LECTURE III-th year Integr.PhD Studium

Modern technologies in surface engineering

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LECTURE "Surface Engineering"

1. Range of scientific area "surface engineering„

2. Modern methods of production technology of surface layers

3. Units of pressure

3a. Vacuum

4. Mechanical methods of surface modification

5. Chemical surface modification methods CVD

6. Crystallization of the coating from the gas phase

7. Plasma

8. Physical methods of surface modification PVD

9. Interaction of ions and electrons with solid surfaces

10. Laser beam-solid interaction

11. Magnetron discharge for thin films plasma processes

12. Surface modification by ion impact

13.Surface modification by plasma ion implantation

14.Surface modification of low-energy and high-current electron beam

15. Laser surface modification by re-melting
16. Laser Rapid Prototyping
17. Pulsed laser deposition using laser ablation
18. Surface cleaning with the use of laser ablation
19. Thermal plasma surface treatment
20. Arc evaporation
21. Diagnostics
    a. spectroscopic method for surface analysis
    b. structural diagnostics (AFM, SEM, TEM, CLSM)
    c. residual stresses and methods of measurement
    d. diagnostic micro-mechanical properties
22. Hard and superhard coatings based on nitrides, carbides, borides and nanocomposites
23. Thermal barrier coatings
24. Polymer film obtained by plasma polymerization
25. Trends in development of surface engineering in the world

1. Range of scientific area "surface engineering”

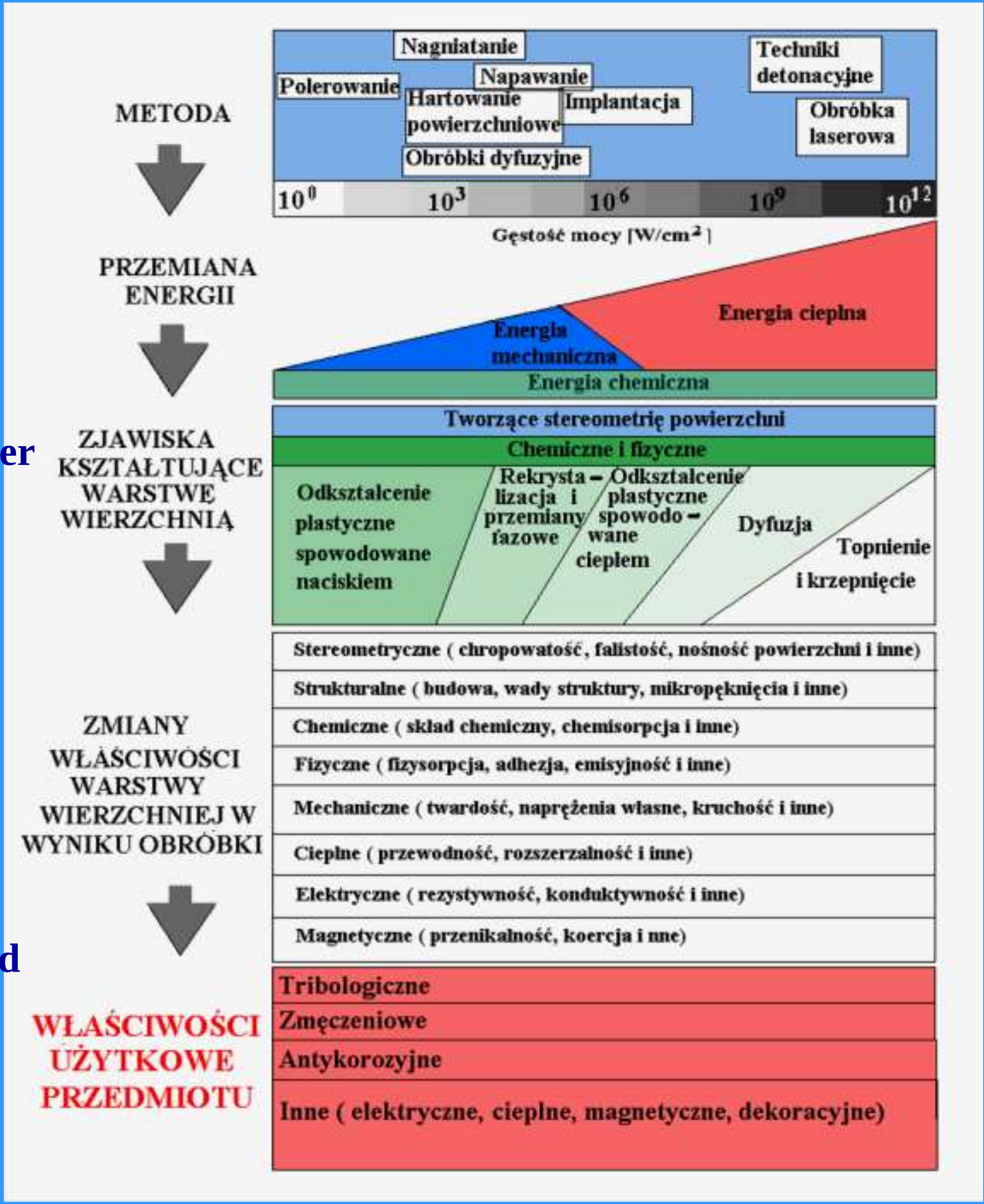
Methods

Energy transfer

Phenomena shaping the surface layer

Changes in the properties of the surface layer by treating

Preformance of manufactured good

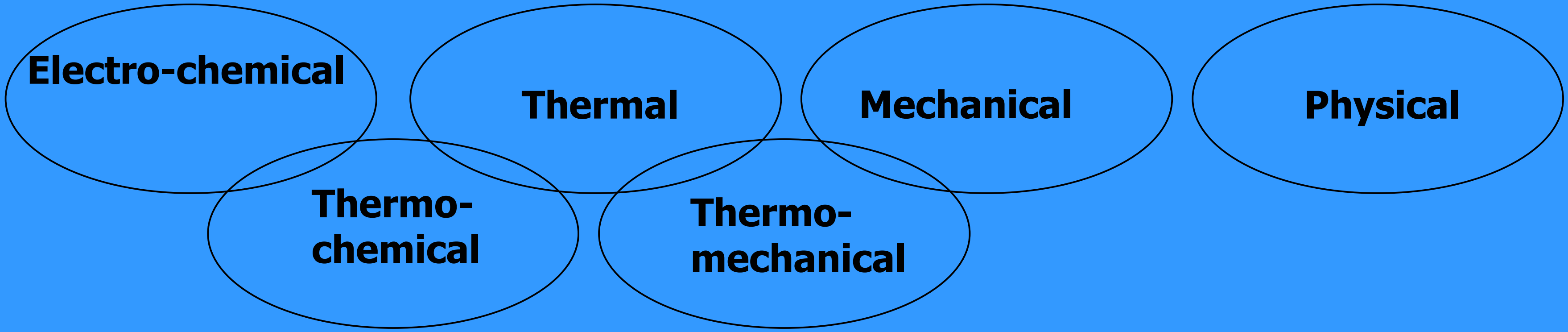


General basis of surface engineering

The coating is a layer of material formed in a natural or artificial way on the surface of an object fabricated with different materials in order to achieve technical or decorative properties

Coatings division due to:
- material
- destiny
- method of preparing

2. Modern methods of production technological surface layers



Electro-chemical

Thermal

Mechanical

Physical

Thermo-chemical

Thermo-mechanical

Modern methods

- **Electron techniques**
- **Laser techniques**
- **Implantation techniques**
- **Glow discharge techniques**
- **Chemical vapour deposition CVD**
- Physical vapour deposition PVD

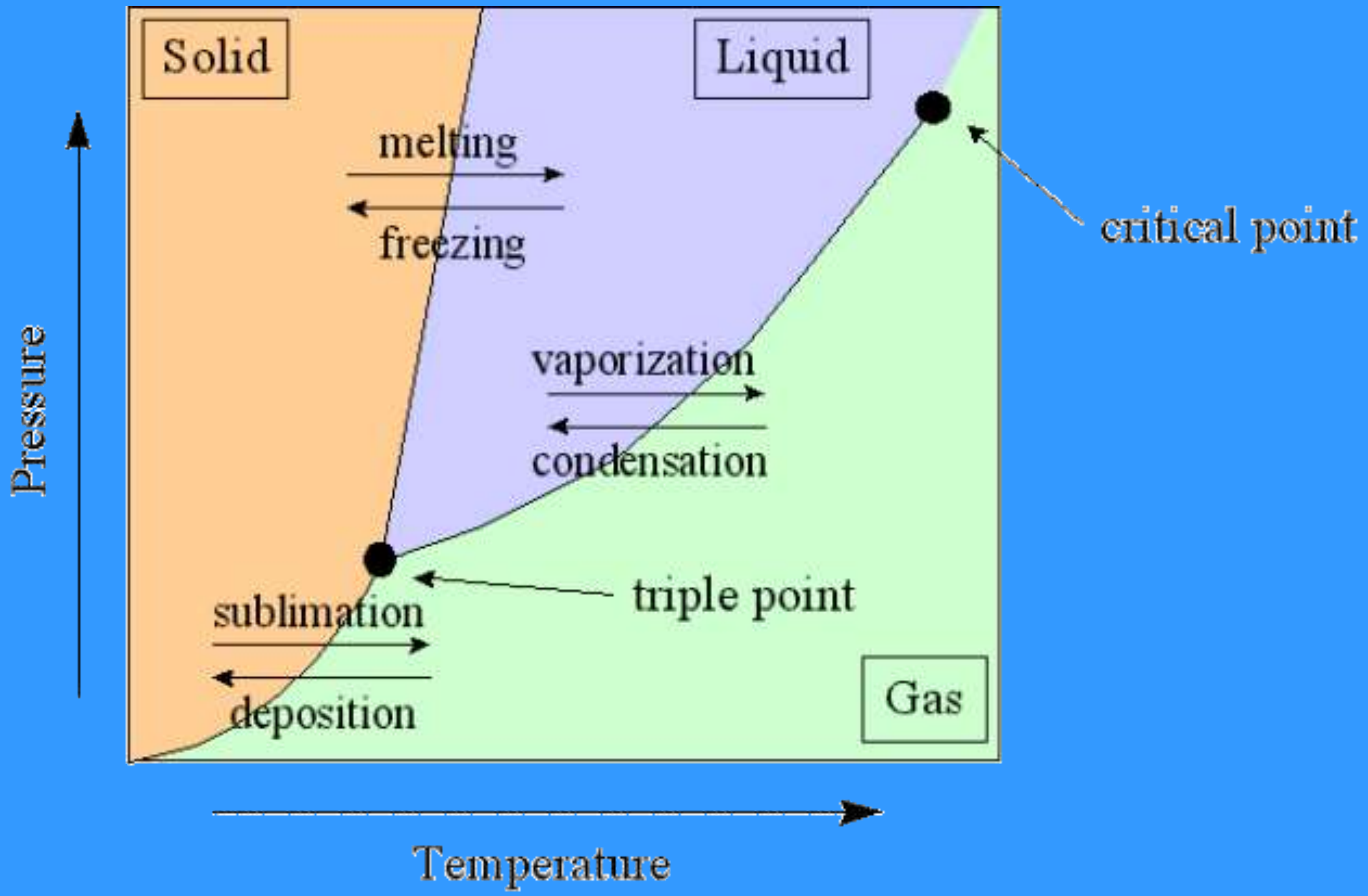
CVD:

APCVD- atmospheric pressure CVD
LPCVD- low pressure CVD
MOCVD- metal organic CVD
PACVD- plasma assited CVD
MWCVD-microwave CVD

PVD:

ARE- activated reactive evaporation
BARE- bias activated reactive evap.
TARE- thermoionic arc evaporation
HCD- hot hollow cathode discharge
ICB- ionized cluster beam deposition

The curves indicate the conditions of temperature and pressure under which equilibrium between different phases of a substance can exist



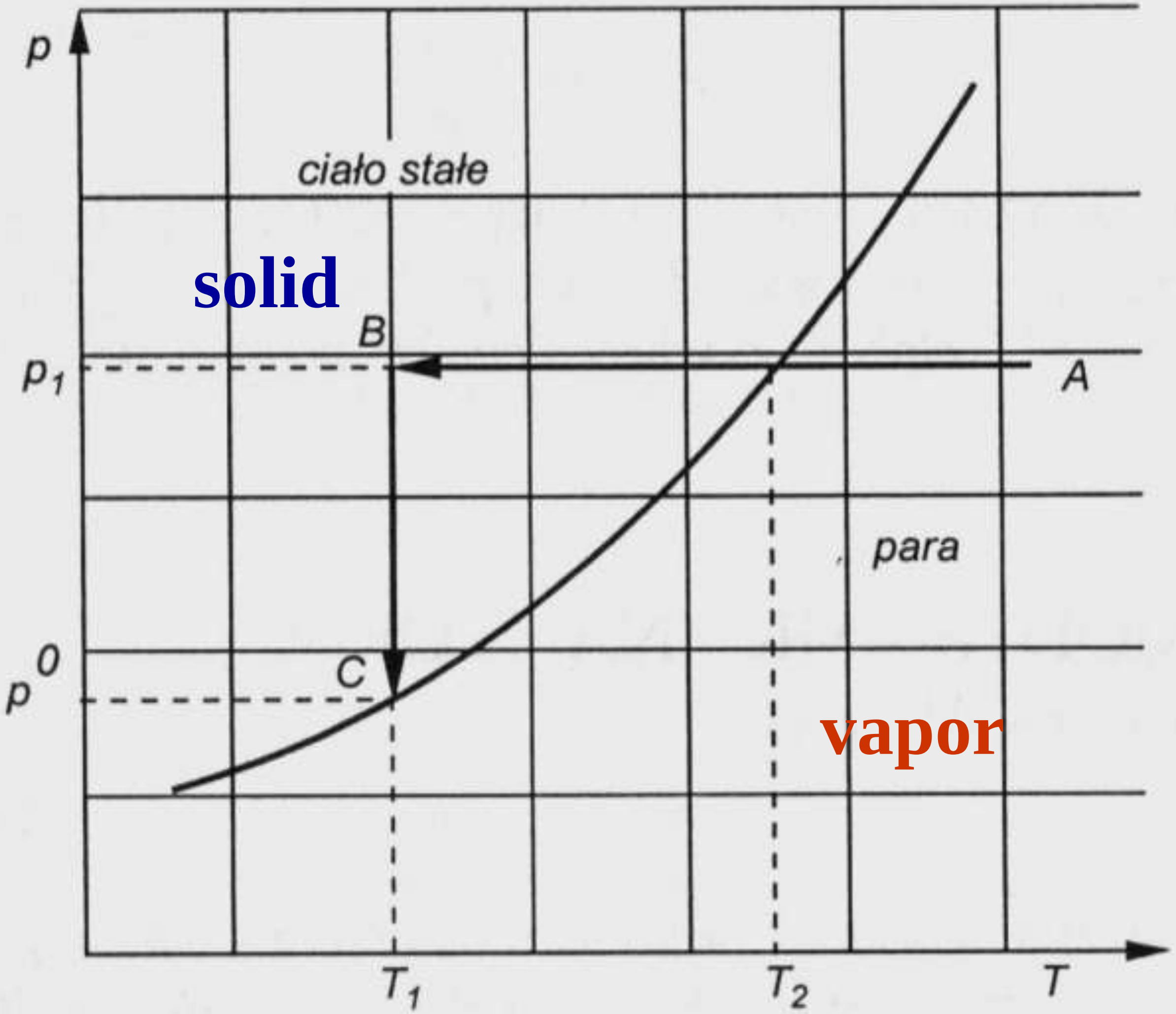


Diagram fazowy para–ciało stałe

Phase diagram vapor-solid

Plasma Treatment – endless possibilities

Plasma can be used in many different cases whenever you would like to better adhere materials together or to change a surface property to suit your needs. With this trend-setting technology it is possible to modify virtually any surface. **Plasma technology** offers several versatile applications, for example:

- **Cleaning** surfaces of any residues, oils, or contamination
- **Activation** of various materials before gluing, painting, etc.
- **Etching** and partial removal of surfaces
- **Coating** of parts with several possible types of layers (PTFE-like, protective barriers, hydrophobic, hydrophilic, friction-reducing, etc.)

Plasma technology is establishing itself in all areas of industry, and new applications are constantly evolving.

Plasma Technology - Convincing Advantages
Compared to other methods, like flame treating or using chemicals to treat a surface, plasma technology exhibits many important advantages:

Many surface properties can be obtained exclusively with this procedure

Can be used in online production or operated independently

environmentally friendly process

Regardless of geometry you are able to treat powder, small parts, discs, fleece, textiles, tubing, bottles, circuit boards, etc.

Fabricated parts will not be mechanically changed

Heating of the parts is minimal

Operating costs are very low

Extremely safe to operate

Process is extremely energy efficient

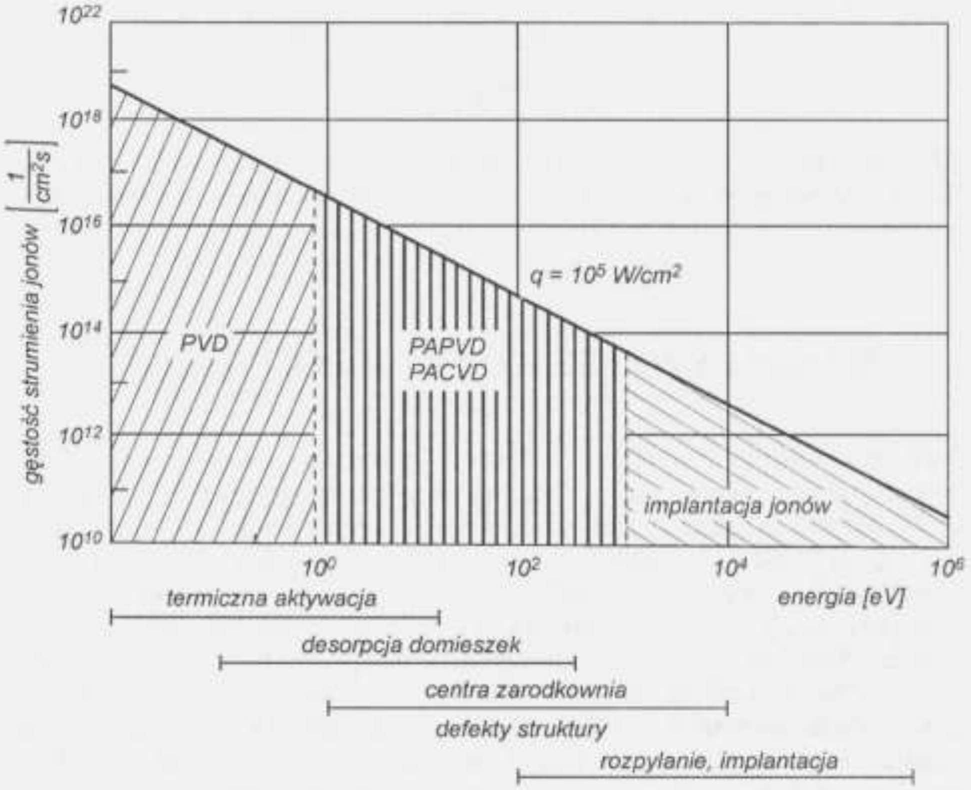
Energia cząstek dla różnych metod nakładania powłok

Metoda	Cząstki docierające do podłoża	Ciśnienie [Pa]	Średnia energia kinetyczna [eV]
Naparowywanie	Atomy, klastery	$< 10^{-5}$	0,2
ARE	Około 1% jony, atomy	$< 10^{-3}$	0,2
IP, TRIP	Około 30% jony, atomy	$10^{-2} - 10^{-1}$	0,2 – 50*
Arc Evaporation	Około 100% jony, klastery, krople	$10^{-5} - 1$	5 – 80*
Impulsowo-plazmowa	Około 100% jony, klastery, krople	> 100	około 100
Rozpylanie jonowe	Około 5% jony, atomy, klastery	$10^{-5} - 5$	5 – 20*

* Energia cząstek zależna od ciśnienia i napięcia między anodą a katodą

Evaporation
Activated reactive evaporation
Ion implantation
Arc evaporation
Pulse-plazma
Sputtering

ARE-Activated Reactive Evaporation
IP- Ion Plating
TRIP- Triode Reactive Ion Plating



thermal activation
desorption of impurities
nucleation centers
structural defects
sputtering, implantation

Effects of the bombing of the solid caused by ions of varying energy

Rysunek 8.3 Skutki bombardowania ciała stałego wywołane przez jony o różnej energii [54]

3. Pressure units (SI - Wikipedia)

1 bar = 1x10^5 N/m^2

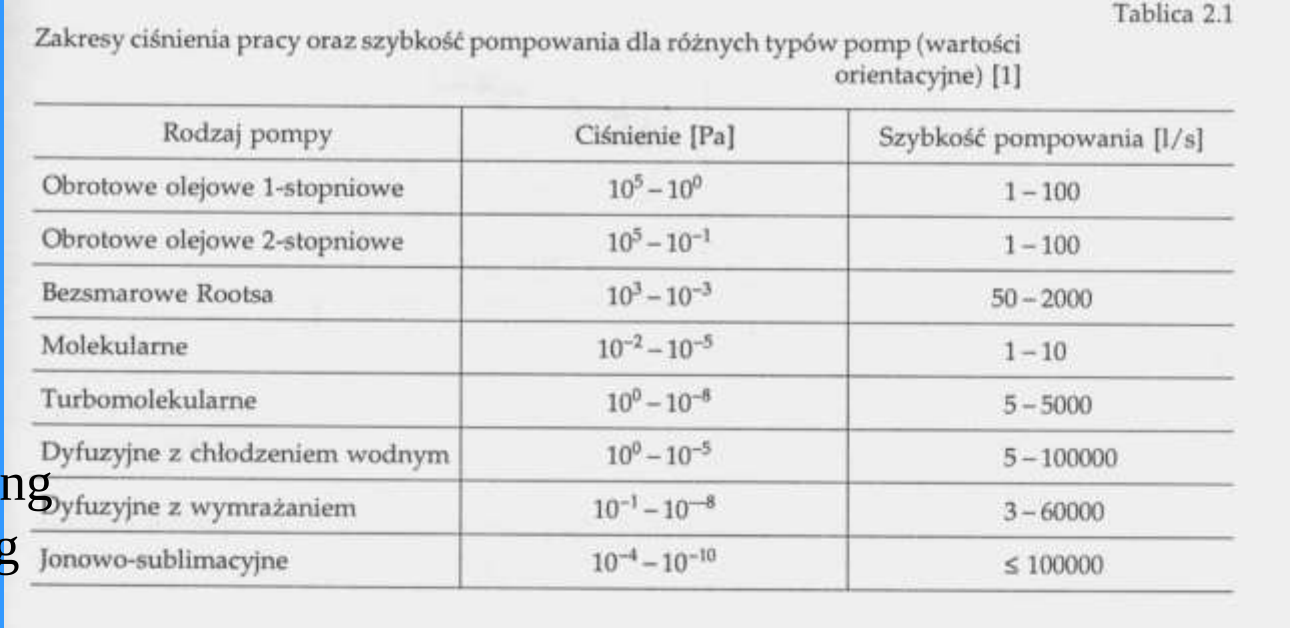
= 1x10^3 hPa = 100 kPa

- 1 bar = 10^5 N/m^2 = 10^5 Pa
- 1 mbar = 1 hPa = 100 Pa
- 1013,25 mbar = 1013,25 hPa = 1 atm (normal pressure)

	Pascal	**Bar**	**Technical atmosphere**	**Physical atmosphere**	**Torr**	**Lb /in^2**
	[Pa]	**[bar]**	**[at]**	**[atm]**	**[torr]**	**[psi]**
	1 N/m^2	1 Mdyn/cm^2	1 kp/cm^2	p_{STP}	1 mm$_{Hg}$	1 lbf/in.^{2}
1 Pa	1	1,0000x10^{-5}	1,0197x10^{-5}	9,8692x10^{-6}	7,5006x10^{-3}	1,4504x10^{-4}
1 bar	1,0000x10^{5}	1	1,0197x10^{0}	9,8692x10^{-1}	7,5006x10^{2}	1,4504x10^{1}
1 at	9,8067x10^{4}	9,8067x10^{-1}	1	9,6784x10^{-1}	7,3556x10^{2}	1,4223x10^{1}
1atm	1,0133x10^{5}	1,0133x10^{0}	1,0332x10^{0}	1	7,6000x10^{2}	1,4696x10^{1}
1torr	1,3332x10^{2}	1,3332x10^{-3}	1,3595x10^{-3}	1,3158x10^{-3}	1	1,9328x10^{-2}
1 psi	6,8948x10^{3}	6,8948x10^{-2}	7,0307x10^{-2}	6,8046x10^{-2}	5,1715x10^{1}	1

3a. Vacuum

Rotary oil 1-stage
Rotary oil 2-stages
Roots oil free
Molecular
Turbolecular
Diffusion of water cooling
Diffusion with freezing
Ion-sublimation



Tablica 2.1

Zakresy ciśnienia pracy oraz szybkość pompowania dla różnych typów pomp (wartości orientacyjne) [1]

Rodzaj pompy	Ciśnienie [Pa]	Szybkość pompowania [l/s]
Obrotowe olejowe 1-stopniowe	$10^5 - 10^0$	1 – 100
Obrotowe olejowe 2-stopniowe	$10^5 - 10^{-1}$	1 – 100
Bezsmarowe Rootsa	$10^3 - 10^{-3}$	50 – 2000
Molekularne	$10^{-2} - 10^{-5}$	1 – 10
Turbomolekularne	$10^0 - 10^{-8}$	5 – 5000
Dyfuzyjne z chłodzeniem wodnym	$10^0 - 10^{-5}$	5 – 100000
Dyfuzyjne z wymrażaniem	$10^{-1} - 10^{-8}$	3 – 60000
Jonowo-sublimacyjne	$10^{-4} - 10^{-10}$	≤ 100000

Pump Types can be broadly categorized according to three techniques:[1]

- Positive displacement pumps use a mechanism to repeatedly expand a cavity, allow gases to flow in from the chamber, seal off the cavity, and exhaust it to the atmosphere.
- Momentum transfer pumps, also called molecular pumps, use high speed jets of dense fluid or high speed rotating blades to knock gas molecules out of the chamber.
- Entrapment pumps capture gases in a solid or adsorbed state. This includes cryopumps, getters, and ion pumps.

