueous, non aqueous, molten salts, ionic liquids

It must contain:

- Metal / compound to be deposited
- Complexing compound (in case the simple metal salt is insufficient)
- Conductive compound (increases conductivity without applying higher V)
- Stabilizing agent (prevents insoluble hydroxides or carbonates by ads. CO_2)
- Buffering agent (prevents change of the Electrolyte PH)
- Brightening Agent
- Wetting agent (inhibit gas release, which otherwise cause pitting)
- Levelling Agent (improves the throwing power of the electrolyte)
- Anode depassivating agent (Prevents Anode Passivation)

Example: Lead plating onto Cu

镀铅 在 电解铜

Quarter Wave Resonators (A case of how Material Science could have been useful)

Each laboratory had its own recipe, mainly empirical and systematically not working if transferred elsewhere

Just after plating the Lead appeared bright, but when drying, the surface started to become yellowish-brown

⇩

The conclusion was that **Lead was unstable** and that

under Lead Plating there was **“Black Magic”**

Plating involved many variants, some of which were:

- Continuous filtering of solution during plating
- Warming of plating solution to 30 C
- Use of anode bags
- Pulse plating (100 Hz)
- Plate-deplate where deplating removes 1/4 to 1/3 of plating (Seattle)
- Use of Pb-covered Cu electrodes (Stony Brook)
- Use of Pb alloys solutions as Pb-Sn or Pb-Bi (Munich)

So when a Lab got a good cavity, the plating procedure was frozen, and any possible failure was attributed to a non-stiff observation of the recipe.

Copper Preplating treatment:

The preparation of the Cu substrate for plating involved a combination of mechanical and chemical steps.

- **Mechanical polish**: abrasive pads and succession of polishing compounds, preferably in a non-imbedding garnet.
- **Washing** in a strong soap solution
- **Rinsing** with deionized water
- **Soaking** in alkaline solution (such as "Contrad 70", Curtin Matheson Scientific, Houston, Texas) for 1-5 mn
- **Rinsing** with deionized water
- **Soaking** in acid solution ("Chempolish 14" and/or "Neutra-Clean", Shipley Co, Newton, Massachusetts) for 1 mn
- **Rinsing** with deionized water
- **Storing** in 0.5 citric acid solution until plating

Then for Lead Plating:

- Plating: 1µm of Pb reguires a charge density of 1.05 C/cm2.

  The most commonly used plating bath is a LEAD Fluoborate solution, available as concentrate, to which is added water, fluoboric acid and a brightener ("Shinol LF-3", Harstan Chemical Division of Chemtech Industries, Brooklyn, N.Y.)
- Rinsing with di-water -Flashing: 10 times for 1 sec at 50-100 mA/cm2
- Plating: 10-15/m if followed by chemical polish (3-12 hours)

  1-1.5jnm if no chemical polish (30 mn)
- Rinsing with deionized water
- Soaking in a chelating solution (sat. EDTA solution diluted 16 to 1)
- Soaking in 1/4 strength chelating solution
- Soaking in acetone or ethanol
- Drying with nitrogen

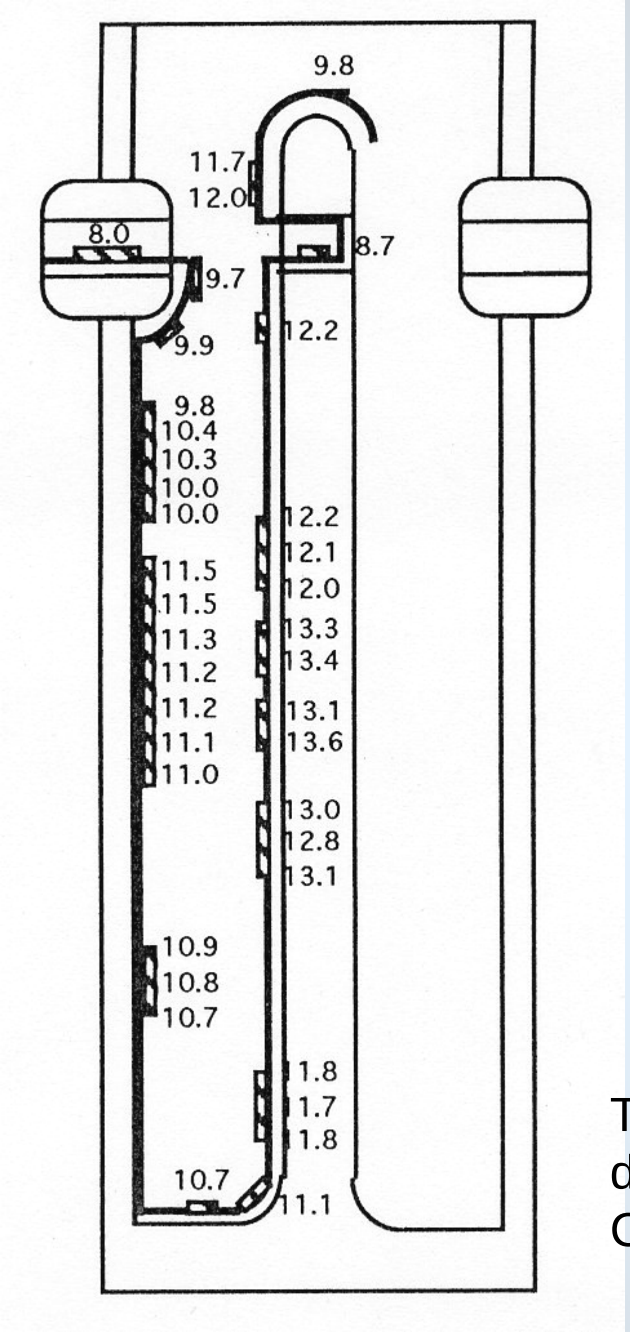
Post-plating treatment (chemical polishing of thick layers):

- Soak in chemical polish solution (1-2 mn)
- Soak in chelating solution
- Soak in 1/4 strength chelating solution
- Soak in ammonia
- Soak in acetone or ethanol
- Dry with nitrogen
- Store in nitrogen or vacuum

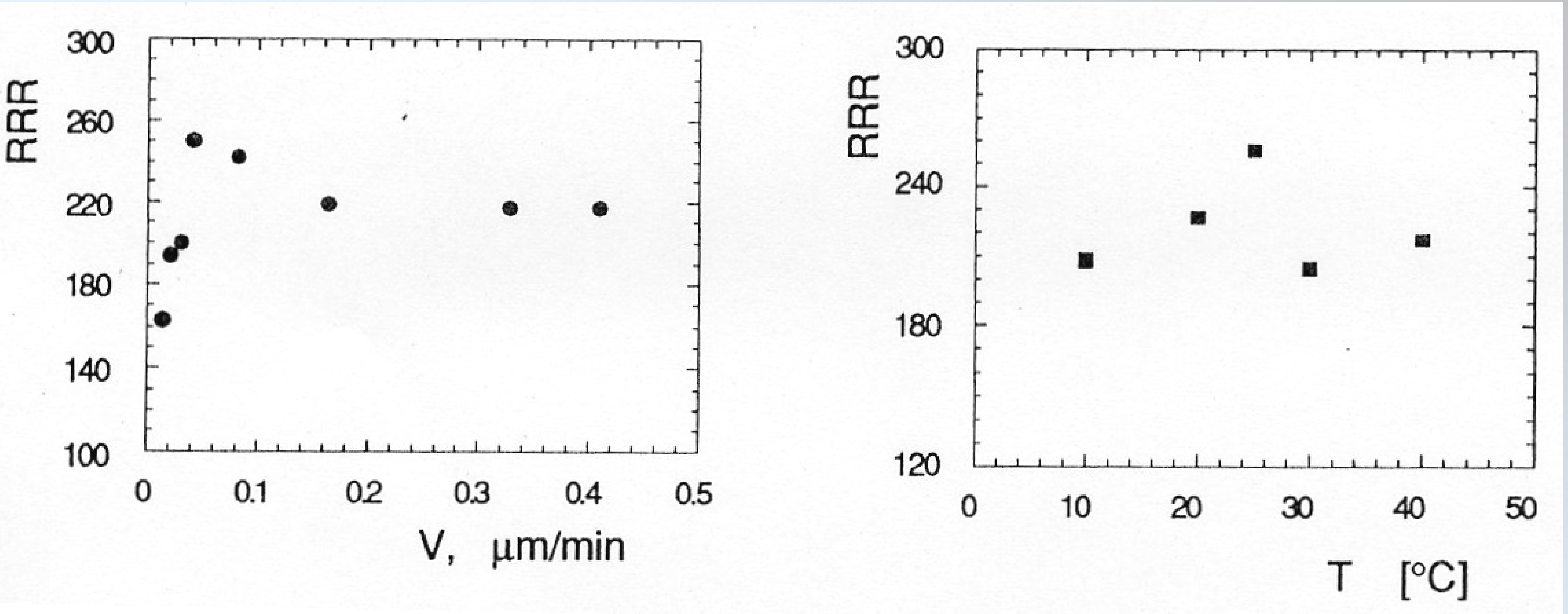
The chemical polish solution is a very weak solution of hydrogen peroxide, EDTA and acids (1/6 acetic acid, 1/3 nitric acid, 1/2 water).

If used fresh, agitation is required, and it is preferable to let it "age" for a day in order to obtain good results by soaking the plated part;

… but aging “seems” to reduce considerably the polishing rate of the solution.

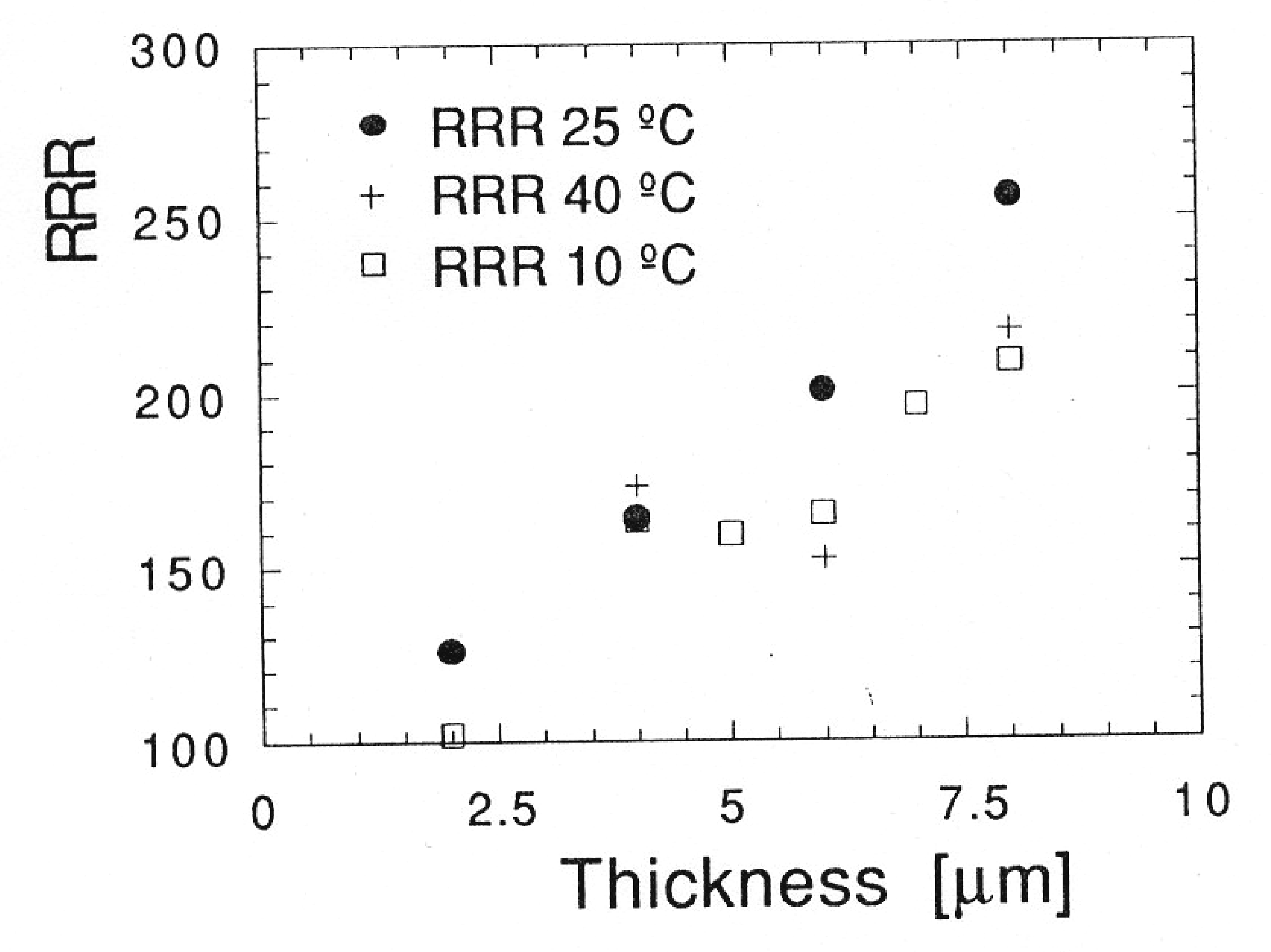


Thickness profile of Lead coating in a dummy resonator equipped with Copper samples.



Residual resistivity Ratio values: a)versus deposition rate,

b)Versus substrate temperature.



RRR values versus thickness for different substrate temperature.

But Lead, ……. has a very stable surface!

The reason for the yellowish-brown surface was due to the dried hydroxide.

The reason for surface instability was due to the porosity of the Pb Coating embedding Tetrafluoborate residuals

So the solution was:

Simply wash the cavity after plating much more than done elsewhere (5-7 times), then passivate with 1% acetic acid solution at 90° and then to rinse again!

High fields were immediately achieved and QWRs remained stable for months also in open air

Nowadays, Pb plating is done by metasulphonate baths!! (StonyBrook, ANU)

The less-common metals are rarely electroplated and can be divided into the following categories:

1) easily platable from aqueous solutions but not widely used, such as **As, Sb, Bi, Mn**, and **Re**;

2) platable from organic electrolyte but not aqueous electrolyte, such as **Al** *(Al hydride in diethylene glycol, dimethil ether o tetrahydrofuran)*;

3) platable from fused-salt electrolyte but not aqueous electrolyte, including refractory metals such as **Ti, Zr, Hf, V, Nb, Ta, Mo,** and **W**.

But now …..

Laser Induced Electroplating 激光触发金属电铸

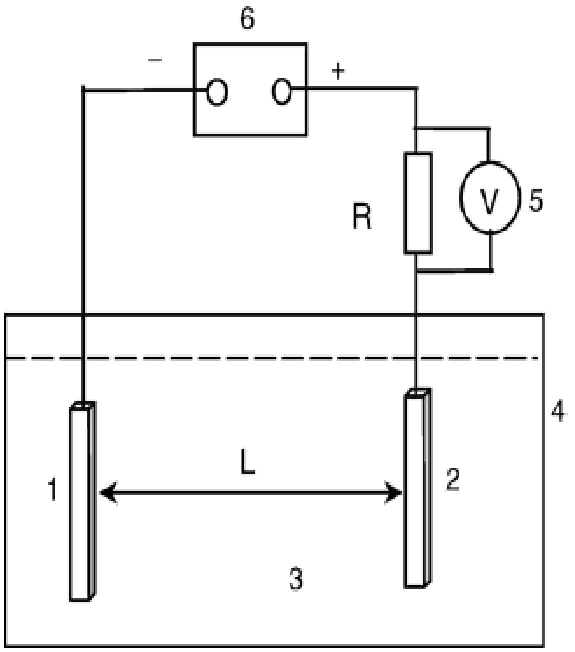
In laser-induced metal deposition, a focused laser beam is used to accelerate the metal deposition. Experiments have shown that the deposition rate can be increased by 1000 times.

The plating equipment mainly consists of a laser head with focusing optics and the electrolytic cell.

The focused laser beam can pass through a hole in the anode through the electrolyte and impinge on the cathode surfaces.

Plasma electrolytic oxidation or Micro-Arc Oxidation

first studied in details by Günterschultze and Betz in the1930s.



1. Cathode
2. Anode
3. Electrolyte
4. Osclillograph
5. Power supply

During the PEO process, the specimen is immersed in a solution, and discrete spark discharge occurs on the surface, when the supplied voltage is higher than a critical value.

The melted materials ejected out of the channel and cooled rapidly due to their immediate contact with the stirring electrolyte.

Plasma electrolytic oxidation or Micro-Arc Oxidation

Compared to vacuum-based plasma processes, the PEO process is preferred for its atmospheric working environment.

The excellent wear resistance, corrosion resistance, electrical, and thermal properties of these coatings are of particular interest to textile machine components, aerospace components, engineering equipment components, and biomedical devices.

Electrophoresis

The immersion of a dispersed solid phase (e.g. inorganic particles or colloids) in the electrolyte is associated to electro-kinetics.

The colloids or dispersed inorganic particles are capable of absorbing other moleculas and ions present in the electrolyte, so becoming positive or negative charged.

When a potential difference is applied, the charged particles start migrating.

It is found that the electrical charge obtained by the dispersed particle depends on the size of the particle, so, by electrophoresis one gets higher deposition rate than in comparison with the Faraday law, ruling standard plating processes.

Electroforming

The deposit does not need to be adherent to the substrate: thus the mandrel can be produced from low melting alloys, dissolvable metals, or collapsible pretreated non-conducting materials.

Indeed the purpose of EF is the reproduction of a particular article as precisely is possible. So the substrate is the negative of the searched form.

- **Sharp angles are a problem.**
- **Thermal strain are a problem** (indeed fused salt are rarely applied)
- **High internal stresses may cause cracking or peeling**

Electroless Plating 无电镀,化学镀

Is the deposition without any applied current of a catalythic metal onto a catalytic or sensitized / activated substrate.

- **The plating thickness tends to be uniform compared to electroplating due to the absence of electric fields and the associated problems in making them uniform;**
- **Coating not as hard as electroplated ones.**
- **Slow deposition rate..**

Example: for Wuppertal Nb_3Sn cavities, the Sn vapour-diffusion process, was preceded by a previous $SnCl_4$ sensitization of Nb in order to enucleate Sn.

Non-Catalytic Displacement Plating (Amalgam)

排代电镀,置换电镀 (汞齐)

An adherent metallic, more noble deposit is formed in a suitable bath, basically by displacement of the less noble/more electronegative substrate metal.

Tipycal Reaction: $\mathbf{Me_x^0 + Me_y^{2+} \rightarrow Me_x^{2+} + Me_y^0}$

The process ends when the substrate is covered **(coatings of few 10ths of a μm)**

Example:

Ag is deposited on a colloidal substrate of Cu (or Pt on collidal Zn).

A non aqueous solution (e.g. Benzene, Ethylbenzene, Toluene, Xylene, may be used as solvent).

Contact plating: 接触电镀

As defined by ASTM, the “Deposition of a metal without the use of an outside source of current, by immersion of the system in a solution in contact with another metal”.

The substrate (e.g. Zn) is hung on a Al wire (the contact metal) in a solution containing a chemical compound of the metal to be deposited (e.g. Sn).

A galvanic couple is created between contact metal, Al, and the Zn substrate, in the electrolyte, thus providing the required potential for the deposition.

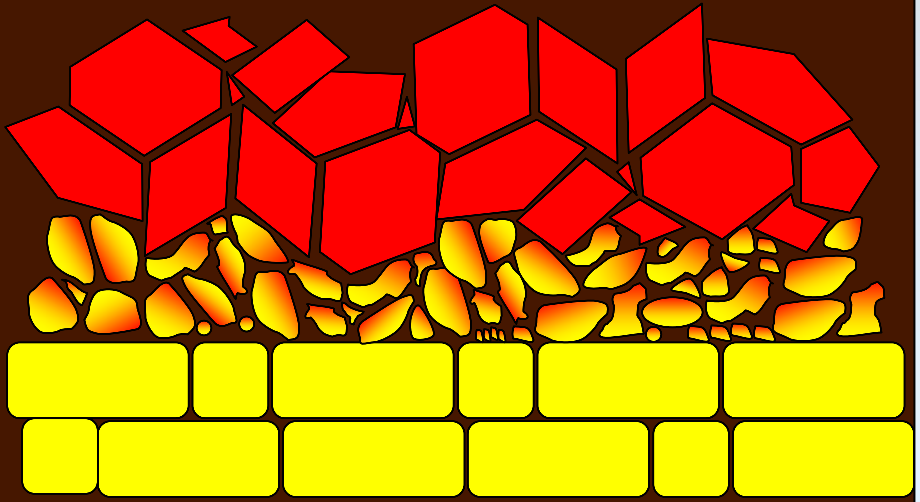
The contact metal Al will dissolve instead of the Zn substrate. Simultaneously both Al and Zn will be plated with the Sn ions that are in the plating solution

Hot-dip in molten metals 热浸涂镀

Physical-Chemical Process based on the coating of a pre-treated (etched or with additional pre-coating) substrate material by immersion in a bath of molten metal/alloy

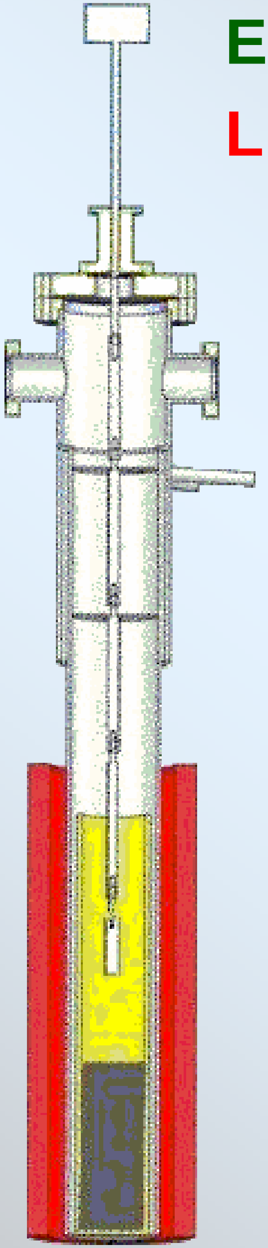
Basically 3 layers:

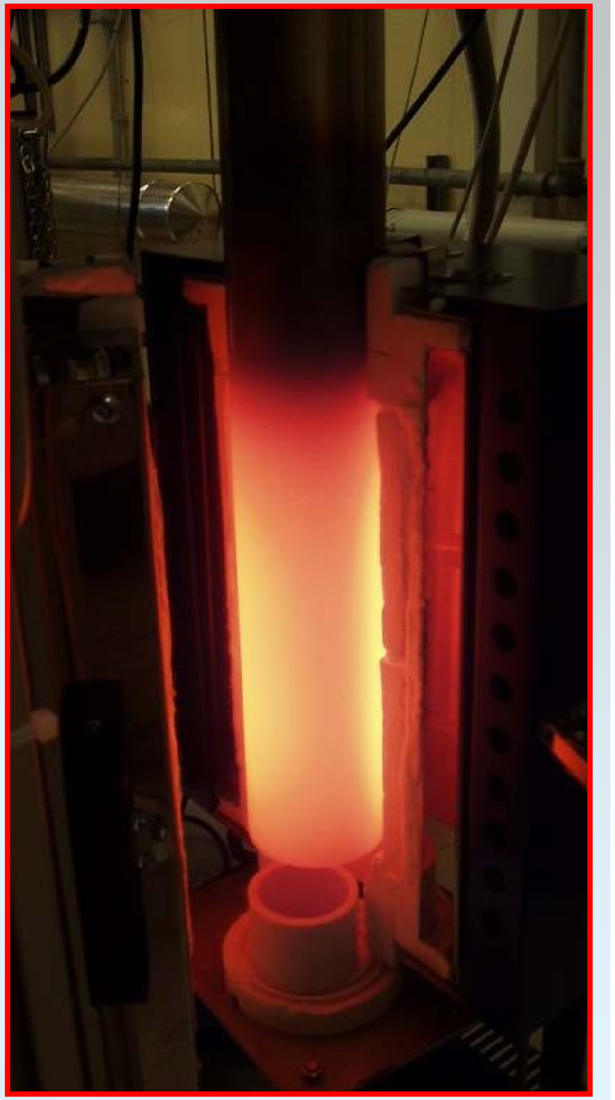
- **The top pure coating**
- The intermediate-diffused chemically bonded zone
- The pure substrate



Example:

Liquid Sn diffusion into Nb cavities





Important note: The oxyde layer must be broken before the Sn dip-coat

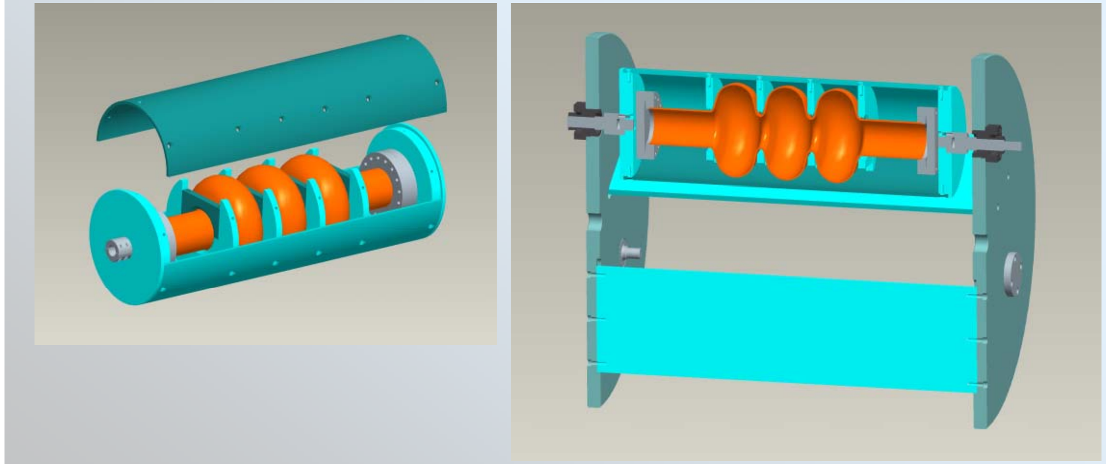
ThyssenKrupp Steel, Dortmund

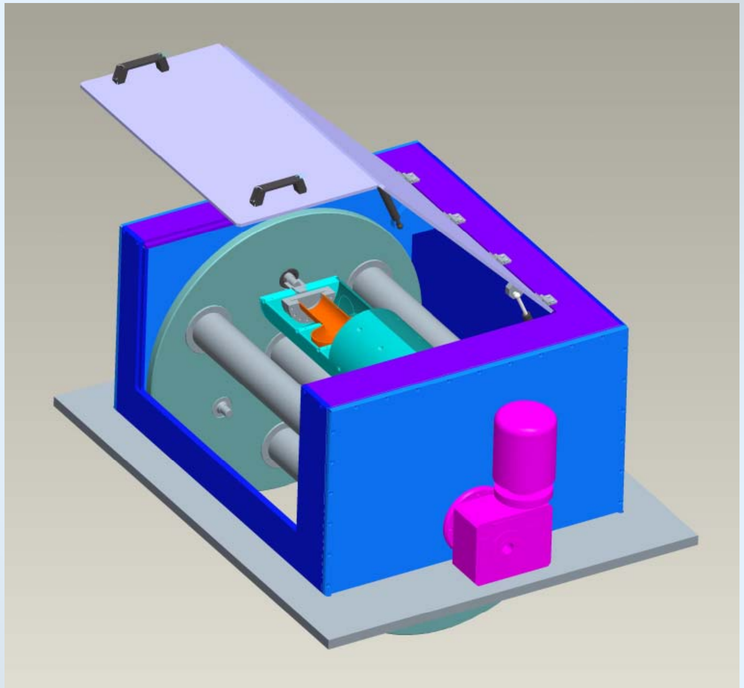
Limiting factor:

- Surface Tension
- Substrate Wettability
- Adhesion
- Difference between T_m of the coating and of the substrate
- Droplets of liquid metal difficult to remove on tricky shapes
- Vacuum degasation of components
- Interdiffusion with the crucible materials at high temperatures
- Furnace often much bigger in dimension than the workpiece

Mechanical Plating (also Impact Plating) 机械喷镀

Impact or centrifugal force is applied to deposit compacted coatings by tumbling both particles of the coating material and an impact media (ceramic balls, porcelain bead) in a suitable solution





Platable materials must remain in stable form without Oxyding and must be more ductile of the substrate material

Example:

Sn coating onto Nb to anneal in order to obtain Nb_3Sn

16-18 μm of Tin coating is obtained in 20 min from solution of Sn salt under action of impact bodies in planetary centrifugal unit, filled with SnCl2, Sn powders, Sodium tartrate (3g/l) and Trilon

Clad Bonding 复合

A physical process of bonding two or more precleaned metals by applying pressure under specific conditions:

It includes:

- **Hot and cold rolling** 碾压
- **Extrusion bonding** 挤压 复合
- **Explosive bonding** 爆炸复合
- **Combination of the above methodes with other technologies:**
  (e.g. Electroplating and extrusion; electrophoretic depositions and roll bonding)

Example: Spinning Nb Clad Cu sheets

The surface must be rid of any surfacial scratch or imperfection, that will be amplified meanwhile spinning.

Hipped-Nb vs Cu, 1:4 thickness.

Poor adesion of Nb onto Cu

By the way, this problem is not visible for Clad Nb/Cu

Diffusion coatings: **Element name …izing)**

There is initially a zone of high concentration of the material to be diffused into the substrate. Then atoms migrate from the high concentration zone to the low concentration one.

Diffusion thus is the equalizing of material concentration

and it mainly dependes by :

- Atomic radius of both diffusing element and substrate material
- Activation energy
- Mutual solubility of alloying

The INTERgrain diffusion across vacancies, dislocations and grain boundaries is order of magnitude higher than the INTRAgrain diffusion

The diffusing element is dispersed in the direction of lower concentration, so the advancing material is the difference between the diffusing amount passing into the substrate and the reversal amount passing from substrate to the element.