- Positive displacement pumps (wyporowe) are the most effective for low vacuums.

- Momentum transfer pumps (wirnikowe) in conjunction with one or two positive displacement pumps are the most common configuration used to achieve high vacuums. In this configuration the positive displacement pump serves two purposes. First it obtains a rough vacuum in the vessel being evacuated before the momentum transfer pump can be used to obtain the high vacuum, as momentum transfer pumps cannot start pumping at atmospheric pressures. Second the positive displacement pump backs up the momentum transfer pump by evacuating to low vacuum the accumulation of displaced molecules in the high vacuum pump.

- Entrapment pumps (adsorpcyjne) can be added to reach ultrahigh vacuums, but they require periodic regeneration of the surfaces that trap air molecules or ions. Due to this requirement their available operational time can be unacceptably short in low and high vacuums, thus limiting their use to ultrahigh vacuums. Pumps also differ in details like manufacturing tolerances, sealing material, pressure, flow, admission or no admission of oil vapor, service intervals, reliability, tolerance to dust, tolerance to chemicals, tolerance to liquids and vibration.

4. Mechanical methods of surface modification

It uses a pressure tool or tools, or the kinetic energy of the particles in order to strengthen the cold surface layer of metal or metal alloy or to receive the metal coating on the cold substrate.

• Burnishing	Nagniatanie
• Shot peening	Kulowanie
• Application of Detonation	Detonacyjne
• Plating	Platerowanie

Burnishing

Plastic deformation of the material in the surface layer by the interaction of the surface of the workpiece with a tool suitable curvature, which can roll without slipping, skidding or collide with the surface of the element.

Performed on machine tools with appropriate equipment as well as using special machine tools for burnishing.

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Static burnishing - the power of the tool element is constant or slowly varying.

Dynamic (Shot peening) - when a collision occurs during the processing of work items and machined surface characteristics of pulse power in a single collision is dependent on the collision energy and the properties of the workpiece.

Layer thickness: up to few mm

static burnishing

- bearings: ball bearings, pulleys, roller chain (normal and orbital

Nagniatanie statyczne

- toczne: kulkowanie, krążkowanie, rolkowanie (zwykłe scylacyjne)

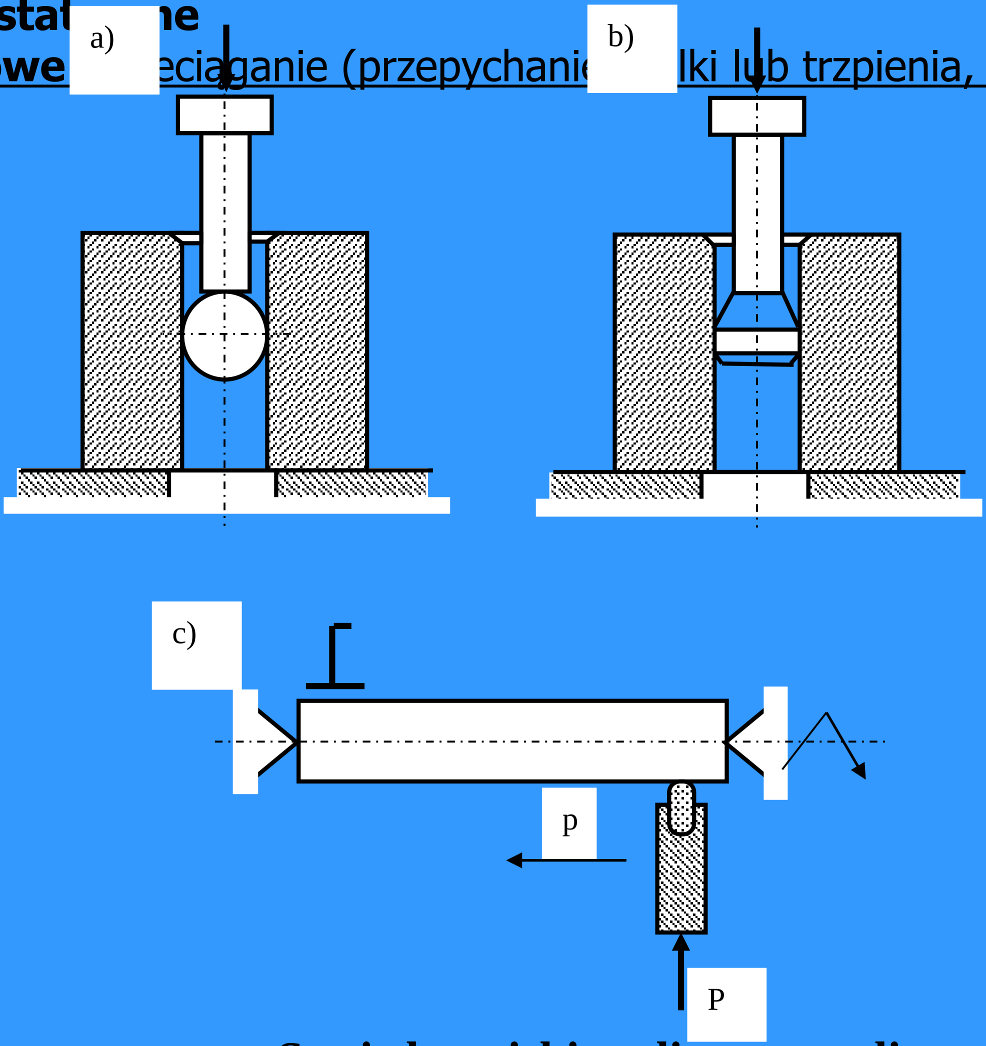
Types of ball burnishing tools, roller and troller

Typy narzędzi do nagniatania kulkowego, rolkowego i krążkowego

Static burnishing - Sliding: drag (pushing) balls or pivot, smooth sliding

Nagniatanie stat ne

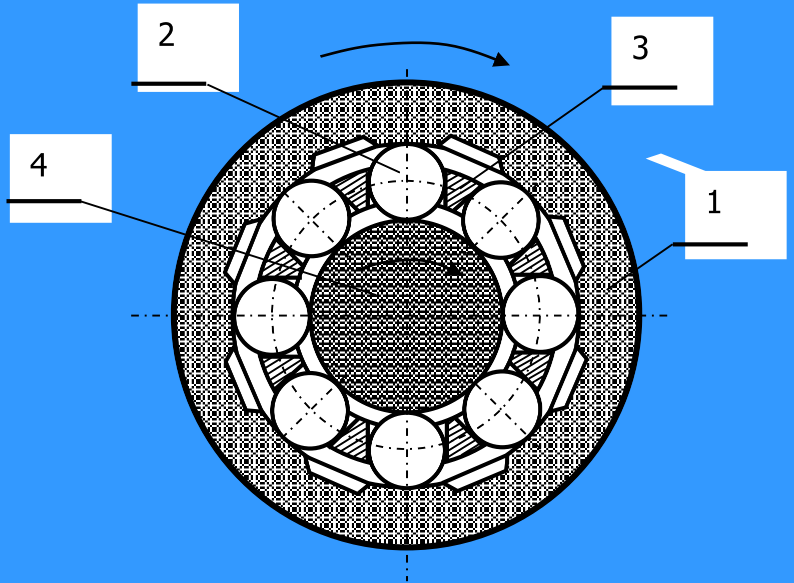
- ślizgowe eciąganie (przepychanie lki lub trzpienia, wygładzanie ślizgowe



Static burnishing diagram - slip

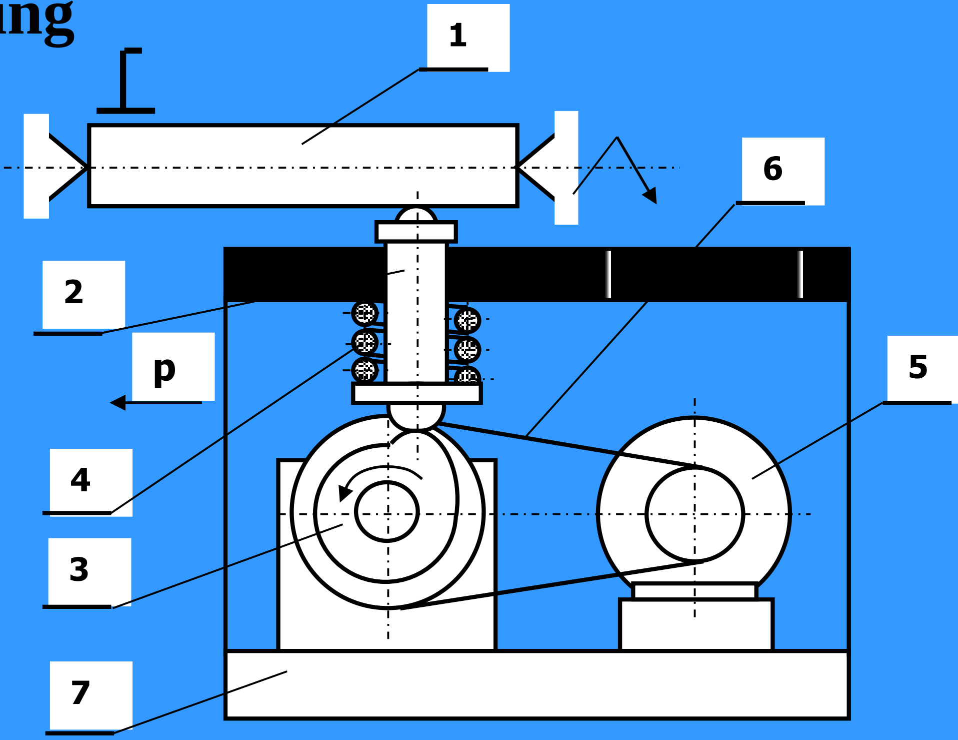
a) pushing balls, b) pushing pivot, c) sliding smoothing tool with carbide tip

Dynamic burnishing
- focused: pulleys, bearings, roller bearings, and centrifugal and pulse hammering



Roller pulsed diagram: 1 - workpiece, 2 - roller, 3 - ring leader, 4 - rotating ring with projections

Schemat rolkowania impulsowego: 1 - przedmiot obrabiany, 2 - element nagniatający (rolka), 3 - pierścień prowadzący, 4 - wirujący pierścień z występami



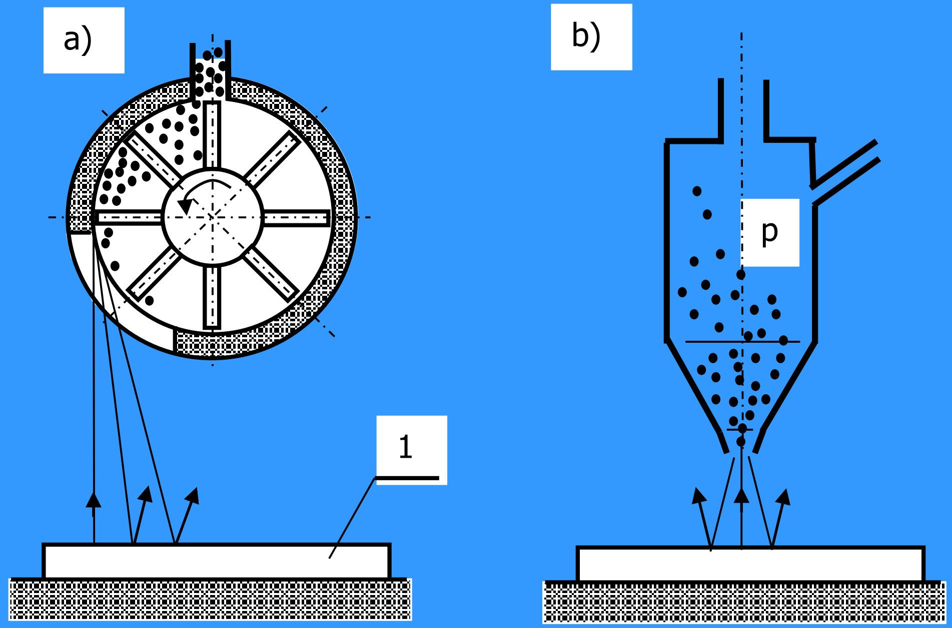
Schematic hammering: 1 - the workpiece, 2 - beater, 3 -, cam, 4 - spring, 5 - electric motor, 6 - belt transmission, 7 - the body of the instrument mounted on the BB machine, p - feed

Schemat młotkowania: 1 - przedmiot obrabiany, **2** - bijak, **3** - krzywka, **4** - sprężyna, **5** – silnik elektryczny, **6** - przekładnia pasowa, **7** - korpus przyrządu mocowany na suporcie obrabiarki, **p** - posuw

Dynamic burnishing

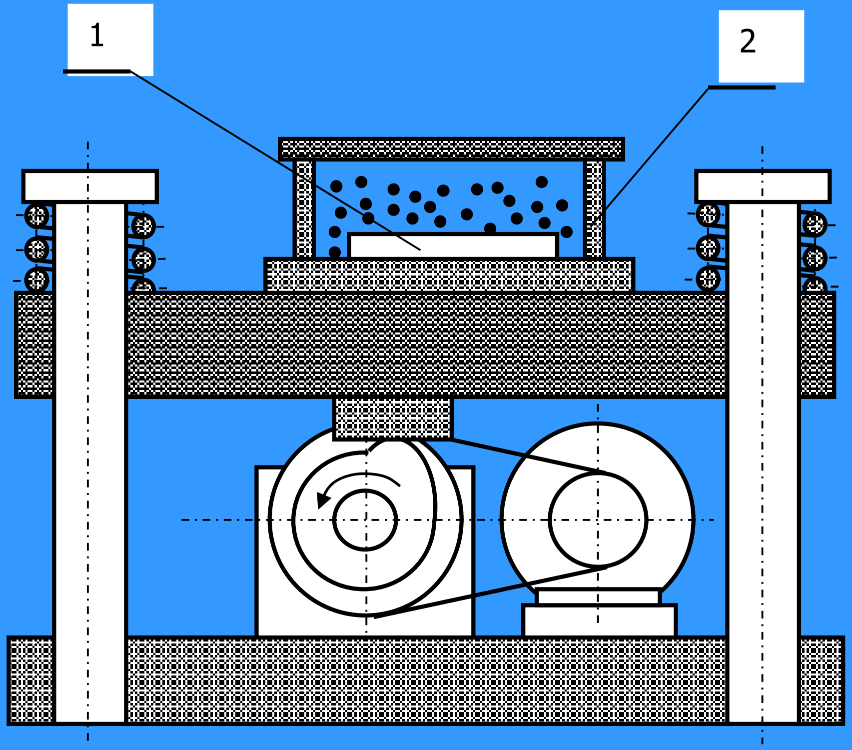
- Scattered - streaming and vibratory ball

Nagniatanie dynamiczne - rozproszone - kulkowanie strumieniowe i wibracyjne



Stream ball: throwing balls with a) or b ejector rotor) with compressed air from a nozzle

Kulkowanie strumieniowe: wyrzucanie kulek za pomocą a) wyrzutnika wirnikowego lub b) z dyszy sprężonym powietrzem



Schematic peening vibration: the workpiece (1) is located in a closed container (2) filled with balls and placed on a mechanical vibrator

Schemat kulkowania wibracyjnego: przedmiot obrabiany (1) jest umieszczony w pojemniku zamkniętym (2) wypełnionym kulkami i ustawionym na wibratorze mechanicznym

Shot peening Kulowanie

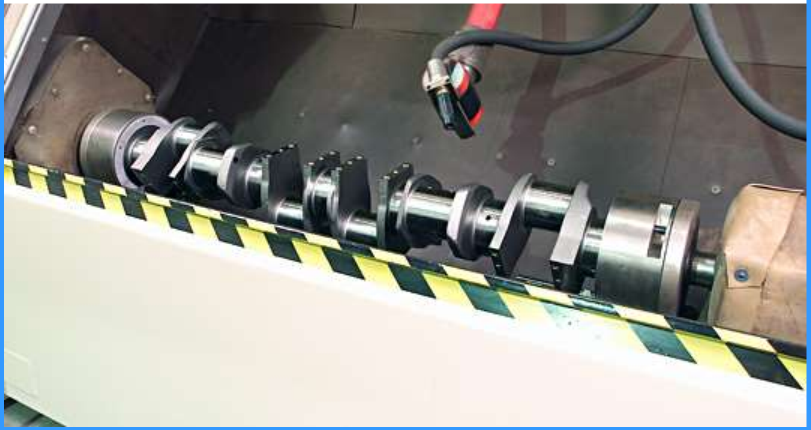
- **Effects on workpiece of stream of round steel shot, ceramic or glass beads**
- **High-casting rotors hurl shot at the outlet of around 80m / s**
- **Stream of pellets have a very high homogeneity, crucial for very uniform treatment of the entire surface elements**
- **Shot hitting the surface of the workpiece to produce plastic deformation causes a depth of a few hundredths of a millimeter to 1.5 mm**
- **The size of deformation is dependent on the intensity of shot peening, and the hardness of the workpiece**

- Działanie na obrabiany element strumieniem okrągłego śrutu stalowego, ceramicznego lub kulek szklanych
- Wysokowydajne wirniki rzutowe miotają śrut z prędkością wylotową wynoszącą ok. 80m/s
- Strugi śrutu posiadają bardzo dużą jednorodność, decydującą o bardzo równomiernej obróbce na całych powierzchniach elementów
- Uderzenia śrutu w powierzchnię obrabianego elementu powodują wytworzenie odkształcenia plastycznego o głębokości od kilku setnych milimetra do ok. 1,5mm
- Wielkość odkształcenia zależy od intensywności kulowania oraz od twardości obrabianego przedmiotu

Shot peening

Application

large gears	duże koła zębate
axles and shafts	osie i wały
turbine blades	łopatki turbin
disc springs	sprężyny talerzowe
coil springs	sprężyny śrubowe
flat springs	sprężyny płaskie
stabilizers	stabilizatory
rankshafts	wały korbowe
rods	korbowody
aircraft parts	części samolotów



Plating Platerowanie

Plating the substrate metal or other metal alloy is by the formation of a coating material by pressing at elevated temperature.

Coating materials: aluminum and alloys, copper and alloys, Mo and alloys, chromium steels, chrome-nickel, precious metals, Monel and other alloys.

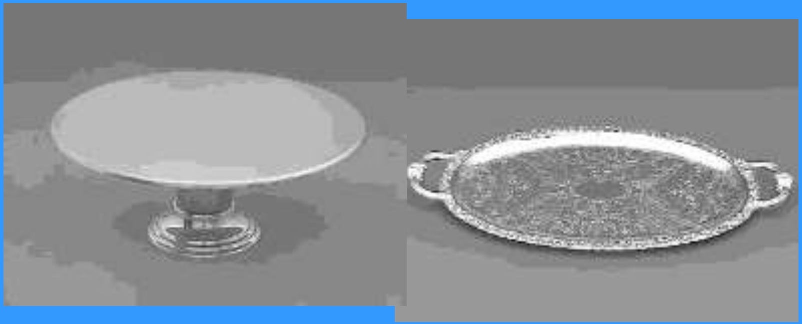
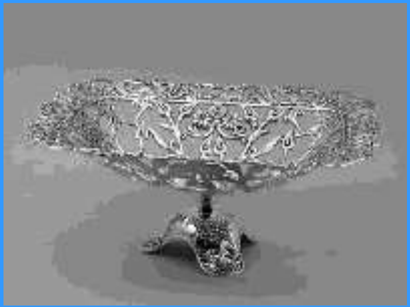
Thickness of layer: from few μm to few mm

OBJECTIVE: Increased resistance to atmospheric corrosion and in high-temperature gas and chemically aggressive environments

Plating - application







Plastic working - strengthening by cold working

OBJECTIVE: The formation or splitting of the workpiece, changing the physical and chemical properties, structure and smooth surface, or creating your own stress

Rolling – plastic deformation of material between rotating cylinders

Forging - material plastically shaped by the impact hammer or static pressure press

Extrusion -is a process used to create objects of a fixed, cross-sectional profile. A material is pushed or drawn through a die of the desired cross-section. The two main advantages of this process over other manufacturing processes are its ability to create very complex cross-sections and work materials that are brittle, because the material only encounters compressive and shear stresses. It also forms finished parts with an excellent surface finish

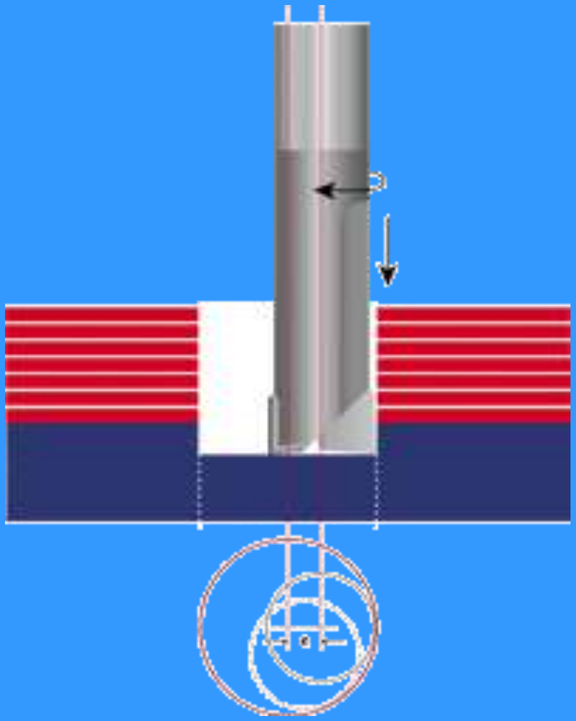
Plastic drawing -sometimes referred to as cold drawing, is the same process as used on metal bars, but applied to plastics

Stamping -Stamping (also known as pressing) includes a variety of sheet-metal forming manufacturing processes, such as punching using a machine press or stamping press, blanking, embossing, bending, flanging, and coining.[1] This could be a single stage operation where every stroke of the press produces the desired form on the sheet metal part, or could occur through a series of stages. The process is usually carried out on sheet metal, but can also be used on other materials, such as polystyrene.

Machining - used pressure tool (blade) to remove some of the material and to obtain the final shape; modern cutting tools, CNC machine tools

Machining is any of various processes in which a piece of raw material is cut into a desired final shape and size by a controlled material-removal process. The many processes that have this common theme, controlled material removal, are today collectively known as subtractive manufacturing, in distinction from processes of controlled material addition, which are known as additive manufacturing.

The precise meaning of the term "machining" has evolved over the past two centuries as technology has advanced. During the Machine Age, it referred to (what we today might call) the "traditional" machining processes, such as turning, boring, drilling, milling, broaching, sawing, shaping, planning, reaming, and tapping.



Detonation spraying

The kinetic energy of the particles in the form of metal powder (ceramic) is transfeerd by gas detonation with a slight warm-up of the workpiece

OBJECTIVE: To obtain a coating of non-metal substrate properties

Powders used for spraying:
powders of metals and their alloys
powders of compounds - oxides, carbides, borides
metal-ceramic powders
ceramic powders

Thickness: 0.3-0.4 mm (up to 1mm

5. Chemical surface modification methods

Chemical Vapour Deposition CVD

Thermally activated CVD coatings
Plasma assisted PE CVD

Methods of CVD (Chemical Vapour Deposition) include processes in which the substrates for coating are transported in the form of volatile compounds to the substrate on which the chemical reaction takes place to form the coating.

Division of CVD methods:

not supported:

APCVD (Atmospheric Pressure CVD)

LPCVD (Low Pressure CVD)

supported by:

selection of appropriate gas atmospheres and the use of organometallic compounds MOCVD (Metal-Organic CVD)

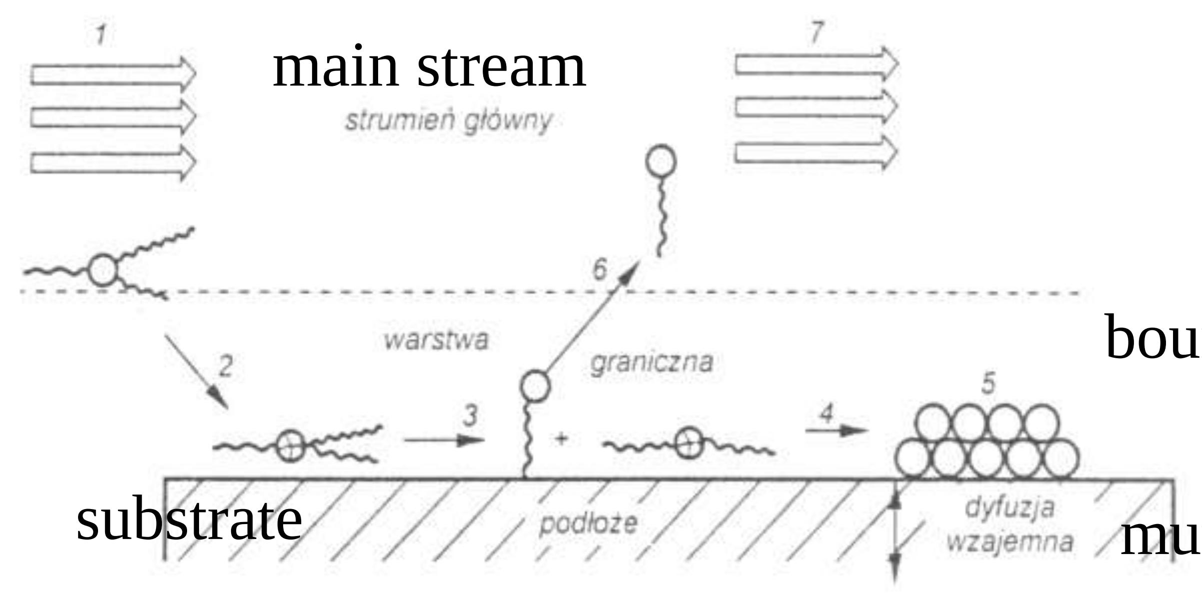
introduction of laser technology Laser CVD

electrical activation of the gas environment using glow discharge PACVD (Plasma Assisted CVD)

CVD methods not supported

Application:

- **electronics industry: production of semiconductor structures with silicon, germanium, compound semiconductors and dielectric layers**
- **coating of cutting tools coated with refractory and hard materials.**



Classified by operating pressure:

Atmospheric pressure CVD (APCVD): CVD processes at atmospheric pressure.

Low-pressure CVD (LPCVD): CVD processes at sub-atmospheric pressures. Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer. Most modern CVD processes are either LPCVD or UHVCVD.

Ultra-high vacuum CVD (UHVCVD): CVD processes at a very low pressure, typically below 10-6 Pascal.

Classified by physical characteristics of vapor:

Aerosol assisted CVD (AACVD): A CVD process in which the precursors are carried to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically. This technique is suitable for use with non-volatile precursors.

Direct liquid injection CVD (DLICVD): DLICVD process in which the precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors). Then the precursor vapors are transported to the substrate as in classical CVD process. This technique is suitable for use on liquid or solid precursors. High growth rates can be reached by using this technique.

Plasma methods:

- Plasma-Enhanced CVD (PECVD): CVD processes that utilize plasma (plasma is a state of matter similar to gas) to boost chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors.
- Remote plasma-enhanced CVD (RPECVD): Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.
- Atomic layer CVD (ALCVD): Deposits successive layers of different substances to produce layered crystalline films.
- Combustion Chemical Vapor Deposition (CCVD): Combustion chemical vapor deposition (CCVD) is a chemical process by which thin film coatings are deposited onto substrates in the open atmosphere.
- Hot wire CVD (HWCVD): Also known as catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). It uses a hot filament to chemically decompose the source gases.

CVD methods not supported

Phenomena occurring during the deposition

1.Transport of gaseous reactants to the frontier
2. Transport of gaseous reactants to the frontier
3. Homogeneous reaction in the gas phase
4. Adsorption of reactants on the substrate surface
5. Heterogeneous chemical reactions
6. Nucleation and growth of coating
7. Desorption of waste products of chemical reactions
8. Transport of gaseous products of the chemical reaction on the outside of the boundary layer
9. Transport of gaseous products of a chemical reaction with the substrate surface to the gas phase, the gas volume

CVD methods not supported

The chemical reactions in the CVD process:

- **high degradation reactions (above 873K) and at low temperature (293-873K), which may be either substrates, inorganic compounds (metal chlorides and some iodides, metal hydrides) and organic compounds (metal carbonyls and organometallic compounds)**

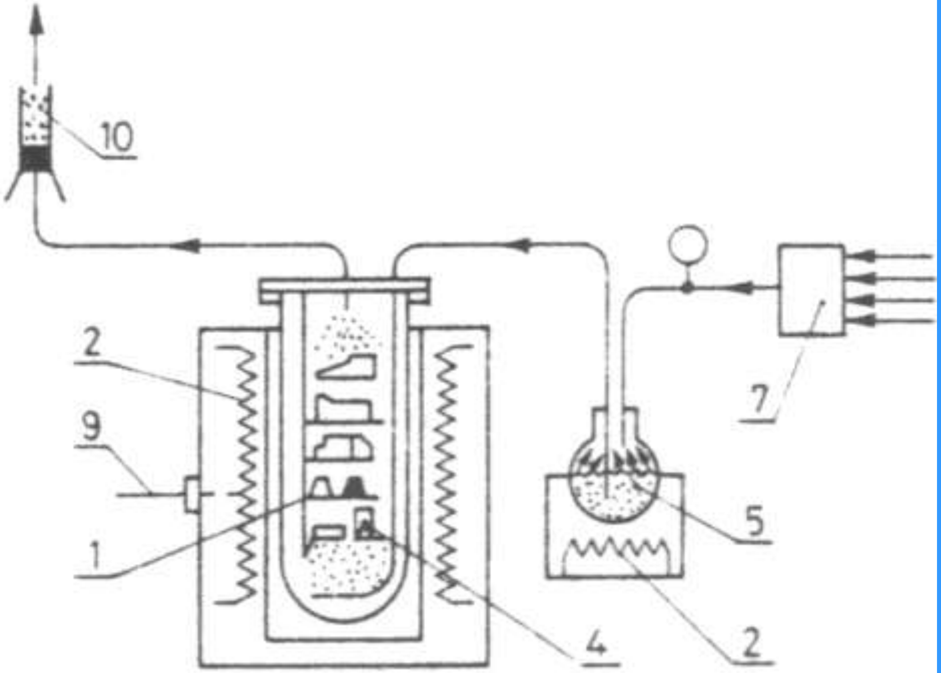
- **reduction reactions with hydrogen halides or metal**

- **transport reactions take place in three stages:**

1. **move the material sources in volatile compound,**
2. **transport of the volatile compound from the source to the substrate,**
3. **decomposition of the volatile compound to form a coating.**

CVD methods not supported

Scheme of apparatus for carrying out the process of CVD



1.working chamber
2.heating resistors
4.batch
5.feeder
7.gas injection system of an agitator
9.temperature gauge
10.gas filter

CVD methods supported PACVD

Glow discharge is used for excitation of the plasma :

DC (Direct Current) power generated by the gas flow between the two electrodes (anode and cathode) under reduced pressure in the range 0.1 - 10^3 Pa. Backup voltage glow discharge depends on the type of gas, pressure, and electrode material. Typical voltage is of the order of several hundred volts and the discharge current of hundreds of milliamps;

Radio frequency RF (Radio Frequency (13.56MHz) is dependent on the type of gas, its pressure, the frequency of the electric field and the size of the discharge chamber. Energy from the power supply can be driven by using electrodes placed on the outside or inside of the chamber (0.2-2kHz);

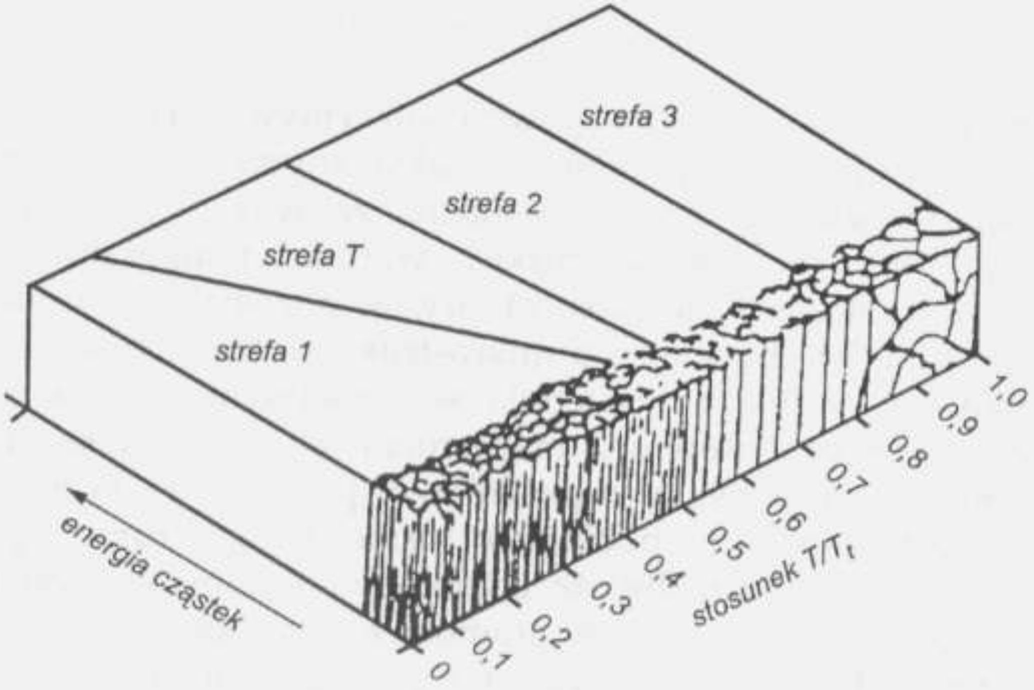
Microwave does not require any electrodes for excitation of the plasma because the process of absorption of microwave energy is concentrated and localized in a specific volume of gas. Microwave energy source is known as microwave magnetron or klystrons (2.45GHz). Microwave discharge energy from the source is fed to the reactor in the form of waveguide electromagnetic radiation.

Zone 1 - porous microstructure, consisting of a prismatic crystallites, between which there are voids

Zone T – super-fine oriented fibrous microstructure

Zone 2 - columnar grain microstructure

Zone 3 - microstructure with equiaxial grains



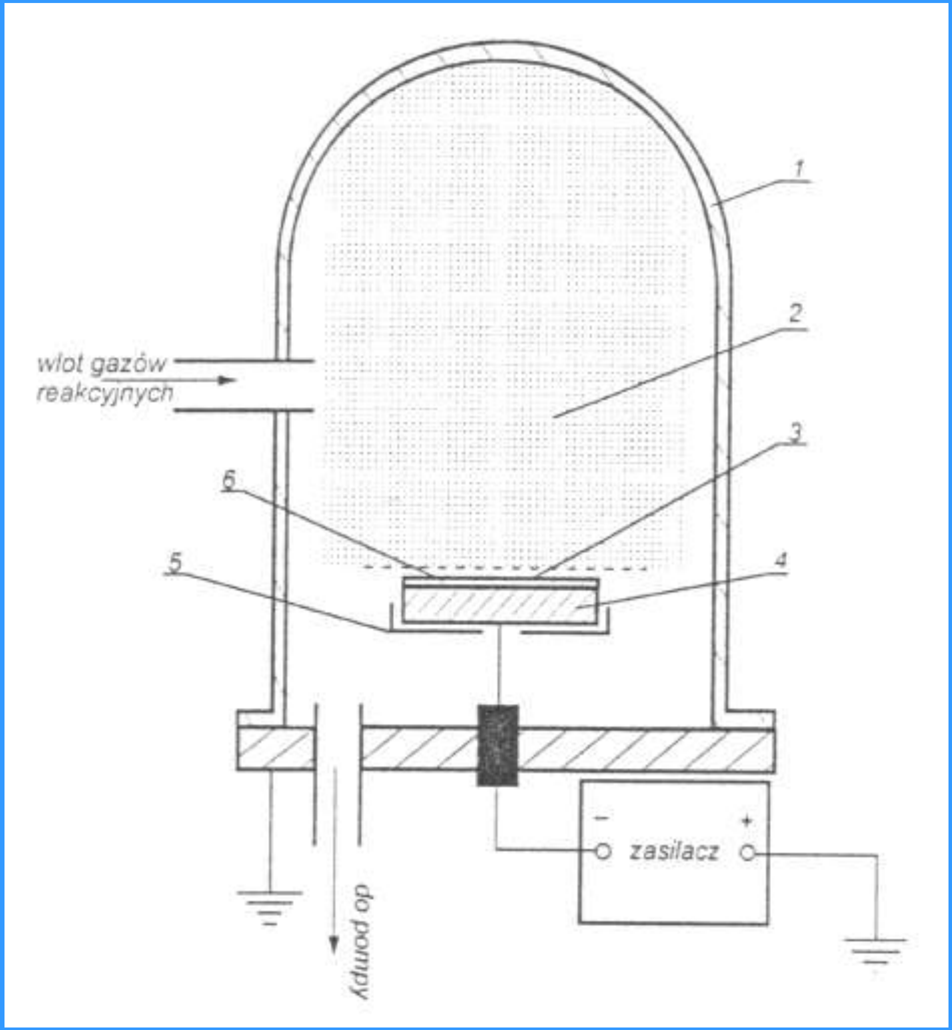
Wpływ energii cząstek i temperatury podłoża na mikrostrukturę powłoki [63]

Thornton diagram

Influence of chamber pressure and homologous coating temperature during deposition on morphology of metallic or ceramic coatings

PACVD

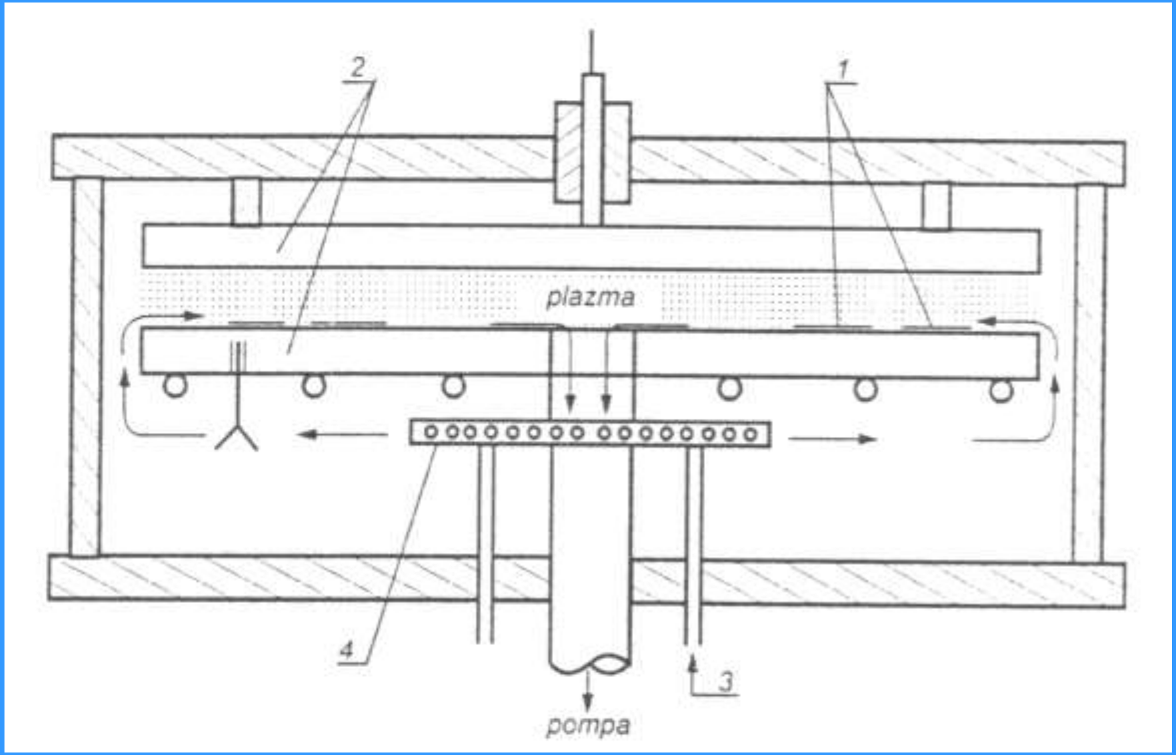
Diagram of apparatus for coating in the plasma-assisted CVD DC



1. reservoir (anode)
2. plasma
3. cathodic darkroom
4. substrate (cathode)
5. grounded screen
6. coating

PACVD

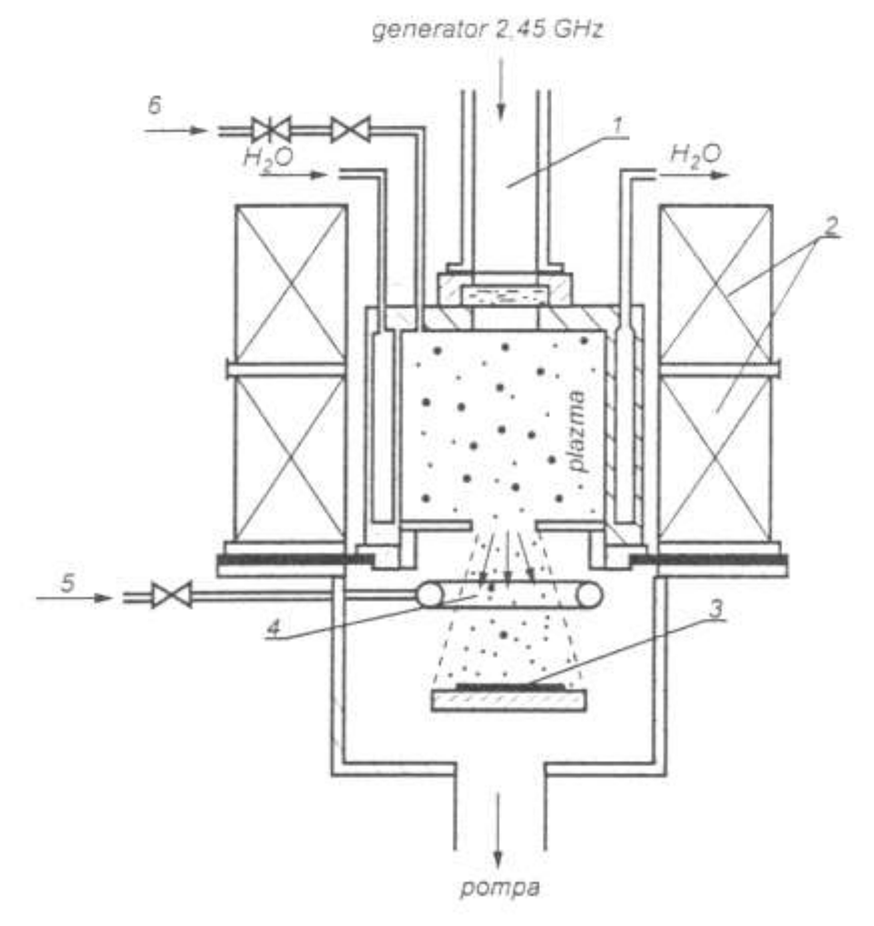
Diagram of apparatus for applying coatings in the RF plasma-assisted CVD excited between flat electrodes



1. substrate
2. discharge electrodes
3. reaction gas inlet
4. gas distribution nozzle

PACVD

Diagram of apparatus for coating in the microwave plasma-assisted CVD



1. waveguide
2. electromagnets
3. substrate
4. plasma jet
5. reactant
6. plasma generating gas

Comparison of CVD
for example, the production of titanium nitride layers

Method	APCVD	LPCVD	PACVD
Method of heating items	Resistive heating of chamber	Resistive heating of chamber	Heating in a glow discharge conditions
Pressure in the working chamber	atmospheric	10 – 500 hPa	3- 13 hPa
Process temperature	1170 – 1220 K	1150 K	770 –820 K
Process time	long	long	short

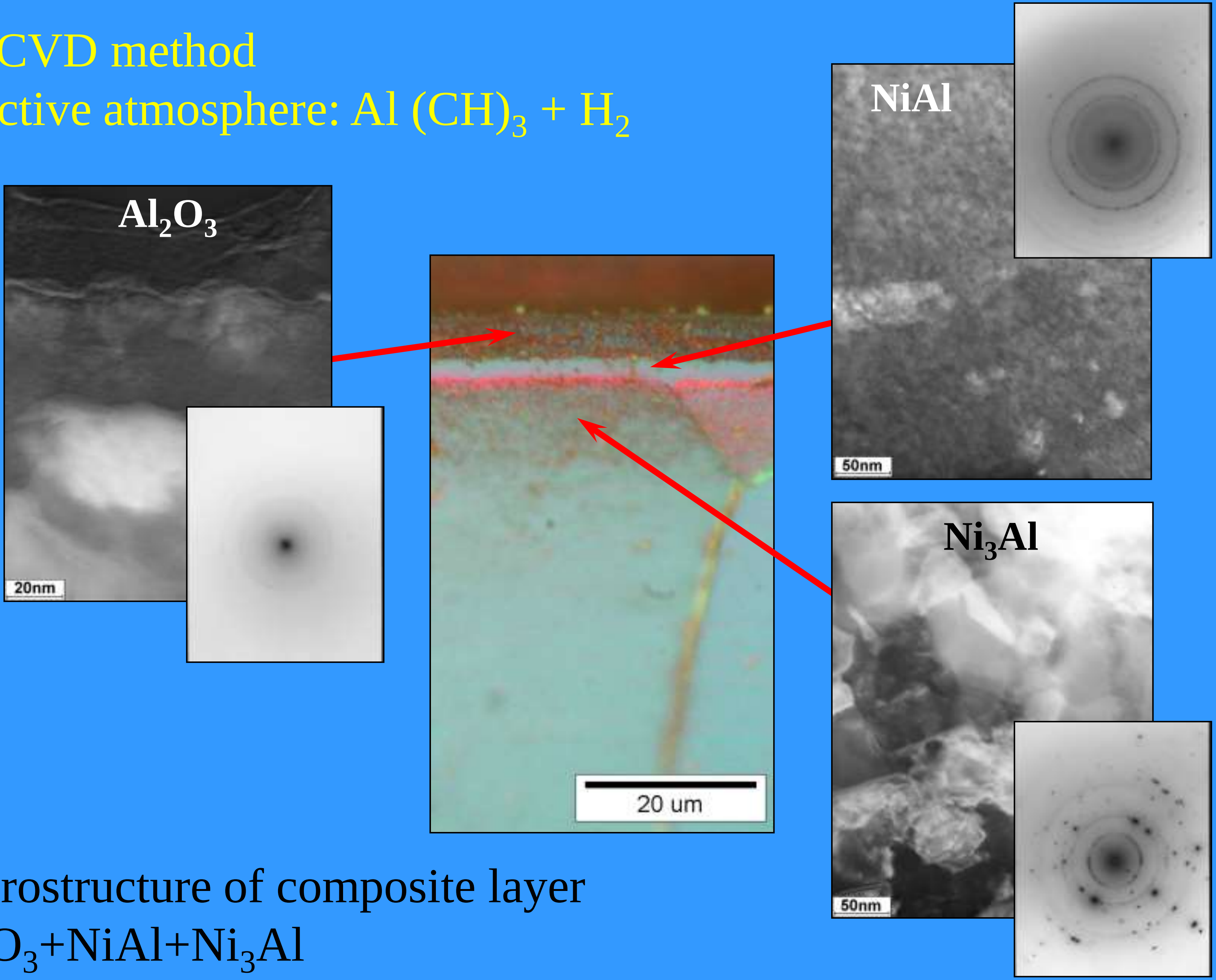
Multiplex processes

The so-called two-step process (duplex, hybrid)

consists of a further combined use of two or more surface engineering technologies to produce a composite layer on the surface with properties not achievable by the use of only one of the known techniques of surface treatments

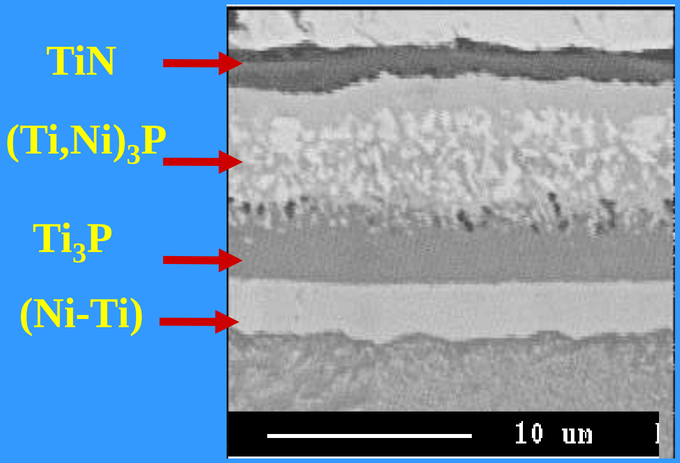
PACVD method

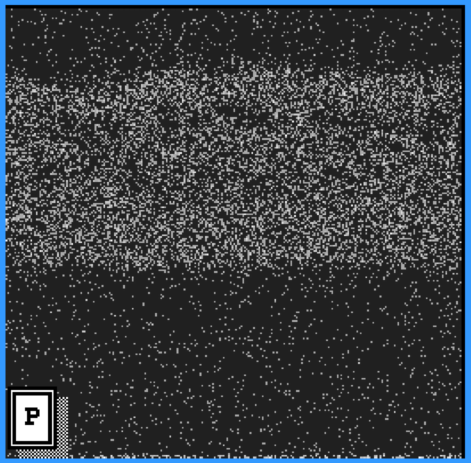
reactive atmosphere: Al $(CH)_3 + H_2$

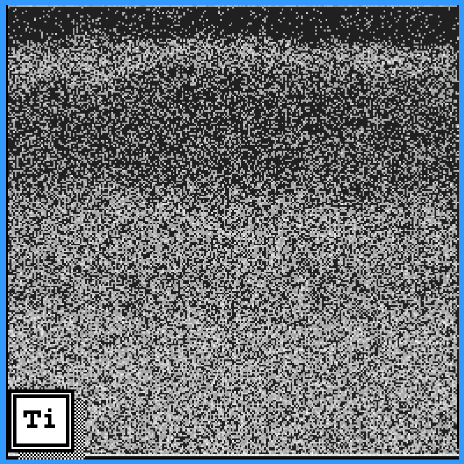


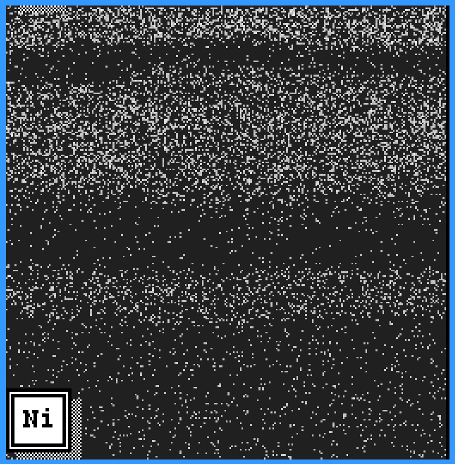
Microstructure of composite layer
$Al_2O_3+NiAl+Ni_3Al$

Structure and distribution of nickel, titanium, and phosphorus in a composite layer of TiN + (Ti, Ni)3P + Ti3P + (Ni-Ti) formed on titanium alloy Ti1Al1Mn