The relation is expressed by Fick's first law:

$$Y = - D \bullet \nabla C = -D \cdot dC/dx$$

where:

Y = amount of diffused element [g/cm^2]

D = Diffusion coefficient [cm^2/sec]

C = Decrease of Concentration per unit length [g/cm^2]

D depends on the frequency, V_0, of atom jumps from one position to another and their atomic diameter, a.

$$D = a^2 V_0$$

The concentration charge of the diffused element is expressed by Fick's second law

$$dC/dx = d/dx\,(D \cdot dC/dx)$$

The Arrhenius law holds for the Diffusion coefficient D

$$D = D_0 \bullet e^{-(Q/RT)}$$

D_0 = Frequency factor [cm^2/sec]

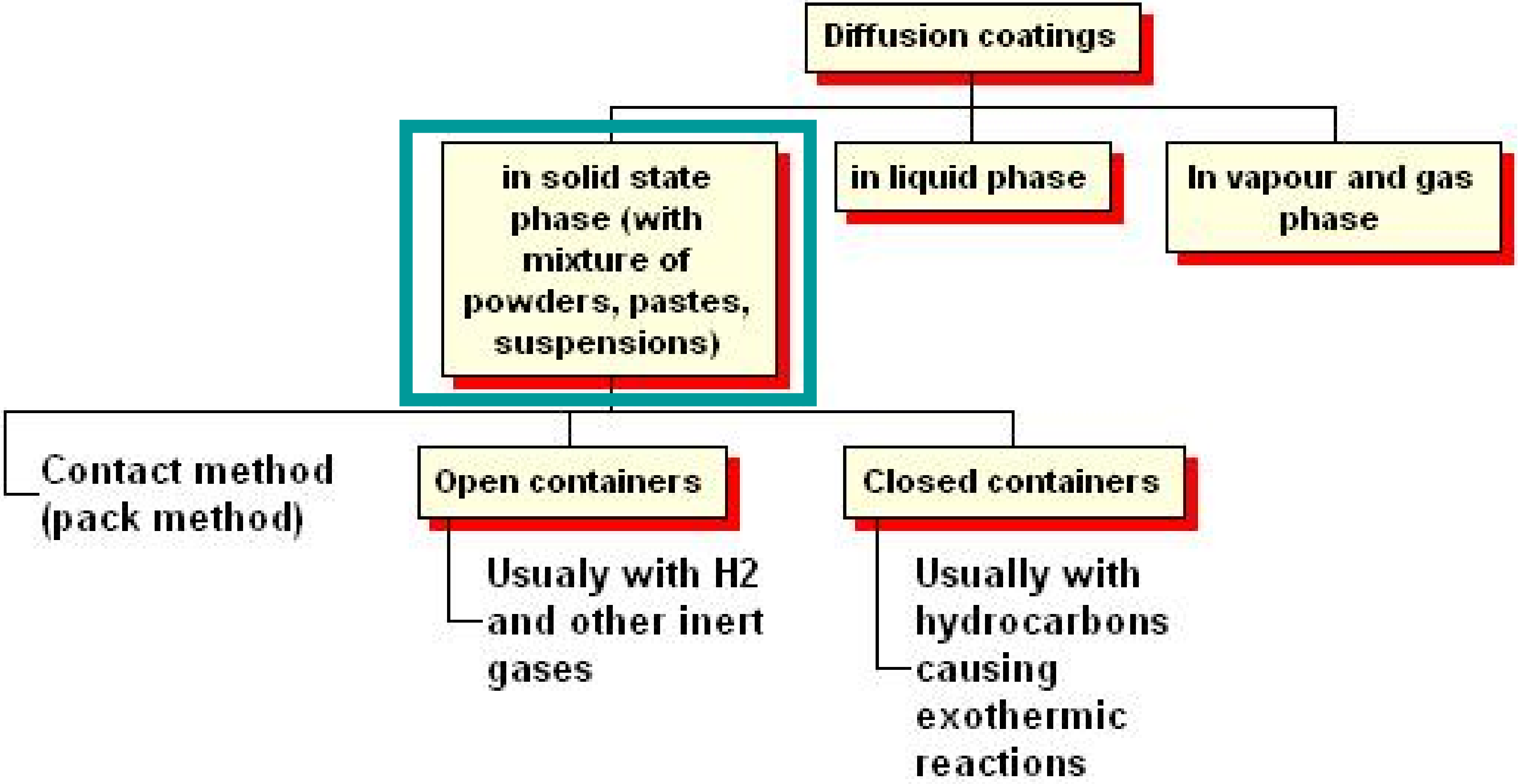
Q = Activation Energy [cal/gm atom]

T = Temperature [K]

In summary:

the diffusion coefficient increase, for :

- Increased Diffusion temperature;
- Increased grain boundary, or lattice defect density;
- Decreased atomic radius of the element to be diffused, and an increase of its concentration;
- Lower diffusion activation;
- When the entire system is stimulated by an additional form of Energy.



Diffusion coatings

in solid state phase (with mixture of powders, pastes, suspensions)

in liquid phase

In vapour and gas phase

Contact method (pack method)

Open containers

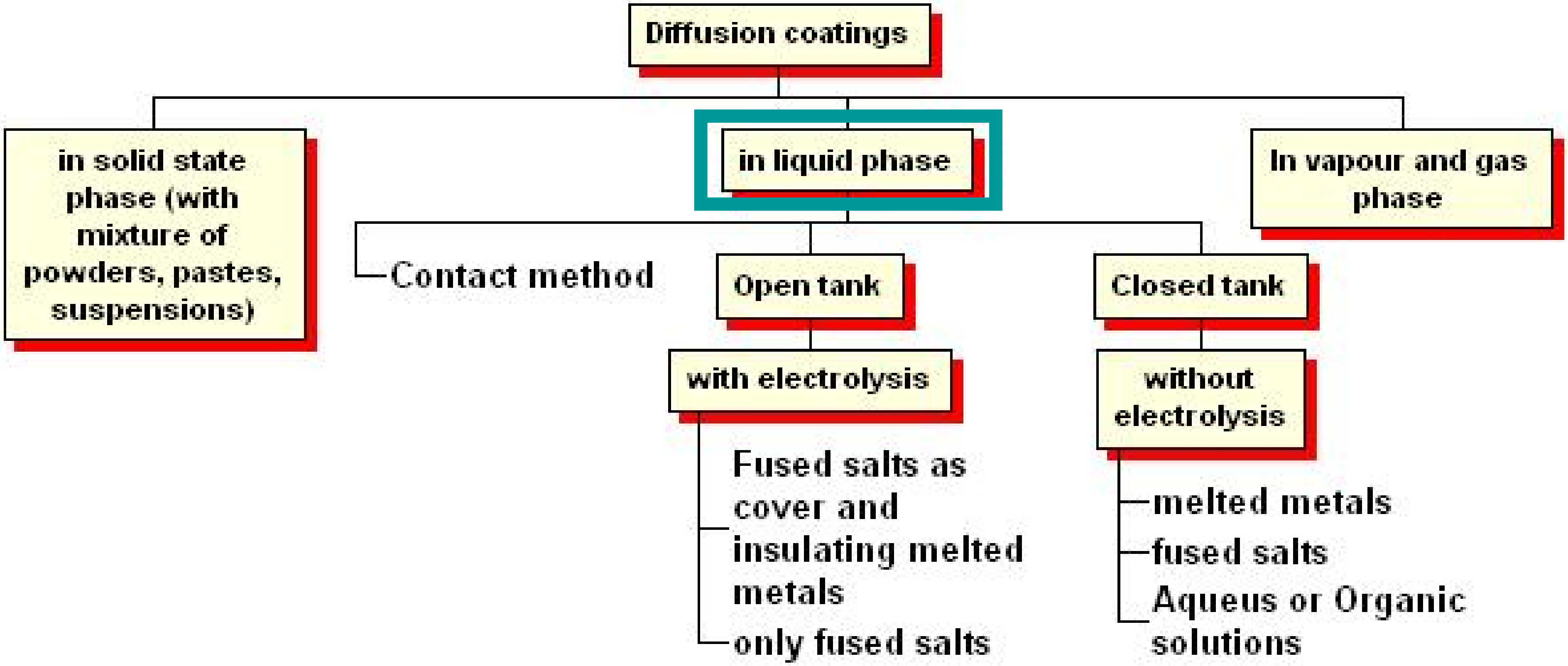
Usualy with H2 and other inert gases

Closed containers

Usually with hydrocarbons causing exothermic reactions

NOTE: The Diffusion Coating Chart should contain other two items:

- The Pretreatment for activating/sensiting the substrate
- Other technologies applied before diffusing: E.g. Electroplating, Gaseous phase plating, mechanical plating, Spray plating, Cladding



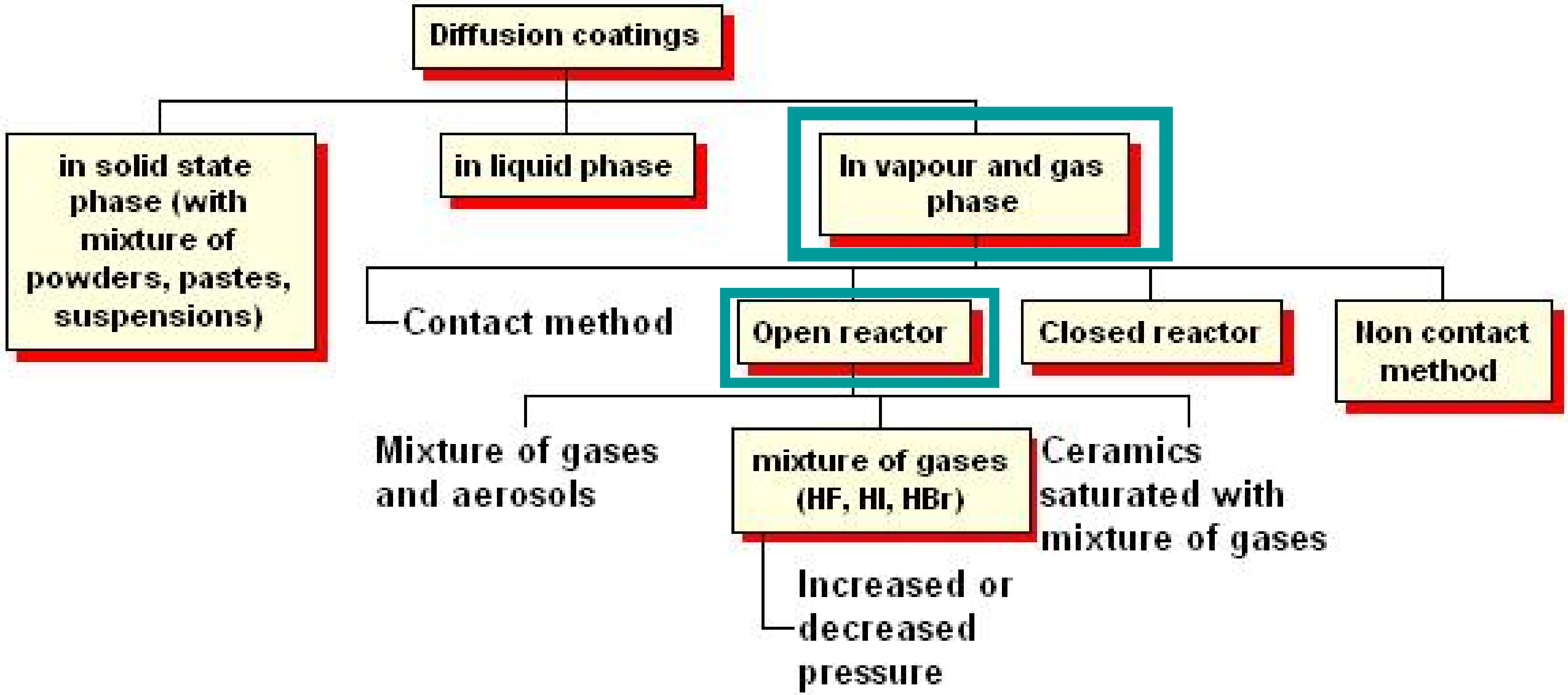
Diffusion coatings

in solid state phase (with mixture of powders, pastes, suspensions)

in liquid phase

- Contact method
- Open tank
  - with electrolysis
    - Fused salts as cover and insulating melted metals
    - only fused salts
- Closed tank
  - without electrolysis
    - melted metals
    - fused salts
    - Aqueus or Organic solutions

In vapour and gas phase



Diffusion coatings

in solid state phase (with mixture of powders, pastes, suspensions)

in liquid phase

In vapour and gas phase

Contact method

Open reactor

Closed reactor

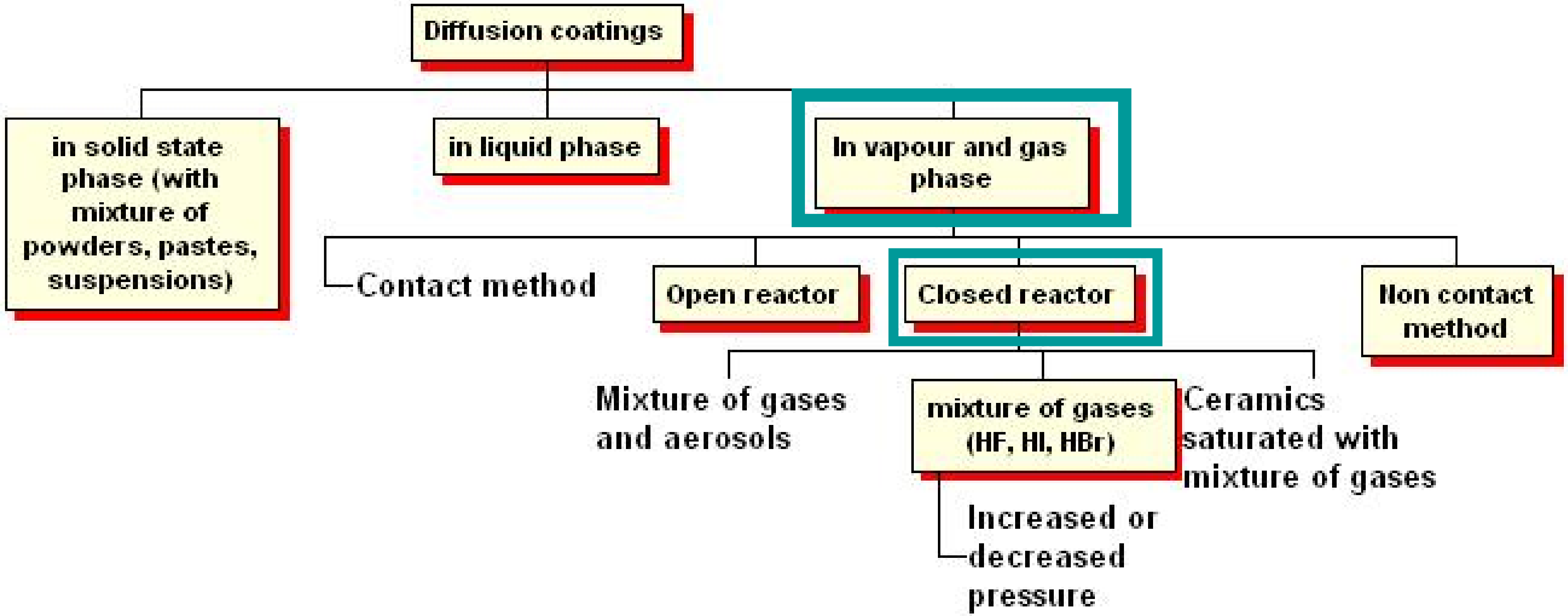
Non contact method

Mixture of gases and aerosols

mixture of gases (HF, HI, HBr)

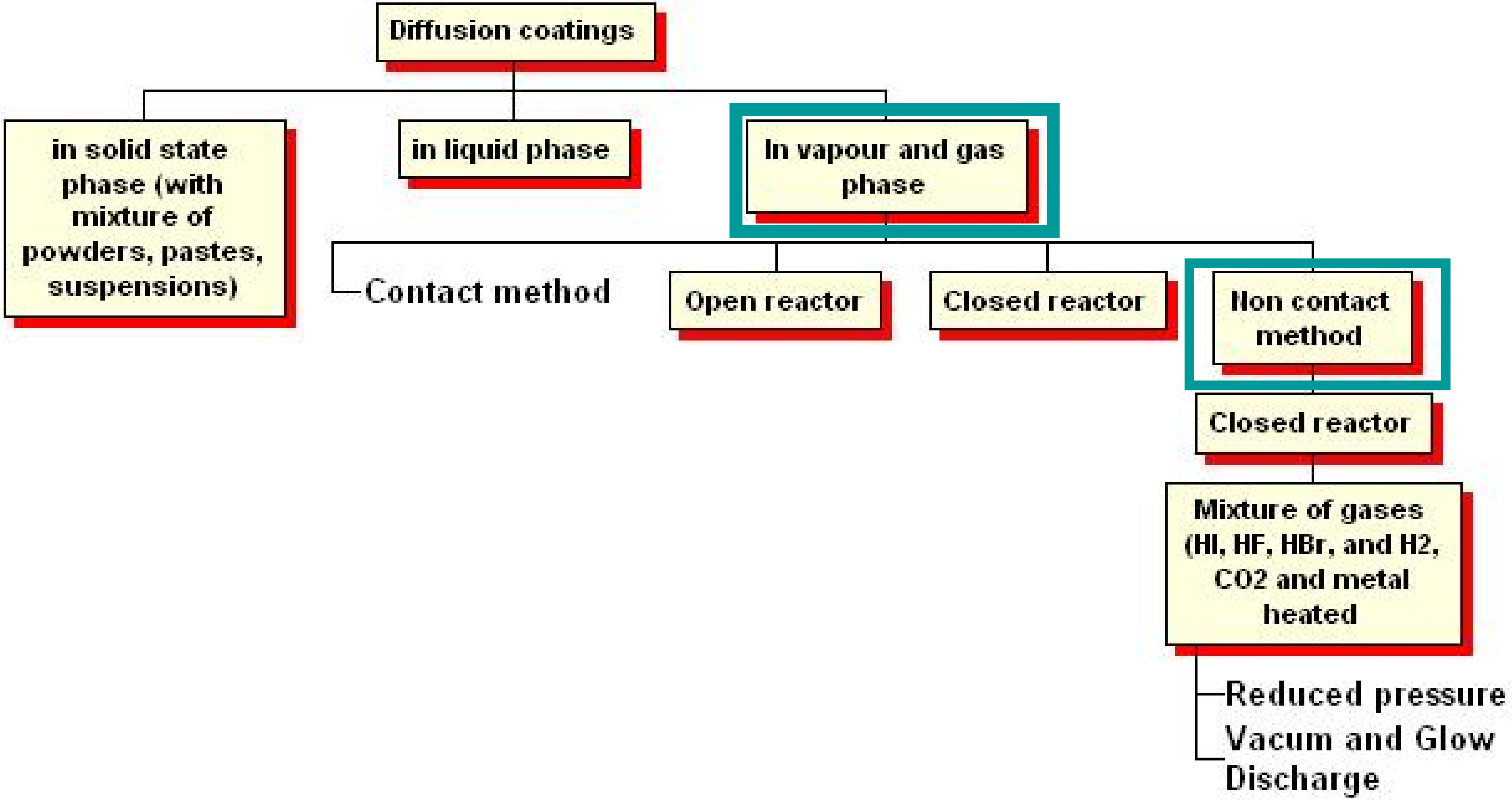
Ceramics saturated with mixture of gases

Increased or decreased pressure



Diffusion coatings

- in solid state phase (with mixture of powders, pastes, suspensions)
- in liquid phase
- In vapour and gas phase
  - Contact method
  - Open reactor
  - Closed reactor
    - Mixture of gases and aerosols
    - mixture of gases (HF, HI, HBr)
      - Increased or decreased pressure
    - Ceramics saturated with mixture of gases
  - Non contact method



Diffusion coatings

in solid state phase (with mixture of powders, pastes, suspensions)

in liquid phase

In vapour and gas phase

Contact method

Open reactor

Closed reactor

Non contact method

Closed reactor

Mixture of gases (HI, HF, HBr, and H2, CO2 and metal heated

Reduced pressure

Vacum and Glow Discharge

Thermal Spray methods:

Deposition by spraying with molten metals

- **Flame spray coatings**
- **Plasma Spray coatings**
- **Electric arc coatings**

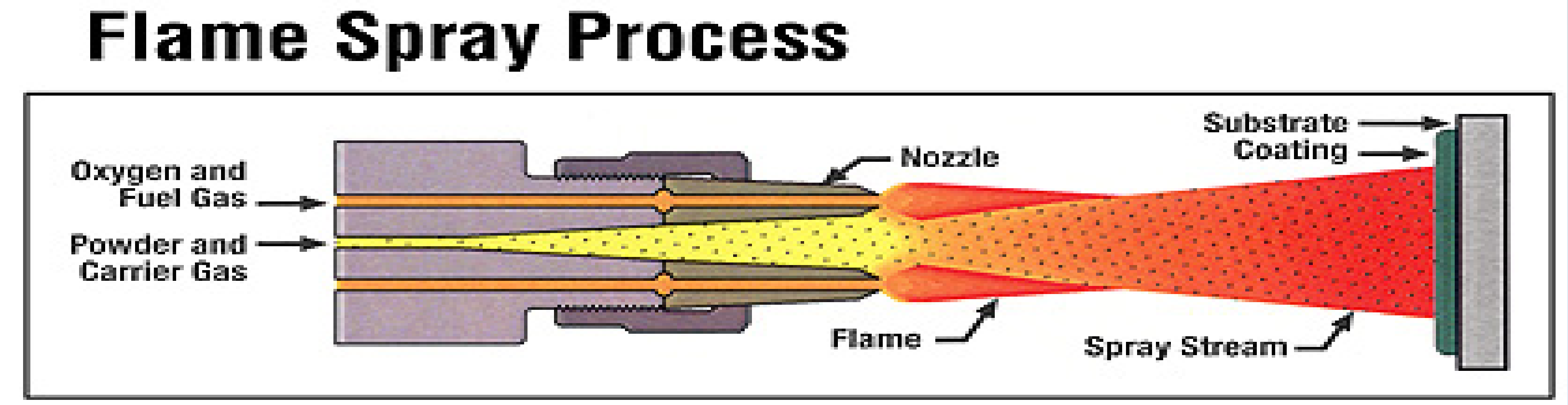
Detonation plating applying high kinetic energy

Deposition by welding: surfacing and hardfacing

FLAME SPRAY PROCESSES 火焰喷镀,喷涂

Fluids may be broken up into very fine particles by a stream of high velocity gas emanating from a nozzle.

Early experiments using this atomizing approach appear to have been directed at producing metallic powders rather than coatings. It was left to Schoop to appreciate the possibility that a stream of metallic particles, formed from a molten source, could produce a coating.



Characteristics:

Flame Temp: Dry-Acetylene, ~3100°C

Oxy-Hydrogen, ~2700°C

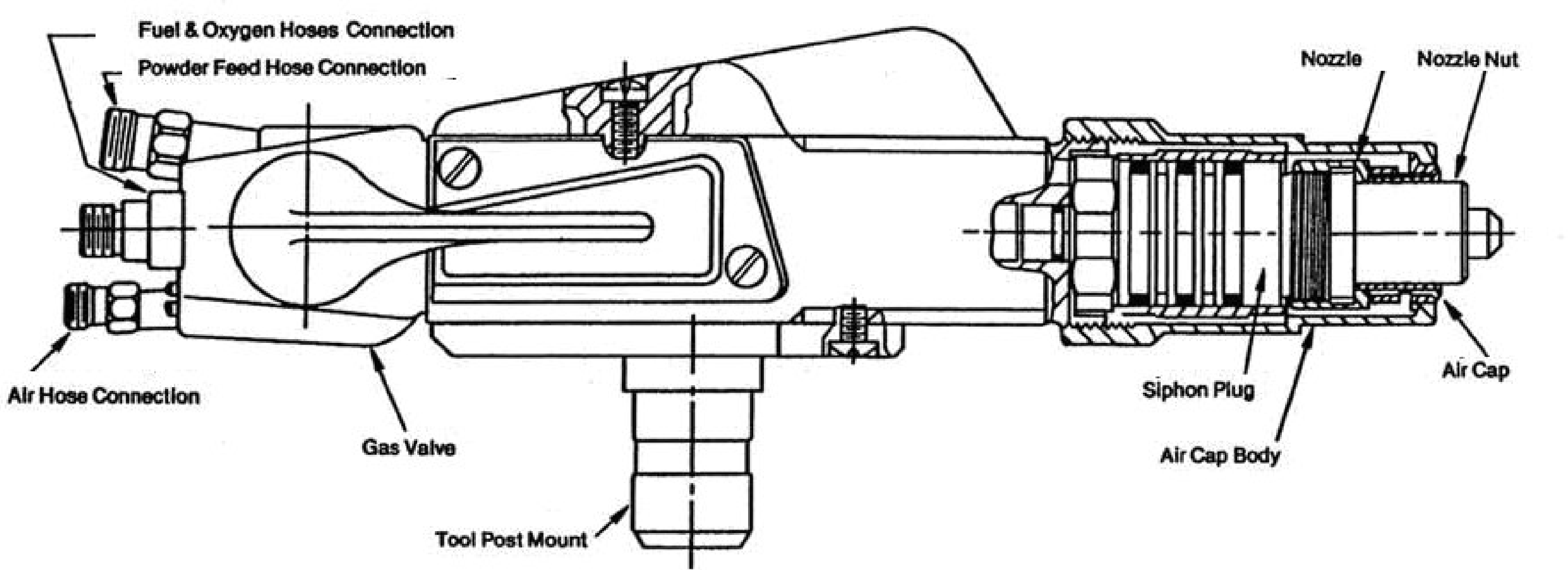
Particle speed: 60-240 mt/sec

Powder Flame Spraying (the simplest of all thermal spray processes)

the material to be sprayed is in powder form

Powder is fed through a nozzle where it melts and is carried by the escaping oxy-fuel gases to the work piece.

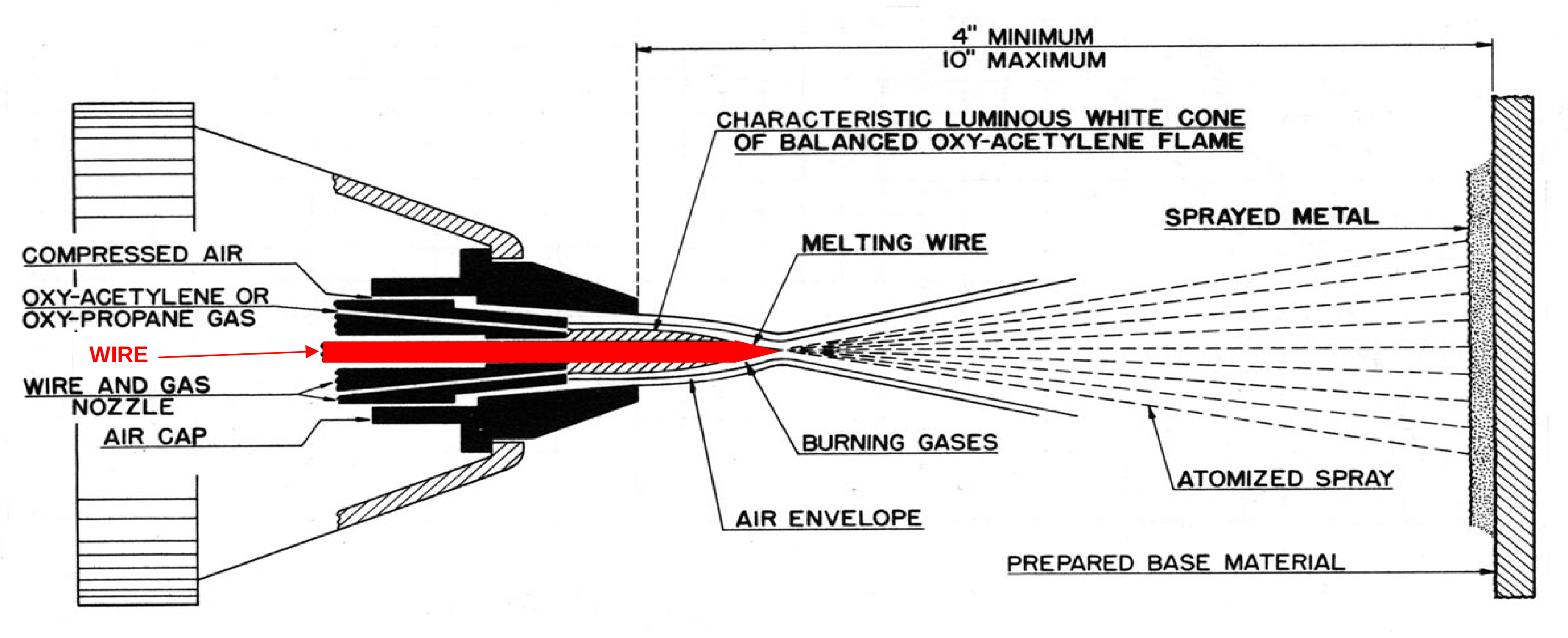
Coatings high in oxides and with void contents approaching 20 vol %



Coating quality can be improved by feeding air to the nozzle, i.e. by reducing the pressure in a chamber, behind the nozzle, that is connected to the powder feed hopper. In this way a weaker gas stream is sucked into the gun

Wire Flame Spraying ("Schoop Process")

A fuel, mainly acetylene or hydrogen, is mixed with oxygen and burned at the nozzle's face. A stream of compressed air surrounding the flame atomizes and propels the liquefied metal.



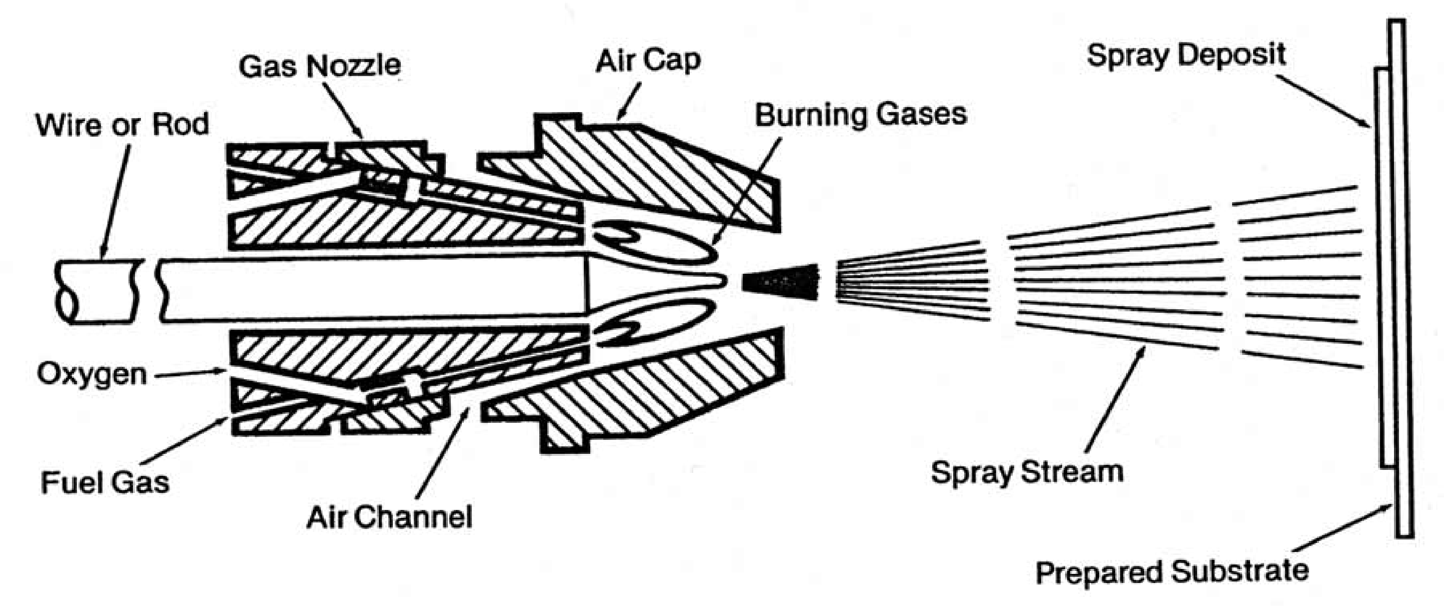
Process continuation depends on feeding the wire at a controllable rate, so it melts and is propelled in a continuous stream

Ceramic Rod Flame Spraying 陶瓷的火焰喷镀

(the material to be sprayed is in ceramic rod form)

The spraying of ceramic rods dates back to the early 1950's when a demand arose for heat resistant refractory coatings (stabilized zirconias, alumina, …)

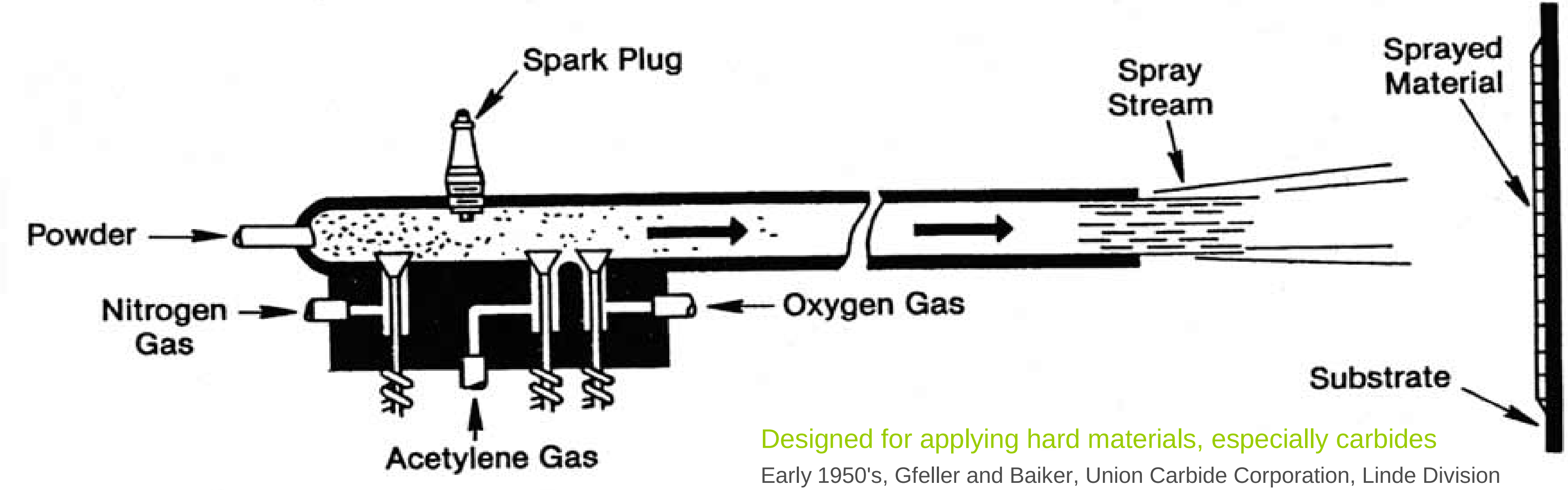
Plasma had not come into its own and flame sprayed powder coatings, due to their porous nature, lacked the integrity and protection required.



A coaxial sheath of compressed gas around the flame atomizes the molten material and accelerates it to the workpiece. Particle velocities in both the wire and rod process are approximately the same ~ 180 m/sec, while coating densities have been measured at approximately 95 v/o.

Detonation Flame Spraying 爆炸涂镀

A thermal spray process variation in which the controlled explosion of a mixture of fuel gas, oxygen and powdered coating material is utilized to melt and propel the material to the workpiece



Designed for applying hard materials, especially carbides

Early 1950's, Gfeller and Baiker, Union Carbide Corporation, Linde Division

Powdered materials are propelled by detonation or shock waves.

“Waves" are produced by igniting a mixture of Acetylene and Oxygen.

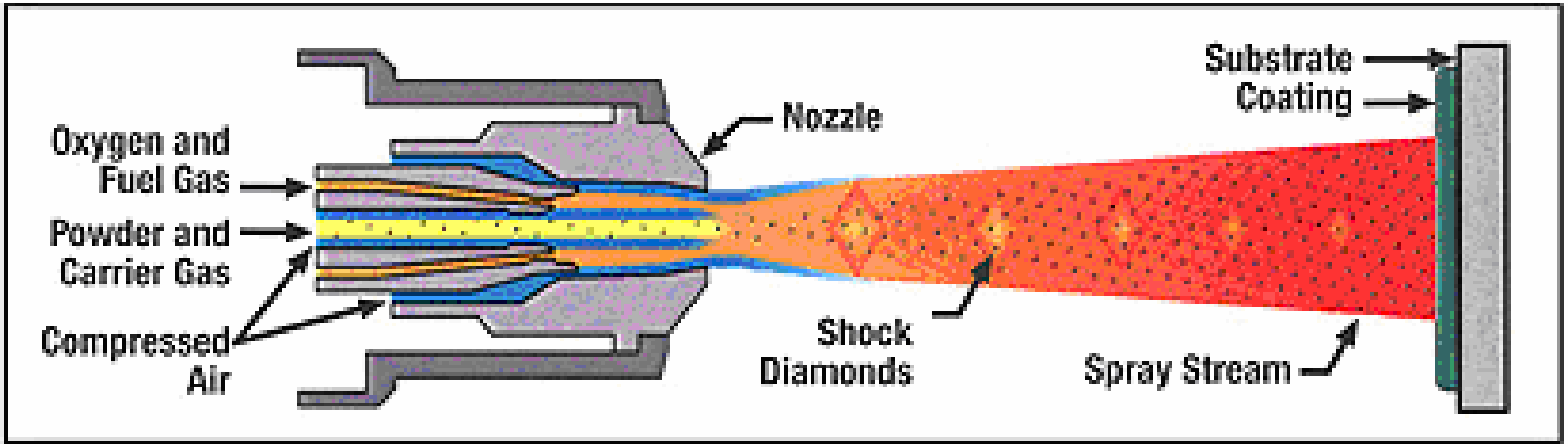
The detonation chamber is an open-end *1 meter long tube* about 1” in diameter

The resulting shock wave accelerates the powder particles to over 731 m/sec

High Velocity Oxy/Fuel Spraying (HVOF)

In early 1980's Browning and Witfield, applied rocket engine technologies, for spraying metal powders.

Inertially driven highly plasticized particles can make coatings approaching the theoretical density.



Flame Temp: ~2750°C **Particle speed: 1400 mt/sec > Mach 1**

Fuel gases: Propylene, or Propane, or Hydrogen, or even Kerosene

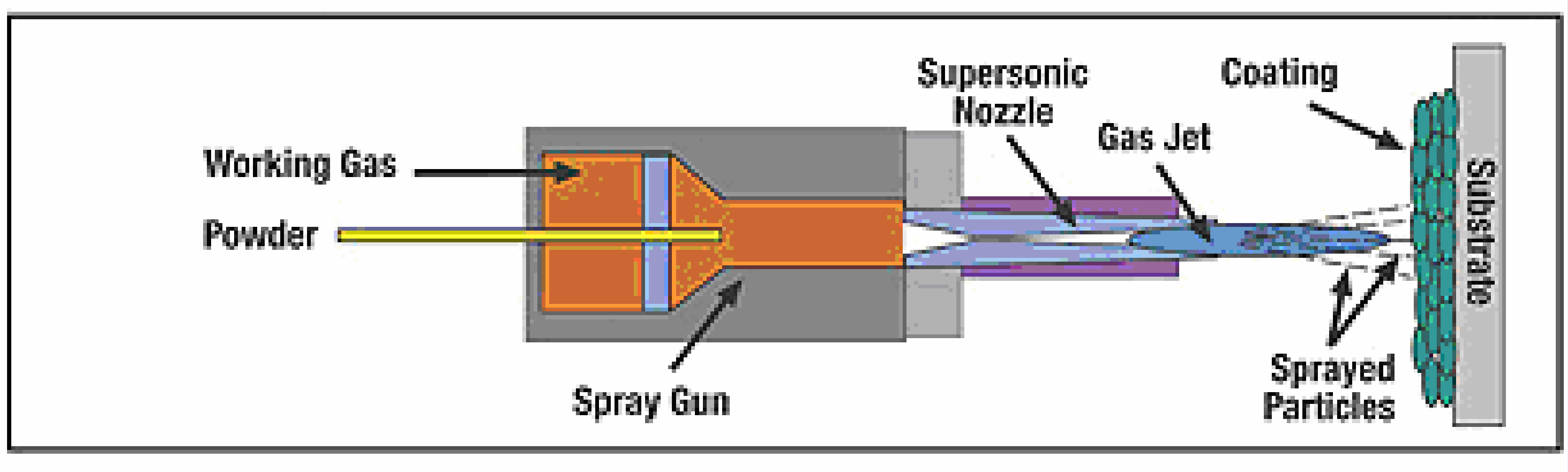
Burning by-products expelled outward through the spray gun orifice can produce "shock diamonds"

Disadvantages include low deposition rates and in-flight particle oxidation

Cold Spray 冷 火焰喷镀

Developed in the former Soviet Union in the mid 1980s by Papyrin, the method has garnered significant research interest after the 2000.

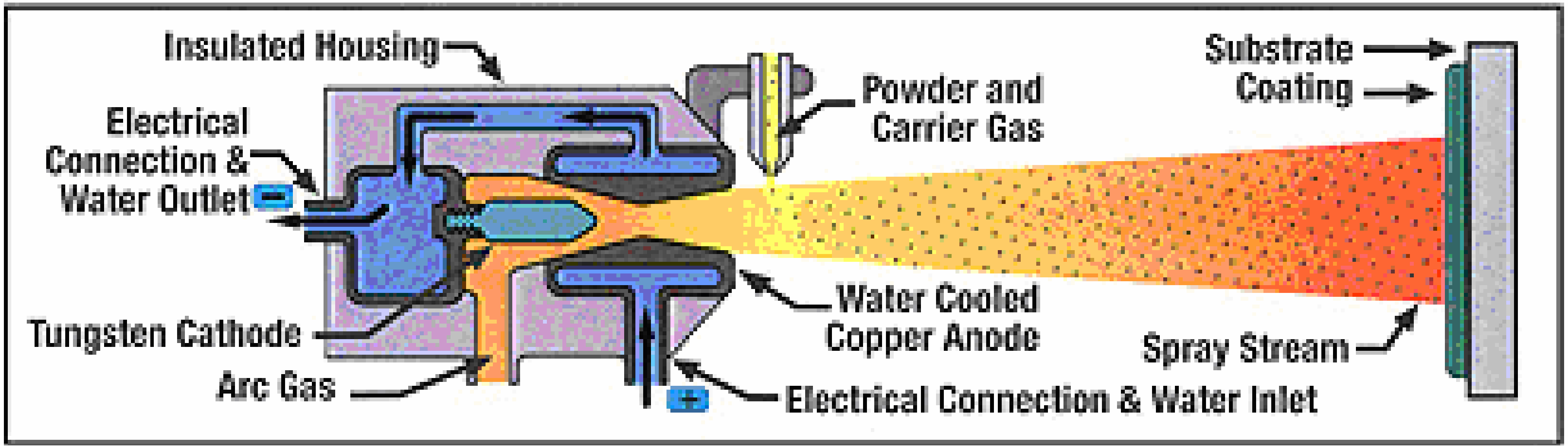
Supersonic jets of compressed gas accelerate near-room temperature powder particles at ultra high velocities. The un-melted particles, travelling at speeds between 500 to 1,500 m/sec, plastically deform and consolidate on impact with their substrate, where deformation and fusion occur on impact to produce dense coatings without significantly heating the feedstock material



This is achieved using convergent-divergent, de Laval nozzles, high pressures (up to 3.5 MPa) and flow rates (up to 90 m3/hr) of gases such as He or N_2. The gases are pre-heated to about 800°C for aiding particle plastic deformation

Non-transferred Plasma Arc Spraying 等离子的电弧喷气切割法

A non-transferred arc is the heat source that ionizes a gas melting the coating material and propelling it to the workpiece



Flame Temp: ~6,000-11,000°C **Particle speed: 240-550 mt/sec** **Fuel gases: Ar/H_2; N_2/H_2**

Plasma guns consist of water-cooled chamber and front-nozzle. At the rear of the chamber is a non-consumable Thoriated Tungsten rear-electrode, also water-cooled.

A port, within the chamber, allows the high-pressure plasma forming gas to enter.

A high-frequency spark initiates operation and is discontinued upon ignition.

Important: the high-pressure gas cools the outer layer of the plasma arc, so extreme heat is kept away from the nozzle bore

Electric Arc Spraying

An arc is struck between two consumable electrodes of a coating material. Compressed gas is used to atomize and propel the material to the substrate.

The electric arc spray process utilizes metal in wire form. This process differs from other thermal spray processes in that there are no external heat sources as in the combustion gas/flame spray processes.

Heating and melting occur when two electrically opposed charged wires, comprising the spray material, are fed together in such a manner that a controlled arc occurs at their intersection.

The molten metal is atomized and propelled onto the prepared workpiece by jets of compressed air or gas.

RF Induction Plasma Spraying

The torch is a, water-cooled, high frequency OFHC copper induction coil surrounding a gas stream into a quartz tube. On ignition, eddy currents are produced within the RF induction coil, which couples to the gas, ionizing it to produce a plasma.

Releasing gas into the tube and energizing the copper helix by a high frequency current that sets up an intense magnetic field inside the tube causing ionization of the gas.

The continuous flow causes gas escaping through the open bottom of the tube. Powder fed into the plasma filled tube is melted and is conveyed to the work surface.
Coatings produced using RF plasma are generally homogeneous and less porous.

In neutral atmospheres, Ca, U, Nb, Ti can be deposited.

What is a Plasma?

‘Plasma' is an ionised gas which contains enough charged particles for the overall behaviour of the system to be dramatically changed from an ordinary neutral gas. It can be fully ionised so that there are few neutral particles left, or it can be a mixture of charged and neutral particles.

Plasmas are classified as the fourth state of matter, after solids, liquids and gases.

Since plasma is the most common state of matter in the universe and everything was plasma just after the big bang, perhaps it should be classified as the 'first' state.

Inductive RF Ar

Hot H Plasma

Supersonic He flow

Galaxy NGC1512

Plasma Thruster

Typical Ne Plasma

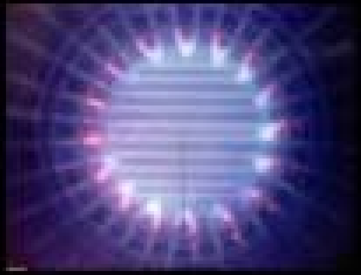
Plasma Torch

Hall Thruster

Aurora (O_2 Colours)

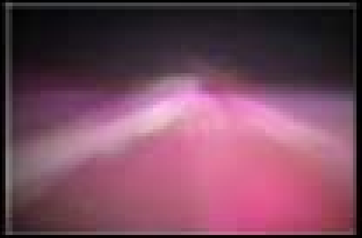
Forked Lightning

Aurora over Finland



Confined Plasma

Underwater Plasma

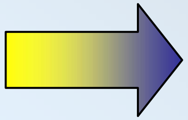


Aurora over Finland (2)

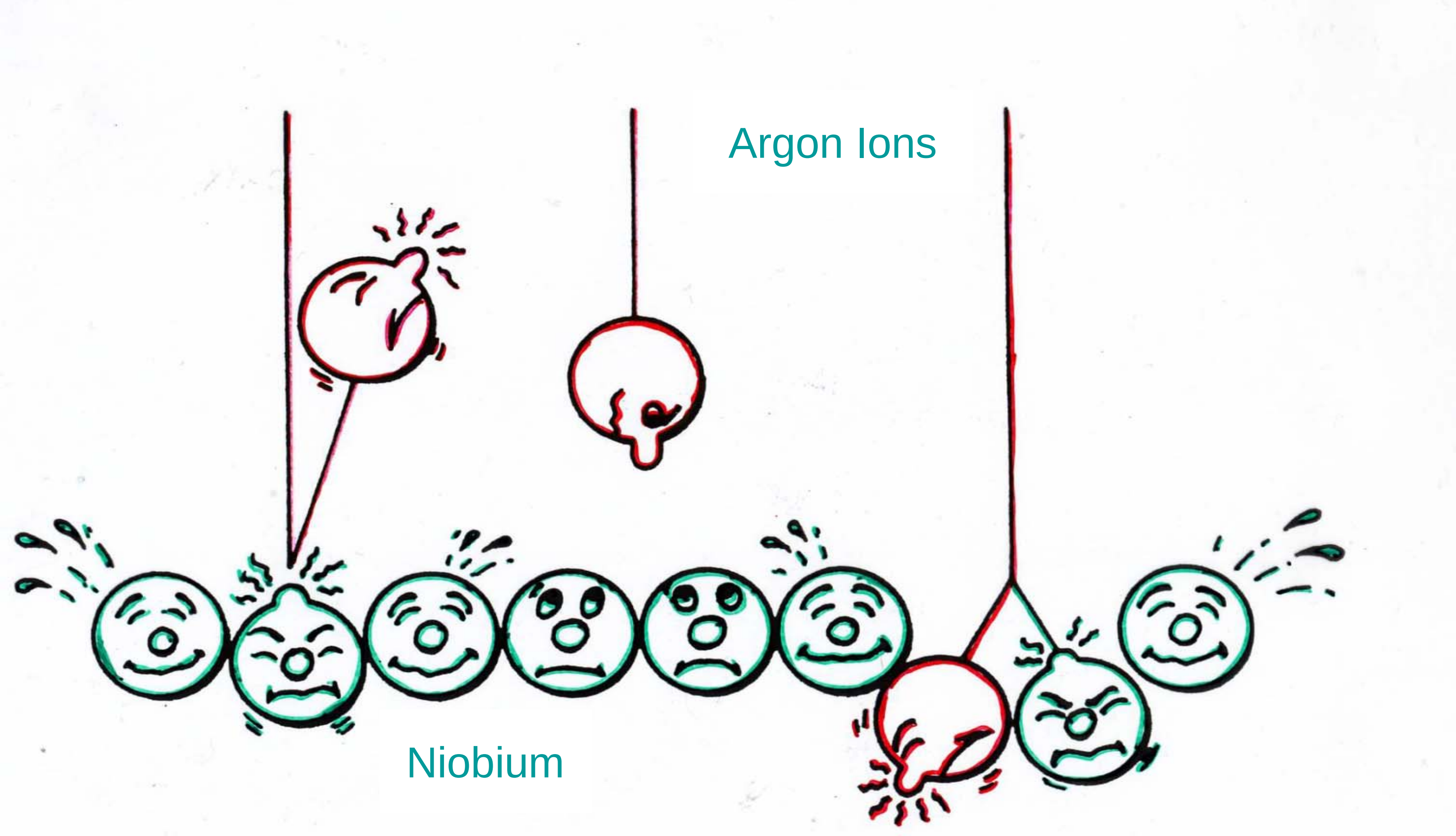
Noble Plasmas

PVD: Sputtering 阴极溅射

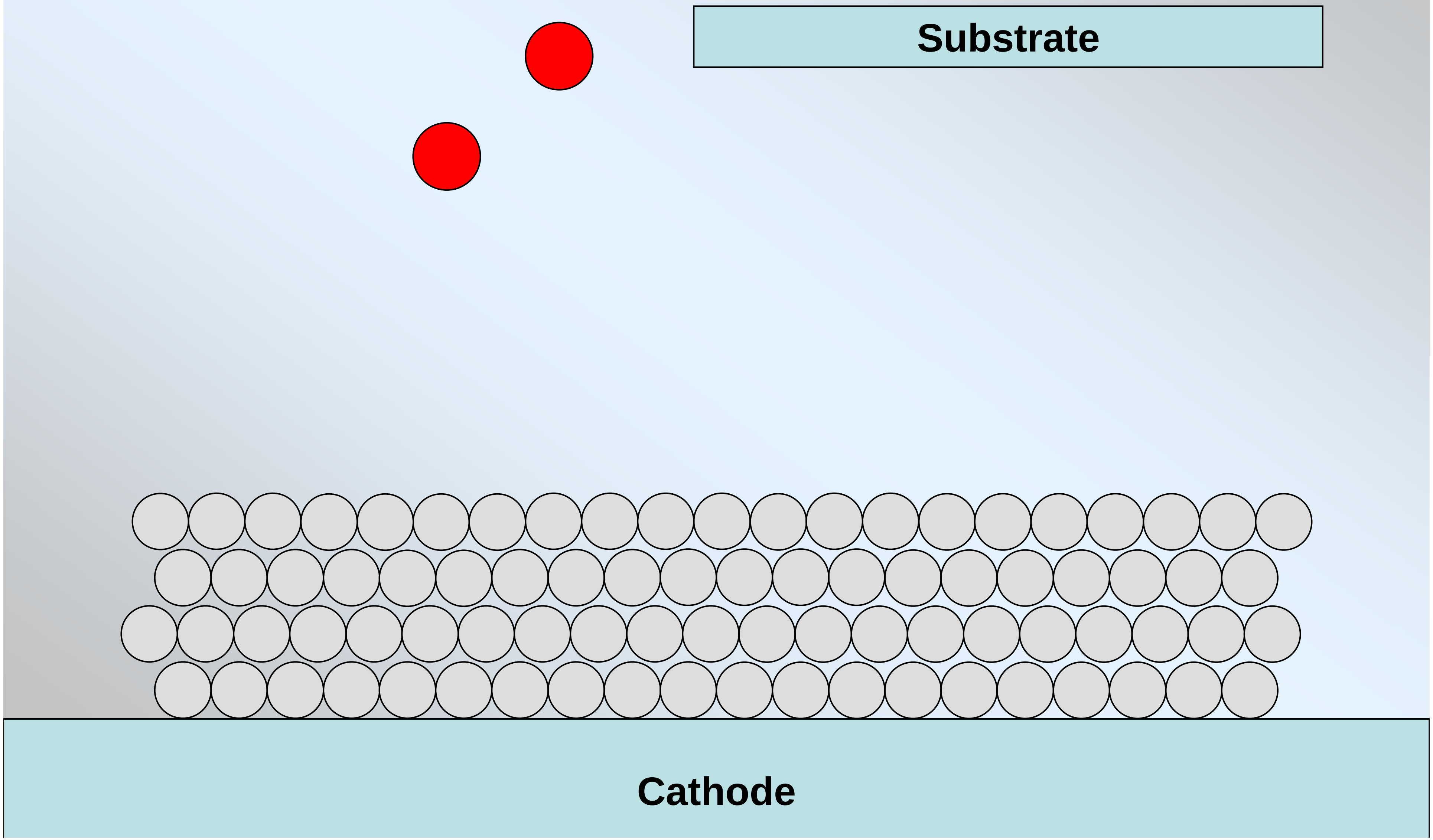
Momentum Transfer from ions to the target atoms



Atoms are ejected from the cathode to the substrate

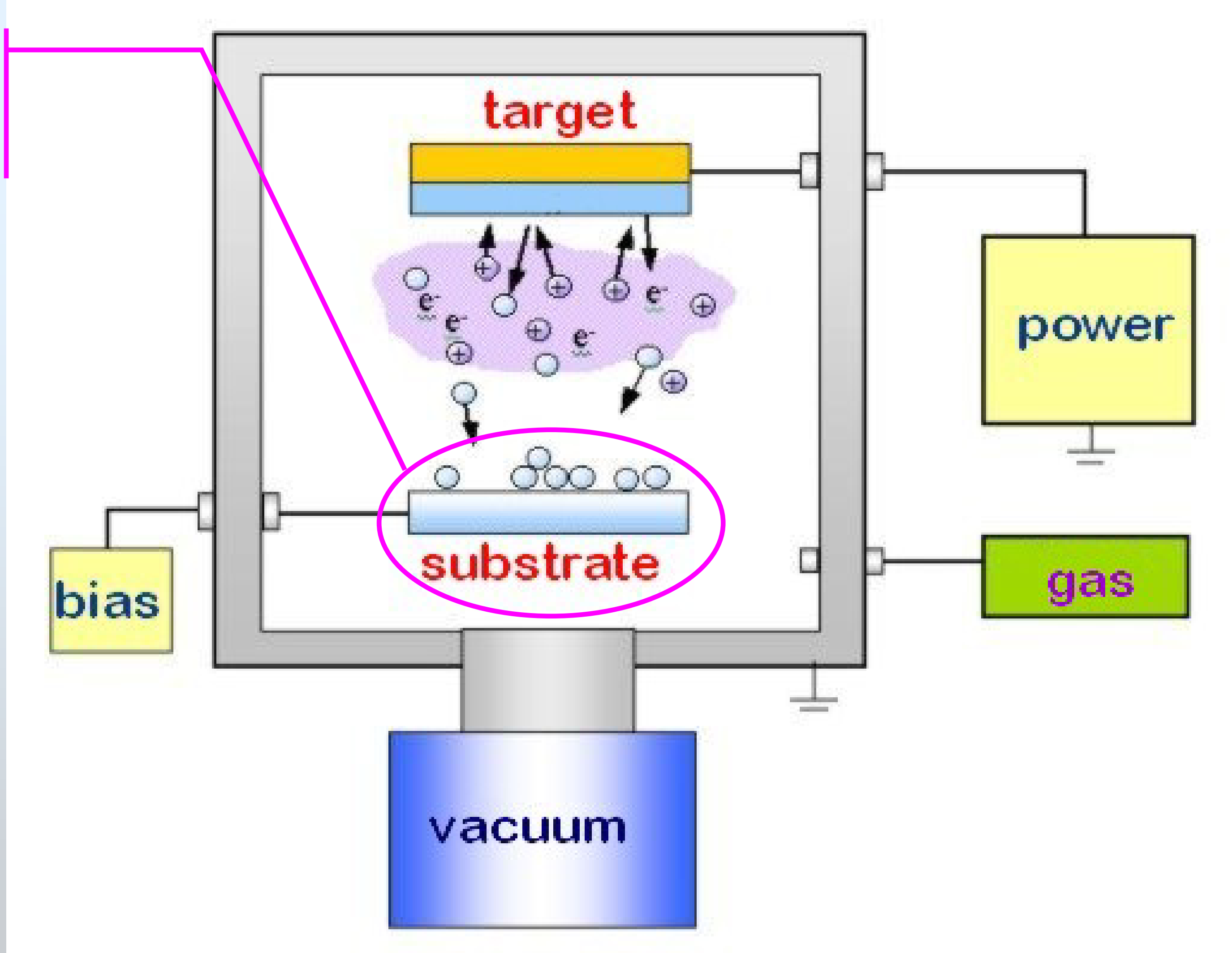


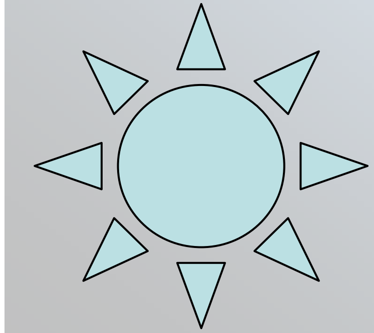
Sputtering



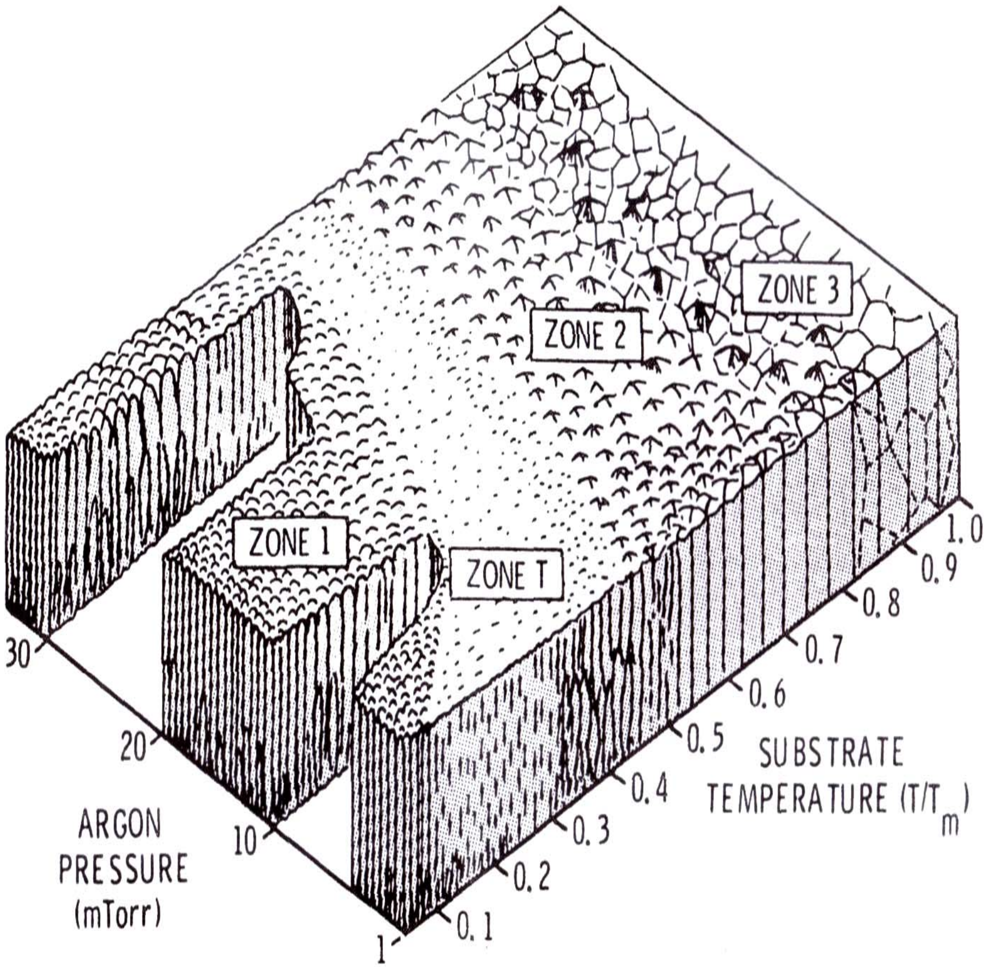
DC Diode Sputtering

The substrate is also the anode

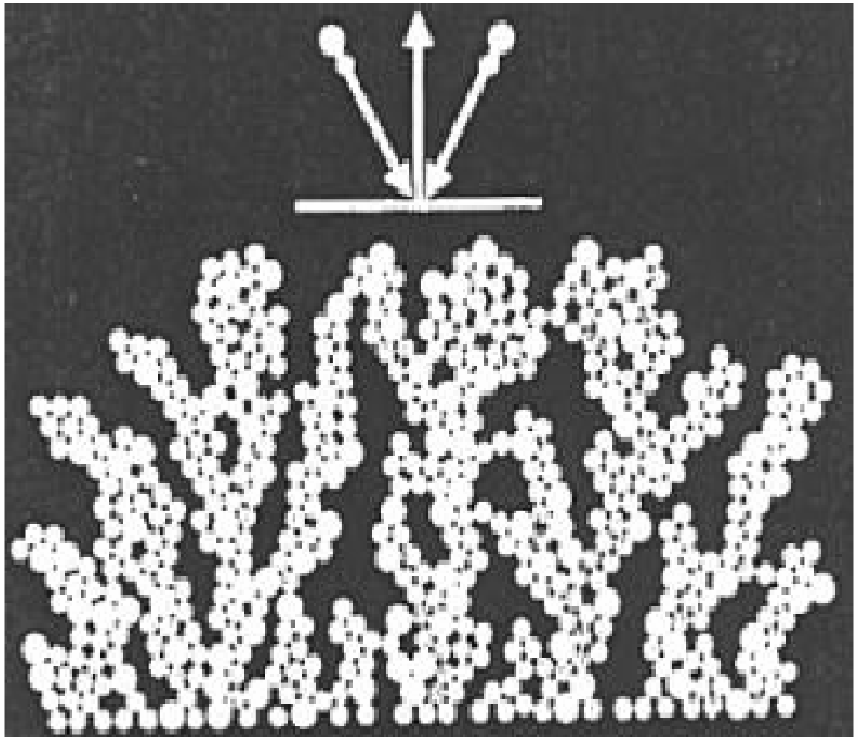




Tornthon Simplified Zone model for a sputtered film

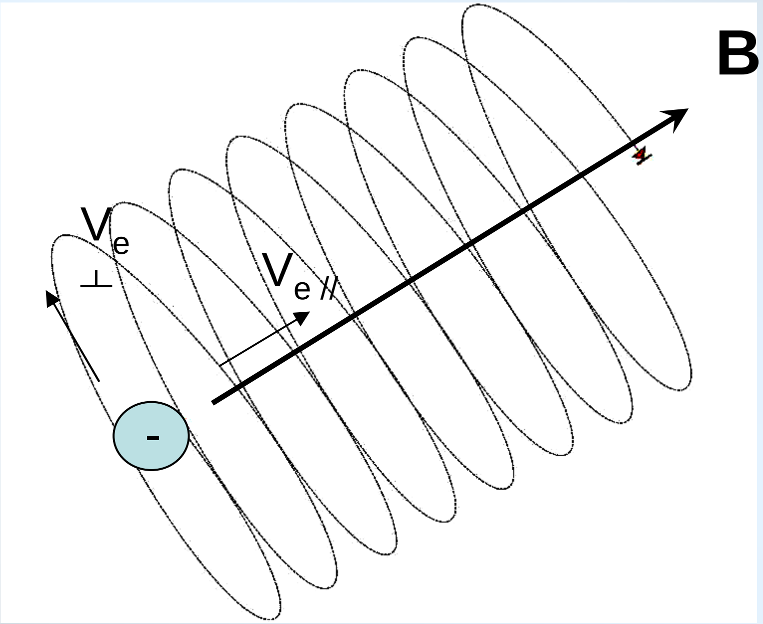


- •ZONE 1: low T/Tm, High P_{Ar} Dome-head rastered Crystals. empty boundaries
- •ZONE T: Dense array of fiber-like grains barely defined, low density boundaries
- •ZONE 2: High T/T_m columnar grains, intercristallyne boundaries
- •ZONE 3: T/Tm ~1 Equi-axed grains, epitaxial growth at high T