Composite layers produced on aluminum alloys

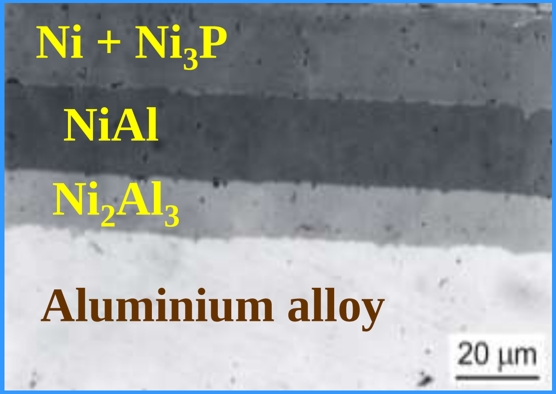
Chemical electroless deposition Ni(P) coating

Glow discharge treatment

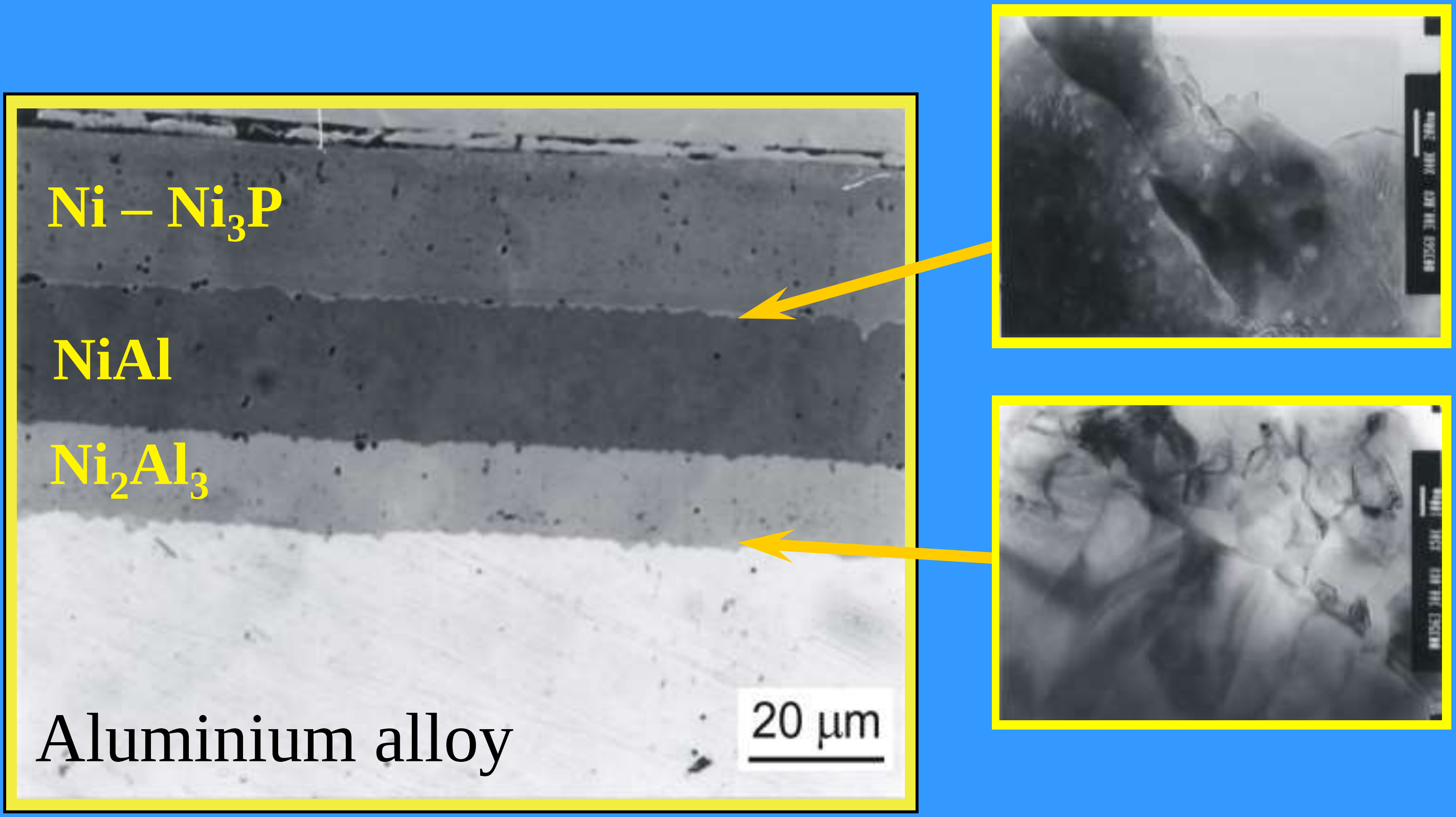
Aluminium alloy

Ni(P) coating

Aluminium alloy



Microstructure


TEM

6. Crystallization of the coating from the gas phase

Supersaturation = ratio of gas pressure in the plasma to the equilibrium pressure p/p0

Gibbs free energy = enthalpy = thermodynamic potential function of the system → $\Delta G = \Delta H - T \Delta S$

Adsorption = process in which one phase particles accumulates on the surface of the second phase, the phase boundary surface. There is no penetration through the boundary components (if absorption).

→ **Physisorption** van der Waals forces → reversible

→ **Chemisorption** bond atomic polarization, ionic chemical reaction → often irreversible

Desorption → inverse process of adsorption

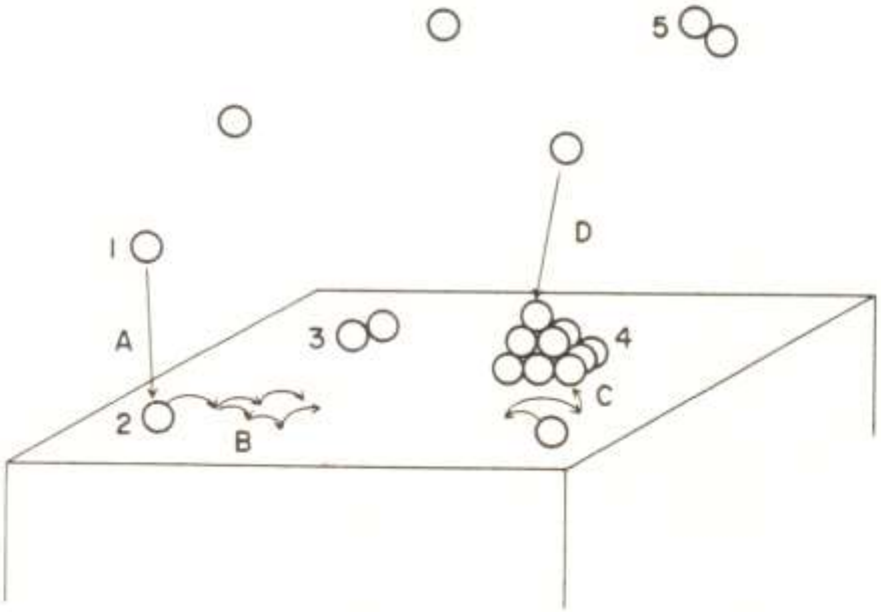
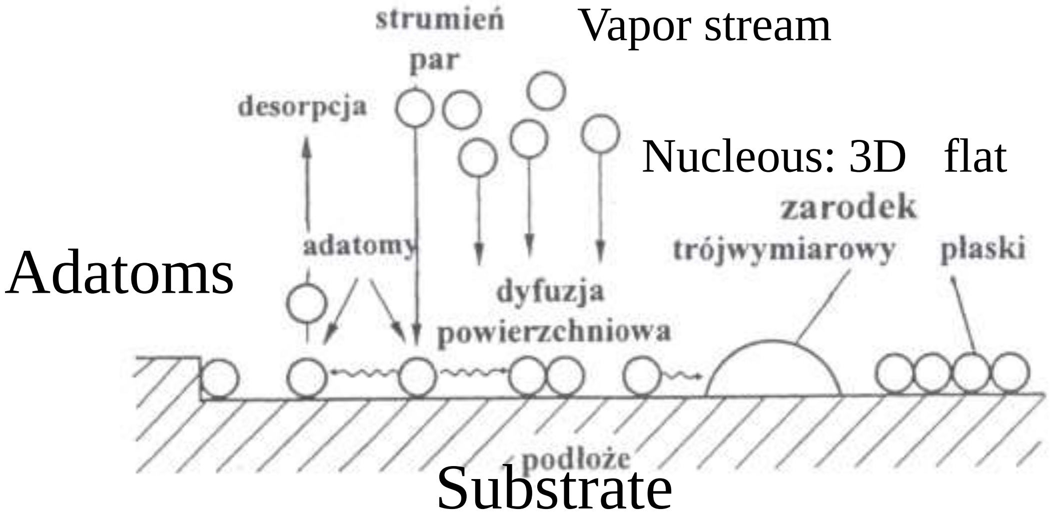


FIG. 1. Schematic illustration of interaction of vapor and substrate showing (1) monomer in vapor, (2) monomer adsorbed, (3) dimer adsorbed, (4) embryo, and (5) dimer in vapor, and the processes of (A) adsorption, (B) surface diffusion, (C) growth of embryo by surface diffusion addition, and (D) growth of embryo by vapor impingement.

reflection
adsorption
diffusion
desorption



Vapor stream

Nucleous: 3D flat

Adatoms

Substrate

Rys. IV.2. Elementarne zjawiska w początkowym okresie wzrostu powłoki z fazy gazowej [Chrisey, Hubler, 1994].

Film growth stages

I. Nucleation = nucleation → with or without energy barrier

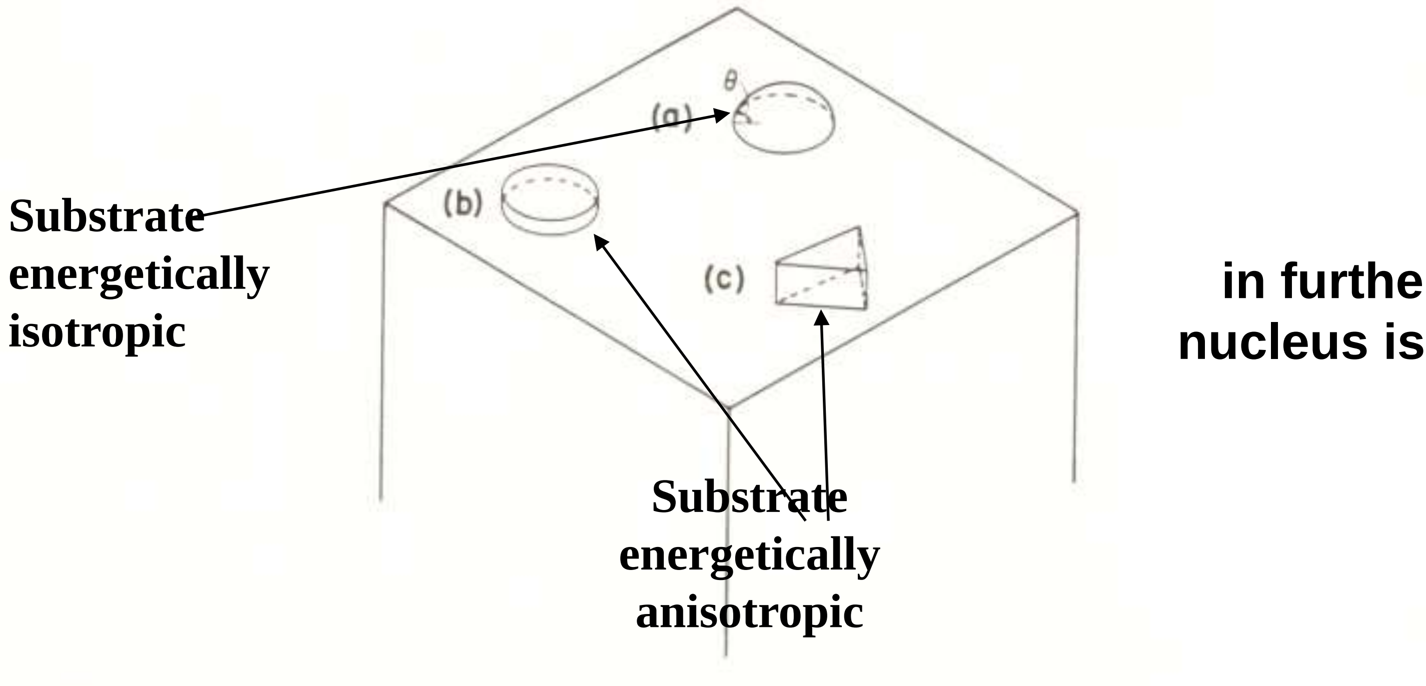
II. The gradual increase in embryos and the creation of a continuous coating

Thermally activated nucleation (diffusion)

- **homogeneous nucleation**
- **heterogeneous nucleation**

Thermodynamic Theory of nucleation = CAPILLARY

- on the substrate surface atom clusters are formed → clusters, aggregates, embryos
- the course of development of the nucleus is examined by determining changes in G
- macroscopic approach→ cluster approach is treated as a continuum phase



Substrate energetically isotropic

Substrate energetically anisotropic

FIG. 3. (a) Spherical cap-shaped nucleus meeting the substrate at a contact angle θ. (b) Disk-shaped nucleus. (c) Polyhedral nucleus.

in further considerations nucleus is taken as the ball

Homogeneous nucleation

Gibbs free energy of the nucleus consists of 2 components

$$G = G_v + G_s$$

G_v = energy (component) volume

G_s = energy (component) surface

The change of free energy Δ G during the growth or decline in the nucleus:

$$\Delta G = \Delta G_v + \Delta G_s$$

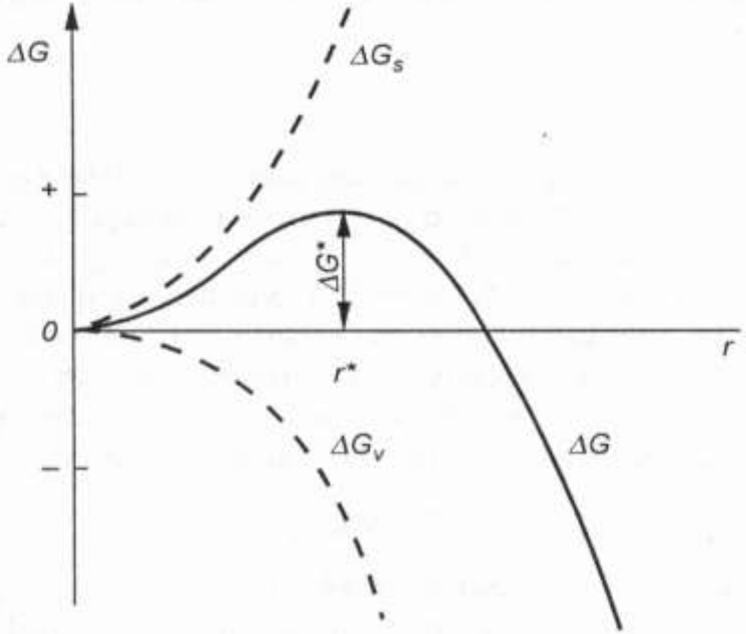
$\Delta G_r = - 4/3\ \pi r^3\ \Delta G_v + 4\ \pi r^{2}$©

r - radius of the nuclus

ΔG_v - the difference between the free enthalpy per unit volume of the crystal and liquid

γ - specific energy of the interface crystal-liquid

dependence on changes in the function of r Δ G



Schemat zmian swobodnej energii tworzenia zarodka

- pronounced maximum at a certain value of the radius
- for connection having a value of cluster Δ G increases up to r * and then decreases

What affects the value of Δ G * and r *

The degree of supersaturation of the gas phase (p/p_0)

the greater the p/p_0 the smaller r * (smaller nuclei become stable)

p/p_0 increases, Δ G * decreases (decreases the energy needed to obtain a stable nucleus)

The substrate temperature

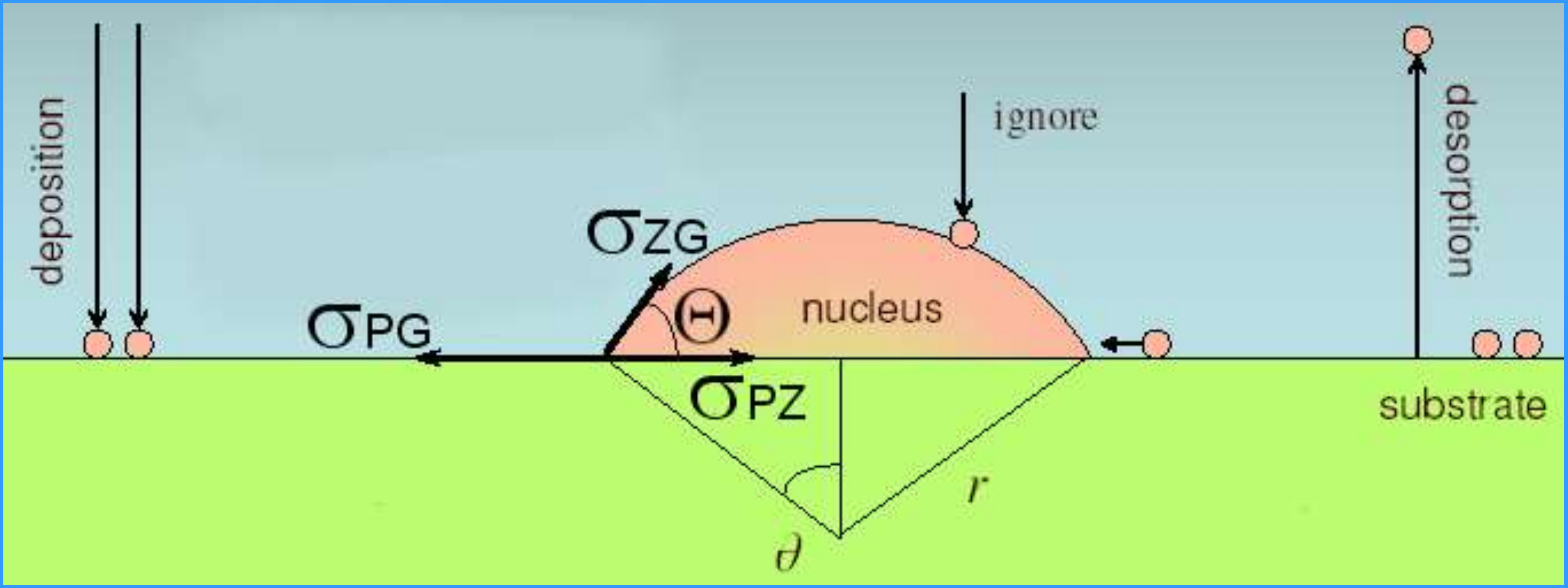
increasing T at a constant stream of carbon deposition increases r *

Heterogeneous nucleation

Steady-state equation determines nucleus - Young equation

$$\sigma_{GP} = \sigma_{ZP} + \sigma_{ZG} \cos\Theta$$

σ_{GP} = surface energy on the phase boarder: gas-substrate
σ_{ZP} = surface energy on the phase boarder: nucleus-substrate
σ_{ZG} = surface energy on the phase boarder: nucleus-gas
Θ = wetting angle



Early growth stages

- ➢surface diffusion is sufficiently large to allow for the rapid migration of atoms
- ➢ structures are able to achieve close to the equilibrium state, in one of three ways

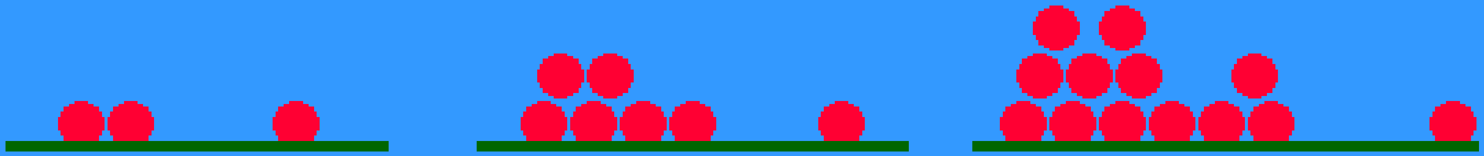
a) Volmer Weber type

b) Frank van der Merwe type

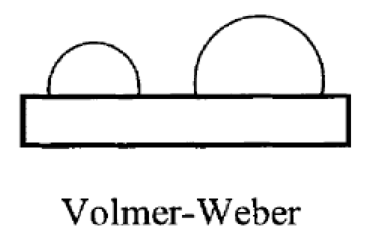
c) Stranski Krastanov type

ISLAND GROWTH; VOLMER WEBER TYPE

- **materiał niejako unika podłoża**
- **the substrate has a lower free energy than the phase boundaries,**
- **atoms of the deposited material produce stronger bond with itself than with the substrate.**
- **cohesive forces are higher than the adhesion**
- **material avoids somehow the substrate**



Mechanism of Volmer Weber type



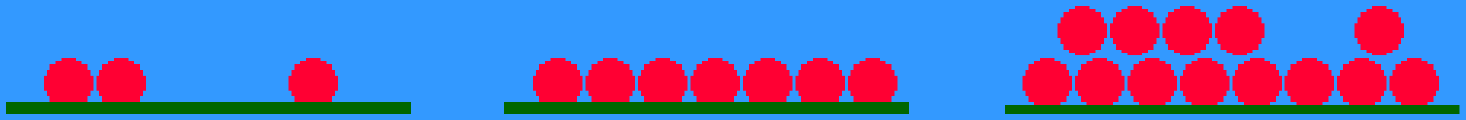
material is more strongly related
to each other than to the substrate
adhesion force greater than
the cohesive strength

- **island growth**
- **material is more strongly related to each other than to the substrate**
- **adhesion force greater than the cohesive strength**

$$\sigma_{PG} \leq \sigma_{ZG} + \sigma_{PZ}$$

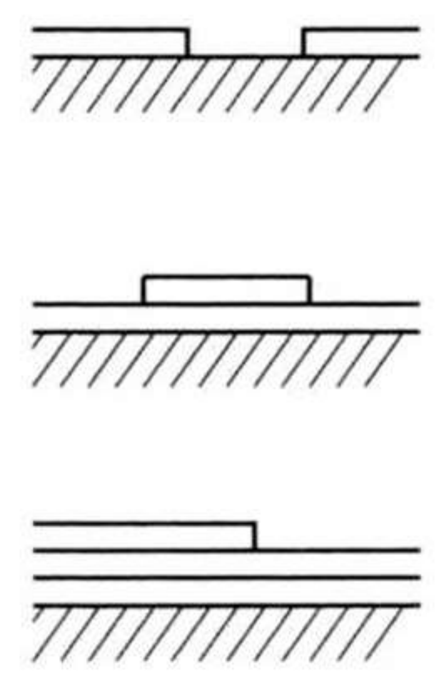
LAYER GROWTH; FRANK VAN DER MERWE TYPE

- strong binding of the substrate-coating, the adhesion forces are much greater than cohesion in the coating material
- low surface energy coating material
- high surface energy of substrate
- fast surface diffusion is a positive factor



$\sigma_{PG} \geq \sigma_{ZG} + \sigma_{PZ}$ and $\Theta = 0$

LAYER GROWTH; FRANK VAN DER MERWE TYPE

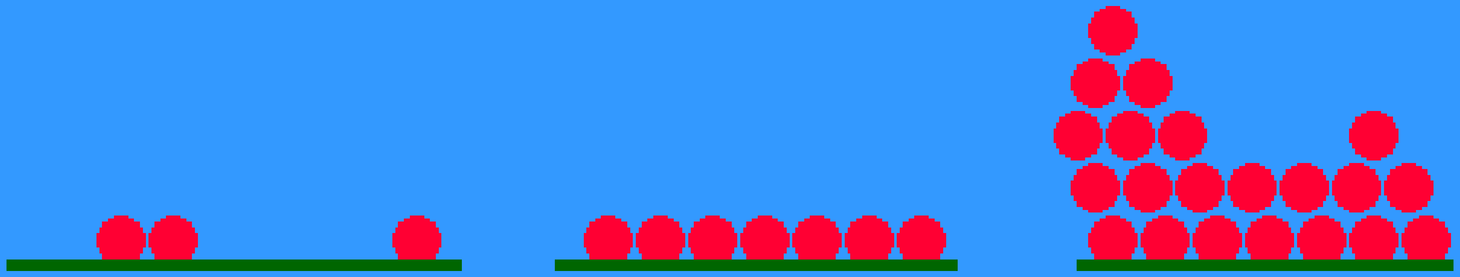


- 2D flat nucleous
- nucleous grow laterally
- there is no barrier to nucleation
- required only that in one place is a certain number of atoms so that they can create a static cluster
- a large number of nucleous on the ground is crucial
- atoms striking the clusters tend to ensure that migrate and establish themselves on the edge of the nucleous, the nucleous grows horizontally, not vertically

MIXED GROWTH; STRANSKI KRASTANOV TYPE

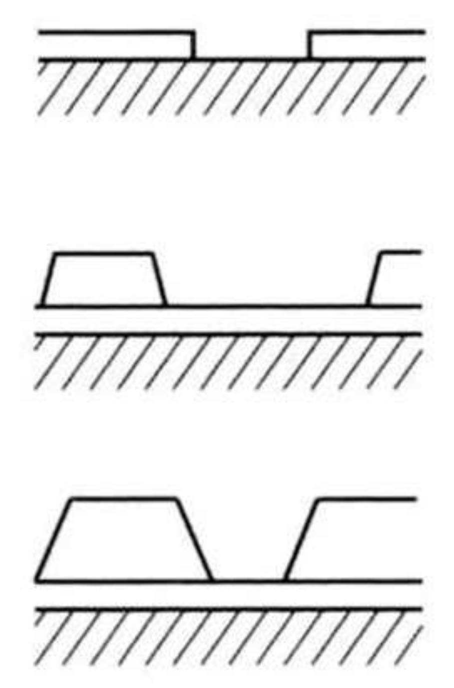
- **in the first phase of deposition of the material forms a continuous monolayer film in accordance with FM mechanism; usually 1-5 layers**
- **these layers are beginning to nucleate 3D islands in accordance with the VW mechanism**
- **both components have already been described**

Examples: Ag on W, Ag on Si or Ge on Si



MIXED GROWTH; STRANSKI KRASTANOV TYPE

- **nucleous lattice parameter significantly different from the lattice parameter of substrate**
- **lattice parameter mismatch creates residual stress in the layer, which increases with increasing coating thickness**
- **after a few monolayers the stress becomes so large that the system with a view to reducing the stress changes the mechanism to the island growth, which leads to a significant stress relaxation**
- **furthermore a strong bond between the substrate and the atoms of the surface changes the surface energy of the layer, which leads to a modification of the growth process and energy conditions**



LATE STAGES OF GROWTH

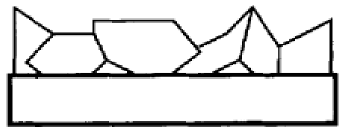
- **growth process begins to be directed by kinetic factors, not the surface diffusion**
- **kinetic effects become important when the grains reach a critical size**
- **diffusion on the surface is extremely limited**
- **slow movement of atoms prevents the achievement of equilibrium states**
- **surface diffusion occurs only to a limited extent**
- **process of growth is controlled by kinetic factors**

LATE STAGES OF GROWTH

a) polycrystalline

b) columnar

LATE STAGE OF GROWTH - POLYCRYSTALLINE

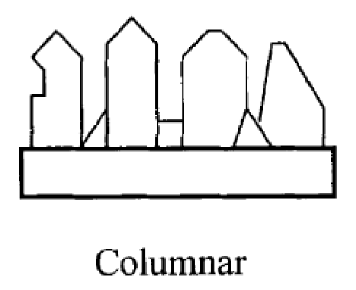


Polycrystalline

- compact layer without a significant amount of voids, but with pronouced grain boundaries

- very often in such cases, the substrate is an amorphous material or a polycrystalline but with a large mismatch of the lattice with respect to the material layer

LATE STAGE OF GROWTH - COLUMNAR



- in this case, the surface diffusion is not substantially observed
- atoms remain in the places, where they have been deposited
- very rough structure
- columnar crystals with diameters of 10-100 nm
- a lot of empty spaces even up to 50%
- the structure departs from the equilibrium state

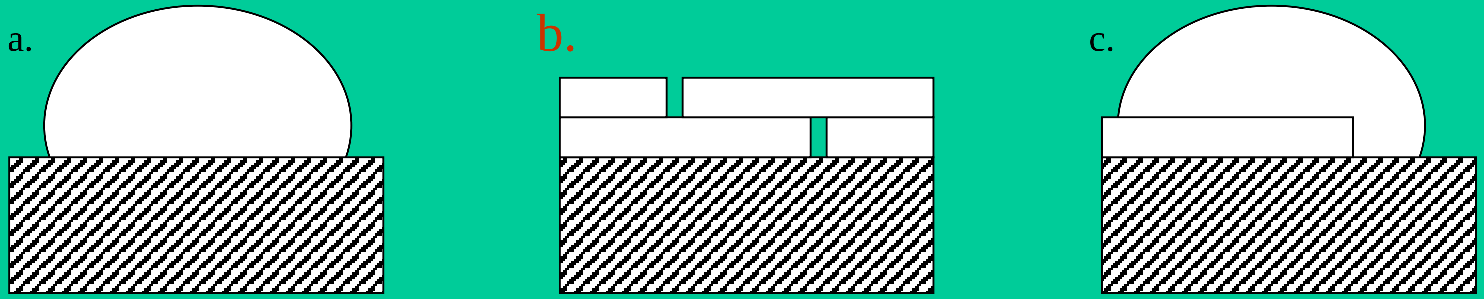
Deposition process design

Models of thin films growth – primary mechanisms

(a) Volmer-Weber-island model

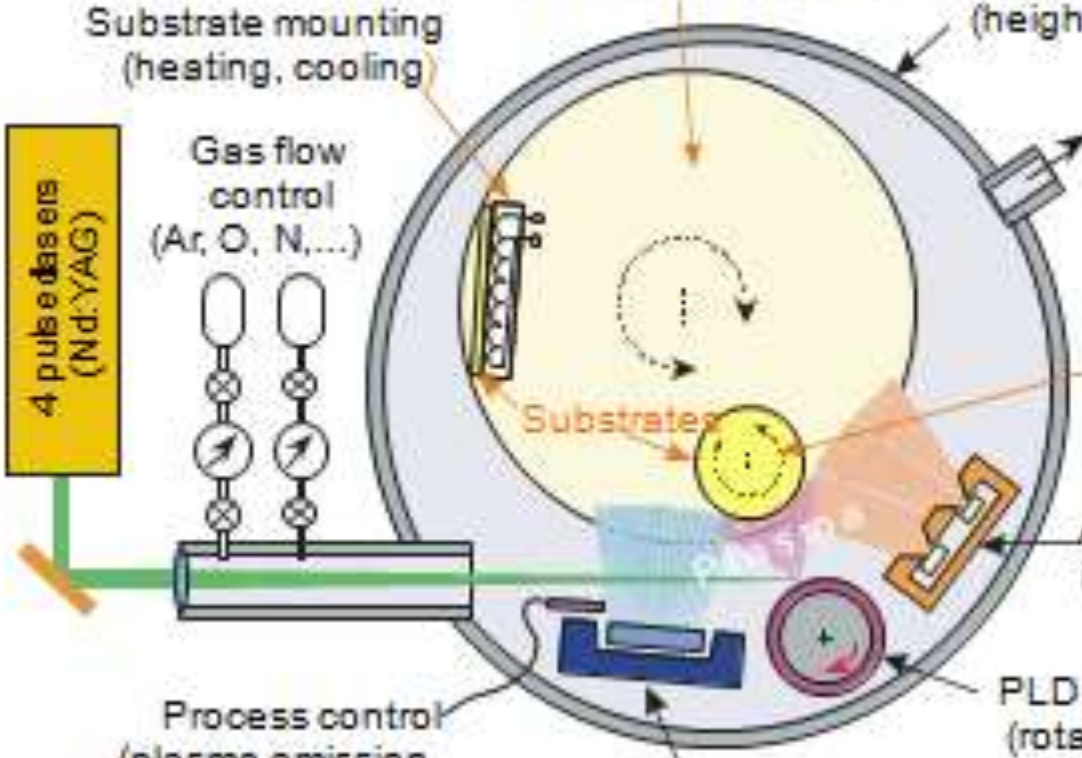
(b) Frank-van der Merwe- layer-by-layer

(c) Stranski-Krastanov- layer-plus-island



Deposition technique

Hybrid PLD coating system



Rotary table (Ø 560 mm)
for substrate movement

Vacuum chamber
(height 650 mm)

Substrate mounting
(heating, cooling)

Vacuum
pump

4 pulsed lasers
(Nd:YAG)

Gas flow
control
(Ar, O, N,...)

Substrate
rotation

Substrates

Plasma

ALS linear
ion source

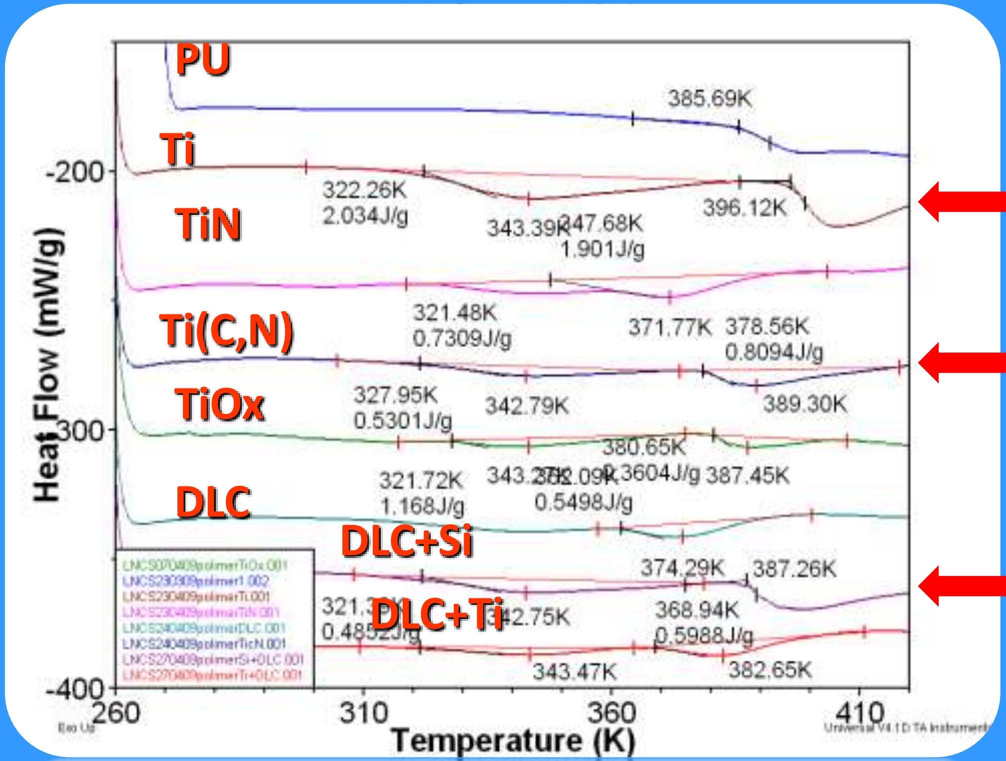
PLD evaporator
(rotating target)

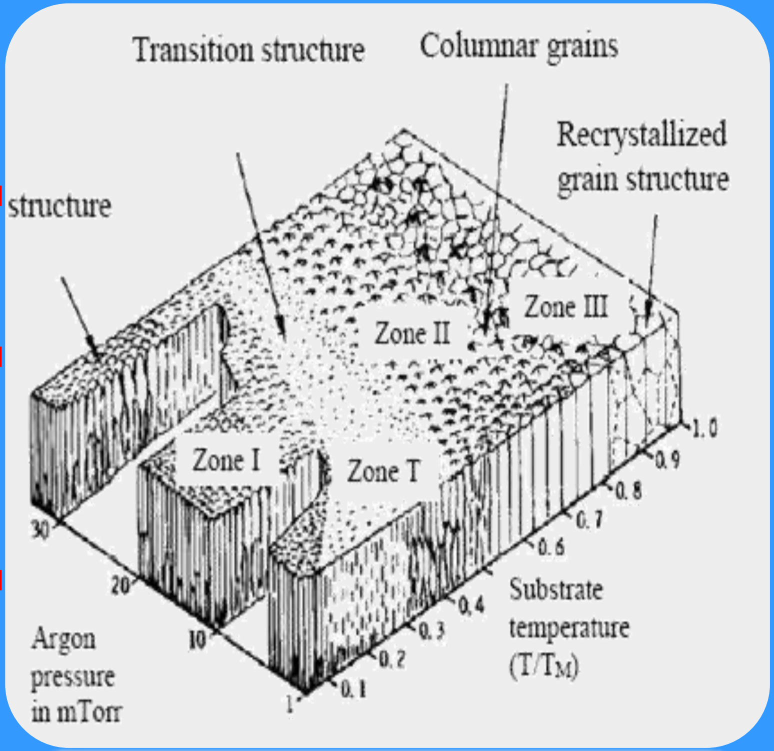
Process control
(plasma emission,
gas analytics
optical plasma spectroscopy,
Raman spectroscopy,
Quartz oscillator,
Temperature, etc.)

Magnetron sputter sources
(RF, MF pulsed DC)
& bias voltage supply

JOANNEUM
RESEARCH

Deposition process design



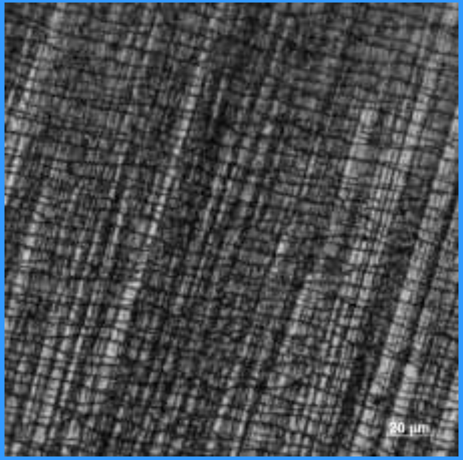


CLSM-surface

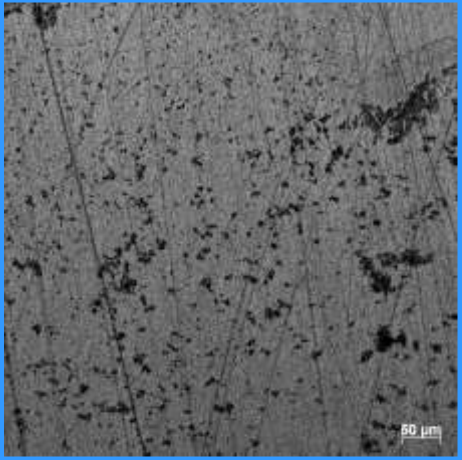
CONFOCAL LASER SCANNING MICROSCOPY

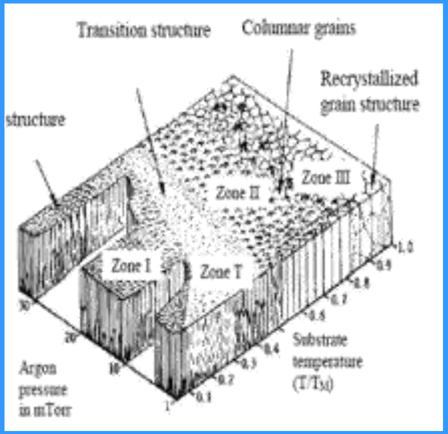
Deposition process design

Ti

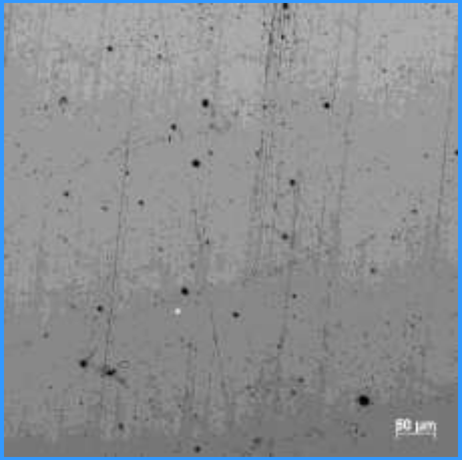


TiN

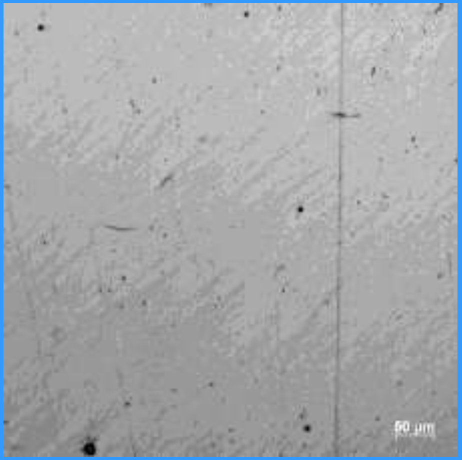




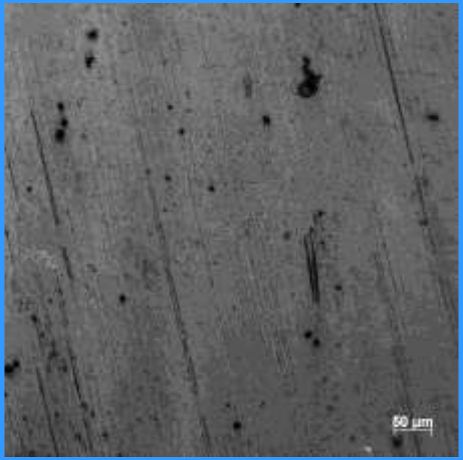
Ti(C,N)



TiOx

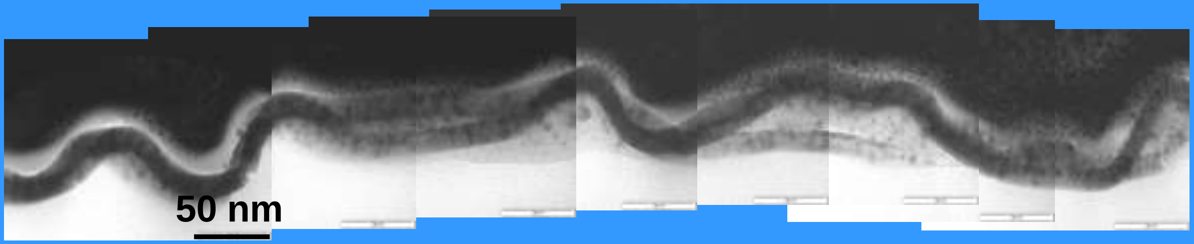


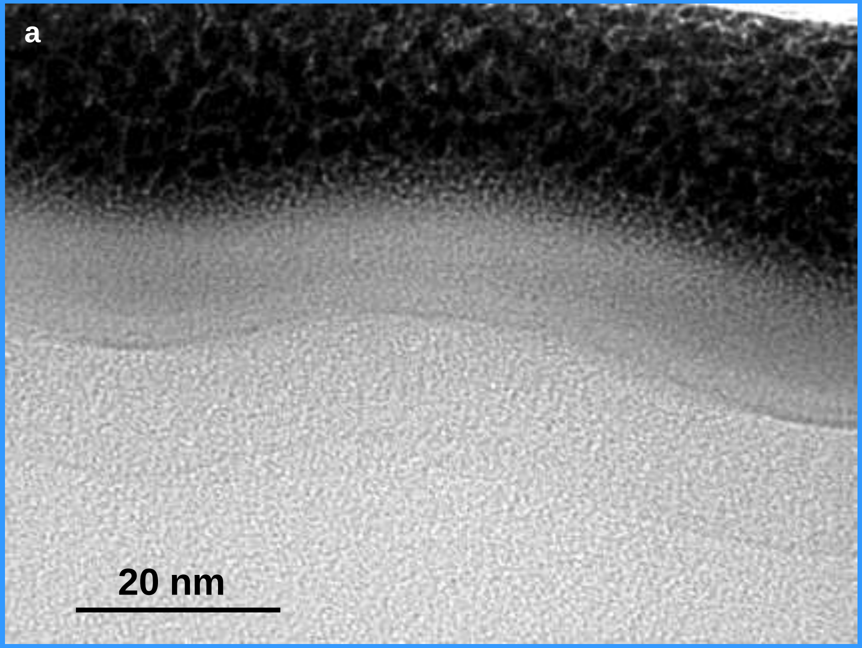
DLC



TEM

Thin layers of TiN-elastic properties of ceramic materials

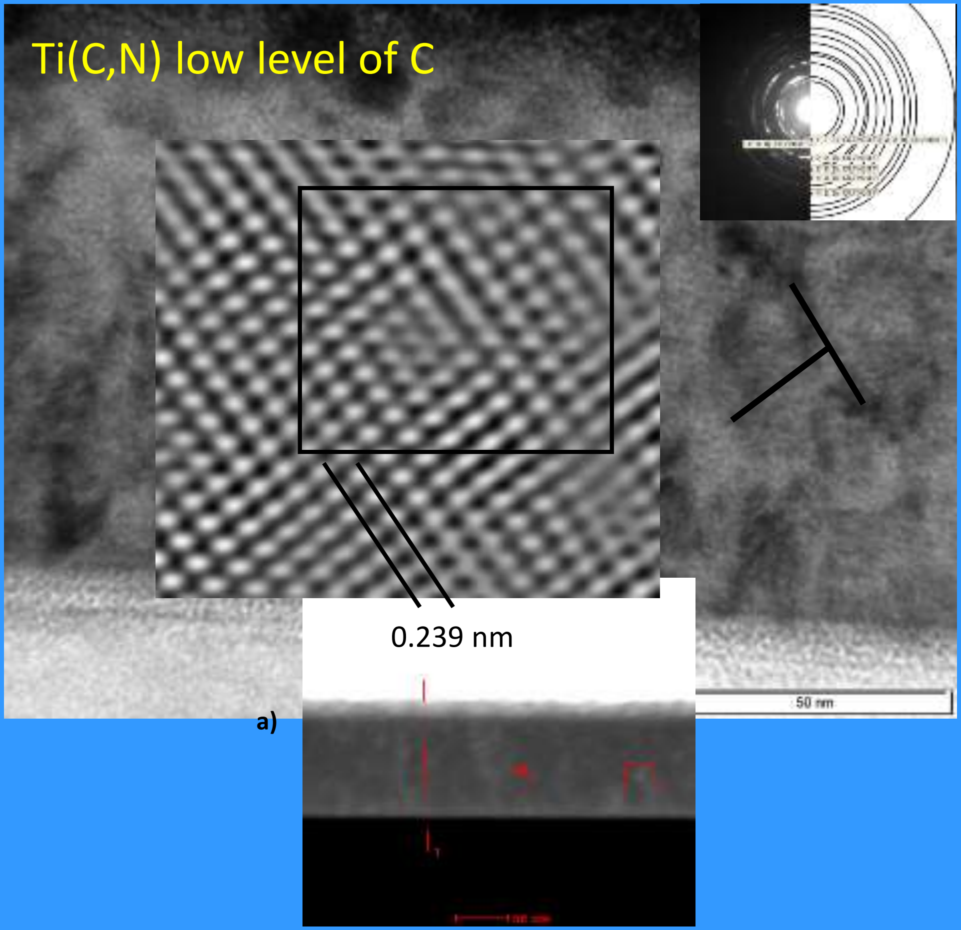


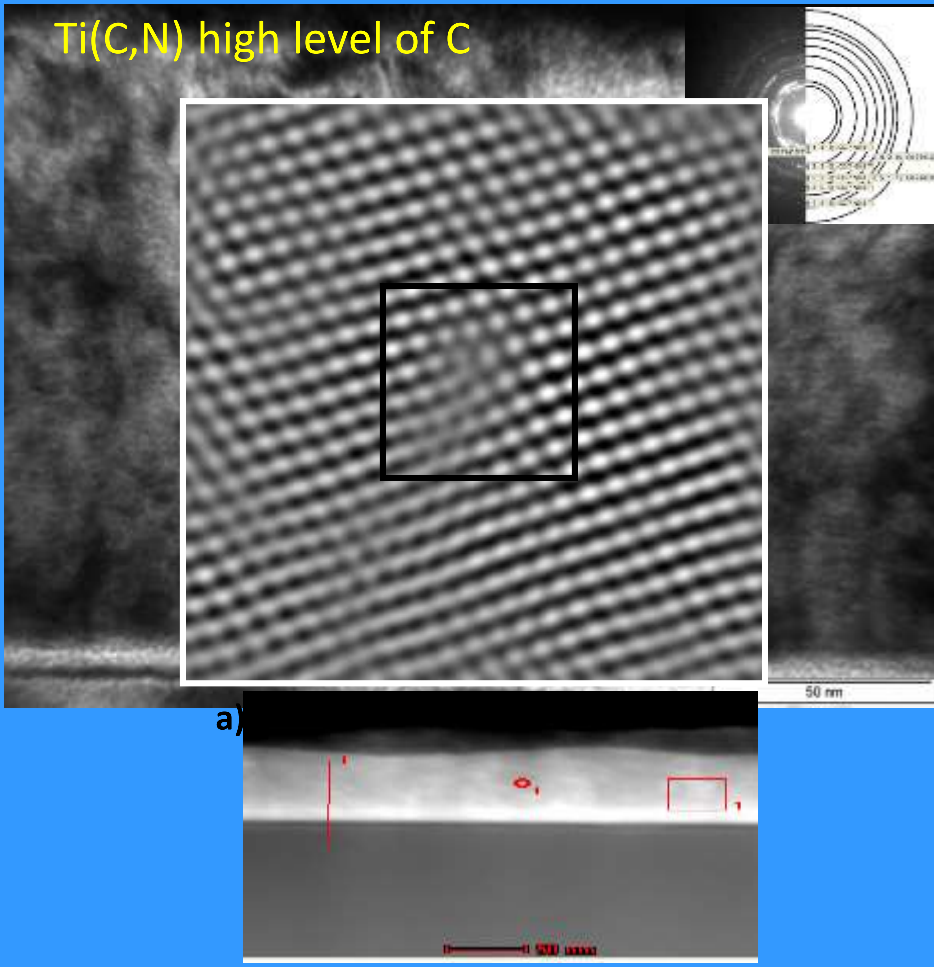


TEM+HREM- microstructure

TRANSMISSION ELECTRON MICROSCOPY

Ti(C,N)