Structure formed by oblique incidence deposition of hard disks from two directions at ± 30° relative to the substrate normal. Disks were allowed to relax to the nearest point of contact with two other disks[12]

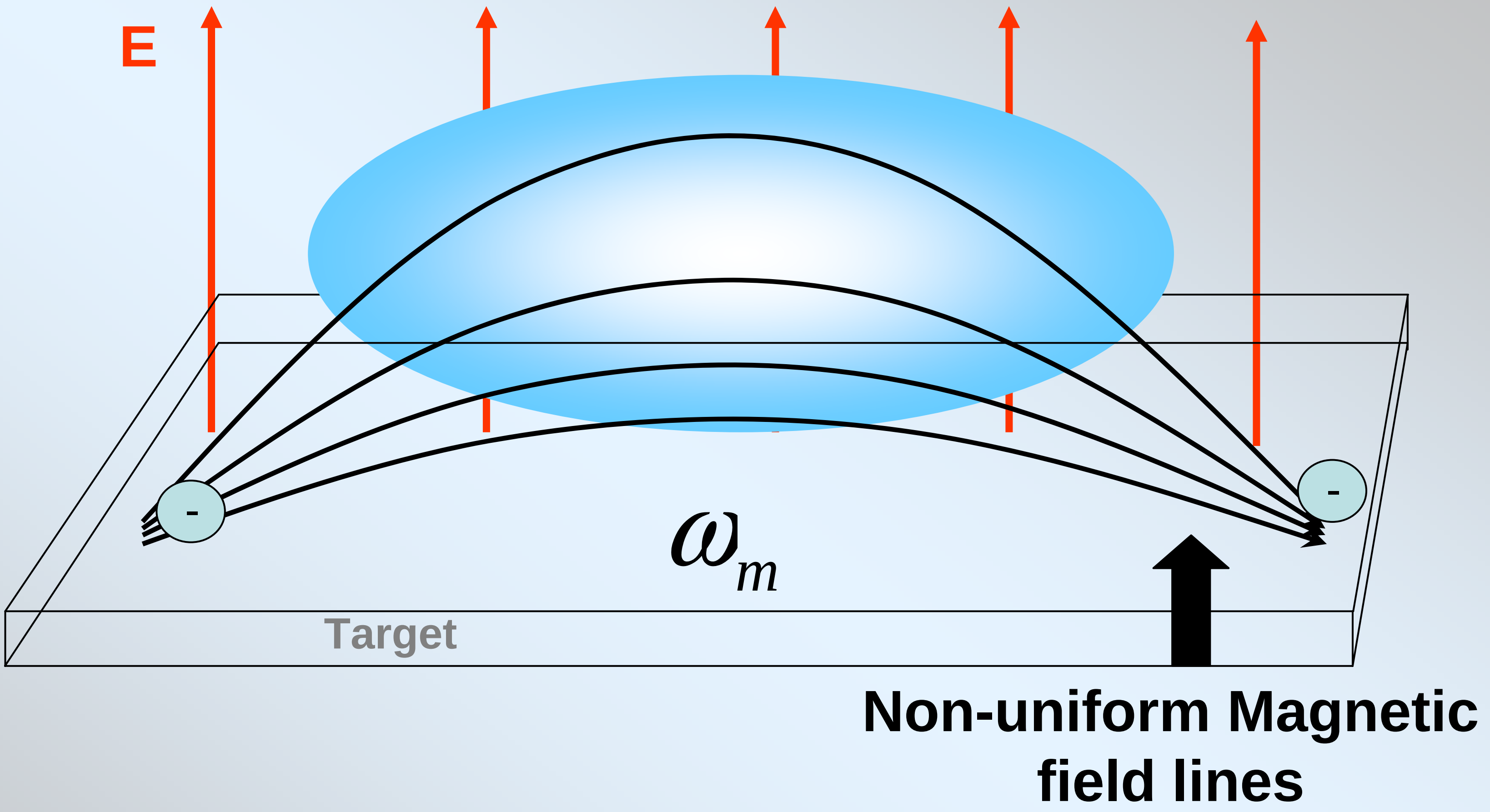
Motion of an electron into a magnetic field



Uniform magnetic field lines

$$\omega_c \propto B$$

Motion of an electron into a magnetic field

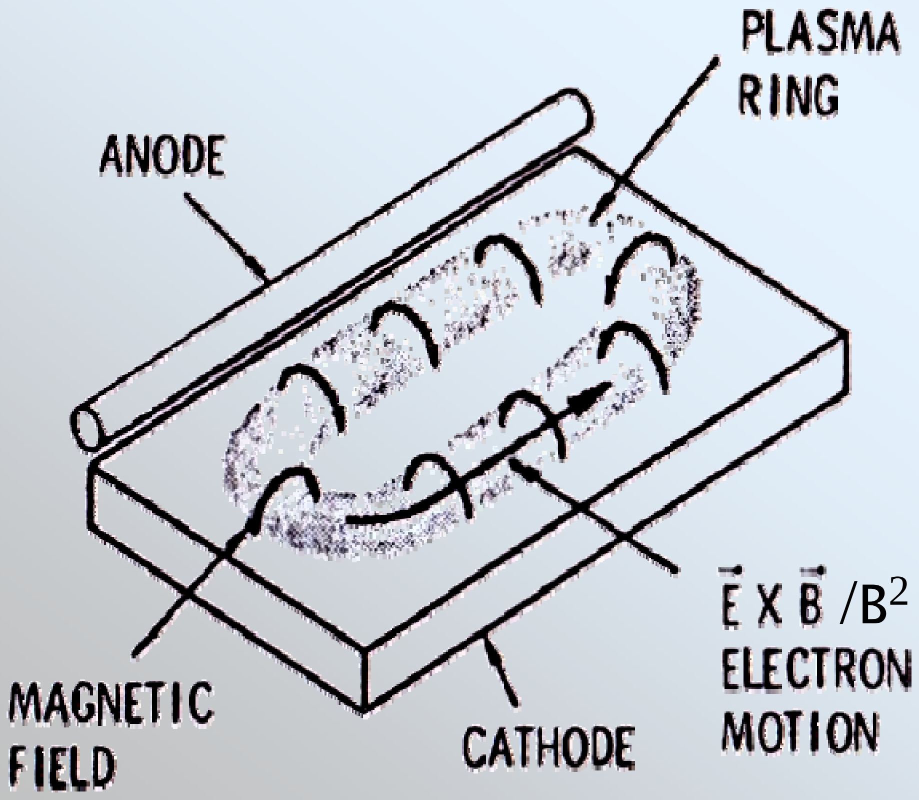


Non-uniform Magnetic field lines

- Electron reflection is due to magnetostatic and electrostatic mirror

Magnetron Sputtering 控管阴极溅射

Electron magnetic confinement



ADVANTAGES:

+ High deposition efficency

+ Low Argon Pressure

+ Low heating and damage of the substrate

A magnetron sputtering source must satisfy the “Penning conditions”:

- An annular-like volume of space is threaded by lines of magnetic field which, at either end, intersect surfaces at cathode potential;

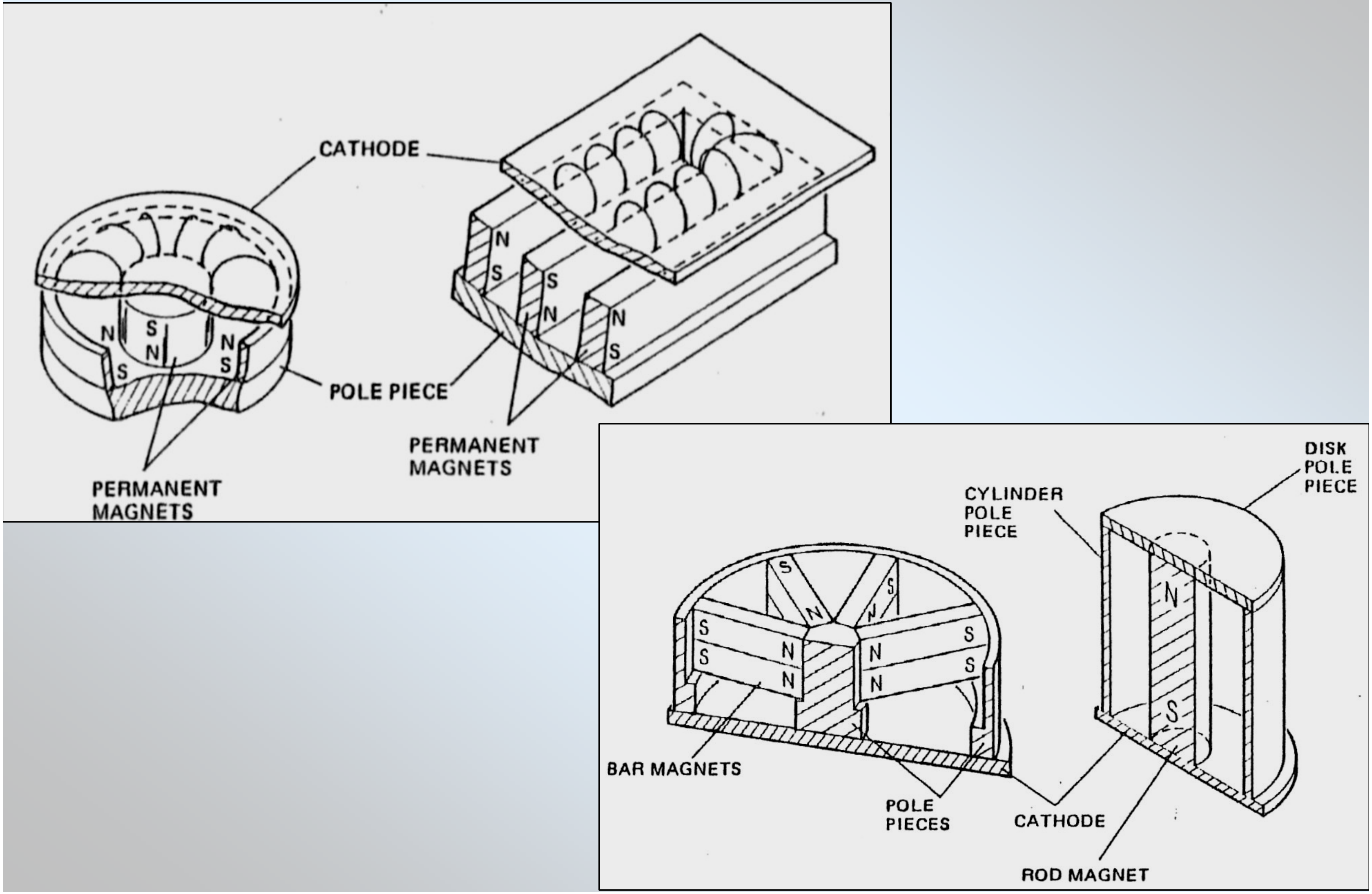
- A glow discharge is sustained by the application of a negative voltage to the cathode surfaces. The dominant voltage drop occurs across positive ion sheaths which forms and adheres to the cathode surfaces;

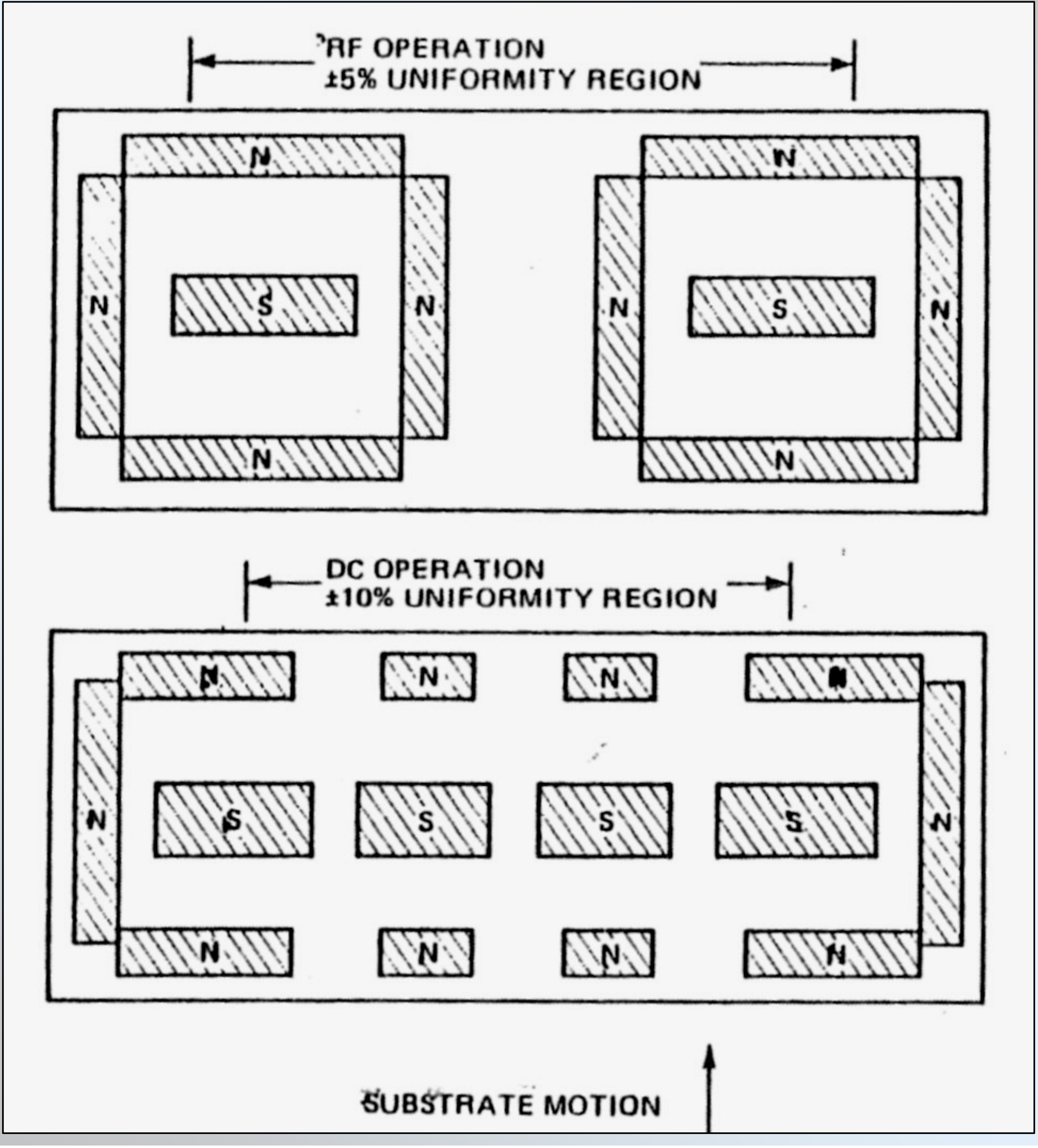
- A magnetic field strength is high enough to “trap” the g-electrons released from the cathode surfaces by ion bombardment, until a substantial fraction of their energy is lost to ionizing collisions with ambient gas molecules;

- A geometry is designed in a way to allow a substantial fraction of the gaseous ions produced in the trap volume to be attracted to, and collected by, the cathode surfaces which delimit such “trap volume”.

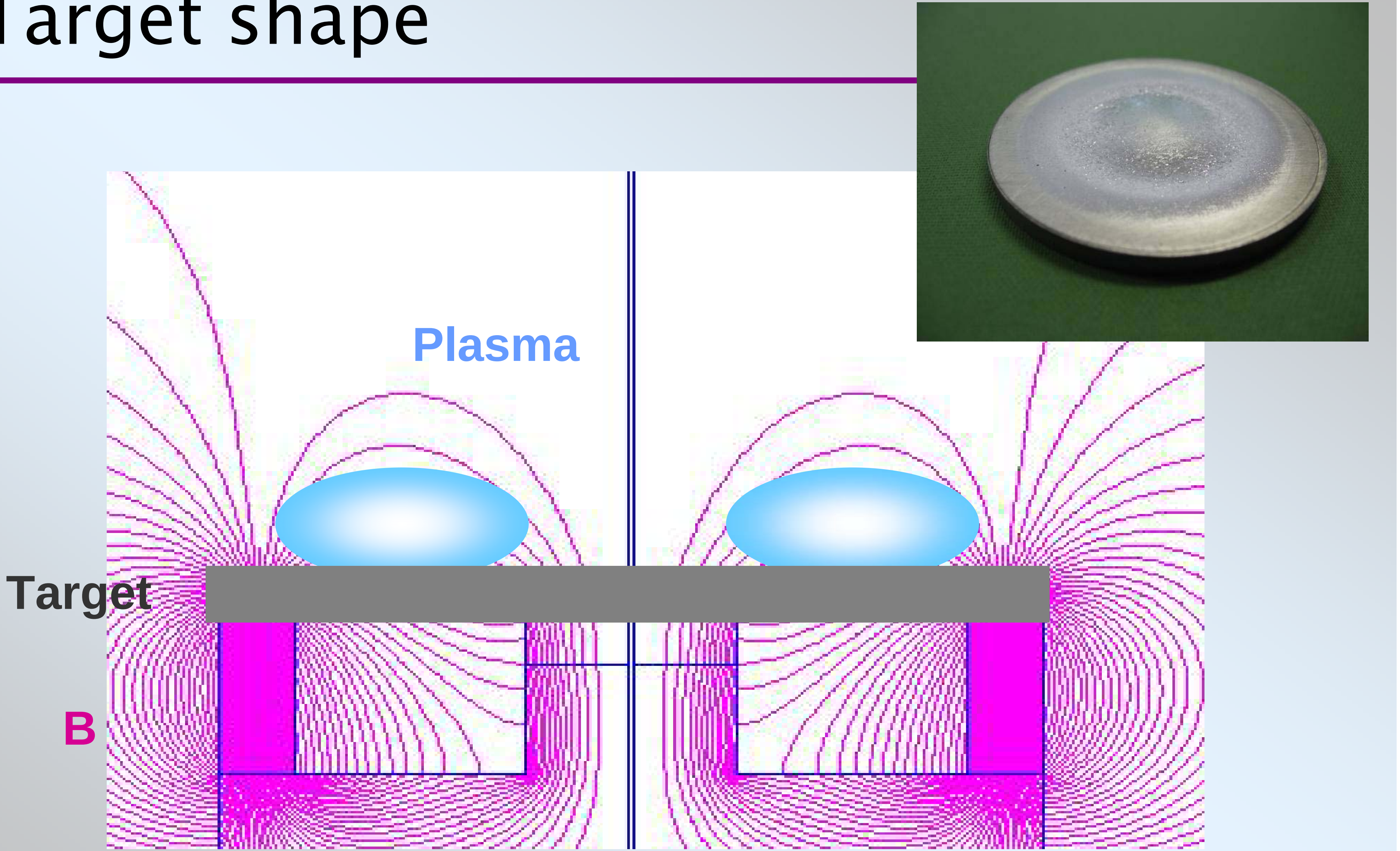
These ions are accelerated to the cathode through the positive ion sheath and cause sputter erosion of cathode material.

Magnetron 控管 Planar Sources

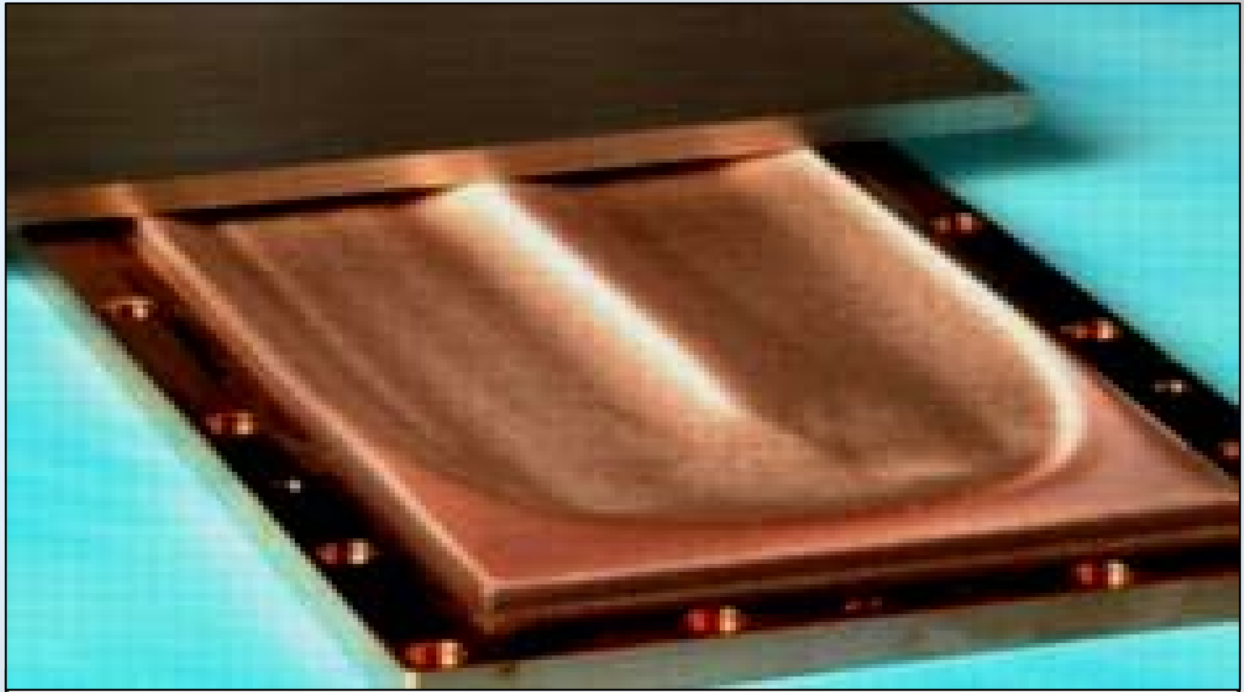



RF OPERATION
±5% UNIFORMITY REGION
N
N
S
N
N
N
N
S
N
N
DC OPERATION
±10% UNIFORMITY REGION
N
N
N
N
N
S
S
S
S
N
N
N
N
N
SUBSTRATE MOTION

Target shape



2 inches planar target



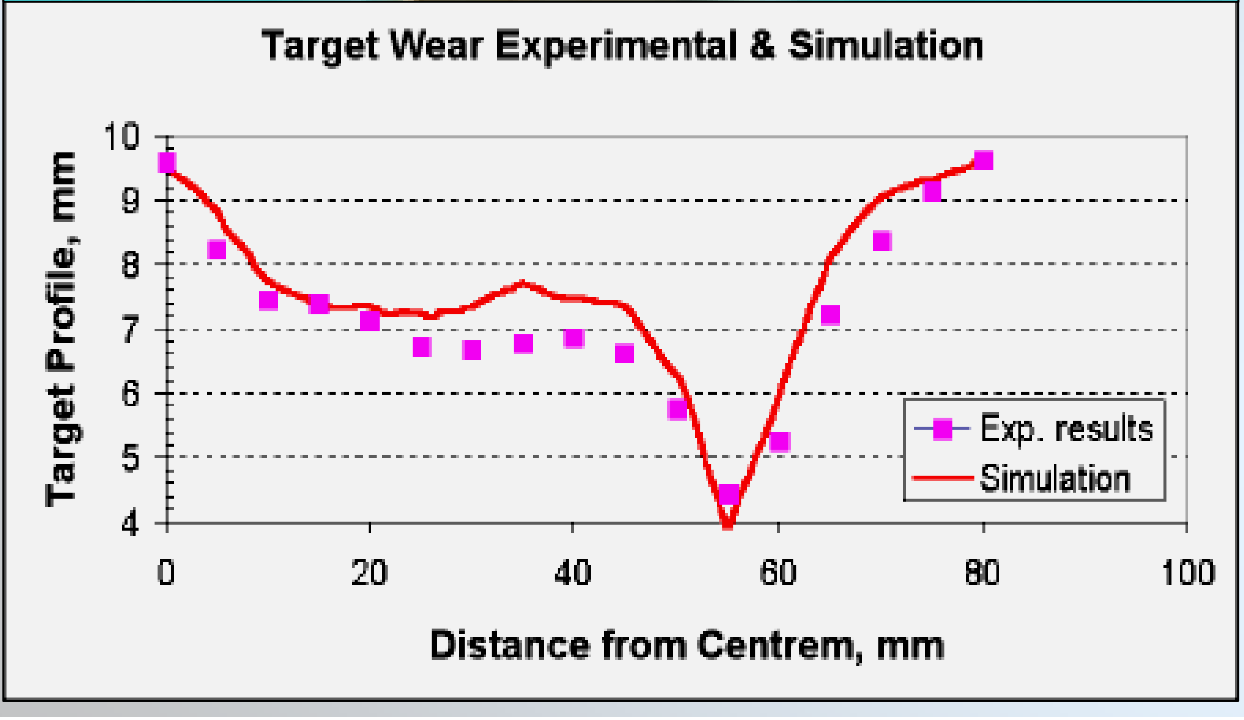

Target Wear Experimental & Simulation
Target Profile, mm
10
9
8
7
6
5
4
0
20
40
60
80
100
Distance from Centrem, mm
Exp. results
Simulation

Рис. 3.11. Базовая конструкция профилированной мишени типа inset до распыления (*а*) и после двустороннего распыления (*б*)

Мишени типа inset выпускаются в виде трех модификаций. Помимо изображенной на рис. 3.11 мишени с X-образной зоной эрозии выпускаются мишени с ε- и μ-образными зонами эрозии. Мишени с ε-образной зоной эрозии предназначены для распыления дорогостоящих материалов (Au, Ag, Pt, Pd и др.). Мишени с μ-образной зоной эрозии наиболее пригодны для распыления материалов с плохой теплопроводностью (Ti, Cr, Ni+7 % V и др.).

Второй способ повышения эффективности ИММ основан на изменении конфигурации магнитного поля с помощью магнитной системы специальной формы, в результате чего существенно увеличивается площадь мишени в зоне интенсивного распыления. Типичным примером реализации этого способа является секционированная магнитная система, полюсные наконечники специальной формы которой создают магнитное поле в виде дорожки большой протяженности (рис. 3.12). При этом зона разряда покрывает значительную часть Δ-образной поверхности мишени, обеспечивая формирование зоны эрозии в виде изогнутой ленты.