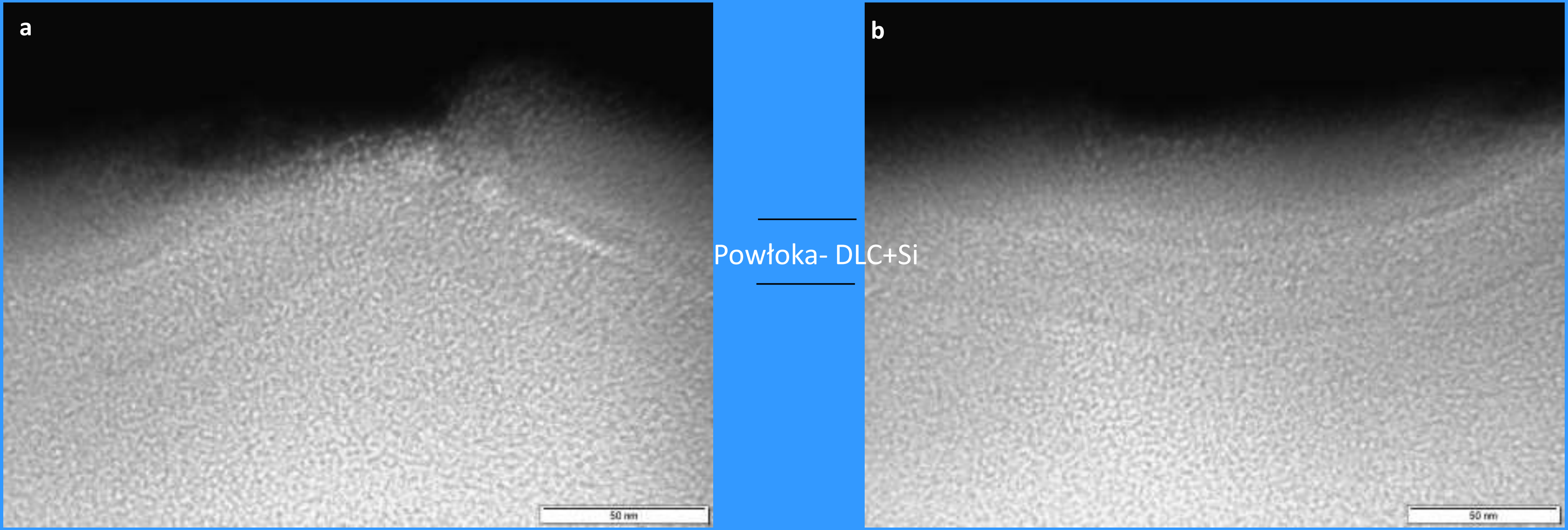




TEM- mikrostruktura

TRANSMISSION ELECTRON MICROSCOPY

DLC + Krzem

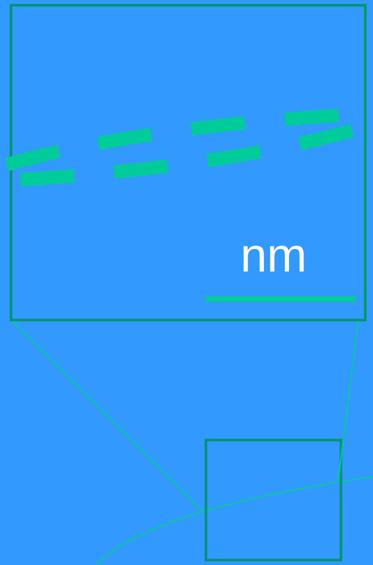


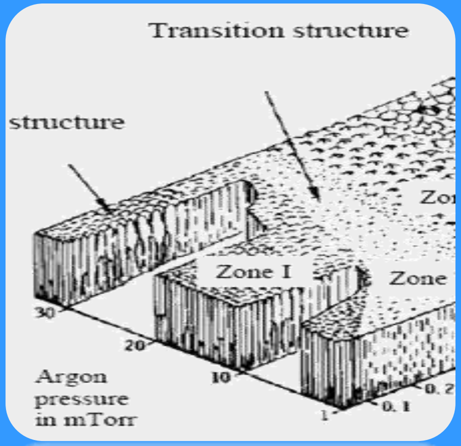
Powłoka- DLC+Si

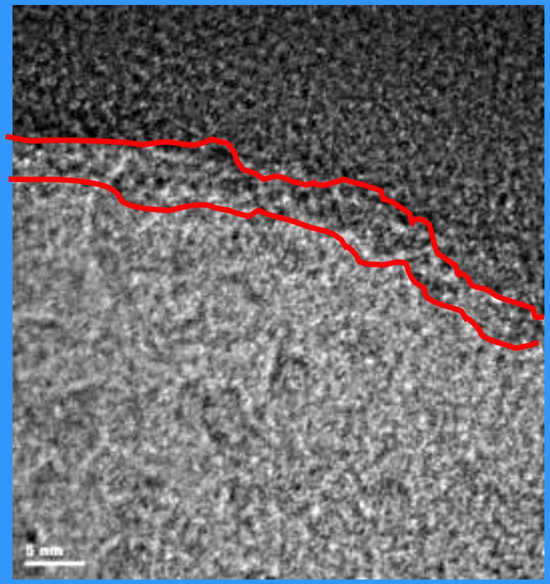
Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor	Absorption Correction
C(K)	95.37	97.96	2.03	0.26	3.940	0.646
Si(K)	4.62	2.03	0.18	0.92	1.000	0.958
Cu(K)	0.00	0.00	100.00	0.99	1.667	0.999
Pt(K)	0.00	0.00	100.00	0.75	81.162	1.000

TEM analysis

Thin layers of TiN-elastic properties of ceramic materials



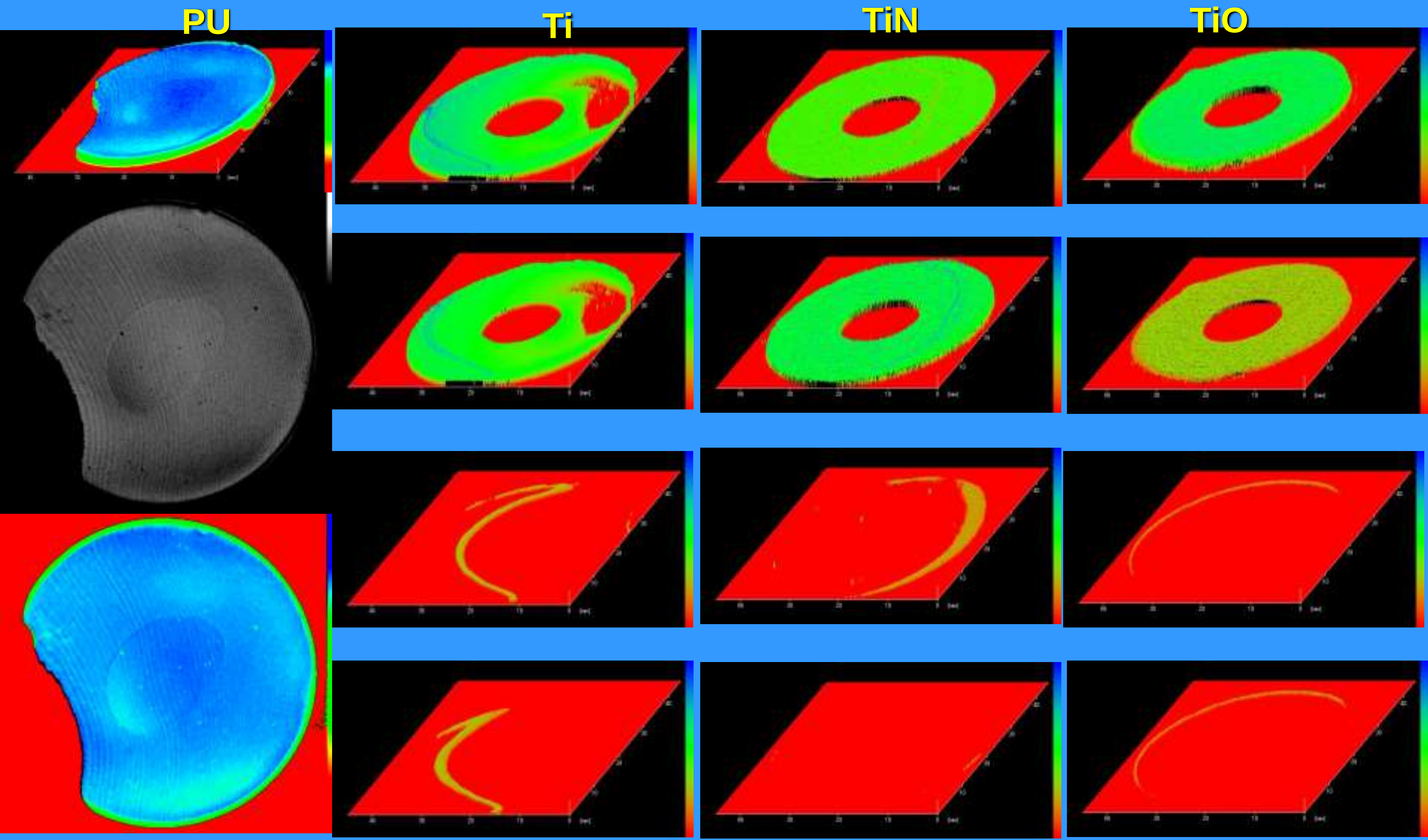




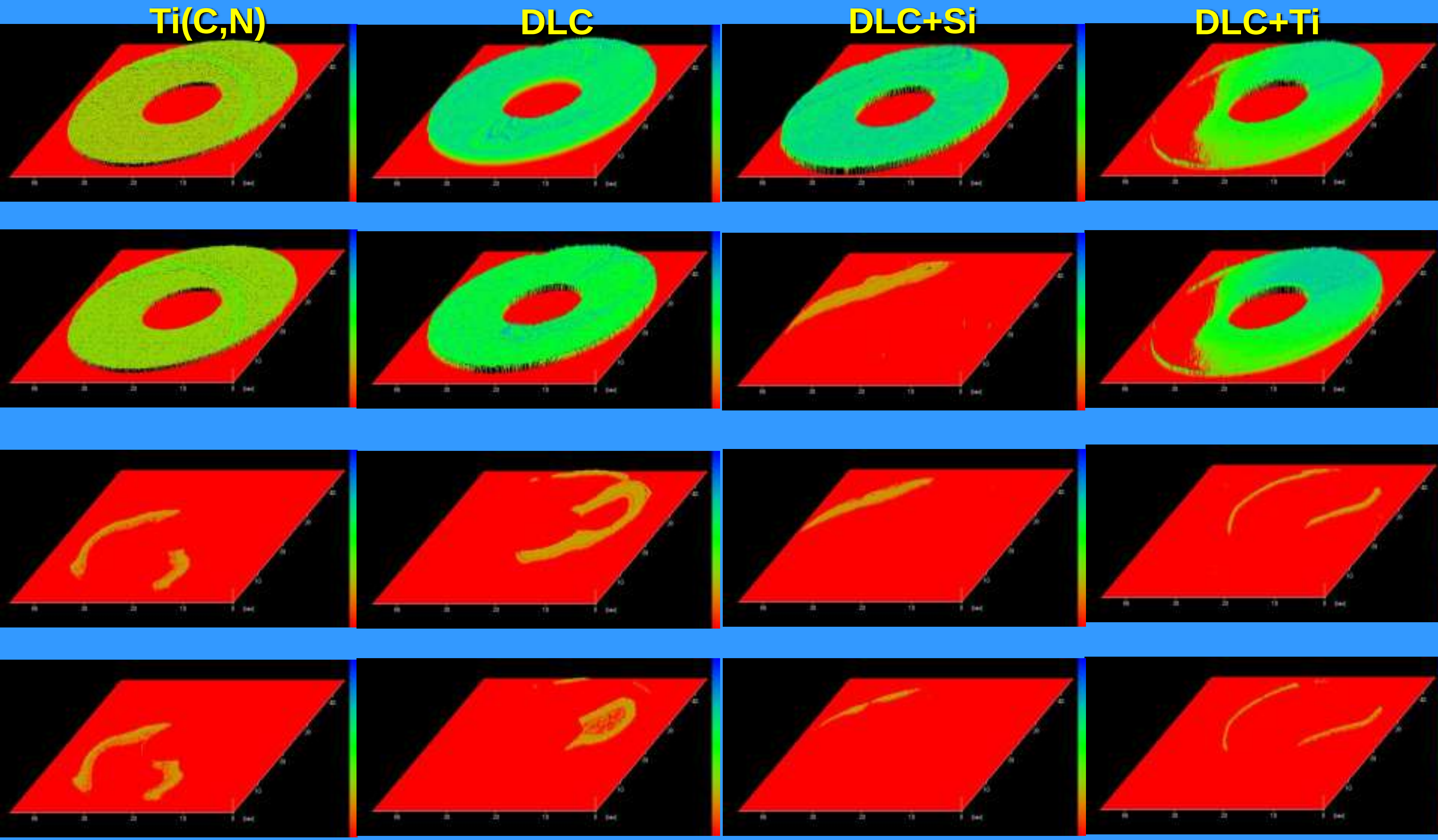
SAM-tomography

SCANNING ACOUSTIC MICROSCOPY

Deposition process design



Deposition process design



Ti(C,N) DLC DLC+Si DLC+Ti

7. Plasma

is one of the four fundamental states of matter (the others being solid, liquid, and gas). /Sir William Crookes 1879/

Def. Partially or completely ionized gas in which the charged particles are in the state of collective impact

The degree of ionization(α)

α = concentration of charged particles / initial concentration of particles

Plasma -> when concentration of large particles is high so that their presence determines the properties of the gas

(plasma is electrically conductive)

Both lightning and electric sparks are
everyday examples of phenomena made from plasma

- **Plasma** (from Greek πλάσμα, "anything formed"[1]) Heating a gas may ionize its molecules or atoms (reduce or increase the number of electrons in them), thus turning it into a plasma, which contains charged particles: positive ions and negative electrons or ions.[2] Ionization can be induced by other means, such as strong electromagnetic field applied with a laser or microwave generator, and is accompanied by the dissociation of molecular bonds, if present.

- The presence of a non-negligible number of charge carriers makes the plasma electrically conductive so that it responds strongly to electromagnetic fields 3. Plasma, therefore, has properties quite unlike those of solids, liquids, or gases and is considered a distinct state of matter. Like gas, plasma does not have a definite shape or a definite volume unless enclosed in a container; unlike gas, under the influence of a magnetic field, it may form structures such as filaments, beams and double layers. Some common plasmas are found in stars and neon signs. In the universe, plasma is the most common state of matter for ordinary matter, most of which is in the rarefied intergalactic plasma (particularly intracluster medium) and in stars. Much of the understanding of plasmas has come from the pursuit of controlled nuclear fusion and fusion power, for which plasma physics provides the scientific basis.

- Plasma is loosely described as an electrically neutral medium of positive and negative particles (i.e. the overall charge of a plasma is roughly zero). It is important to note that although they are unbound, these particles are not ‘free’. When the charges move they generate electrical currents with magnetic fields, and as a result, they are affected by each other’s fields. This governs their collective behavior with many degrees of freedom.312 A definition can have three criteria:1314

- **The plasma approximation**: Charged particles must be close enough together that each particle influences many nearby charged particles, rather than just interacting with the closest particle (these collective effects are a distinguishing feature of a plasma). The plasma approximation is valid when the number of charge carriers within the sphere of influence (called the *Debye sphere* whose radius is the Debye screening length) of a particular particle is higher than unity to provide collective behavior of the charged particles. The average number of particles in the Debye sphere is given by the plasma parameter, "Λ" (the Greek letter Lambda).

- **Bulk interactions**: The Debye screening length (defined above) is short compared to the physical size of the plasma. This criterion means that interactions in the bulk of the plasma are more important than those at its edges, where boundary effects may take place. When this criterion is satisfied, the plasma is quasineutral.

- **Plasma frequency**: The electron plasma frequency (measuring plasma oscillations of the electrons) is large compared to the electron-neutral collision frequency (measuring frequency of collisions between electrons and neutral particles). When this condition is valid, electrostatic interactions dominate over the processes of ordinary gas kinetics.

- Plasma parameters can take on values varying by many orders of magnitude, but the properties of plasmas with apparently disparate parameters may be very similar (see plasma scaling). The following chart considers only conventional atomic plasmas and not exotic phenomena like quark gluon plasmas:

Preparation of plasma

(electric discharges in gas)

due to the conditions of discharge (not-spontanous, spontaneous)

because of the time (stationary, not-stationary)

due to the physical mechanism (fluorescent, arc, RF, MW)

Factors affecting the nature of the discharge:

electrical voltage

current intensity

pressure

Gas penetration - the voltage at which the discharge ignition

The transition in the plasma state:

- gas heating
- electric discharge
- absorption of electromagnetic radiation

1eV = 1.602 10-19J = k 11.600 K

Quasi-neutrality of plasma

Stored electrical energy = energy of thermal motion

$e^2 \, ne \, \lambda^2_D / \varepsilon_0 = kT_e$

Debye radius - λ_D

size at which the charged particles can separate in the plasma

The transition in the plasma state:

- gas heating
- electric discharge
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Debye radius - λ_D

size at which they can separate the charged particles in the plasma

8. Physical methods of surface modification

Physical Vapor Deposition PVD

Vapor with plasma

Thermal deposition - ions (atoms) are deposited and partially reflected, this leads to the deposition of thin films

Sputter- or Beam-Assisted Deposition - there is the high thermal energy to 1eV, raises the temperature of the deposited particles in the environment during several ps, leading to an increase of the surface diffusion, the deposition process is still the dominant

Sputtering - from a few eV to MeV, striking ions have energy enough to penetrate the target mainly due to elastic collisions, emission of target atoms occurs

Ion implantation - implanted ions lose energy through electron and nuclear interaction with the substrate atoms

Radiation damage, phase transformation, ion beam mixing - there is a slowing down of ions by collisions with the atoms of the target giving structural effects (vacancy, re-arranging of atoms, mixing, alloying)

Electron bombardment of solids - electrons penetrate the surface layer and sputtering processes occur, the penetration is associated with phenomena: generation of X-ray, Auger electrons and back-reflected electrons, secondary electrons emitted from the surface

Elastic electron-spraying can be approximated by the wave propagation and performed calculation of cross-sectional differentiation on the basis of quantum mechanics

Inelastic electron-spraying leads to ionization, valid empirical formula of Bethe for energies above 1keV

(Pau 1.13)

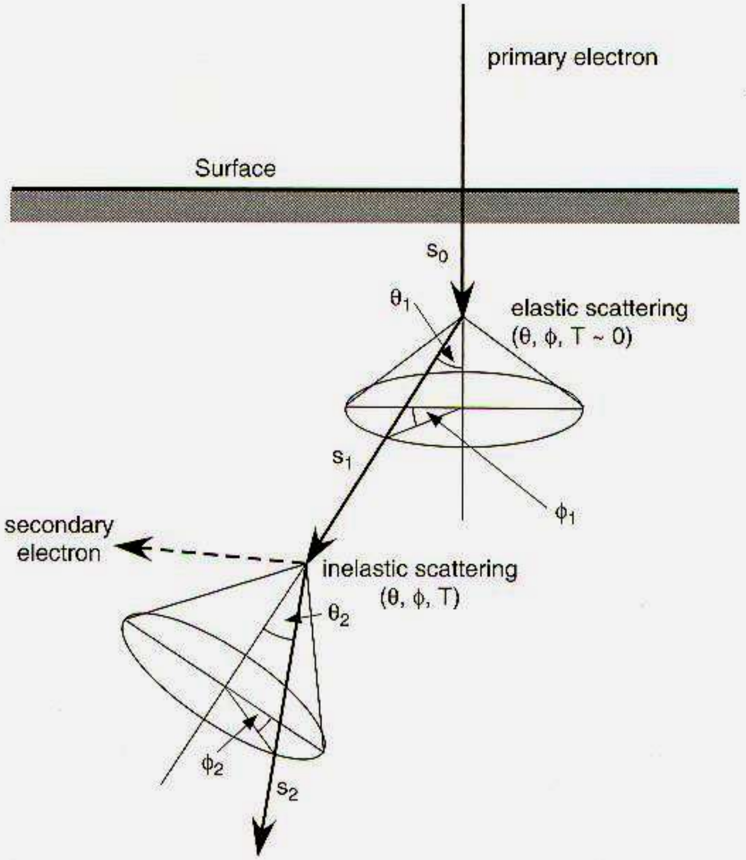
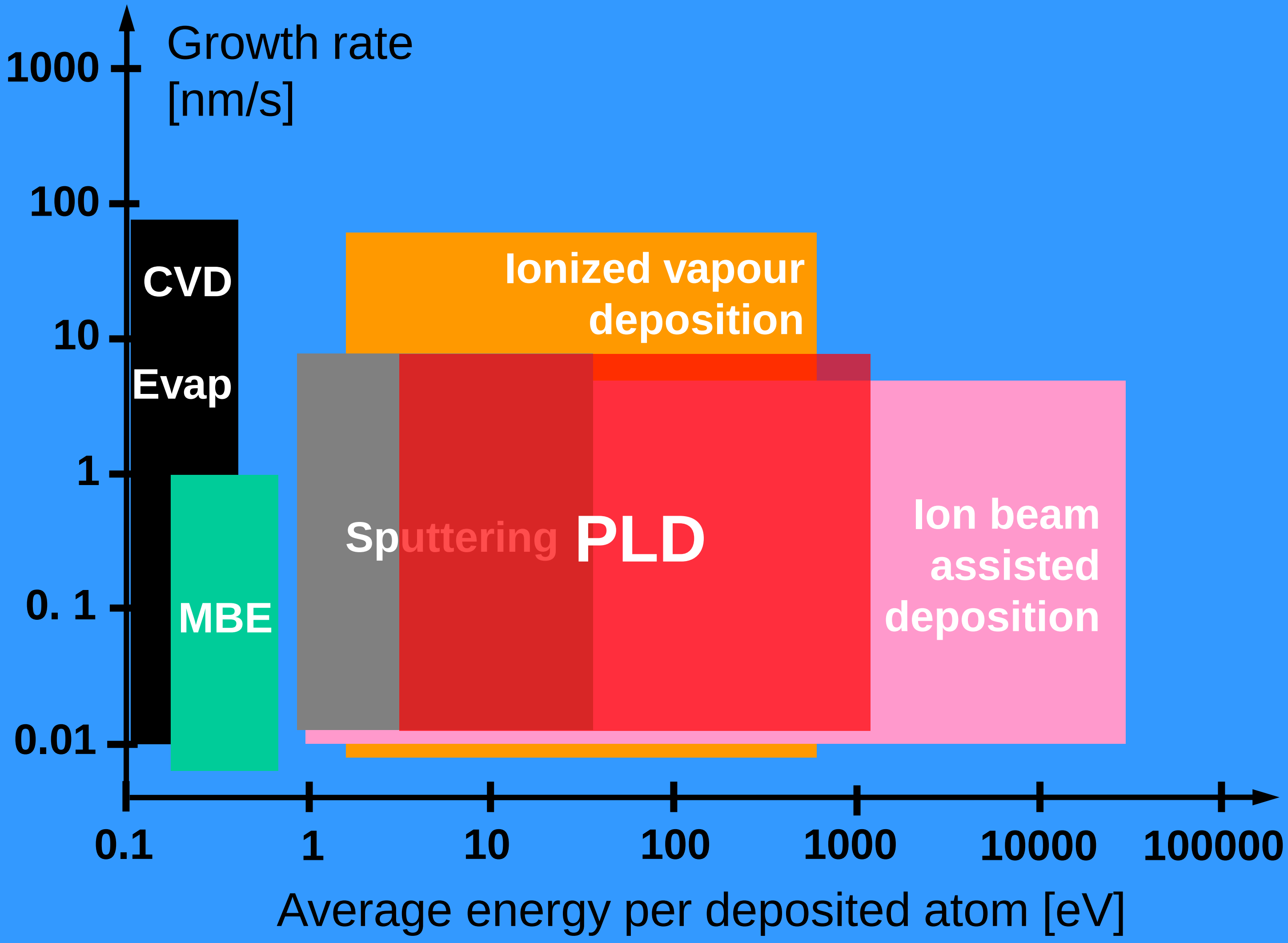
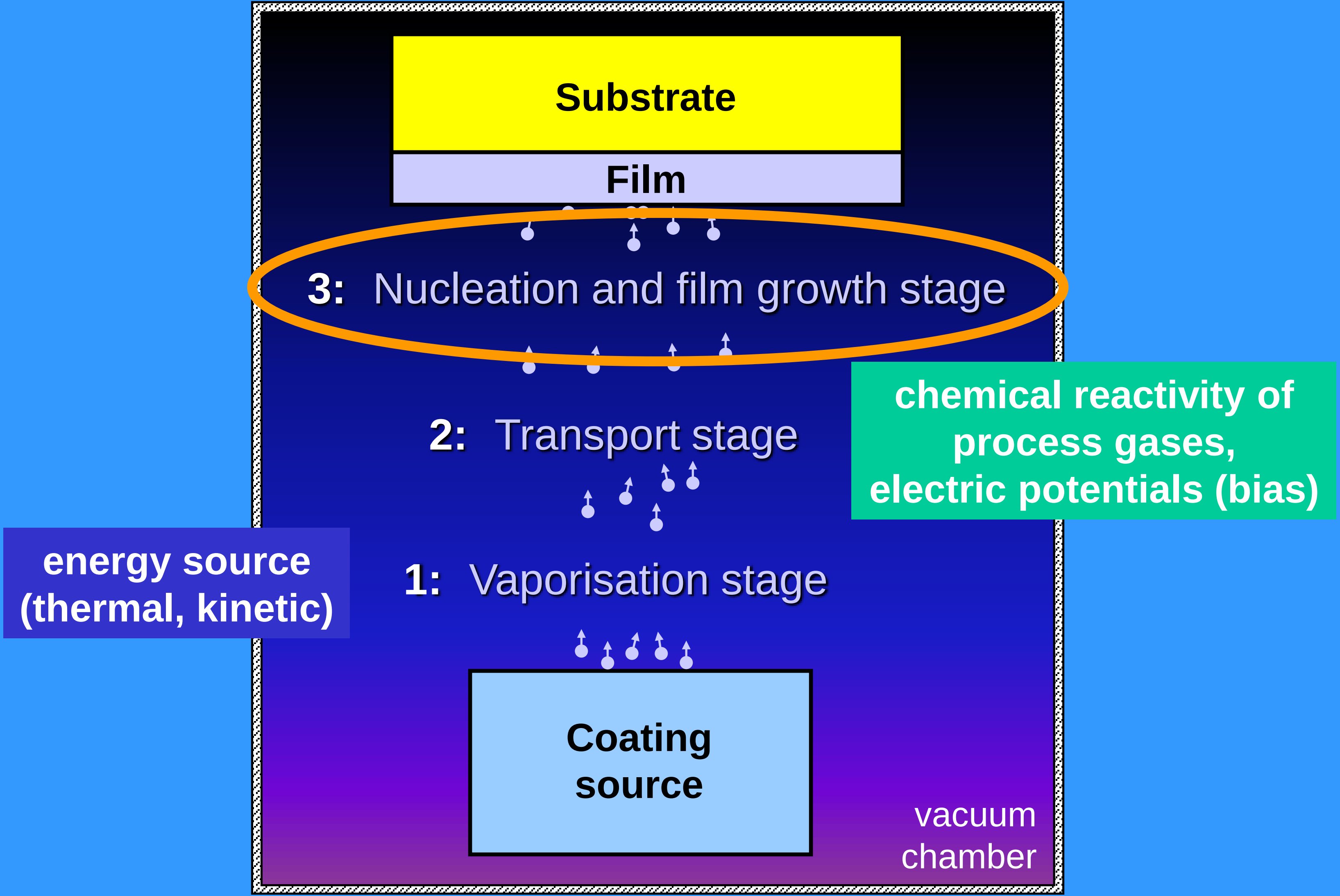


Figure 1.13: Schematic view of an electron trajectory in an MC simulation. *T* is the energy loss of the incident electron in an inelastic collision.

Vapour energy (energia par)



Principles of vacuum coating



Substrate

Film

3: Nucleation and film growth stage

2: Transport stage

1: Vaporisation stage

Coating source

vacuum chamber

energy source (thermal, kinetic)

chemical reactivity of process gases, electric potentials (bias)

Demands – industrial coating

economically competitive

Low temperature

(new materials: polymers, biomaterials, light metal alloys; and for preventing distortion)

high reproducibility

of optimized film properties

high-rate

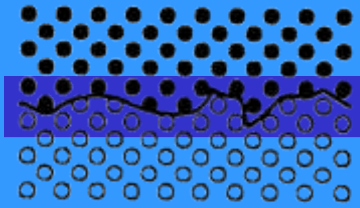
High functionality

Combination of tribological, sensoric, decorative, optical, electrical … properties

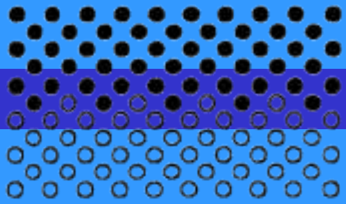
large-area

J.M.Lackner; Surface & Coatings Technology 200, p. 1439-1444, 2005

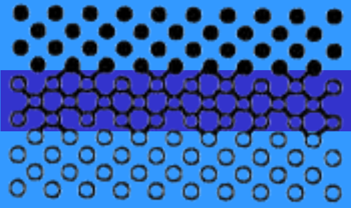
Additional demand



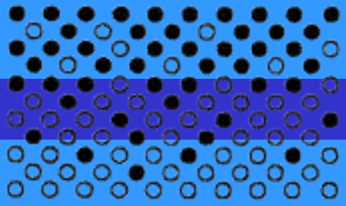
Mechanical interlocking



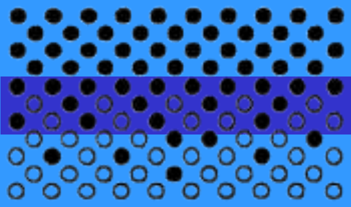
Abrupt



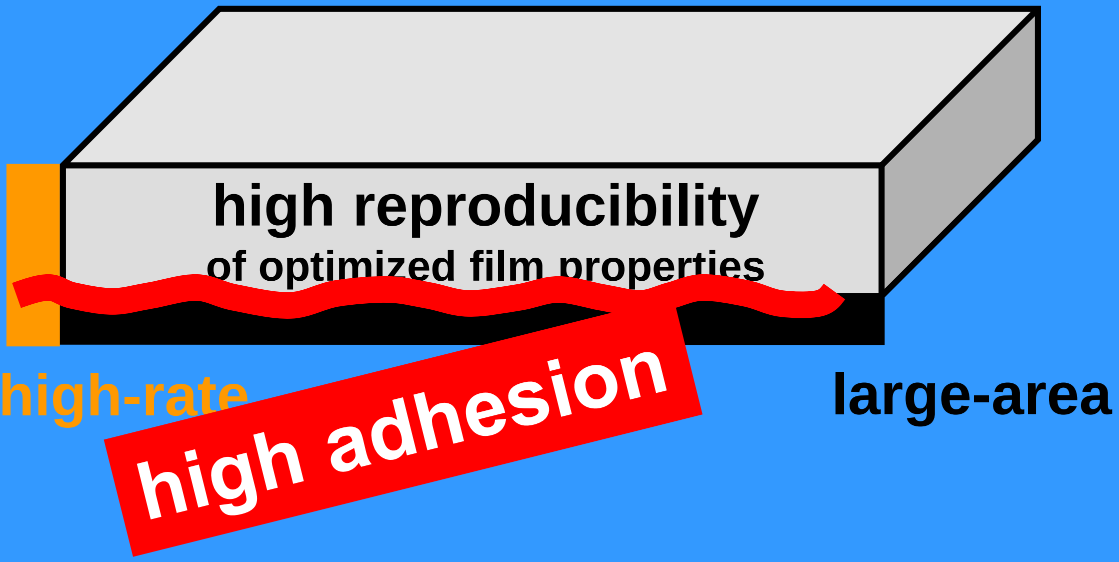
Compound



Diffusion



Pseudodiffusion



high reproducibility

of optimized film properties

high-rate

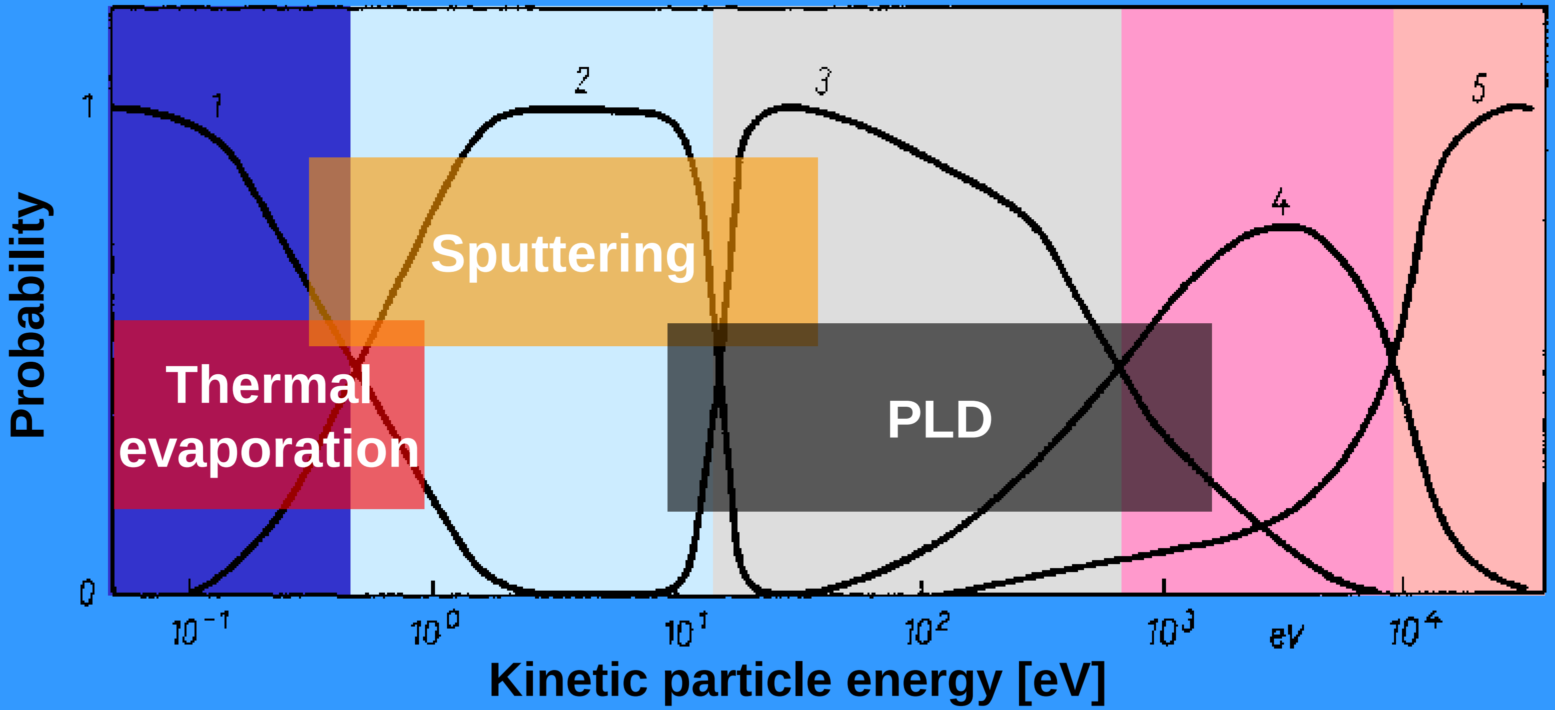
large-area

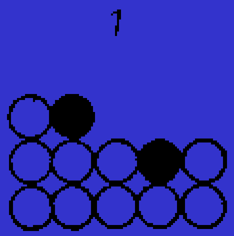
high adhesion

Dependent on:

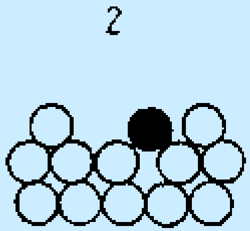
- surface topography
- deposition temperature
- energy of vapour (particles)
- etc.

Energetic aspects in thin film growth

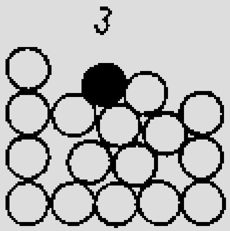




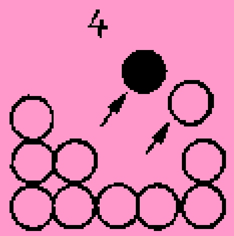
adsorption



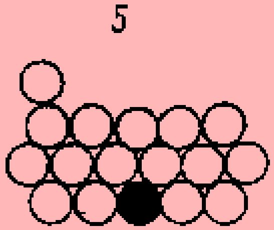
inclusion



energetic peaks



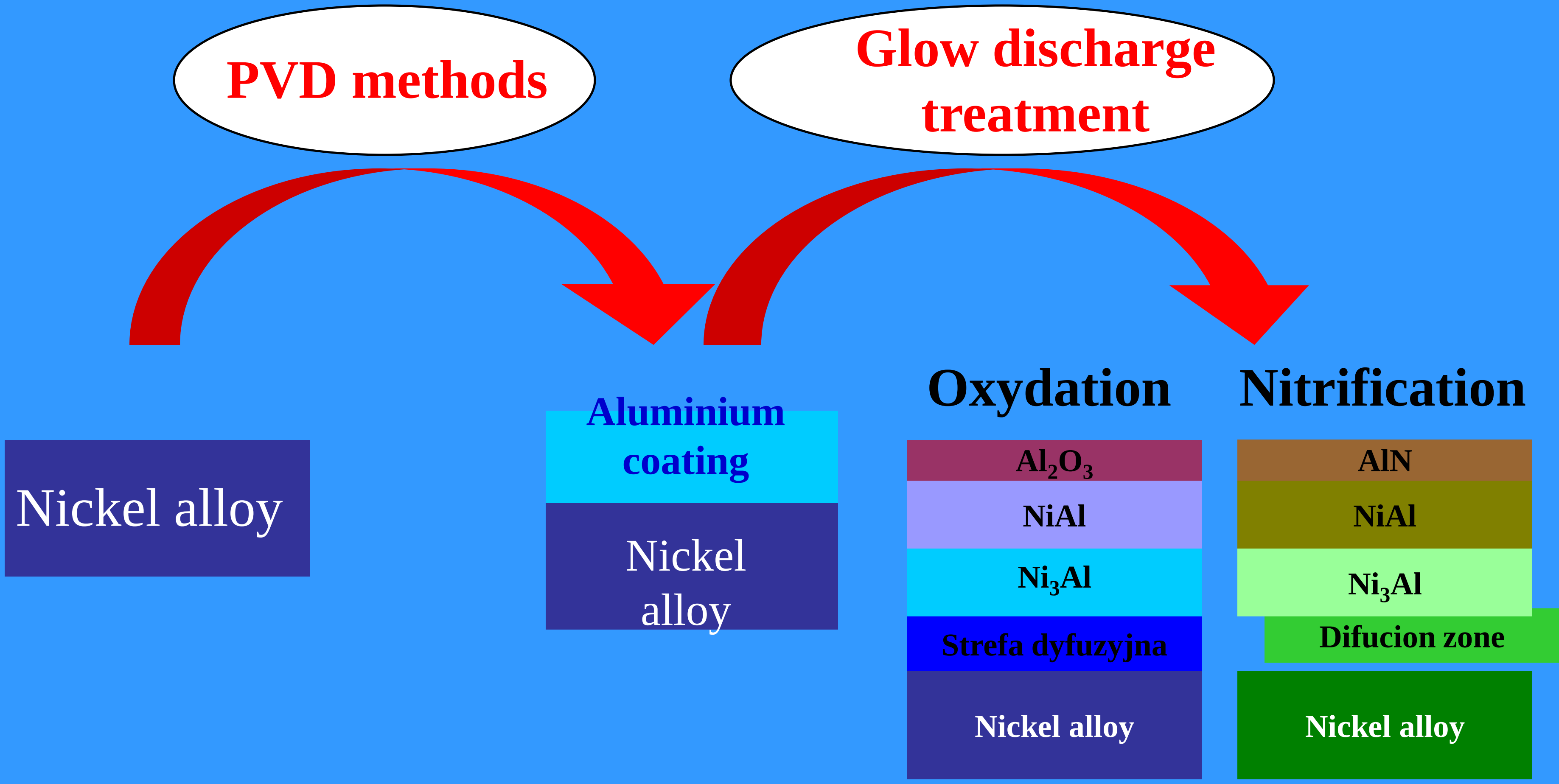
sputtering



implantation

Two stages (hybrid) method

Composite layers fabricated on nickel alloys



PVD methods

Glow discharge treatment

Nickel alloy

Aluminium coating

Nickel alloy

Oxydation

Al_2O_3

NiAl

Ni_3Al

Strefa dyfuzyjna

Nickel alloy

Nitrification

AlN

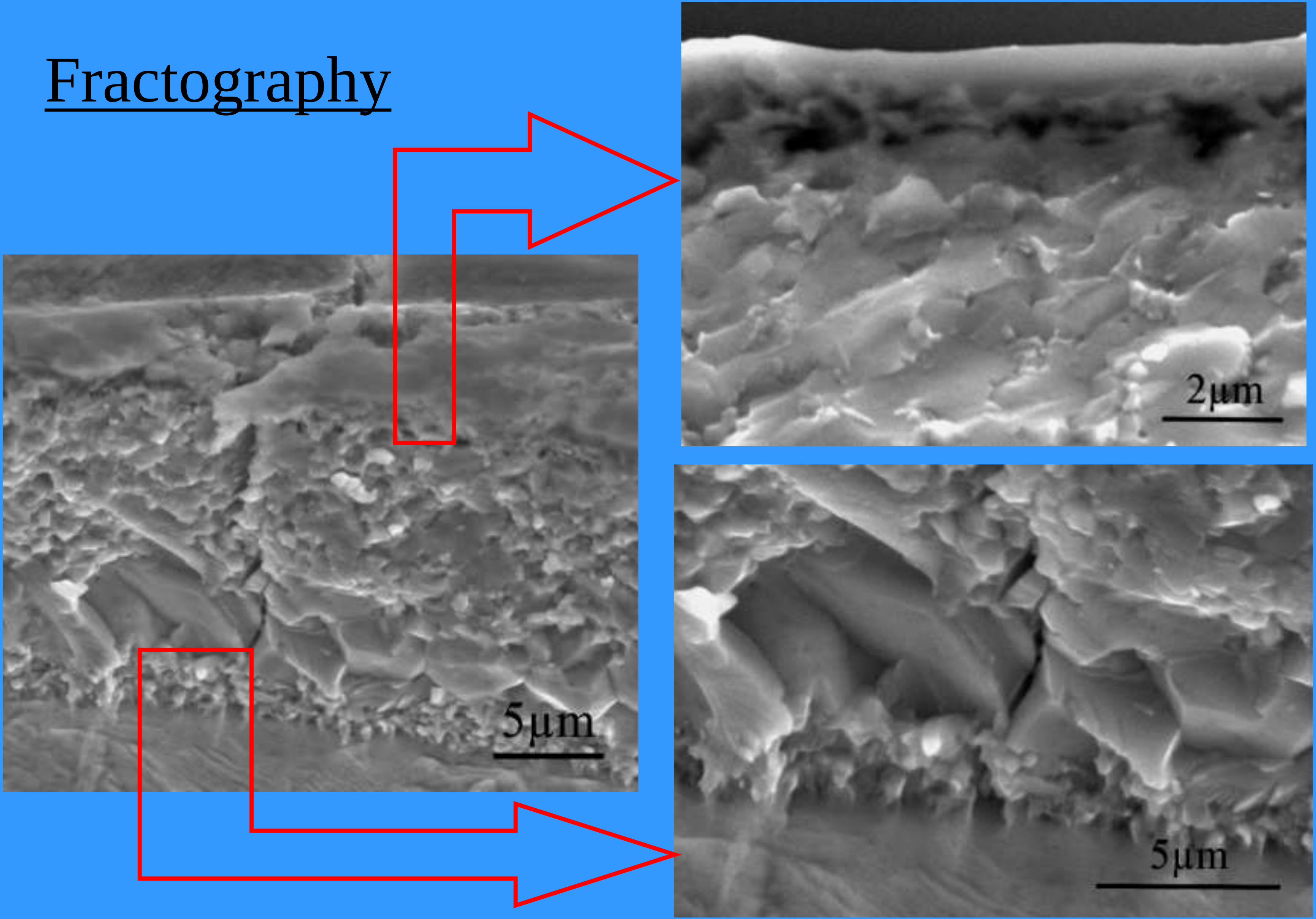
NiAl

Ni_3Al

Difucion zone

Nickel alloy

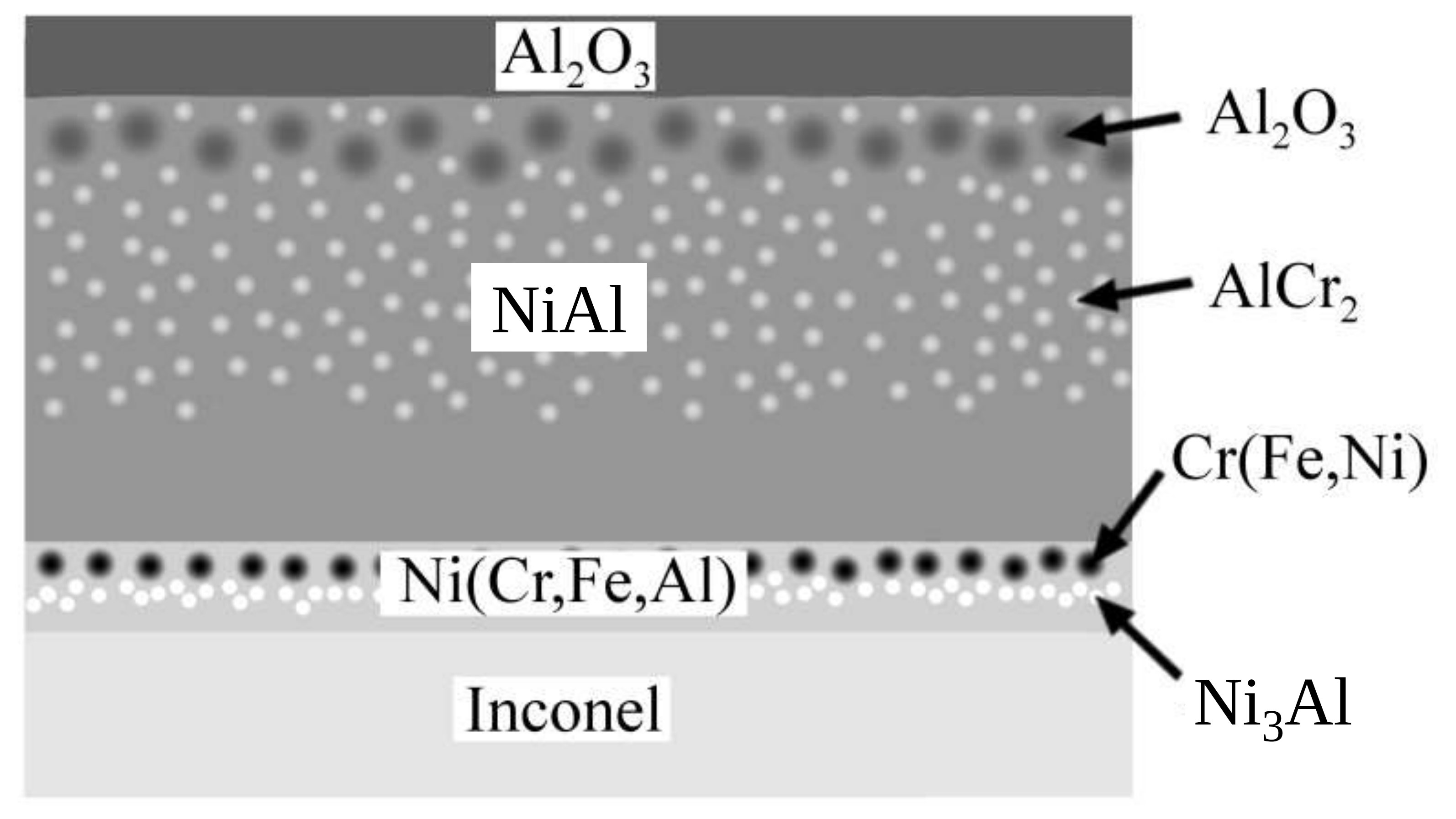
Fractography



Composite layer of type:

$\mathbf{Al_2O_3+AlCr_2+NiAl+Ni_3Al+Cr(Ni,Fe)+Ni(Cr,Fe,Al)}$

Model of composite layer on Inconel



Inconel Element (% by mass) Ni(50-70) Cr Fe Mo Nb Co Mn Cu Al. Ti Si C S P B

9. Interaction of ions and electrons with a solid surface

(Pau1.1)

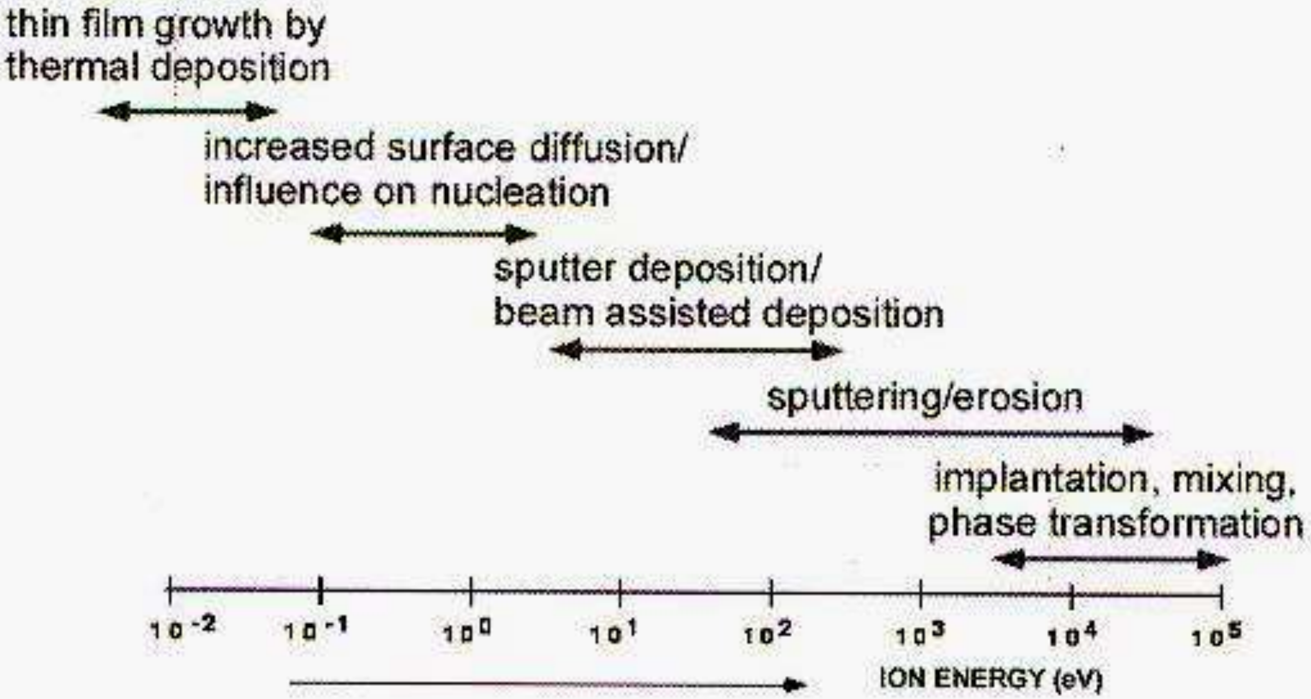


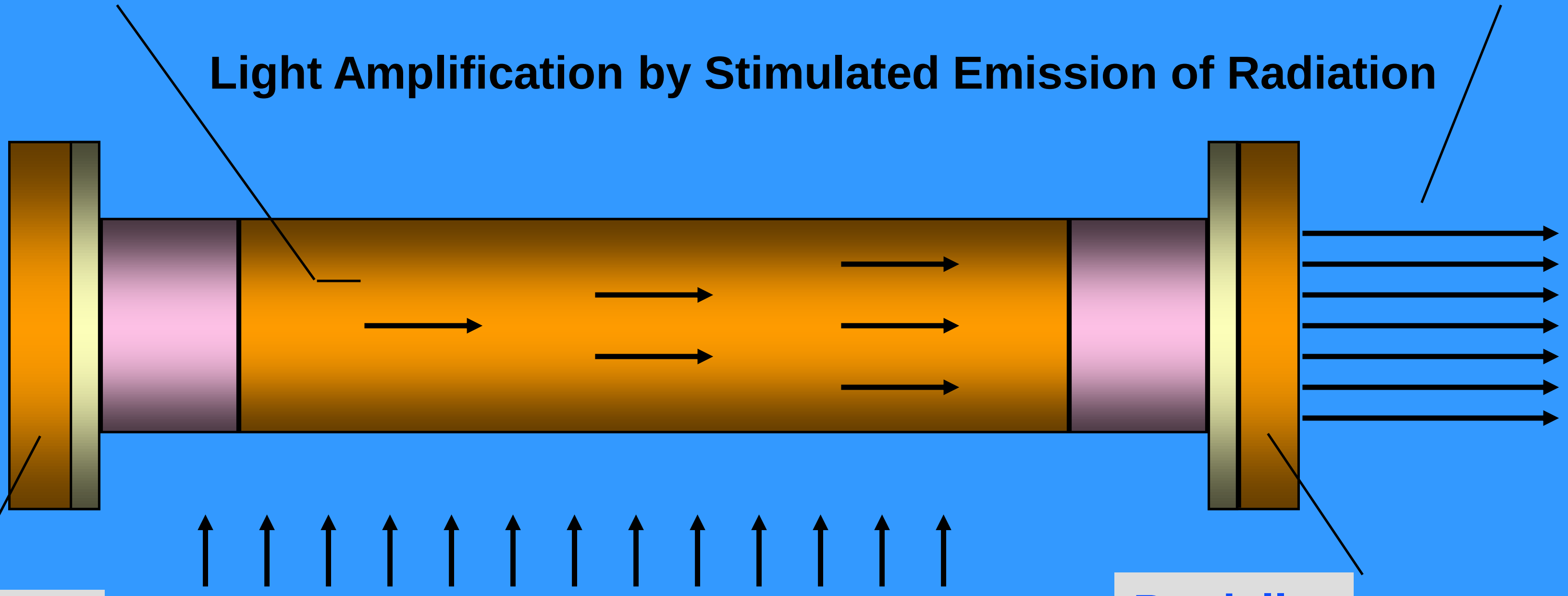
Figure 1.1: Different processes occurring under ion bombardment of a solid depending on ion energy.