Для повышения эффективности использования материала мишени могут применяться движущиеся относительно поверхности мишени магнитные поля, создаваемые постоянными или электрическими магнитами. Получение такого профиля, при котором зона распыления охватывает большую часть поверхности мишени, возможно несколькими способами: смещением поля постоянного магнита путем на-

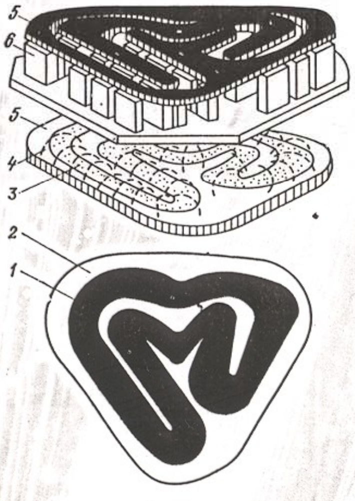


Рис. 3.12. Базовая конструкция мишени Δ-образной формы с секционированным магнитным полем:

1 — зона эрозии мишени; *2* — мишень; *3* — зона плазмы; *4* — силовые линии магнитного поля; *5* — полюсные наконечники; *6* — магниты

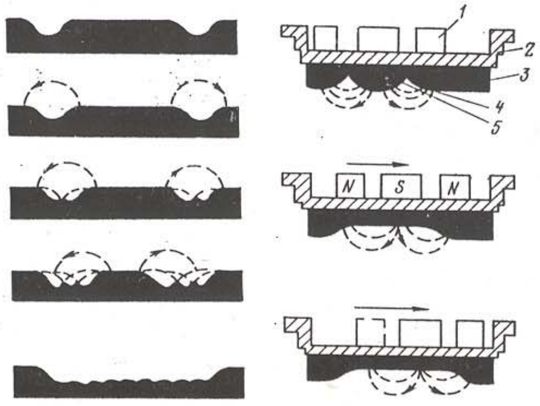


Рис. 3.13. Последовательность расширения зоны эрозии мишени с помощью подвижной магнитной системы:

1 — магнитная система; *2* — держатель мишени; *3* — катод-мишень; *4* — линии магнитного поля; *5* — зона эрозии

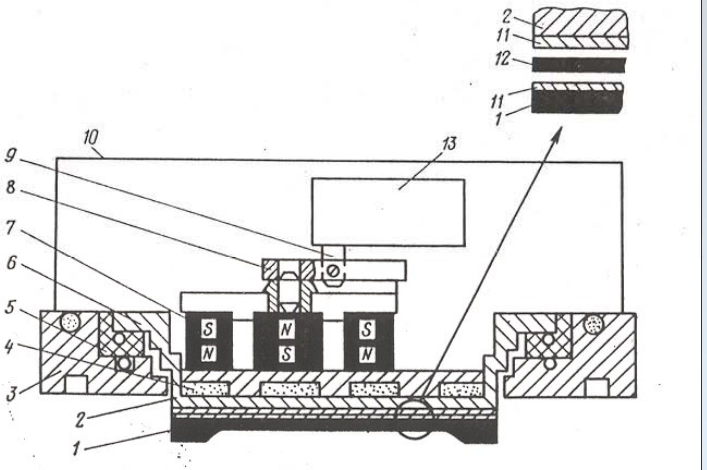
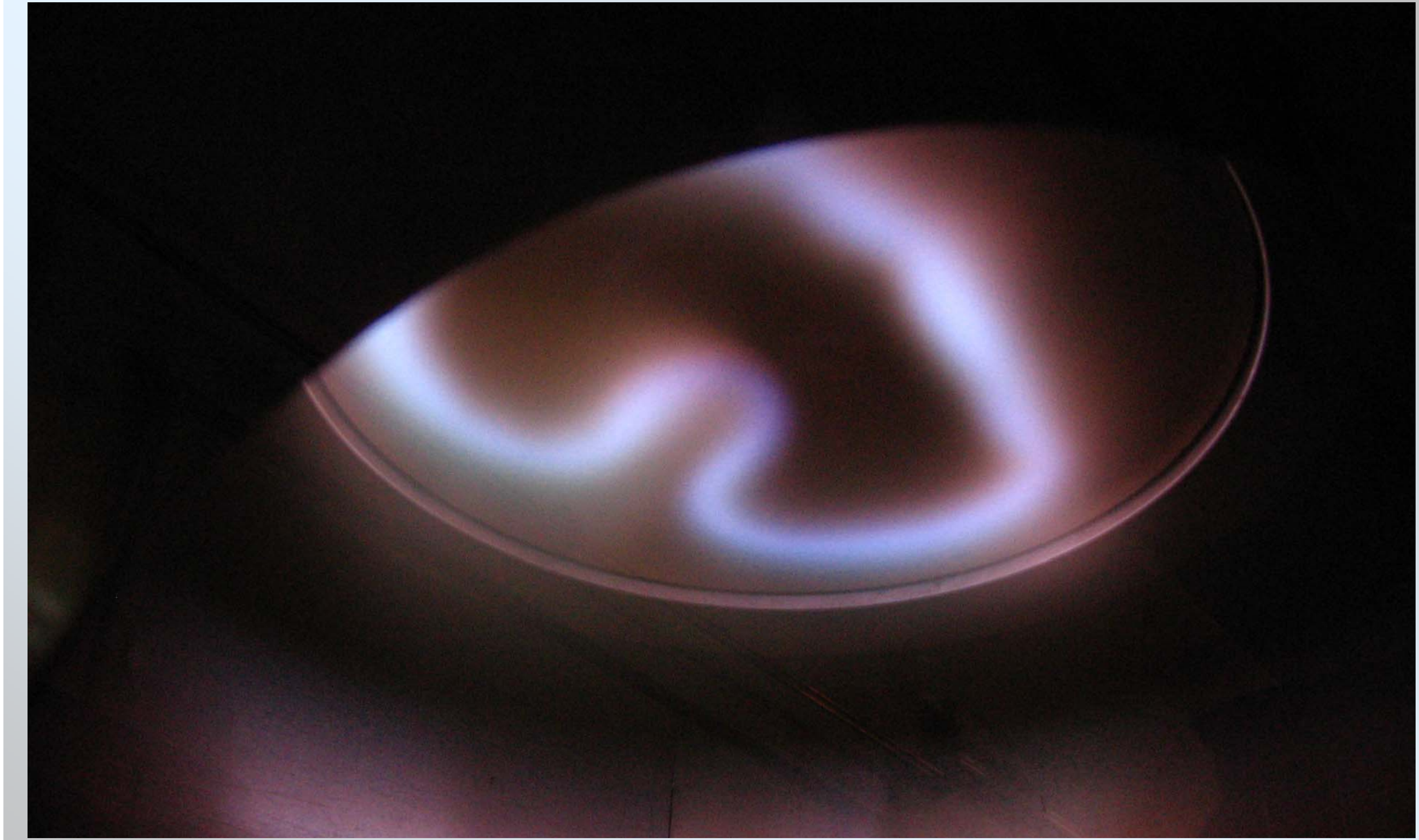


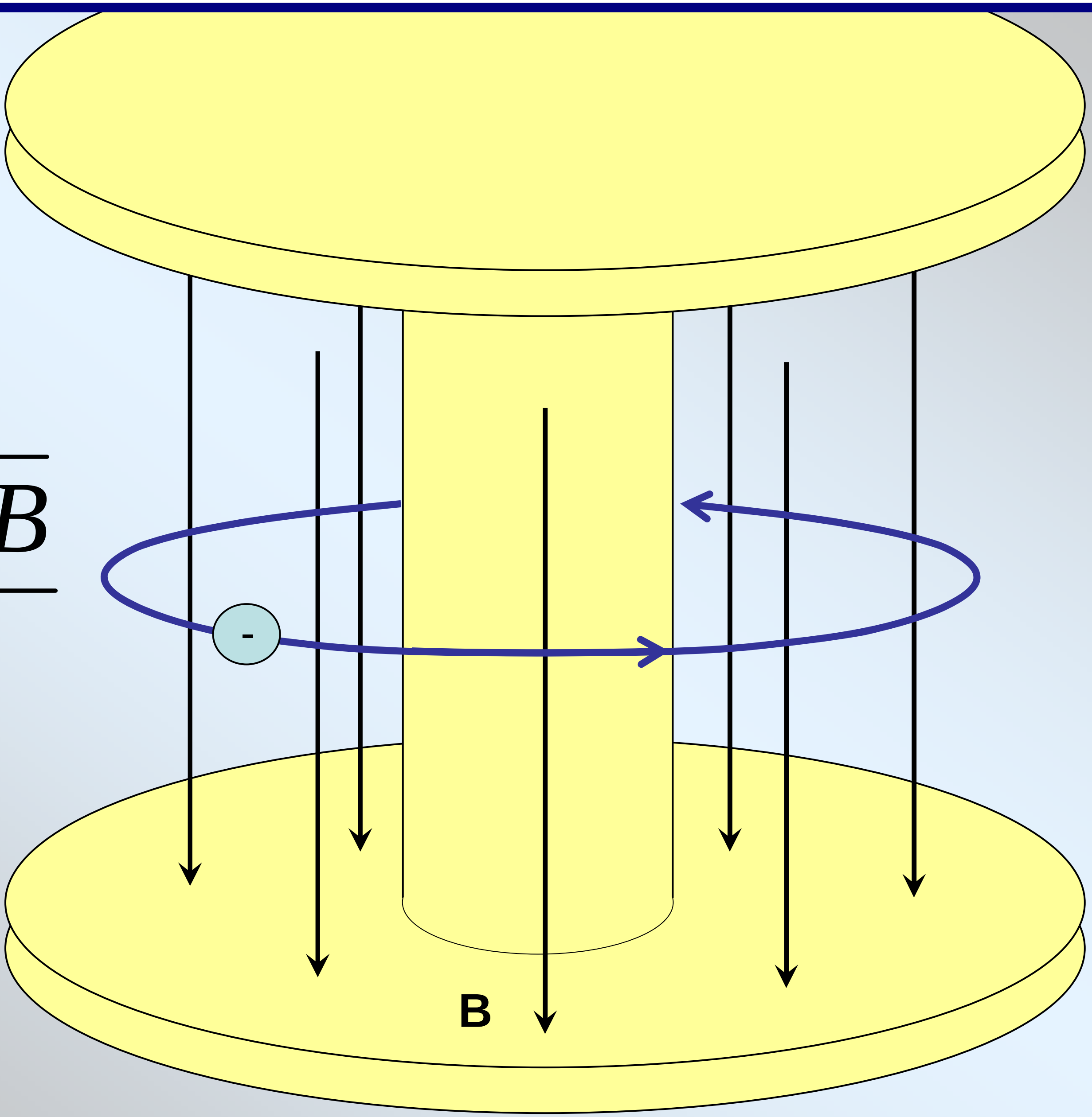
Рис. 3.14. Базовая конструкция МРС типа orbitorr:

1 — мишень; *2* — держатель мишени; *3* — анод; *4* — канал охлаждения; *5* — кольцевые уплотнения; *6* — фланец; *7* — магнит; *8* — эксцентрик; *9* — привод; *10* — крышка; *11* — металлизация обратной стороны мишени; *12* — легкоплавкий металл; *13* — электродвигатель



Cylindrical Post magnetron sputtering

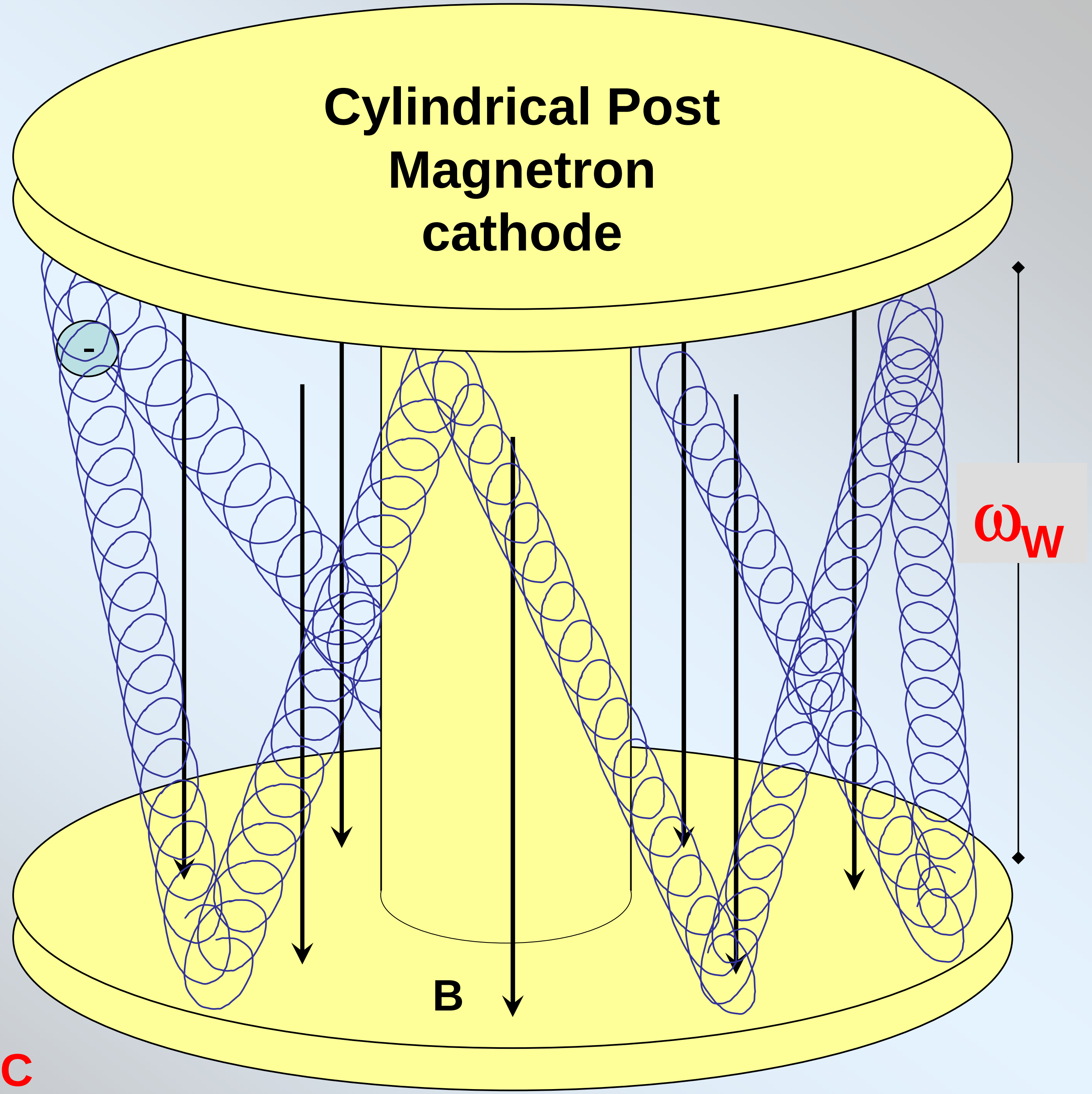
$$\omega_D \propto \frac{\overline{E}\times\overline{B}}{B^2}$$



If

$E \perp B$

Higher ionisation efficiency



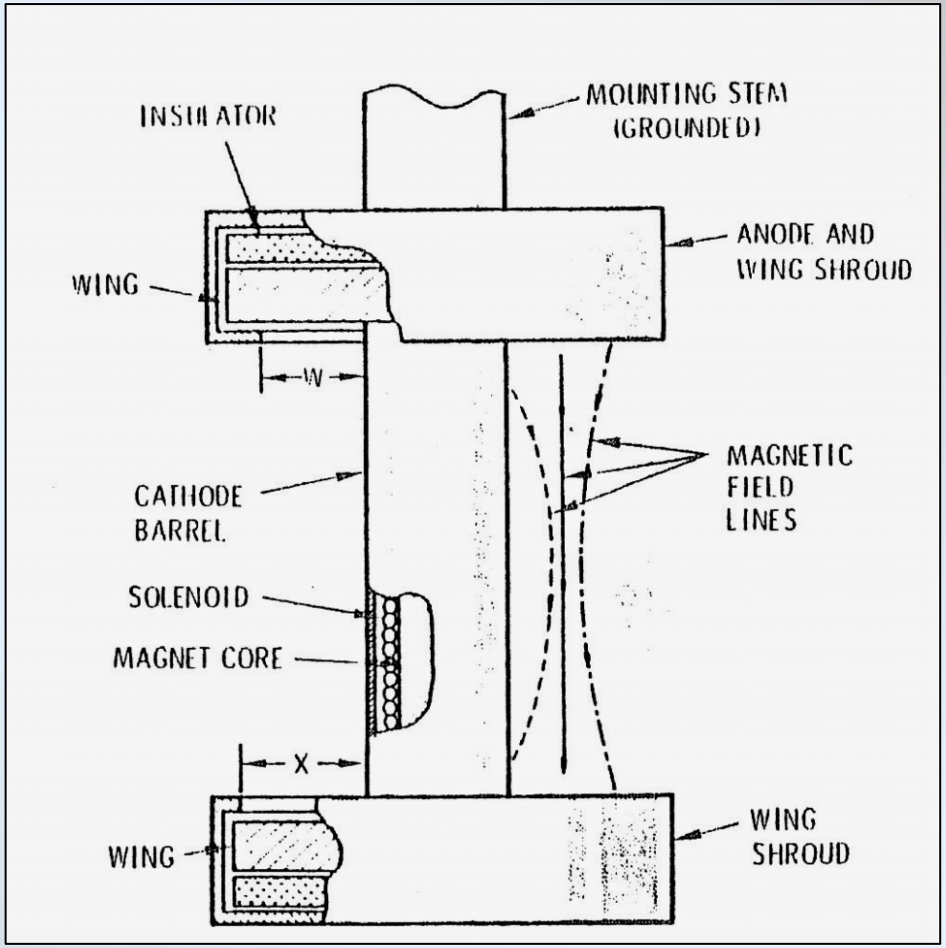
$\omega_D < \omega_W < \omega_C$

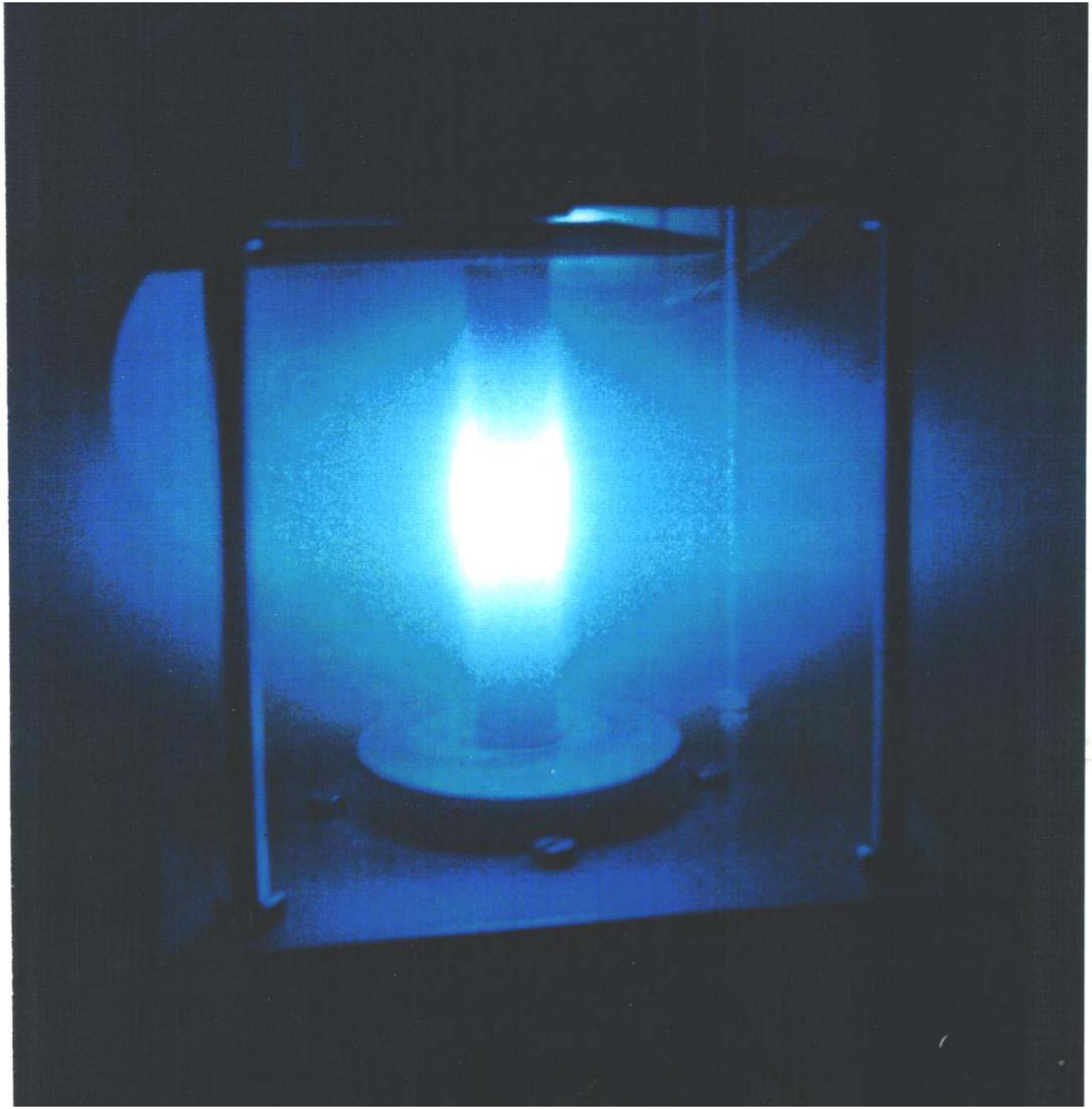
Magnetron

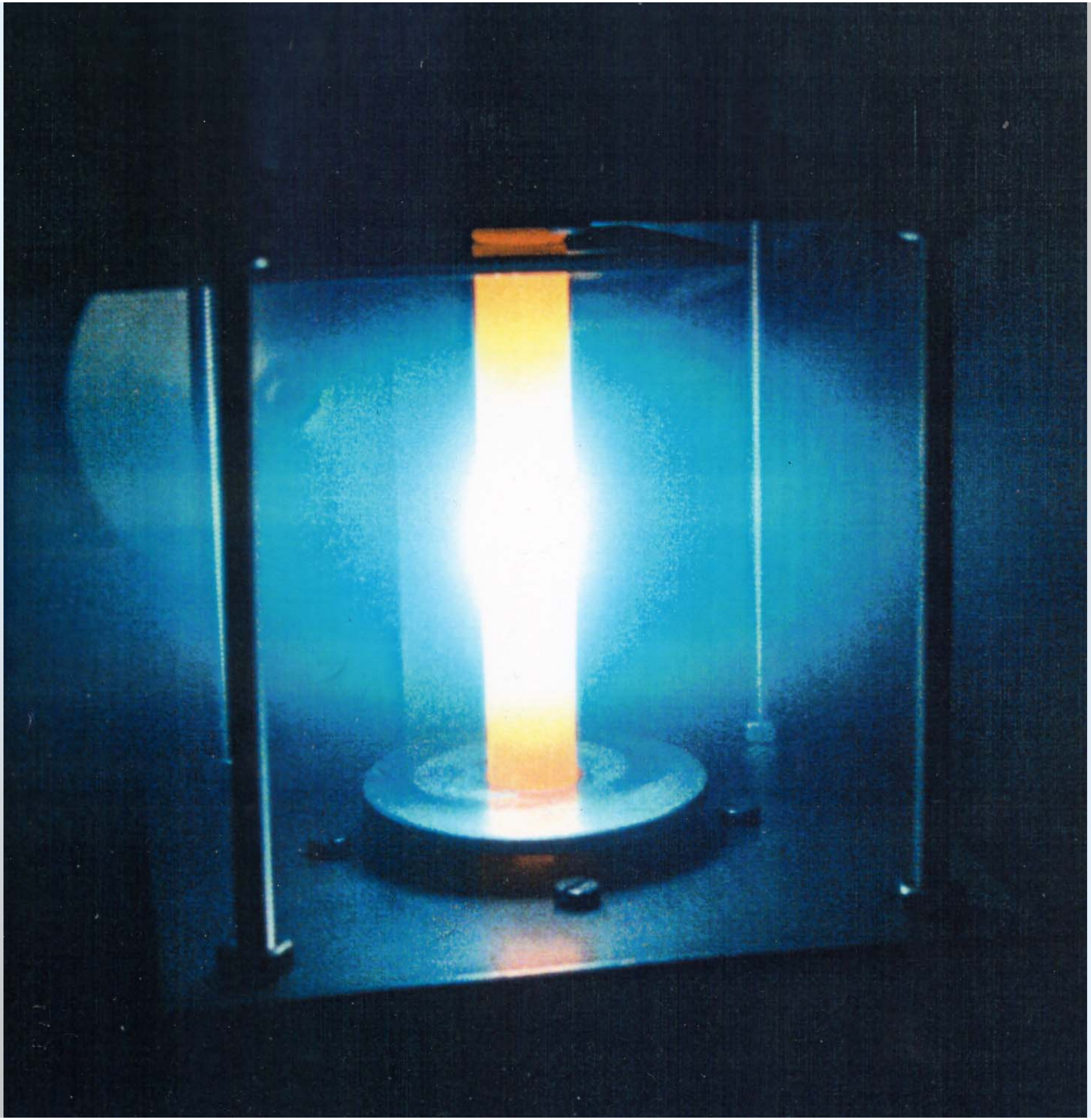
Sorgenti cilindriche: Cylindrical Post-Magnetrons

Due to the magnetic field generated, an intense discharge is confined along the cilindrical cathode

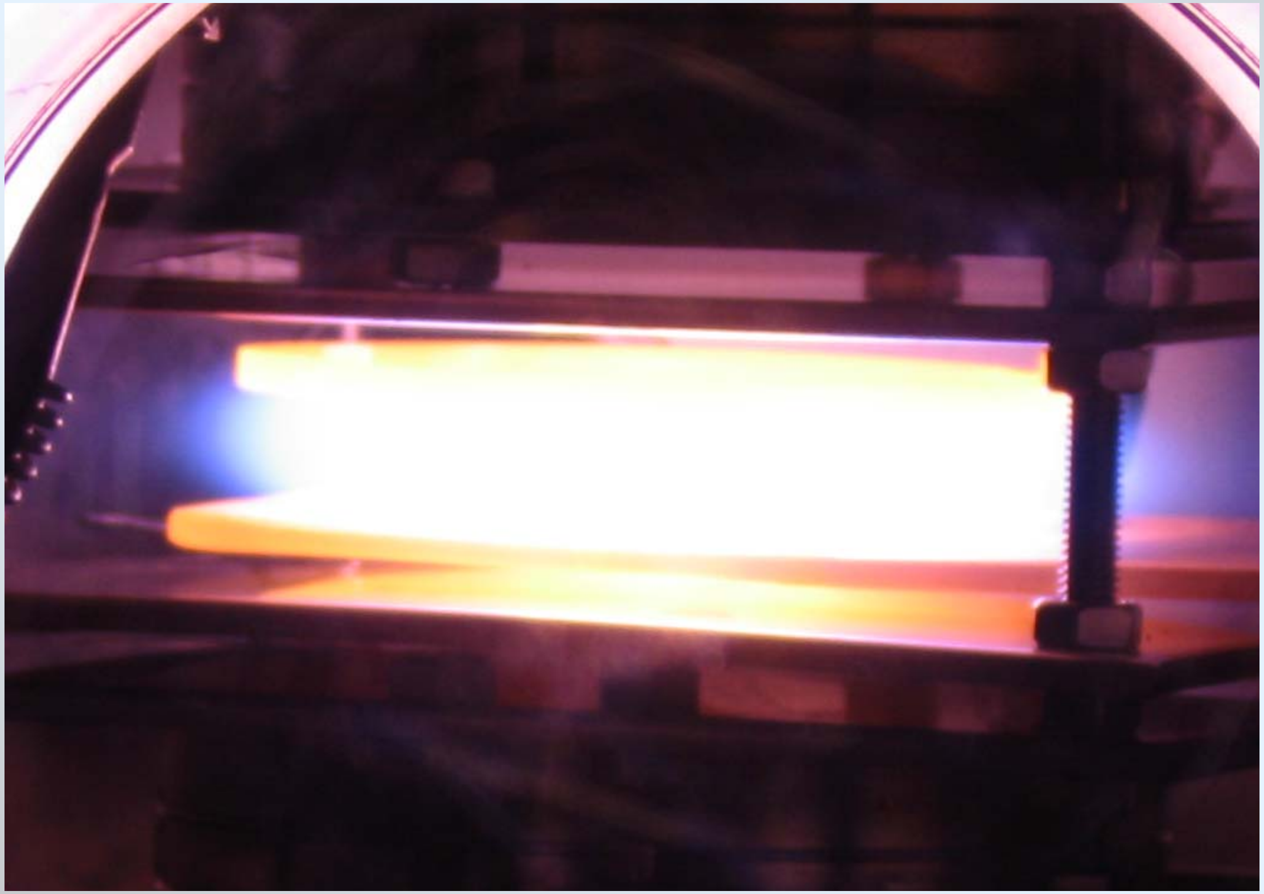
$$\boxed{W \geq 10\left(\frac{V^{1/2}}{B}\right)}$$



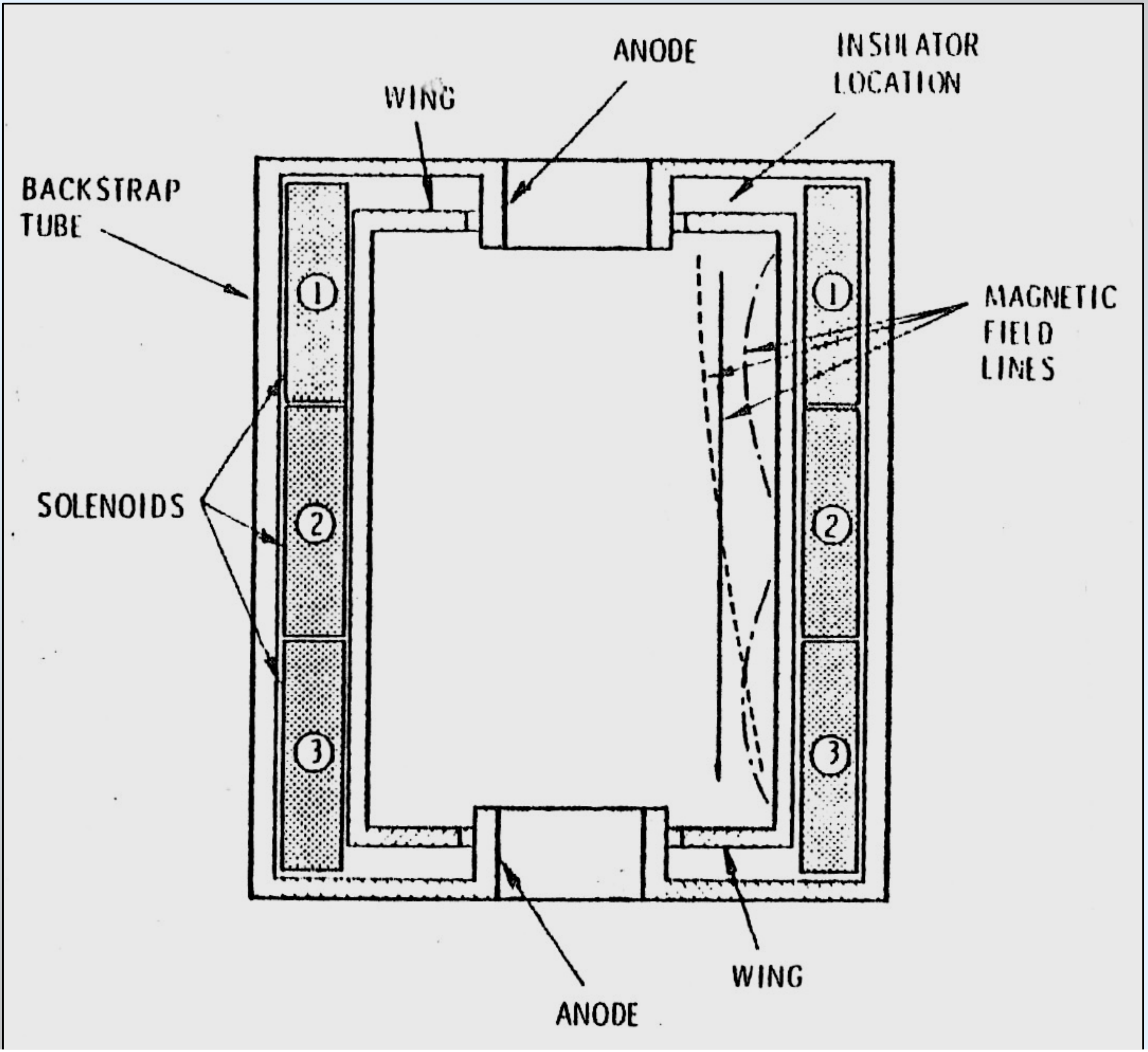


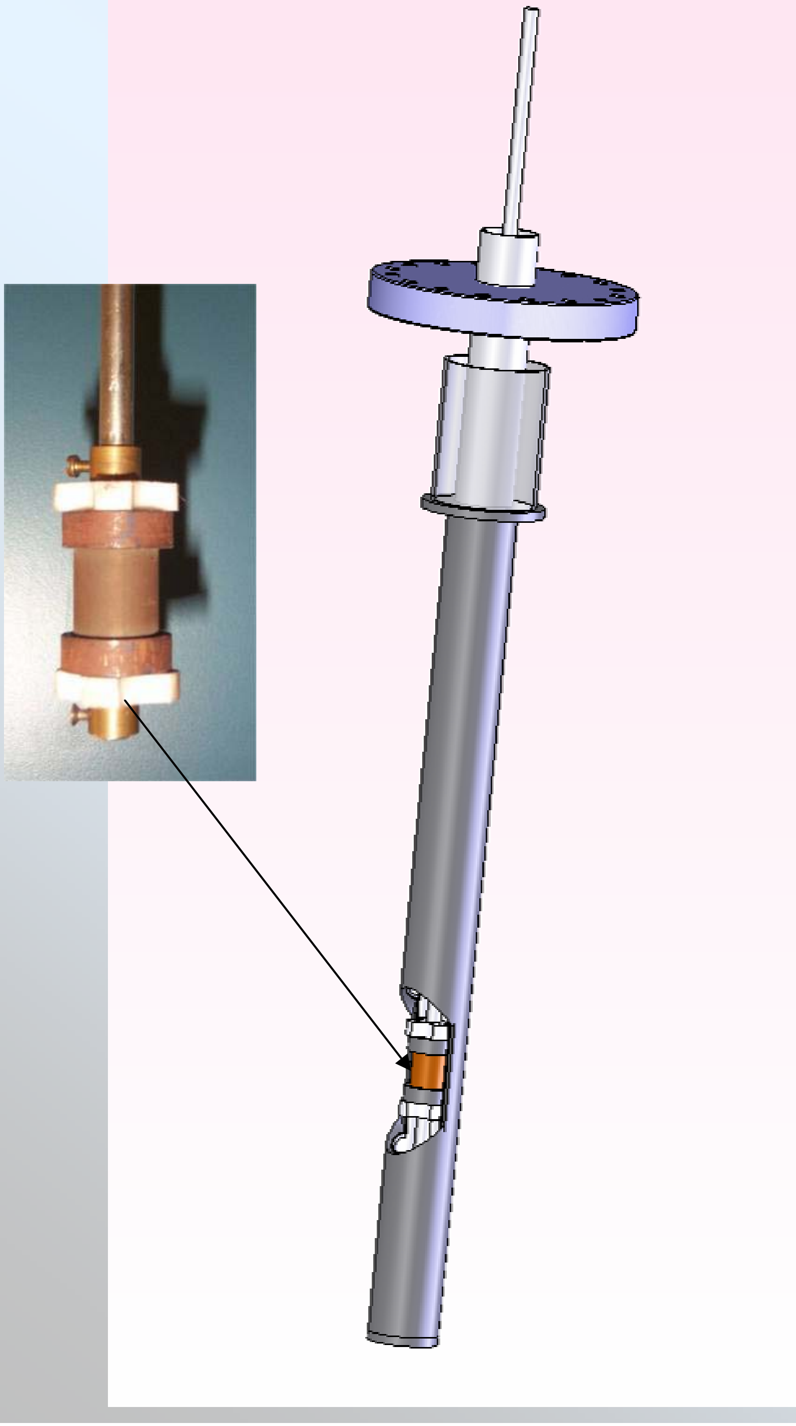


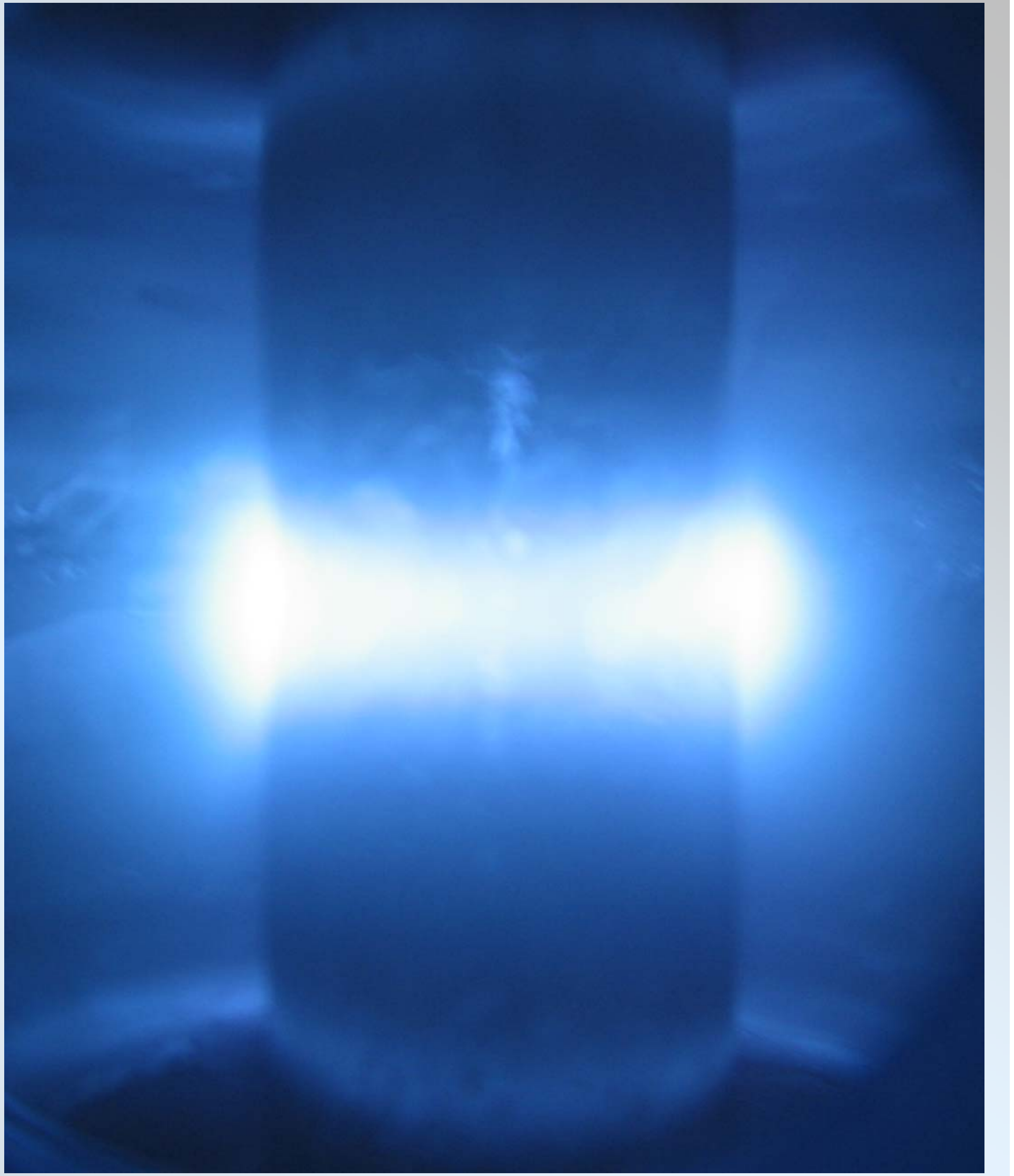
High Rate Sputtering



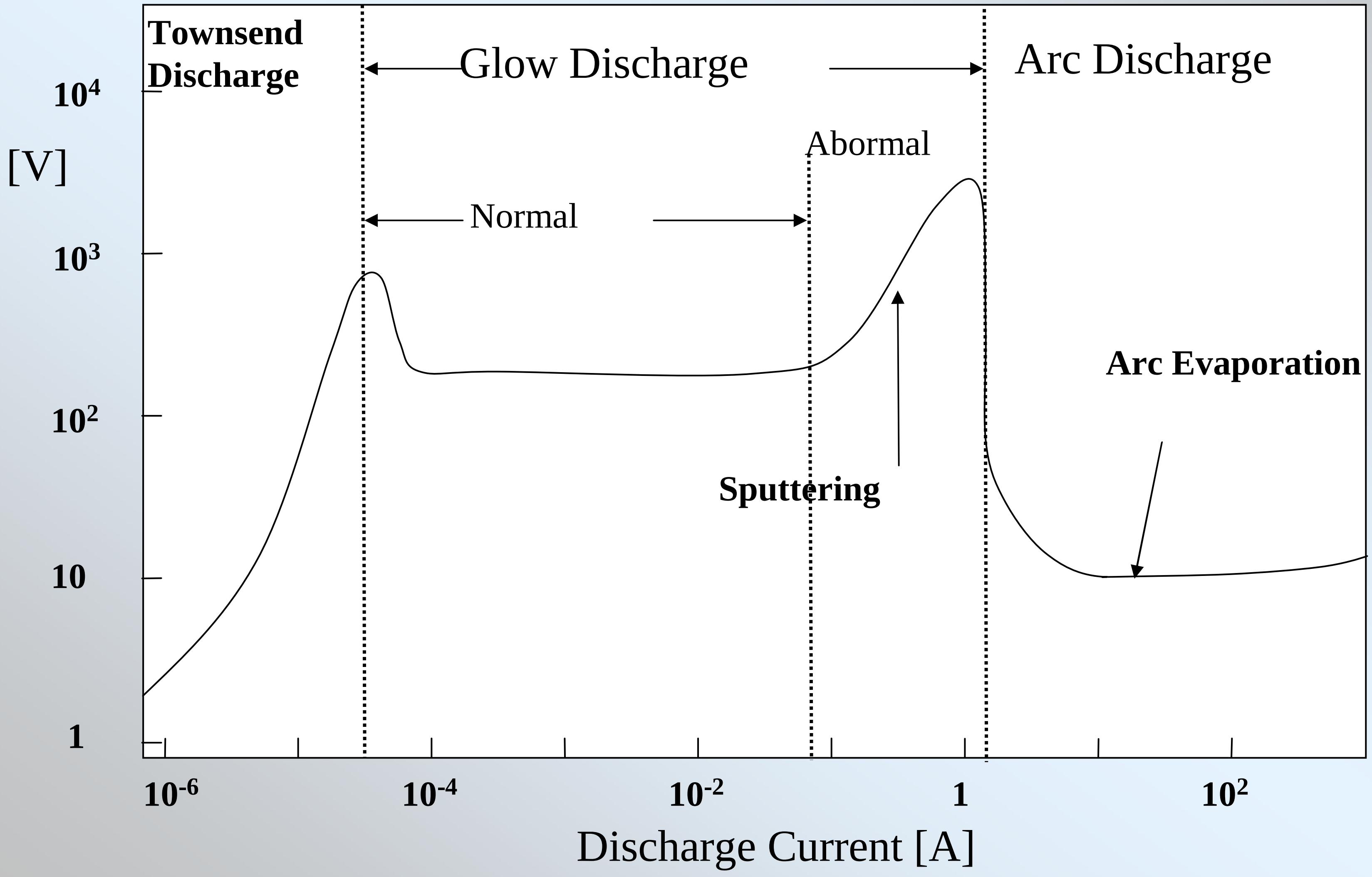
Cylindrical Hollow Magnetrons





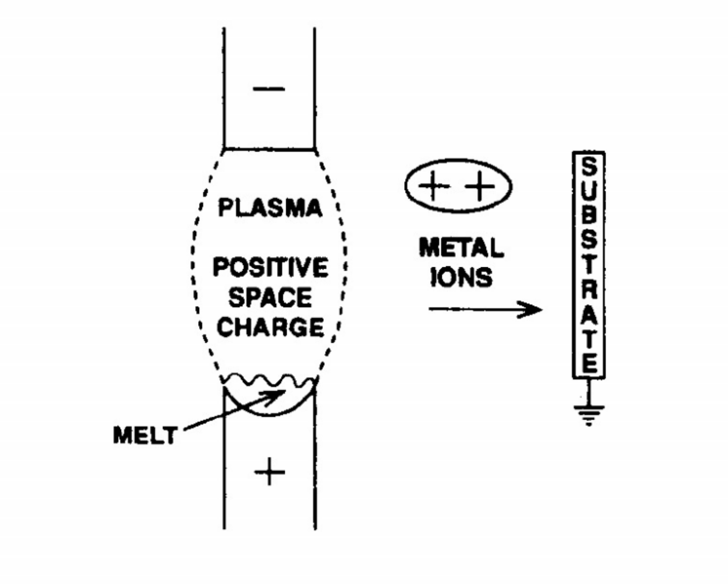


Arc Evaporation Regime



Vacuum Arcs

Arc vaporization in a low pressure vacuum occurs when a high current-density, low voltage electric current passes between slightly separated electrodes in a vacuum, vaporizing the electrode surfaces and forming a plasma of the vaporized material between the electrodes



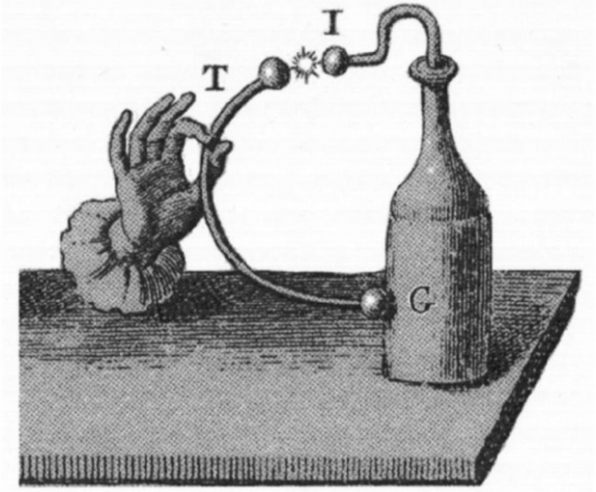
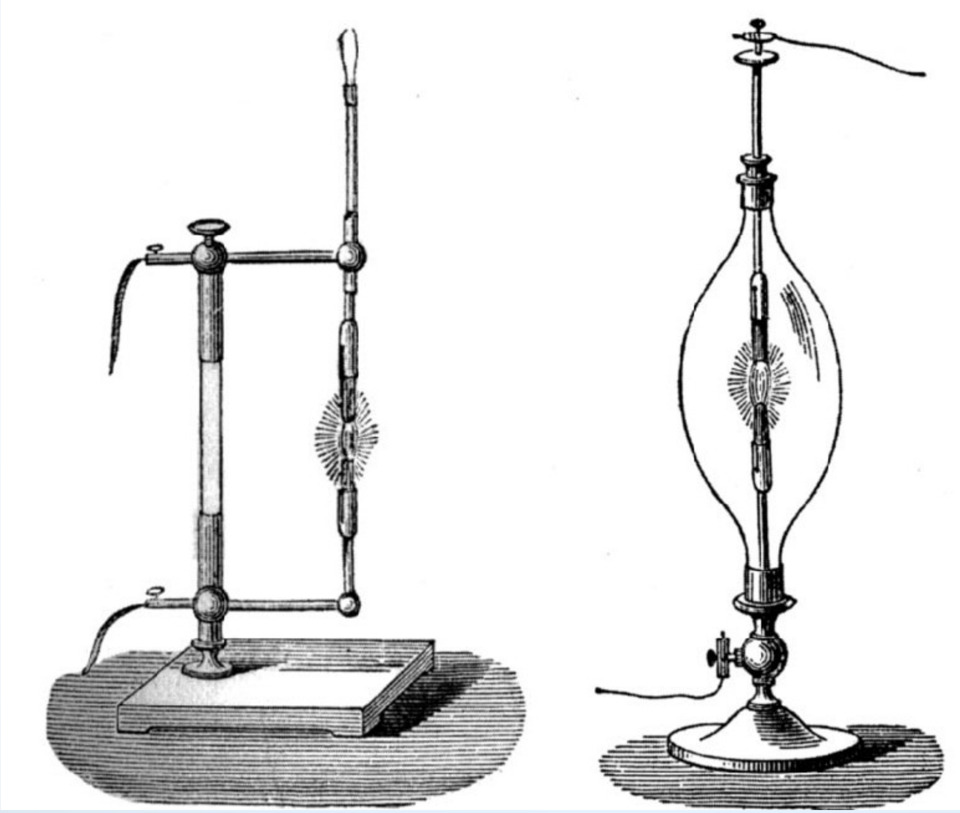


Fig. 4. Short-circuit discharge of a Leyden jar, producing a “spark” or oscillating discharge (segment of an engraved plate from Alessandro Volta to Joseph Priestley, 1775 [4, p. 31]).

First vacuum arc in 1836

By doing the discharge in vacuum it was possible to demonstrated that the discharge was due to electric field and not to burning carbon.



From Anders IEEE TRANSACTIONS ON PLASMA SCIENCE, 31(2003)1060

Vacuum Arc

- In order to initiate the arc, usually the electrodes are touched, and then separated by a small distance. On the cathode a “cathode spot” is formed that has a current density of 10^4 –10^6 A/cm^2.

- This current density causes cathode erosion by melting and vaporization and by the ejection of molten or solid particles.

- On the anode the current density is much less but can be sufficient to melt and evaporate the anode.

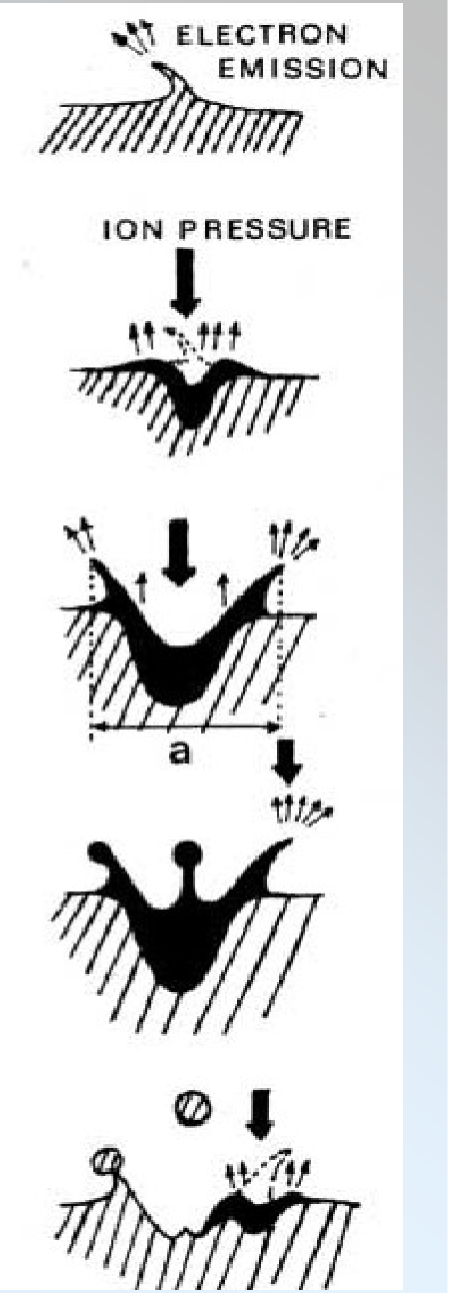
- A high percentage of the vaporized material is ionised in the arc and the ions are often multiply charged.

Gaseous Arcs

- In gaseous Arc one or more gases are injected in the vacuum chamber
- In some cases gas molecules help to sustain the discharge increasing the limit of arc stability (current and distance cathode-anode)
- Reactive gas (nitrogen, oxigen, etc) allows deposition of compounds (nitride, oxide)

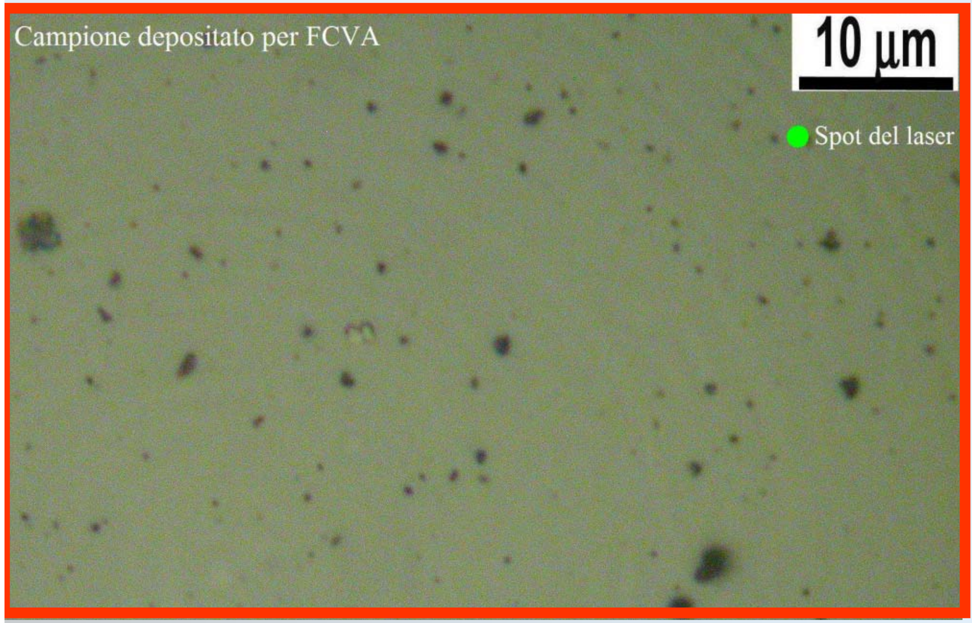
Macroparticle formation

- Ion bombardment of the cathode can melt the surface layer
- the melted surface is subject to the momentary, “pulsed” ion pressure
- Macroparticles are formed as part of the explosive plasma formation
- Typical: Material is ejected from the liquid pool between plasma and solid



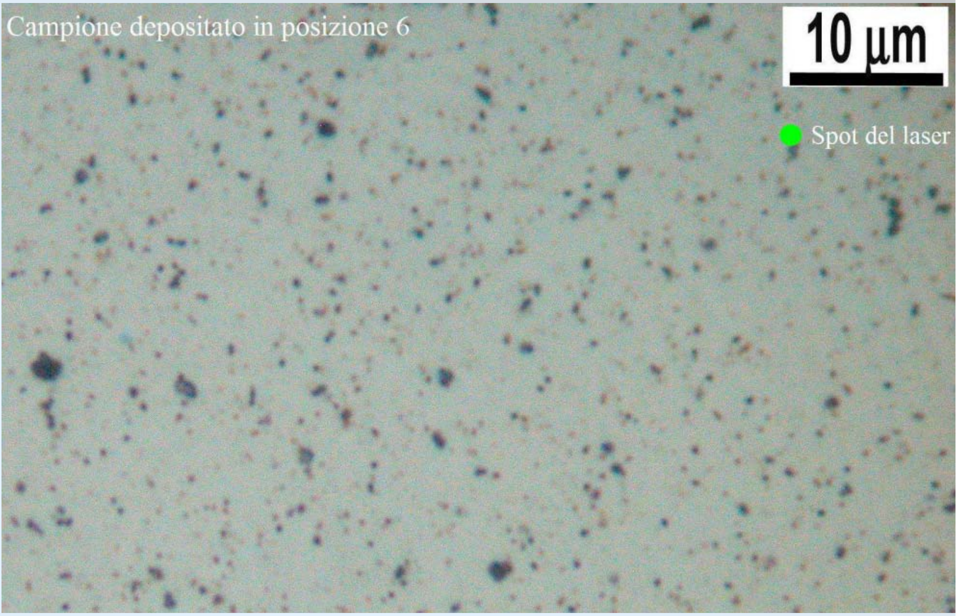
Optical Microscopy

FILTERED ARC



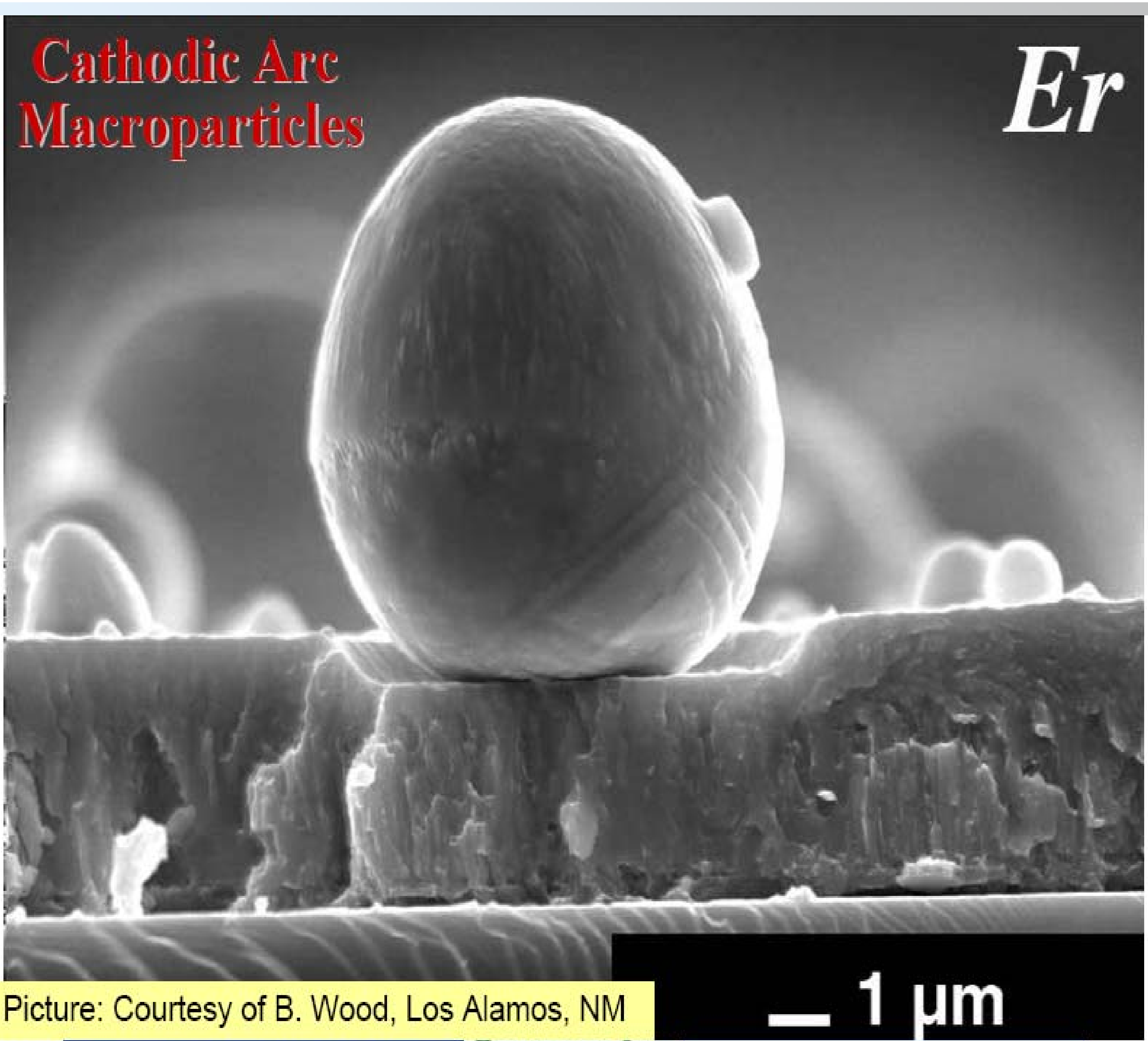
Deposition time 6 min

UNFILTERED ARC



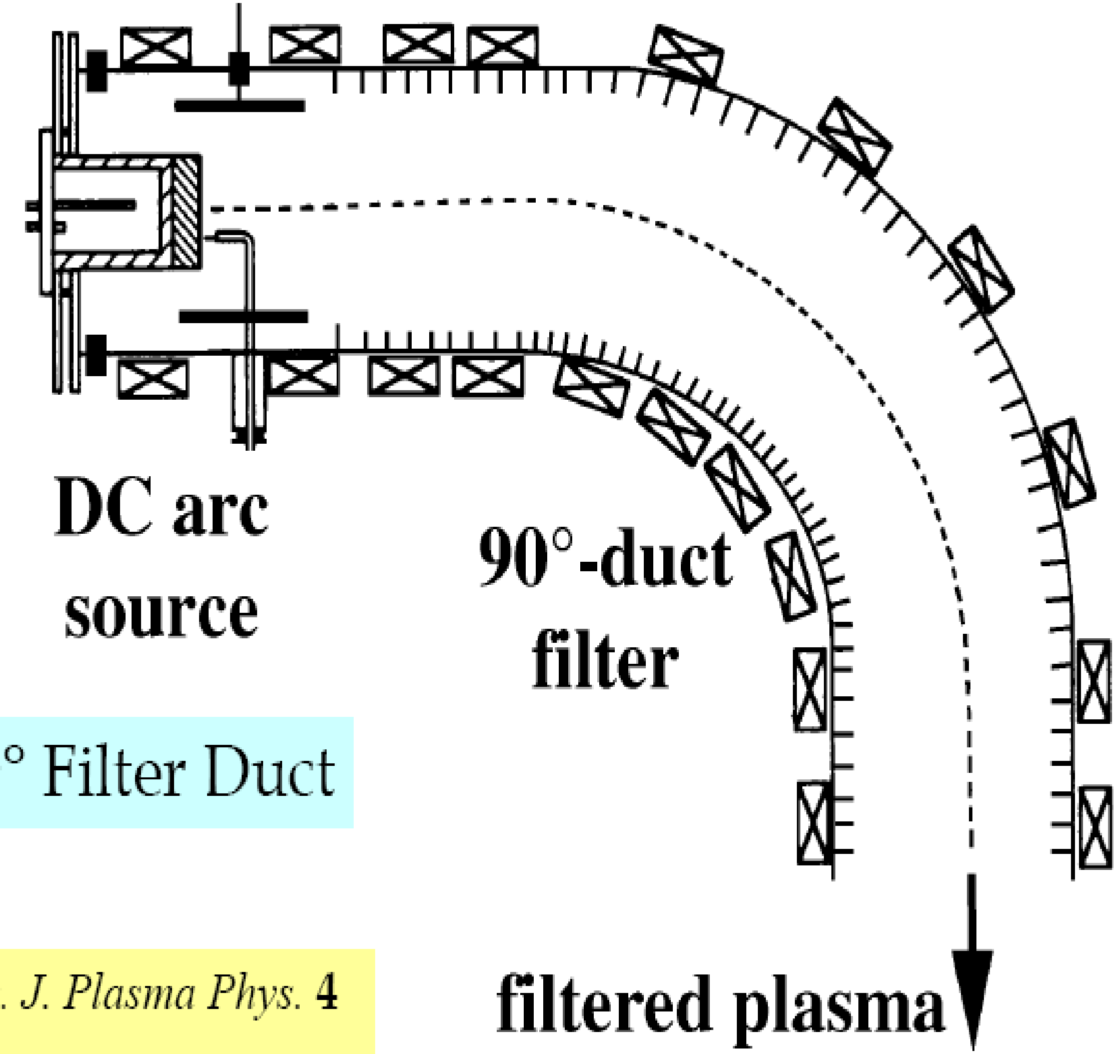
Deposition time 90 sec

Cathodic Arc Macroparticles



Picture: Courtesy of B. Wood, Los Alamos, NM

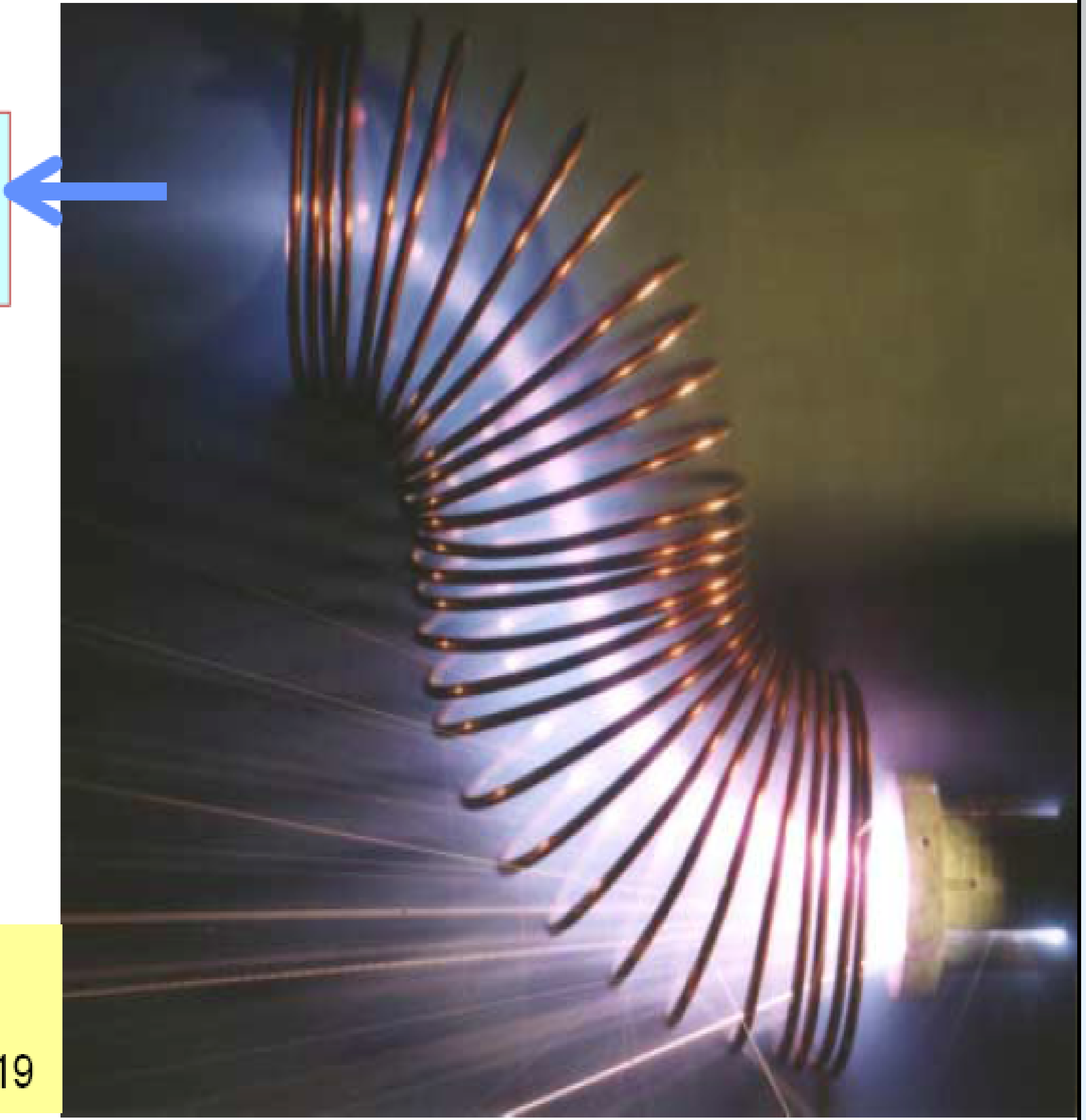
Macroparticle Removal by Magnetic Filtering



"Classic" 90° Filter Duct

I.Aksenov, *et al., Sov. J. Plasma Phys.* **4** (1978) 425

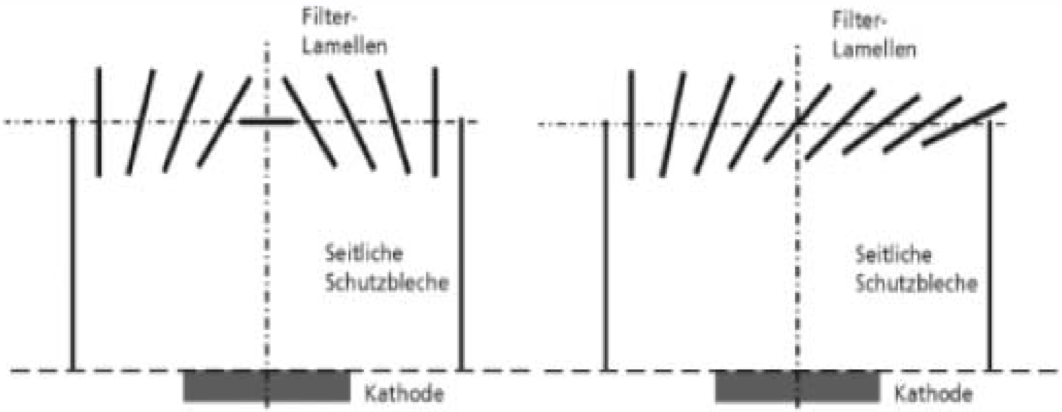
Open Filter for Cathodic Arcs



streaming, clean metal plasma

review on filters:
A. Anders, *Surf. Coat. Technol.* **120-121** (1999) 319

Venetian Blind Filter

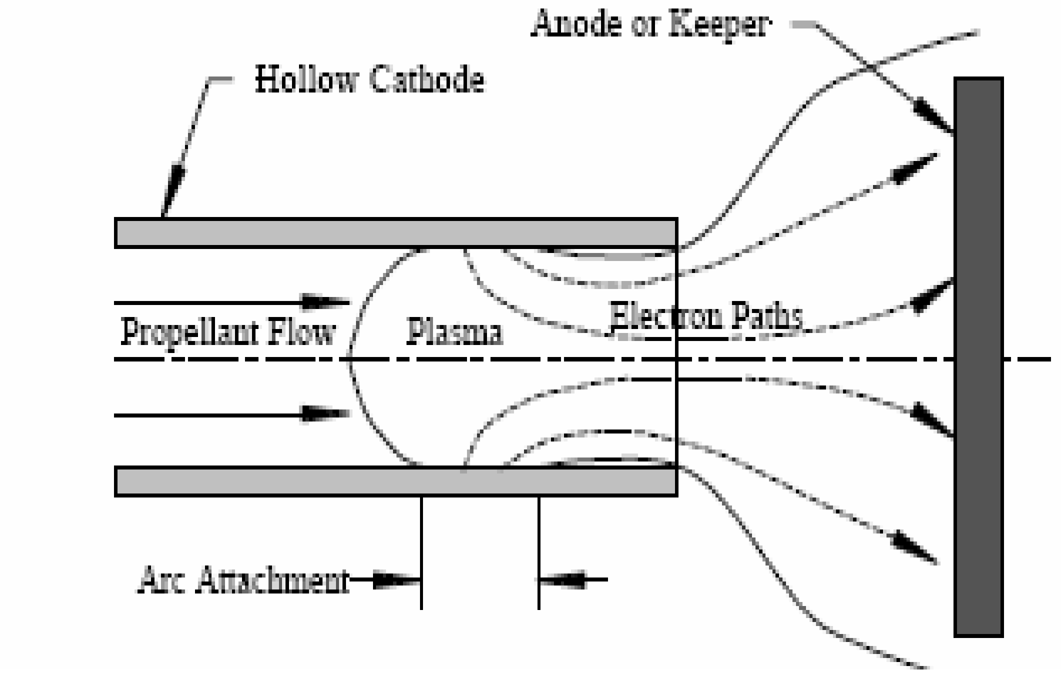


- Ryabchikov and Stepanov, *Rev. Sci. Instrum.* **69** (1998) 810
- M. Bilek, *et al.*, *IEEE Trans. Plasma Sci.* **27** (1999) 1202.
- O. Zimmer, PhD Thesis, Ruhr-Universität Bochum, 2002.

Hollow Cathodes 空心阴极放电

Thermo-ionic devices which rely on electron bombardment ionization of a neutral gas to generate a plasma.

The arc attaches upstream of the cathode exit plane, and these devices typically operate above 1500 ºC due to the high work function of the tube material.



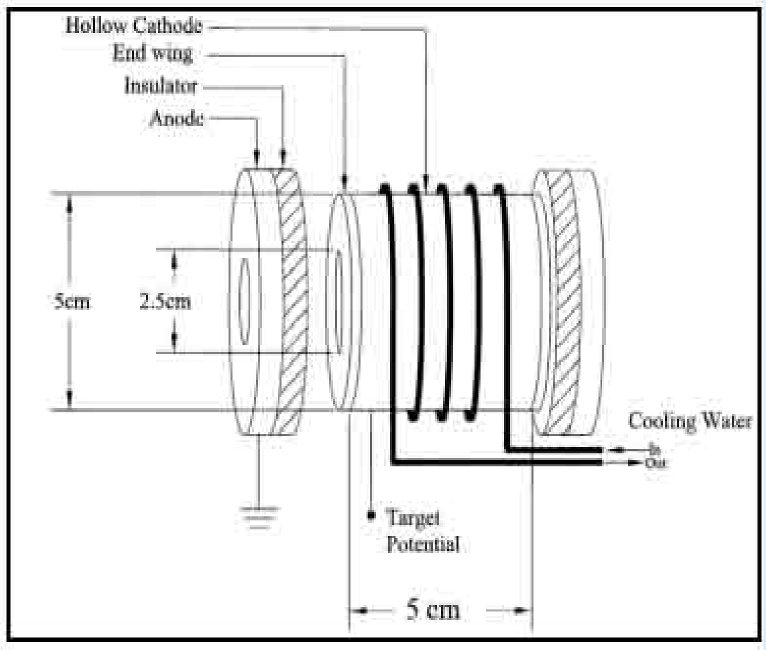
Open-channel hollow cathode, one of the simplest HC devices

Hollow cathodes used for thin film depositions consist of a refractory metal Ta, or even Nb, tube with an orifice plate welded to the downstream en. A low work function insert emits electrons to create the insert plasma which flows downstream.

A cathode heater is used initially to heat the insert to emission, and self heating sustains the discharge following ignition. The keeper is typically used to initiate the discharge and maintain it when the emission current, the current to beam or space plasma, is insufficient to provide the self-heating for stable operation.

***R**eactive sputtering* is an industrially important technique used to deposit binary oxide and nitride films for applications such as optical, tribological, electrical and decorative coatings.

However, conventional reactive sputtering is a complex non-linear process and lot of effort is required to negate problems such as hysteresis and low compound deposition rates. Ismat Shah has developed a new source called the d.c. Hollow Cathode Source (HCS) which can eliminate hysteresis and deposit compounds at extremely high rates, similar to those obtained with conventional sources operated at 1000 times higher power densities.



Selected Publications:

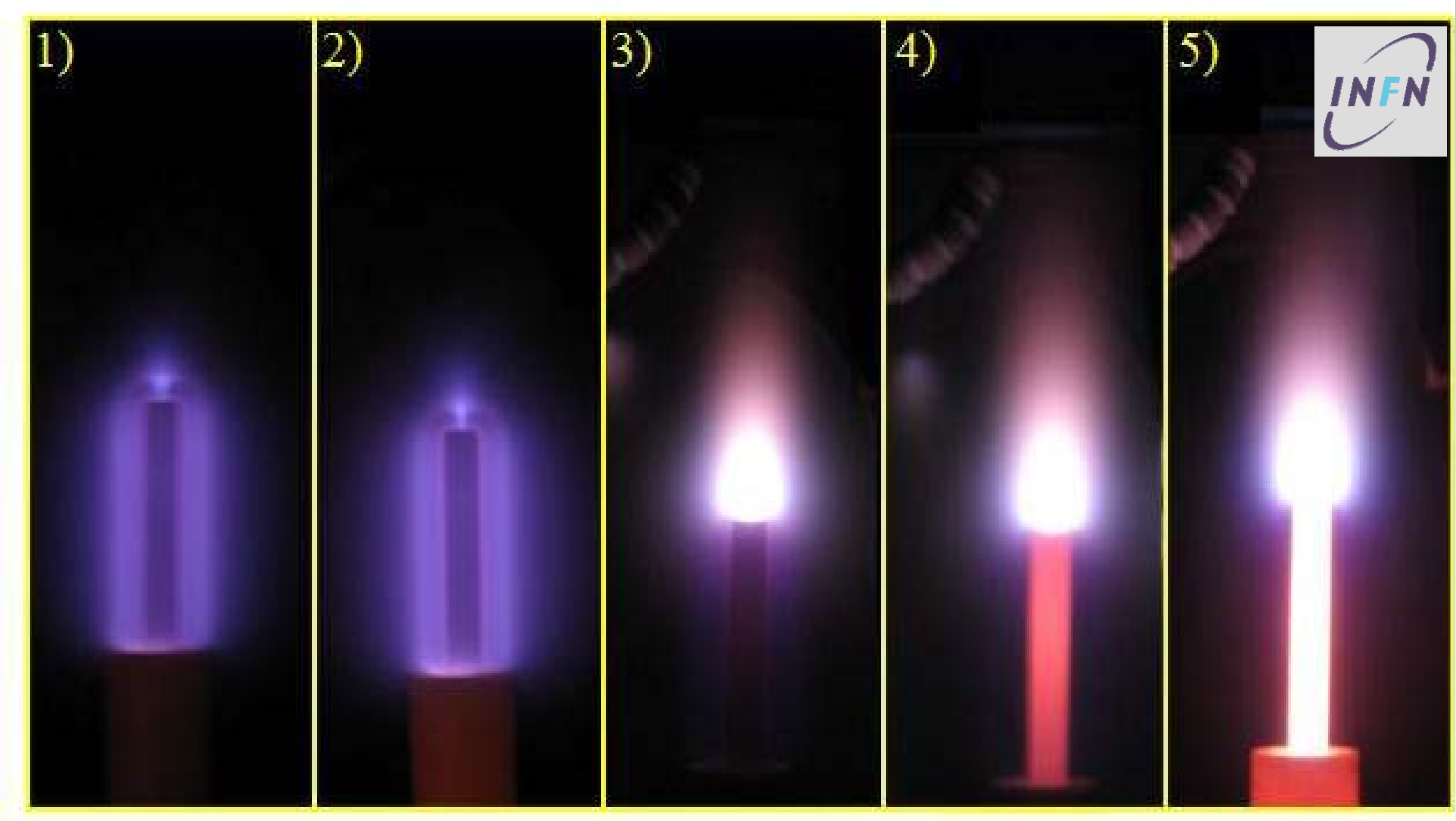
"Reactive sputter deposition of alumina thin films using a hollow cathode sputtering source" Anshu A. Pradhan, S. Ismat Shah and Karl M. Unruh, Rev. Sci. Instrum., 73 3841 (2002).

"High Deposition Rate Reactive Sputtering with Hollow Cathode" Anshu A. Pradhan and S. Ismat Shah, Proceedings of the Annual SVC Technical Conference (2002), p.96

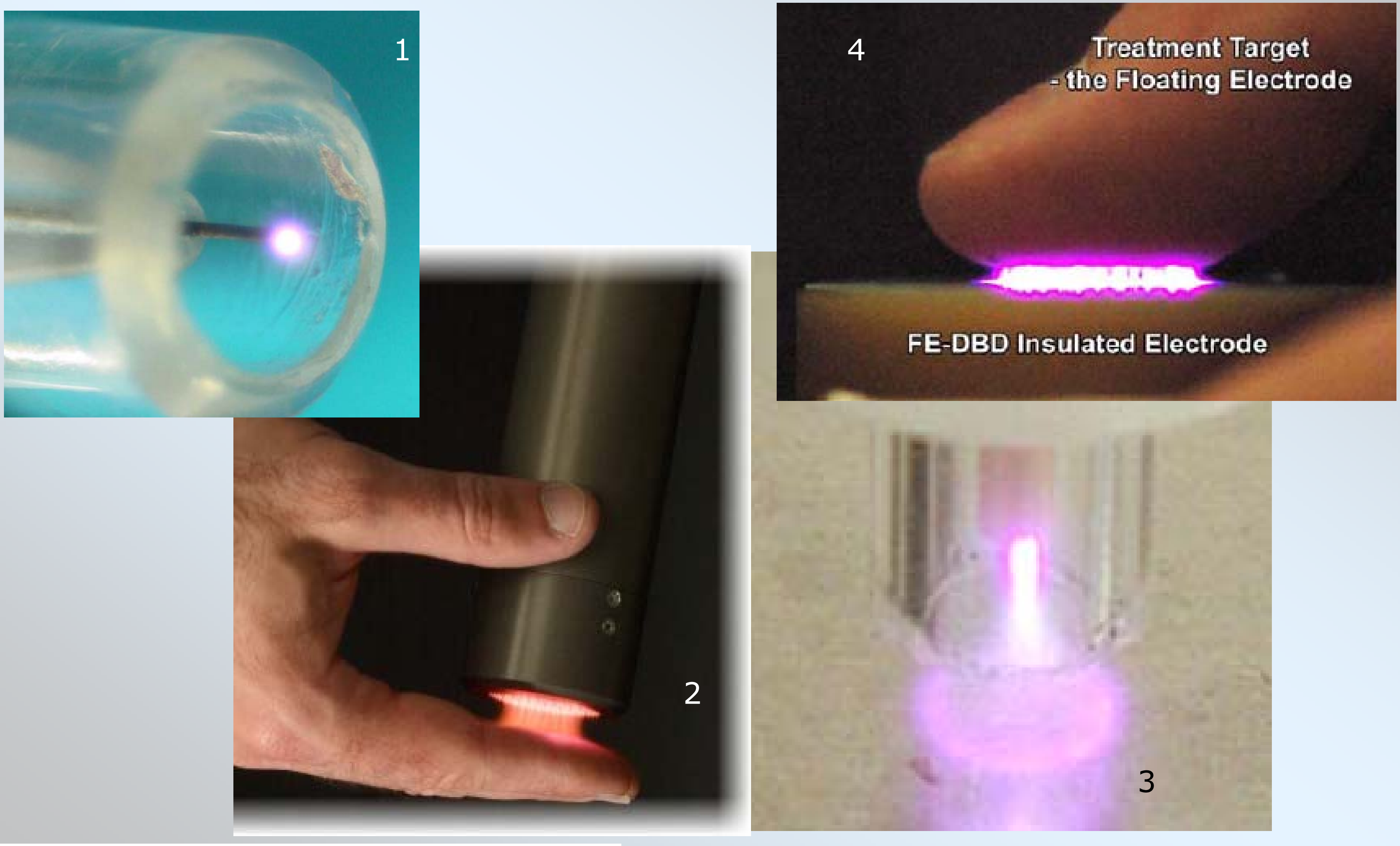
"Static Mode Hollow Cathode Reactive Sputtering" Anshu A. Pradhan and S. Ismat Shah, Proceedings of the Annual SVC Technical Conference (2003). (in press)

http://www.udel.edu/mse/research/shah-RHC.htm

Hollow cathodes are used in a wide variety of applications (Electric propulsion devices, plasma contactors, lasers), where high current densities, low cathode-fall voltages, and extended lifetimes (thousand of hours) have been demonstrated are required.



Different atmospheric plasmas



1) I. E. Kieft, Electrical and optical characterization of the plasma needle

2) Atomflo™ 225C, www.surfxtechnologies.com

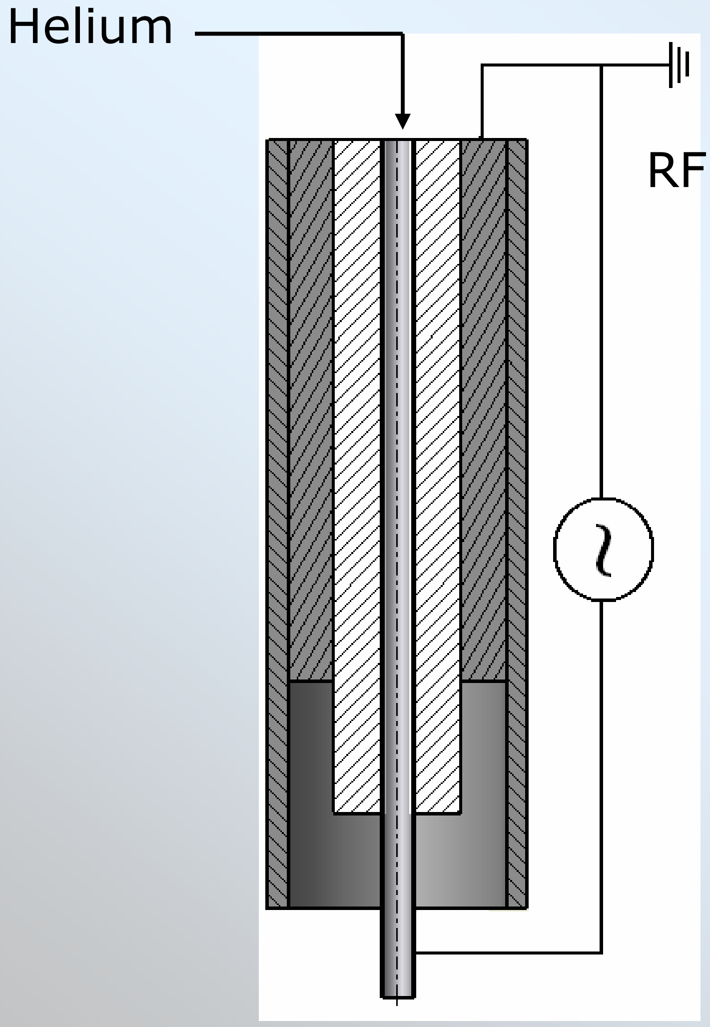
3) J. Goree, Biomedical applications of plasma treatment

4) G. Fridman, Bio-Medical Applications of Non-thermal Atmospheric Pressure Plasmas

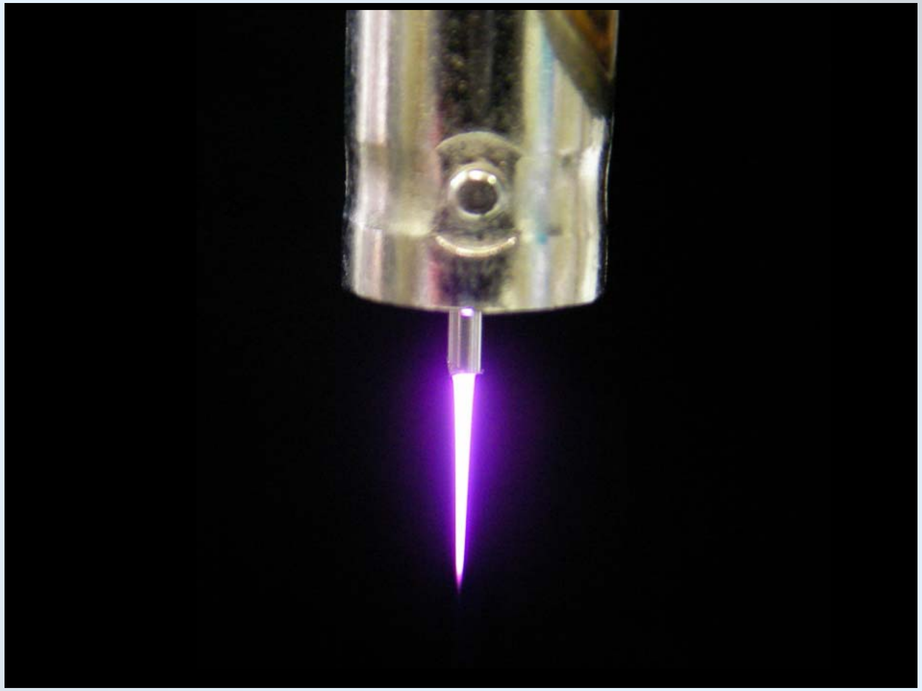
(Safety) requirements

- Cause no damage to biological tissue due to an electric shock, thermal damage, UV-radiation or any other yet unknown effect
- Stable, reliable, and controllable plasma generation
- Sufficient active plasma species production
- Low dimensions
- Operable at atmospheric pressure/open air

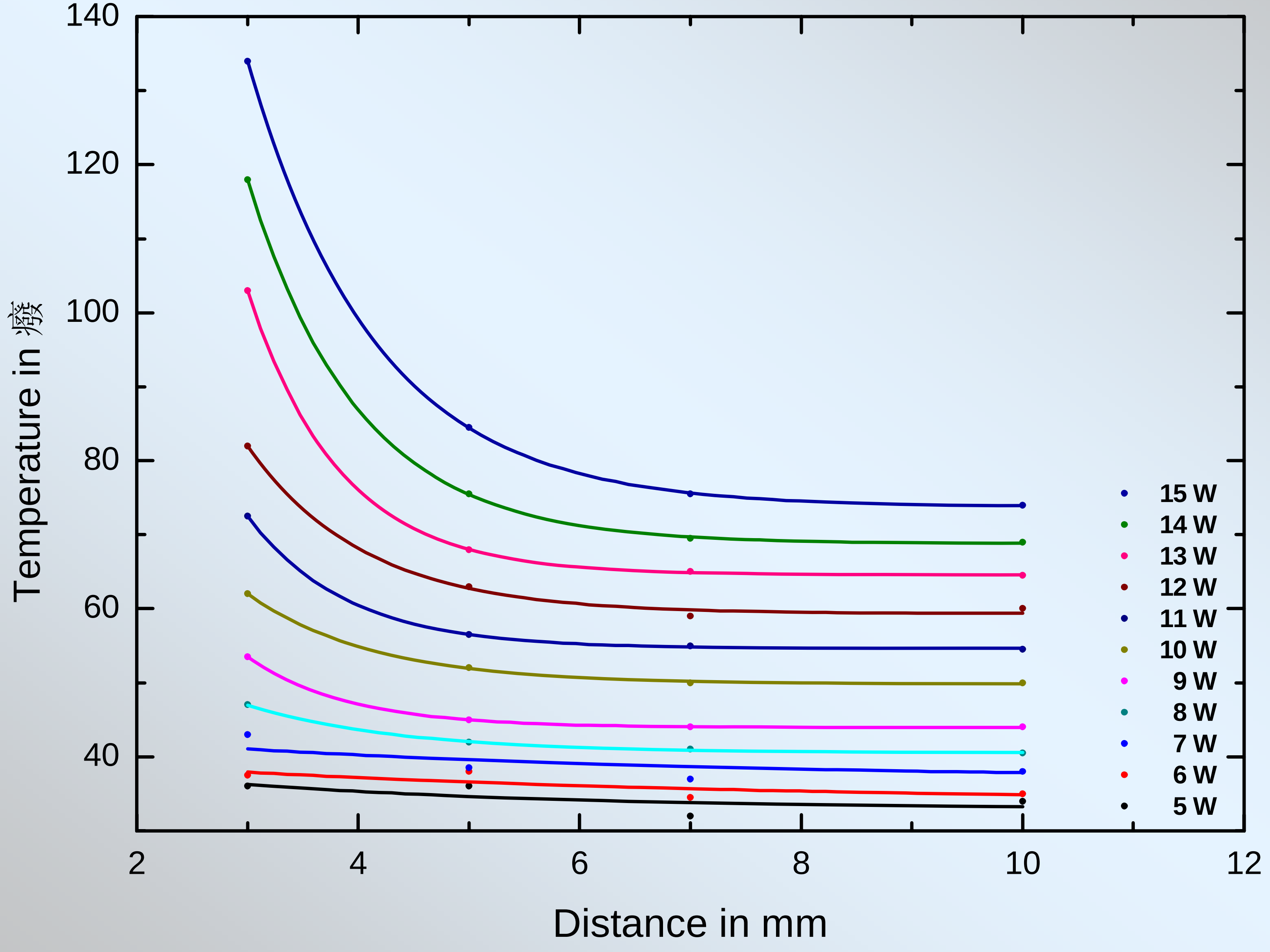
Helium plasma



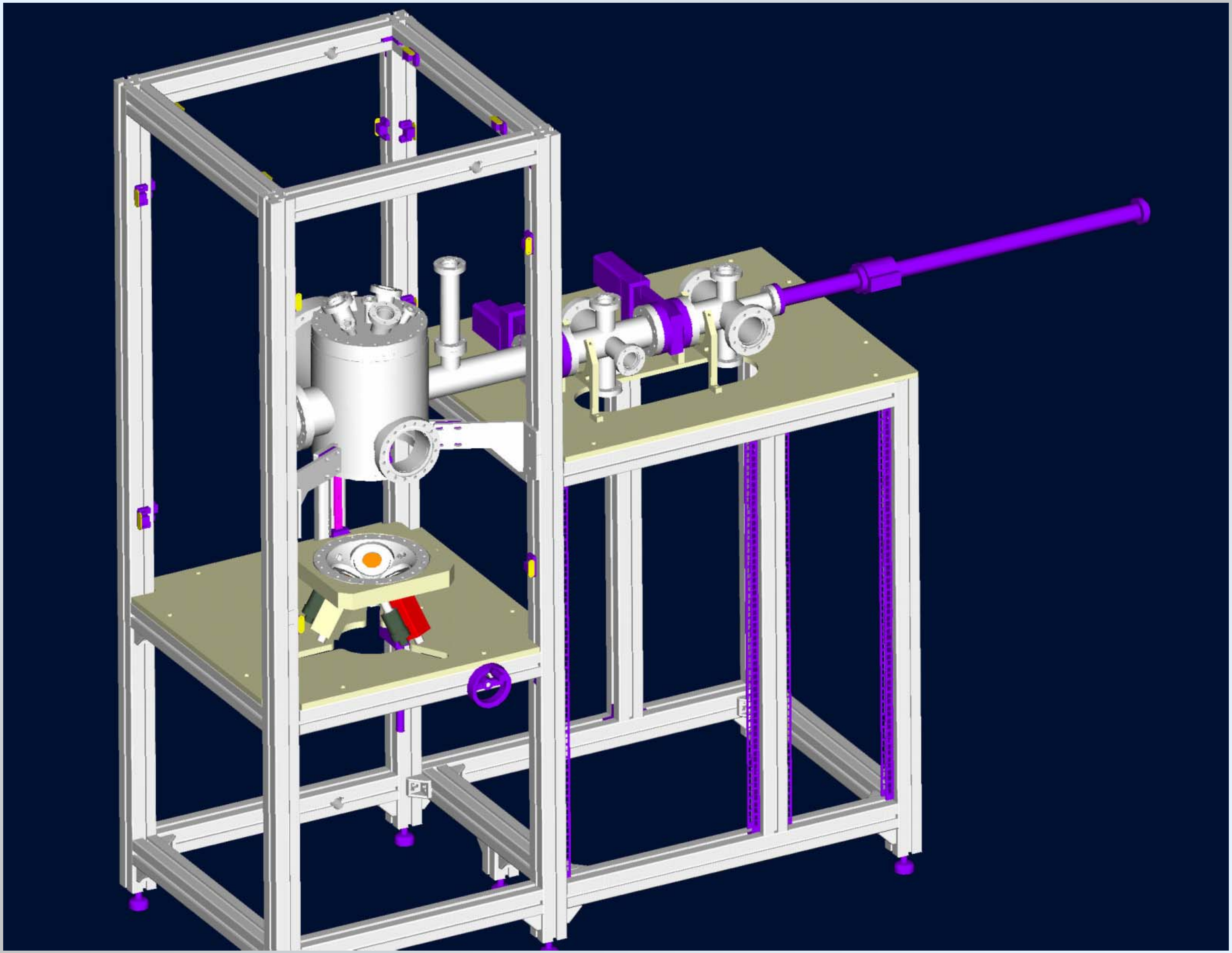
RF- excitation at 13.56 MHz



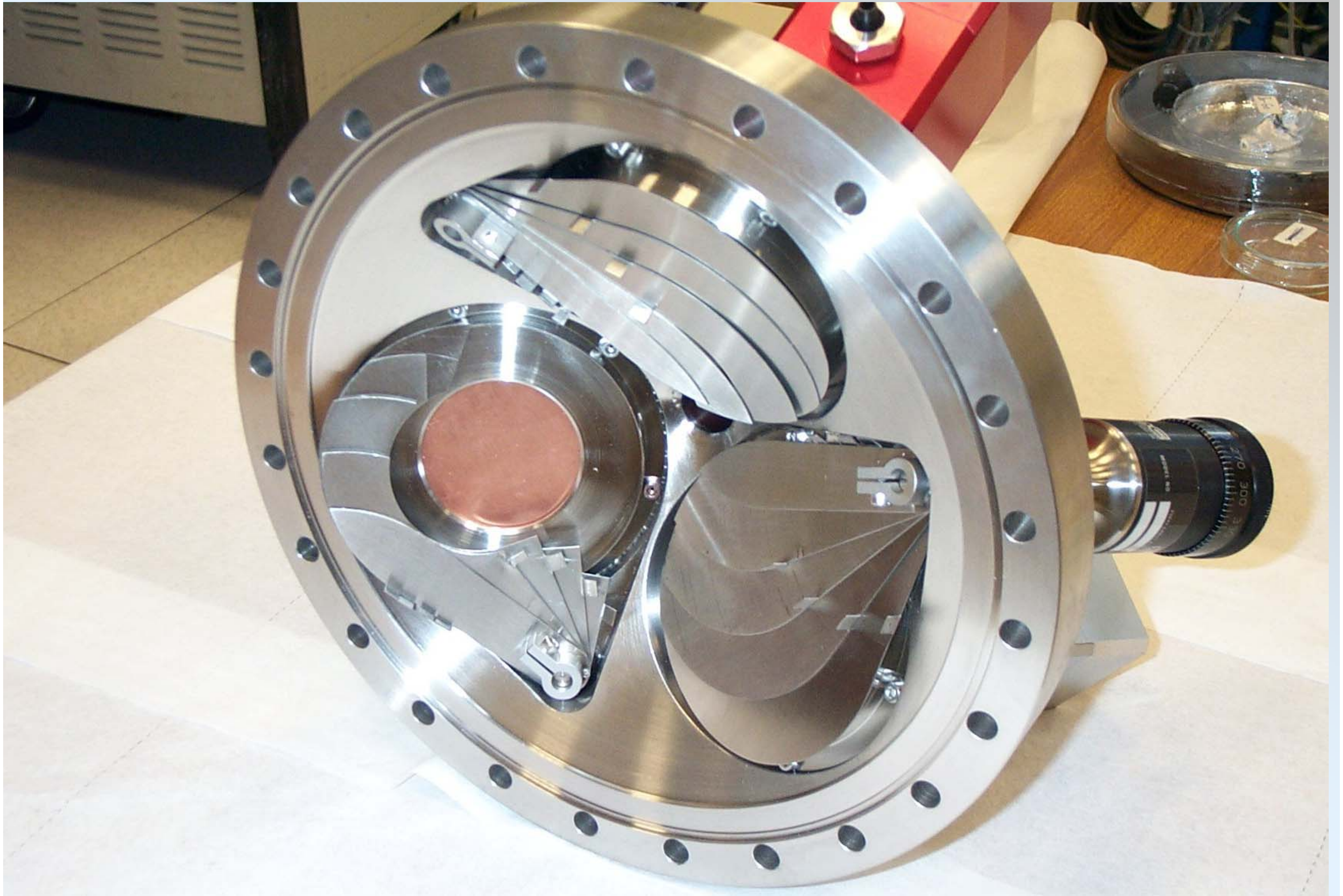
Temperature vs. distance

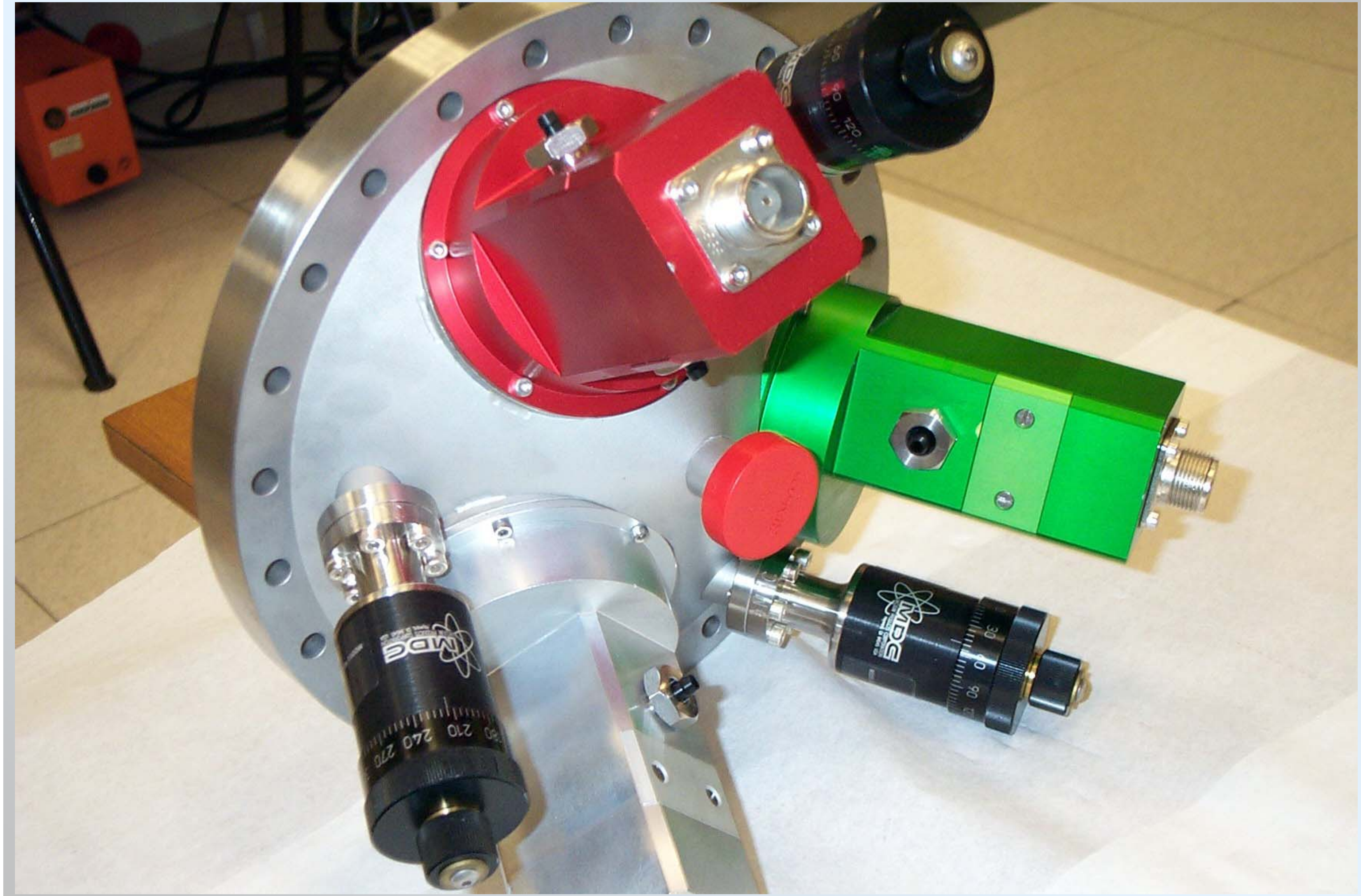


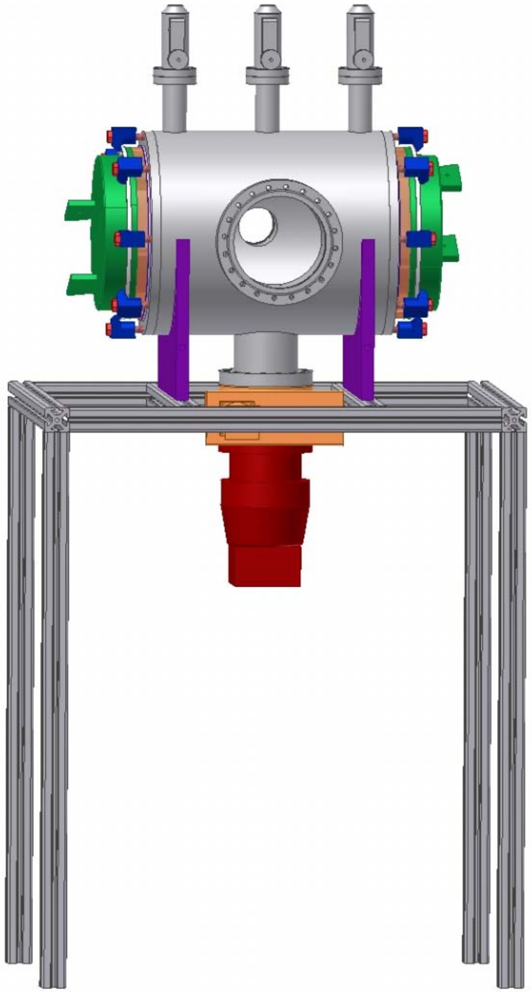
Some example of the PVD machines built at INFN-LNL

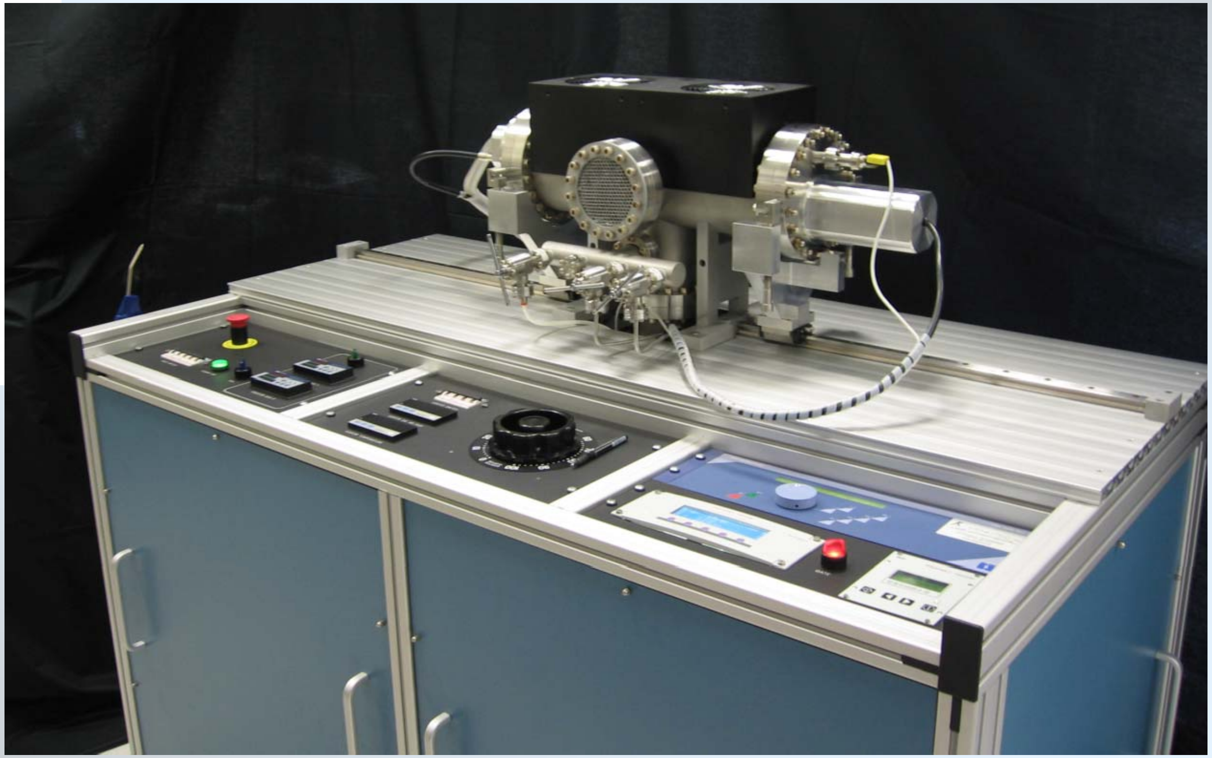


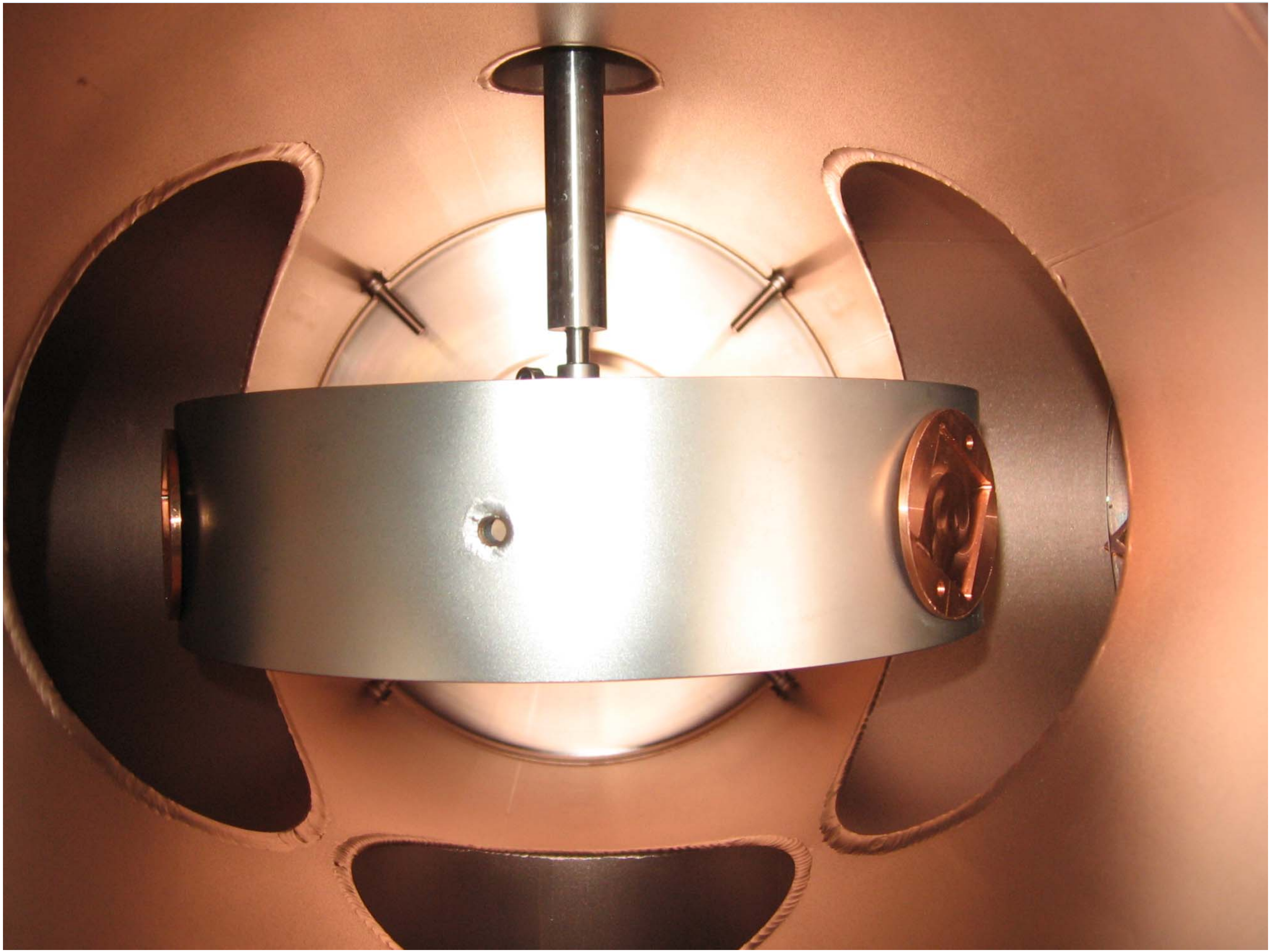

ARRESTO EMERGENZA

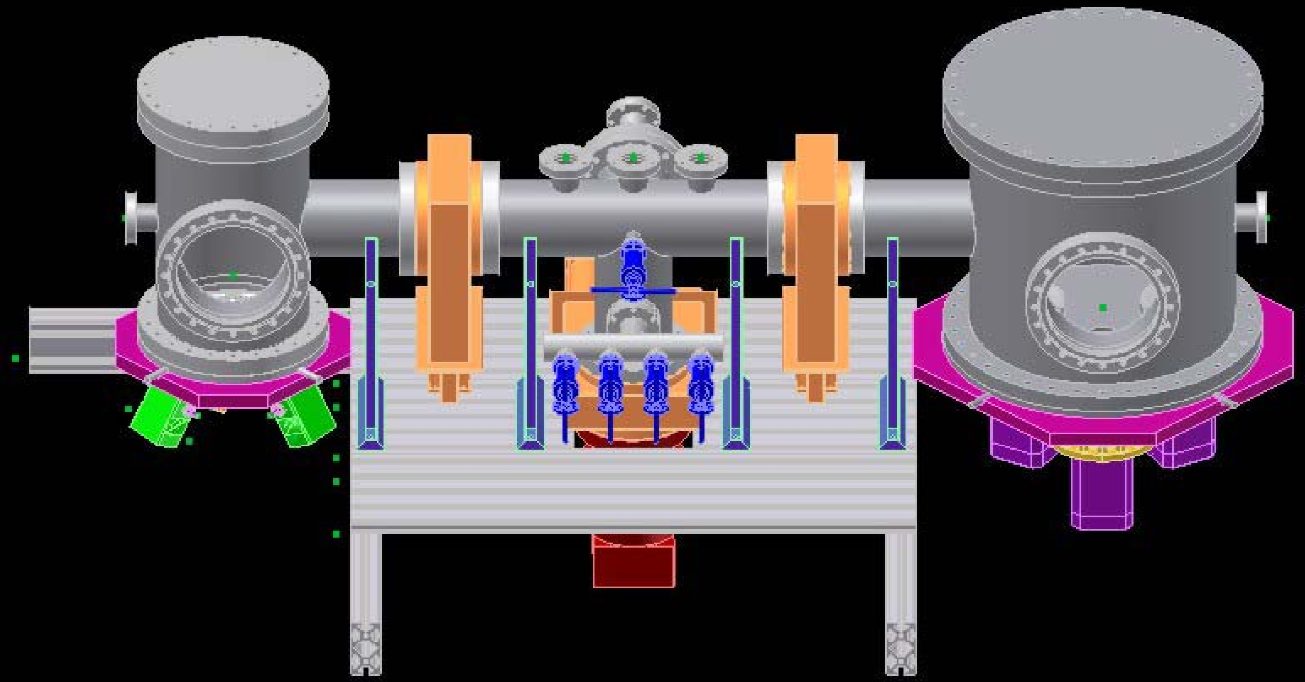


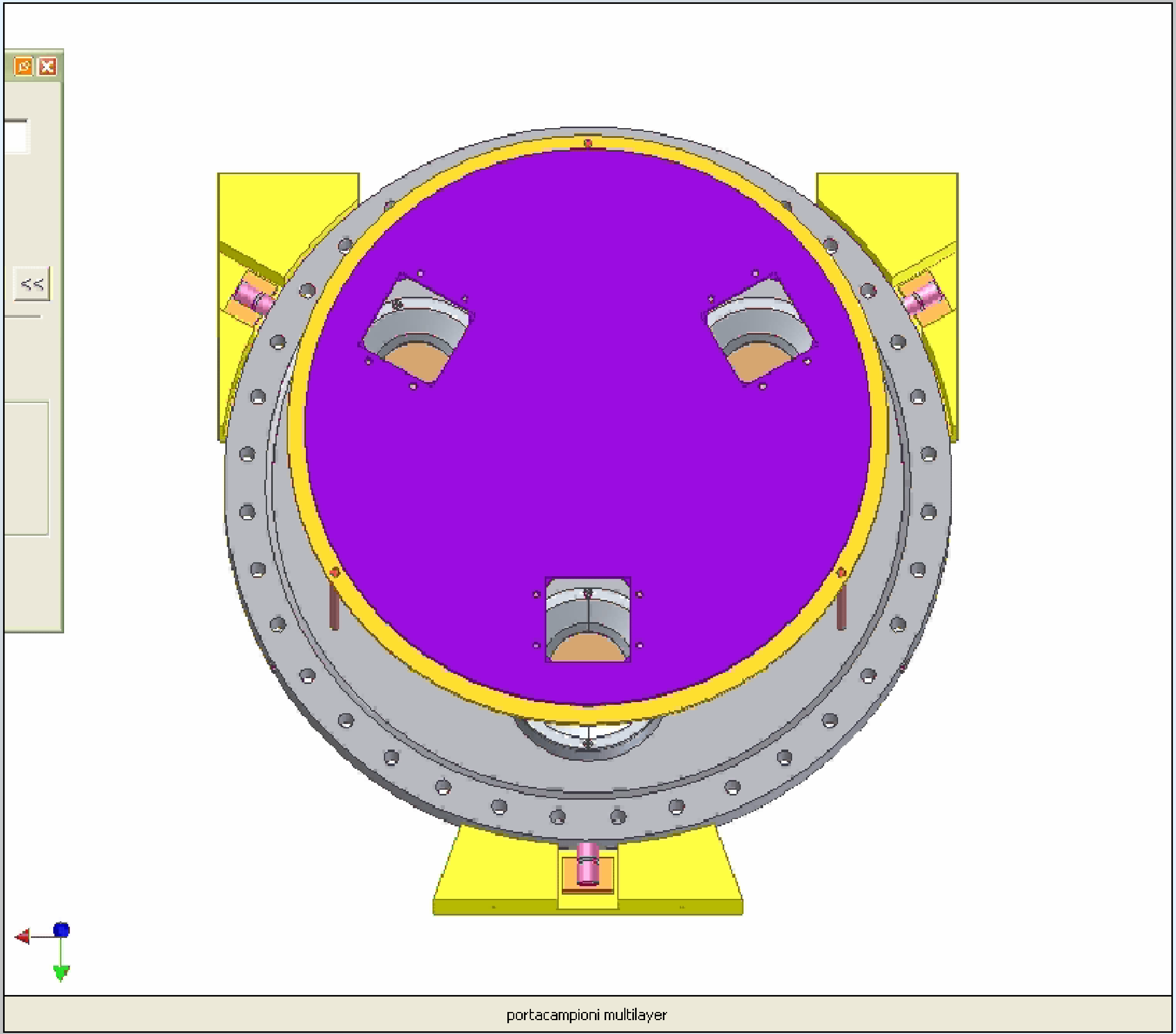

MDC
MDC
210
240
270
30
60
90
120



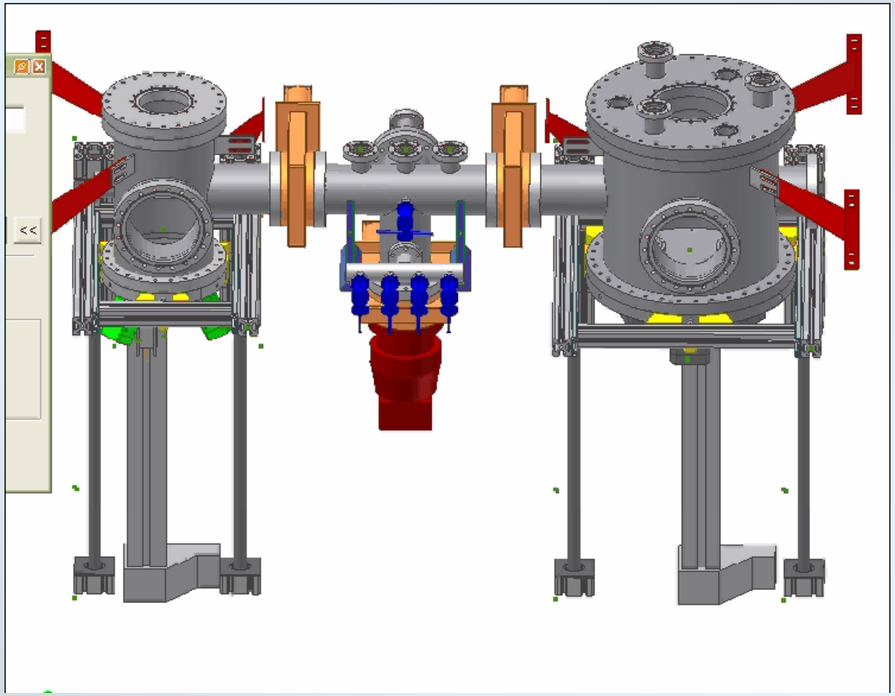


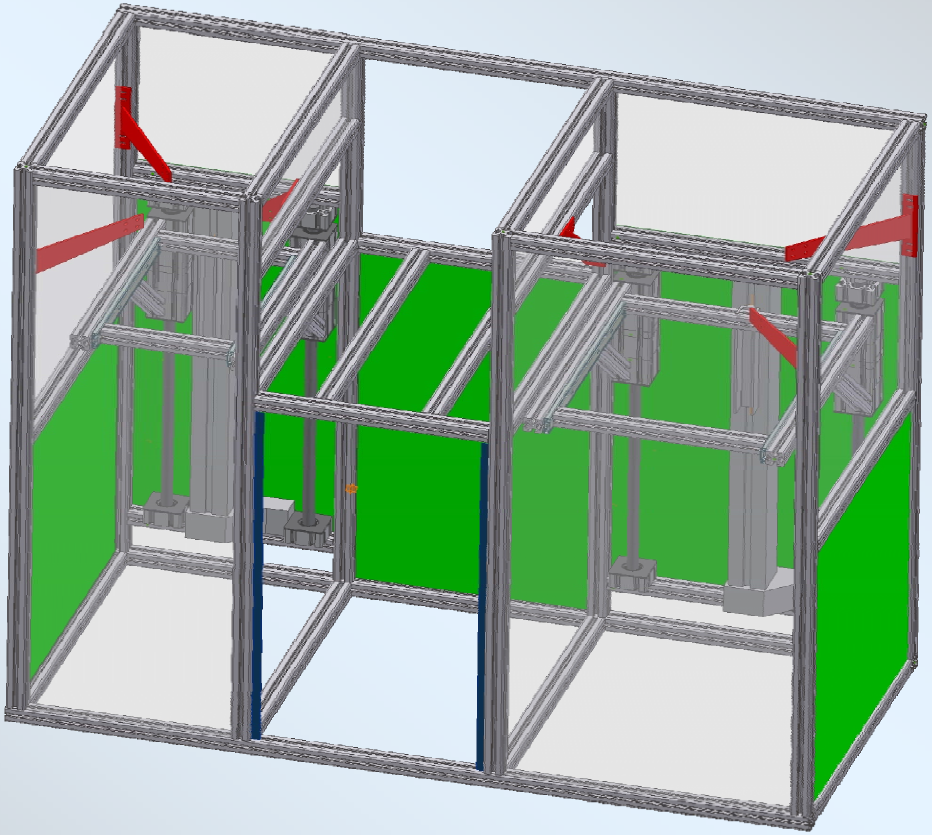


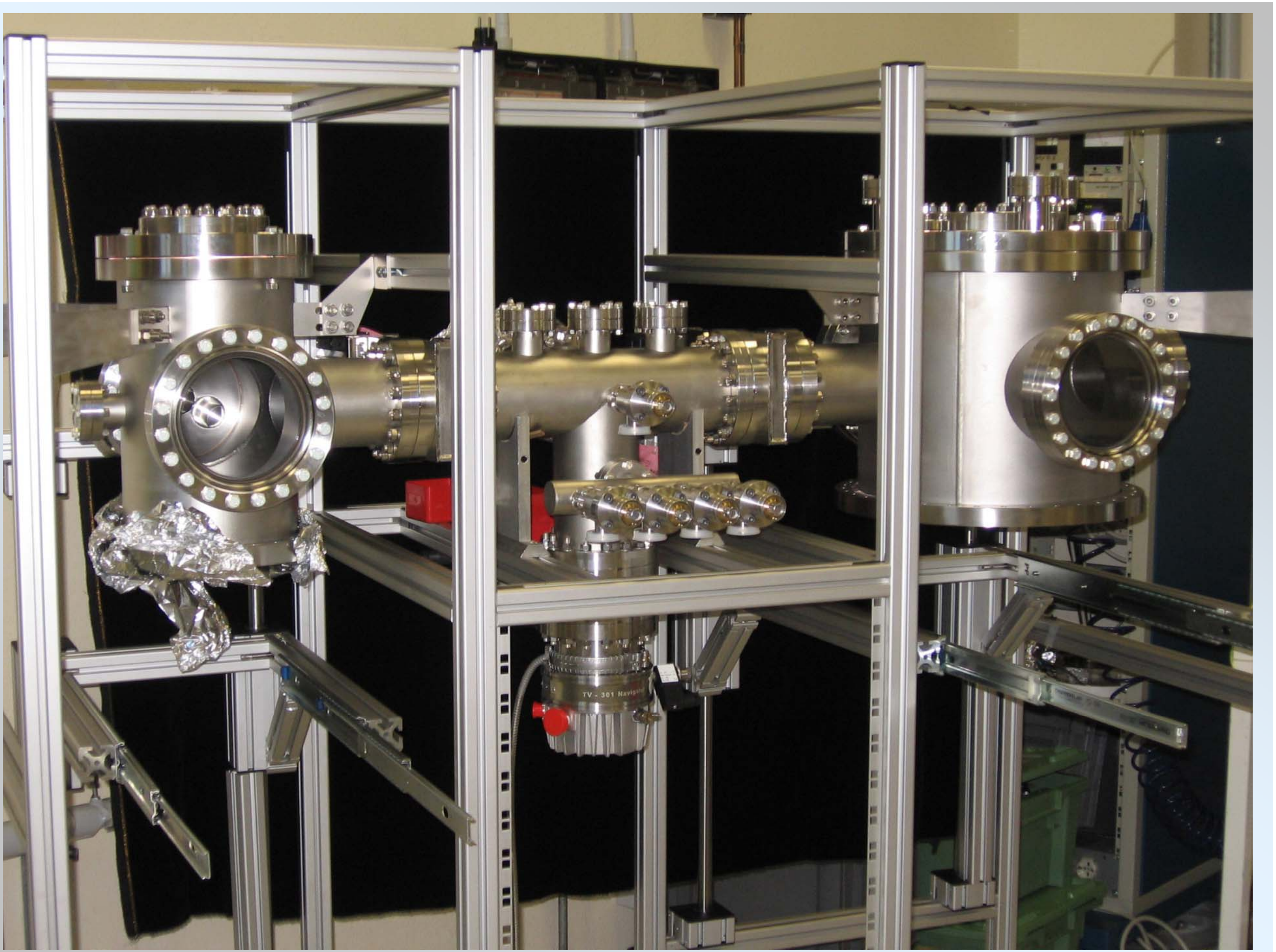




portacampioni multilayer



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CONTROL PANEL
GATE L
GATE R
L1
L2
L3
R1
R2
R3
GATE C
LOCK L
LOCK R
TURBO PUMP
EMERGENCY
OFF
MAIN
POWER ON
NITROGEN
WATER
IN
OUT
POWER

- Evaporation
- Ion implantation
- Ion beam Dep.
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- CVD
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