10. Interaction of laser beam with the surface

Laser application in materials engineering

- **Cutting**
- **Welding**
- **Surface heating and hardening**
- **Drilling**
- **Surface melting or alloying**
- **Laser rapid prototyping**
- **Ablation and pulsed laser deposition**

Laser construction



Laser output;
parallel, monochromatic, coherent

Laser medium

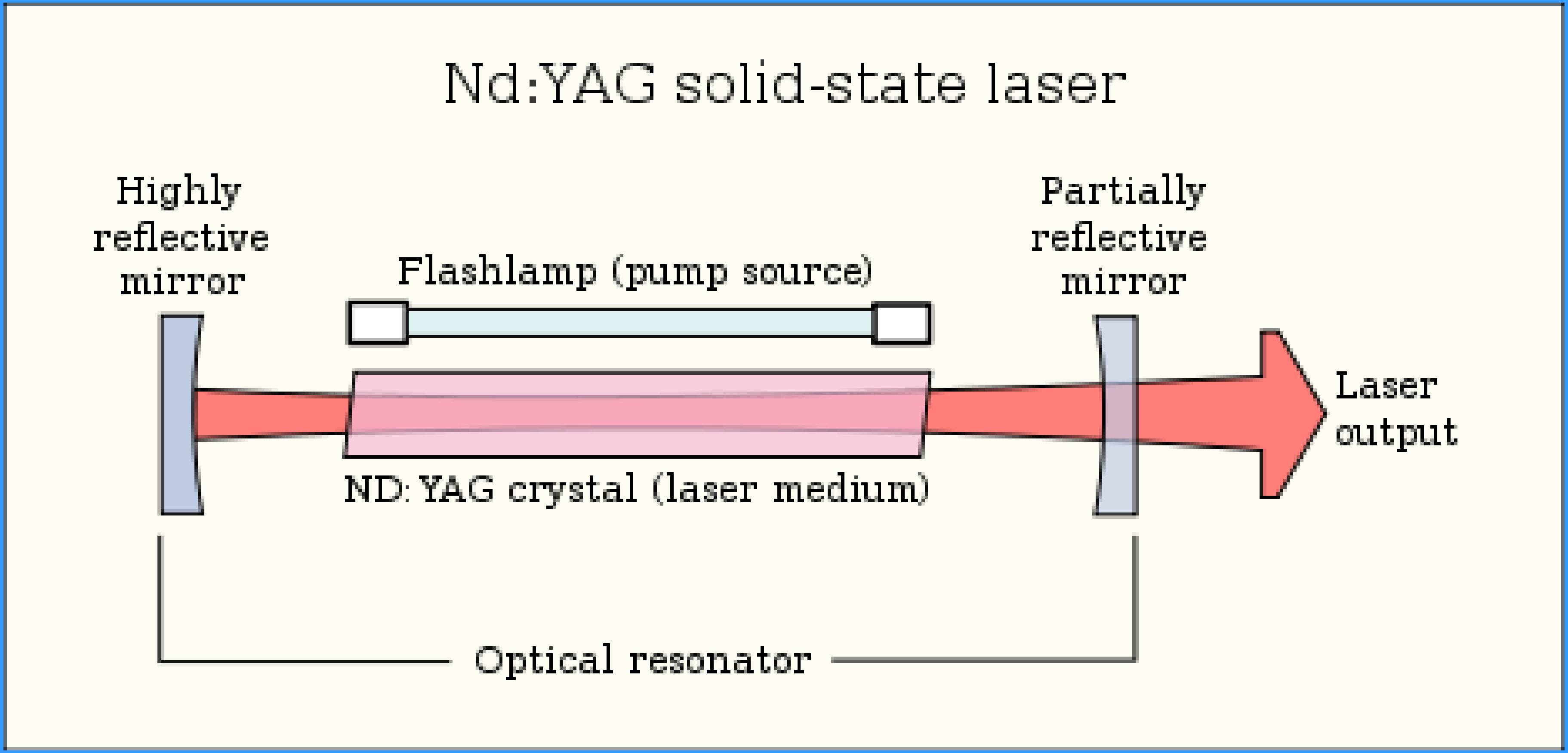
Light Amplification by Stimulated Emission of Radiation

Highly Reflective mirror

Pump source

Partially reflective mirror

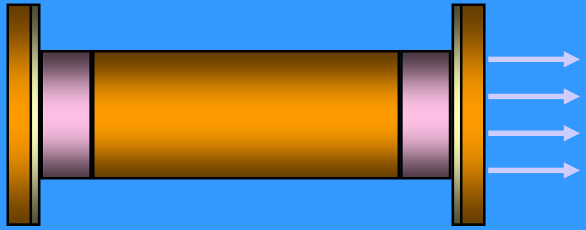
Laser outline



Properties of laser beam

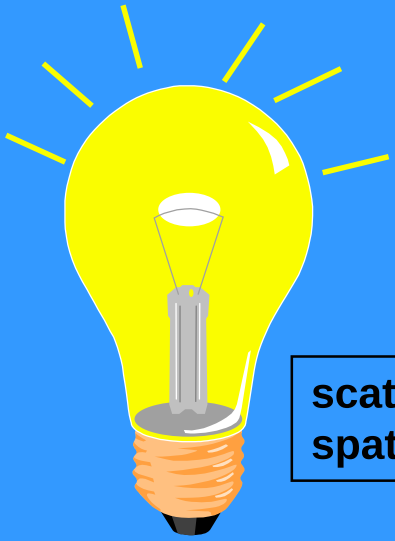
Low divergence

Laser



tightly focused, parallel

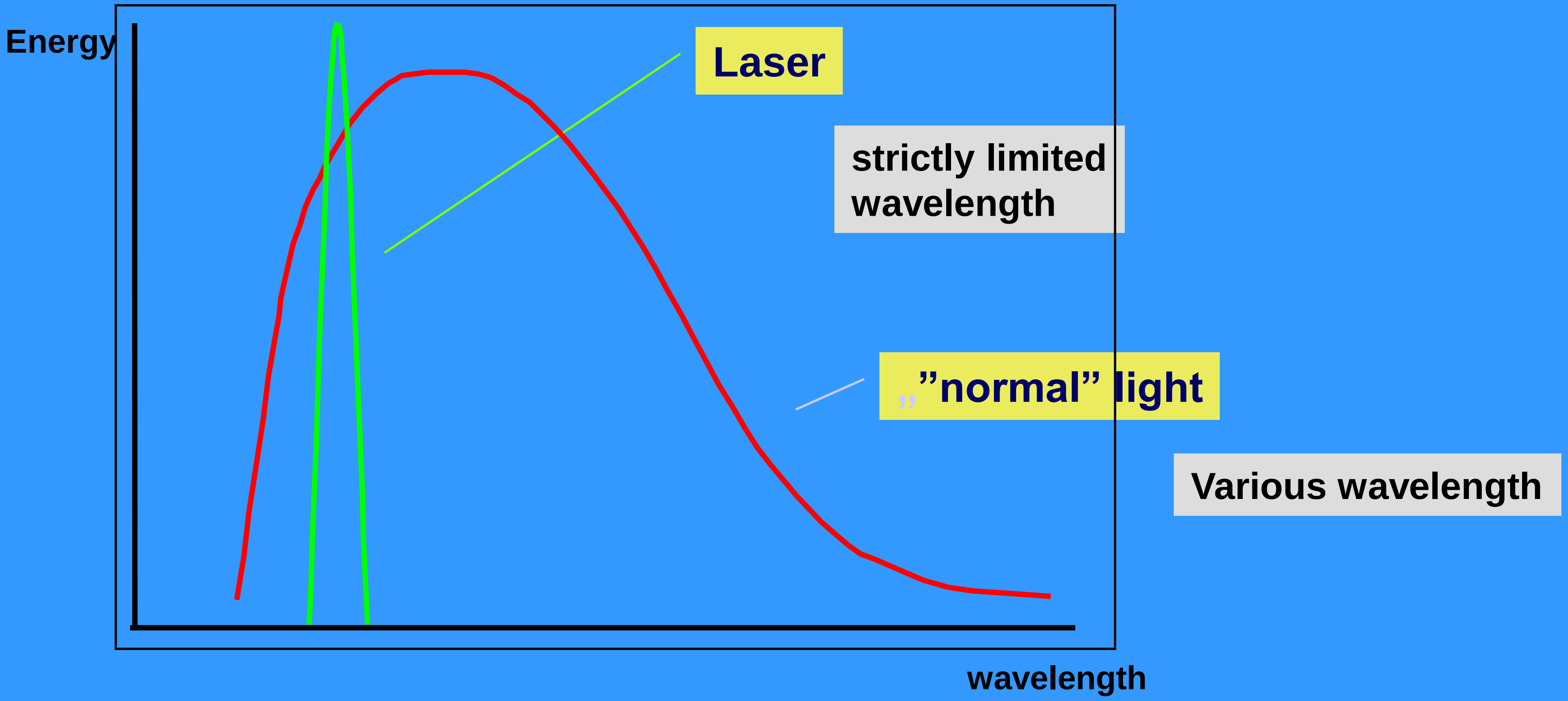
„Normal” light



scattered, spatial

Properties of laser beam

Monochromatic (unicoloured)



Laser

strictly limited wavelength

„”normal” light

Various wavelength

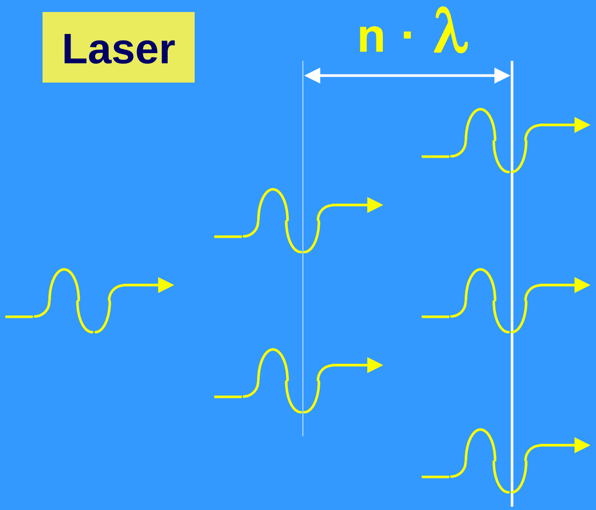
Properties of laser beam

Cohesion (time and spatial)

"Normal" ligth

"Normal" light,
waves differ in phase,
spatially spread

Laser

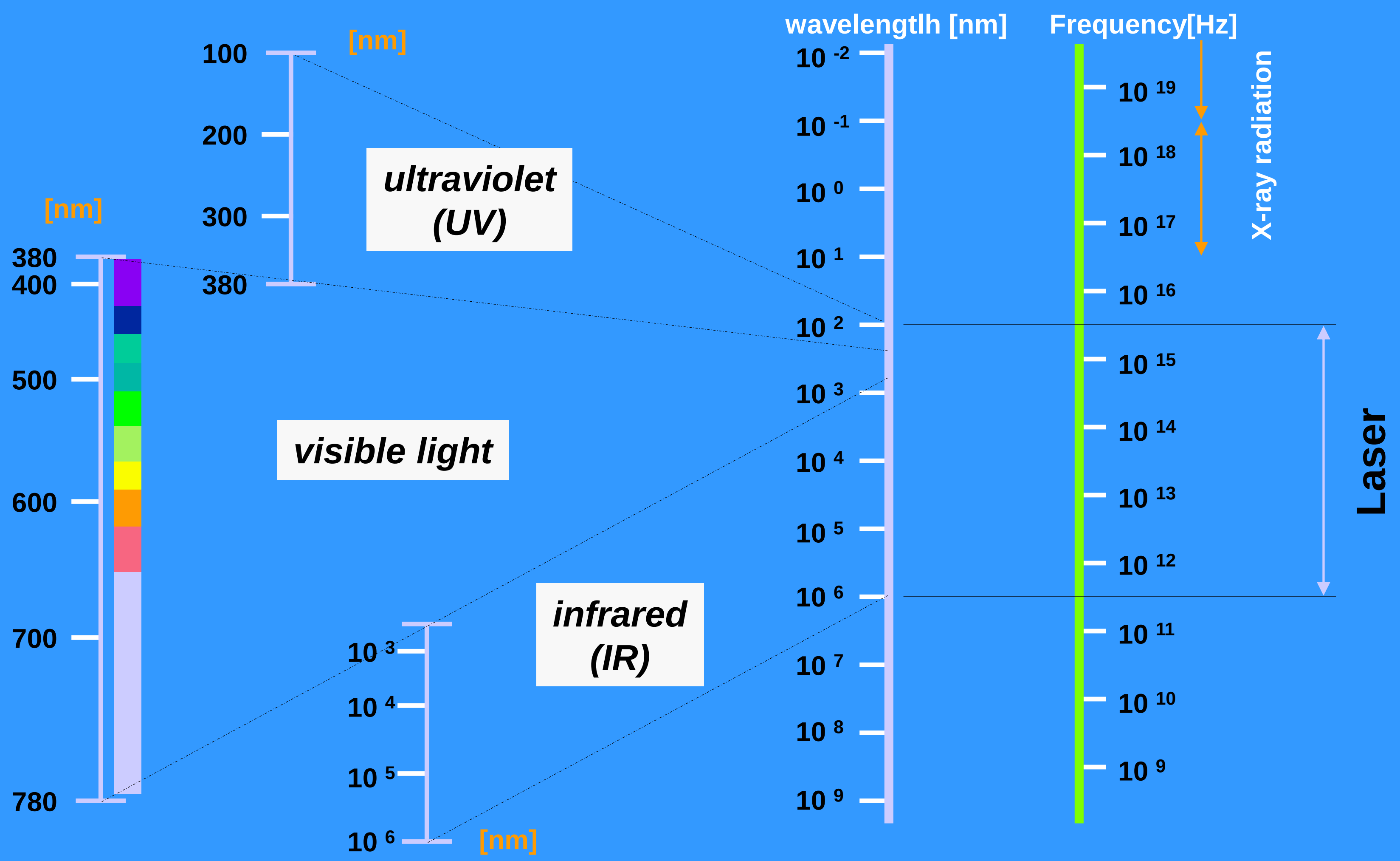


Laser radiation,
waves in the same phase,
and
amplitude

Laser types

Laser	Costruction	Laser medium	Application
Hel-Neon	gaseous	Ne	Measurement, Holography, Treatment of materials
Argon	gaseous	Ar	
Carbon dioxide	gaseous	CO_2	
Rubin	solid	Cr	Treatment of materials, Precision treatment of materials
Nd-YAG	solid	Nd	
Dyeing	liquid	Organic dye	Spectroscopy
Semiconductor	solid	Ga As	Optical transmission of information, Treatment of materials

Wavelength Range

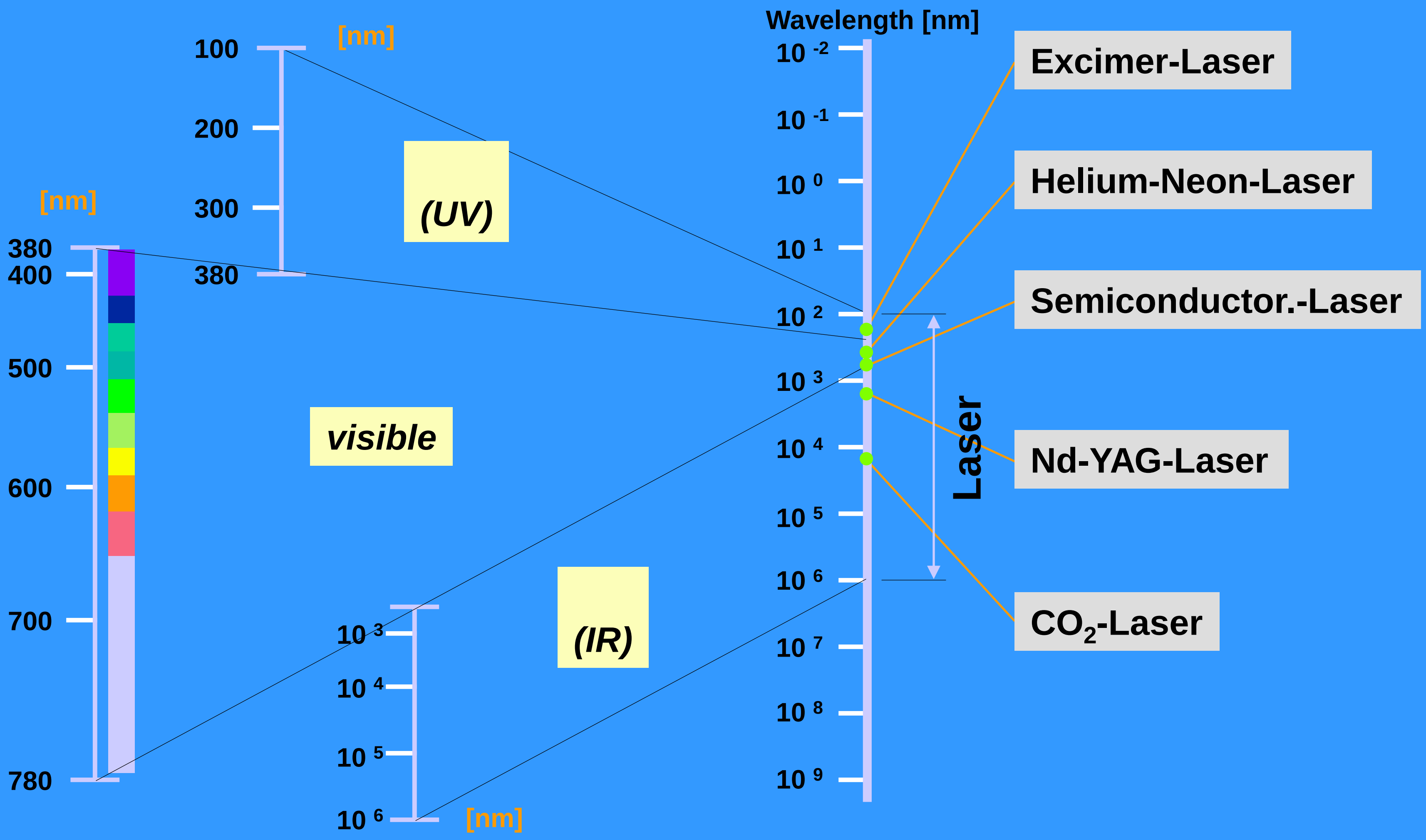


ultraviolet (UV)

visible light

infrared (IR)

Wavelength Range



Excimer-Laser

Helium-Neon-Laser

Semiconductor.-Laser

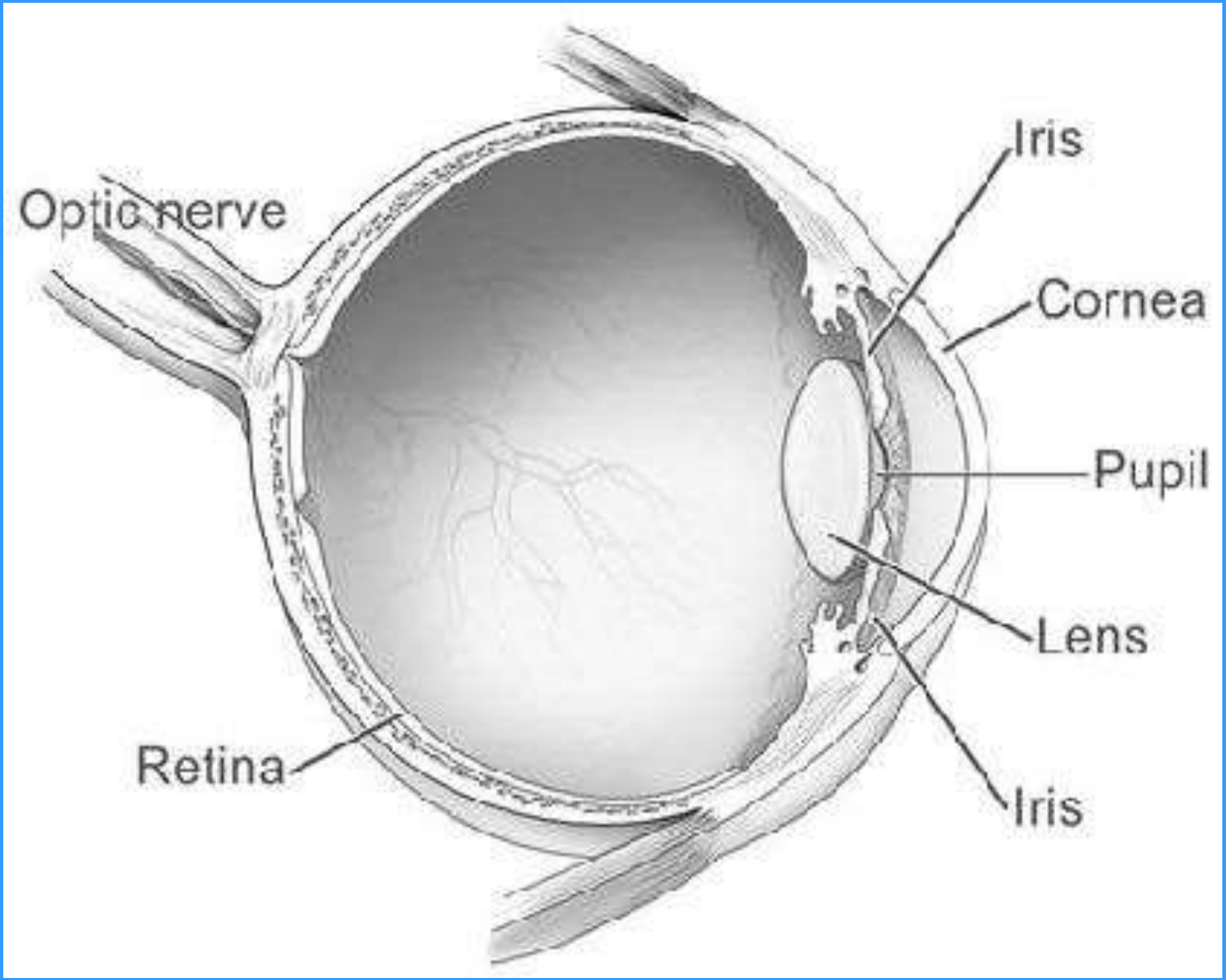
Nd-YAG-Laser

CO_2-Laser

The impact of the laser radiation

Wavelength Range		Impact to eye	Impact to skin	
100-315 nm	*UV*	inflammation of the cornea (rogówki)	Burn, accelerated aging	Excimer-Laser
315-380 nm		clouding the lens	Strengthening pigment	He-Ne-Laser
380-780 nm	*Visible*	damage of the retina (siatkówki)	Darkening pigment, inflammation	
780-1400 nm	*IR*	clouding the lens, damage of the retina	inflamation	Nd-YAG-Laser
1400-3000 nm		lens clouding, inflammation cornea		diode laser-high power
3000-100000 nm		inflammation of the cornea		CO_2-Laser

Eye layout



The impact of the laser radiation

Laser pulses- the mechanism of destruction (high energies and powers)

Exposure time	Pulse type	Mechanism of destruction
Shorter than 10^{-9} s	Coupled mode	Electric break-down
10^{-9} do 10^{-1} s	Giant pulses	Acoustic shock wave, Evaporation, Thermal processes
0,1 do 10 s	Pulsed laser, Over 0,25 s Linear laser	Thermal processes
Longer than 10 s	Linear laser	Thermal processes, Photochemical processes

Absorption of the laser light

Laser radiation spreading in various centers under the laws of reflection, refraction, polarization and absorption

When monochromatic radiation, forming a parallel beam passes through the absorbing medium, its intensity decreases as the radiation penetration into the depths, and the change in the intensity of radiation describes Lambert law:

$$I = I_0 \ e^{-\alpha x}$$

I_0, I – initial intensity and after passing the layer of a thickness x

α - radiation absorption coefficient of the medium; depends on the wavelength

As a result of absorption of laser beams the electromagnetic energy is converted into electrical, thermal, chemical and mechanical energy

Absorption mechanisms of the laser light

- classical
- multiphoton

Classical absorption mechanism

the wavelength λ = 10.06 microns to λ = 0.53 microns

/ second harmonic Nd: YAG /

called „Inversebremsstrahlung" - a process opposite to the braking of electrons

/ braking radiation - due to inhibition of the electron in the electron nucleus generates electromagnetic EM /

Classical absorption mechanism causes the acceleration of electrons in the EM wave laser beam, the electrons collide with atoms and ionizing it, and then escape from the plasma region by creating an electric field for accelerating electrons, ions that follow, there is a heating of the peripheral areas of the plasma to the relatively high temperatures, resulting in melting and evaporation followed by a large quantity of material

To initiate the classical mechanism of absorption, free electrons are needed, they must be released in the process of multiphoton absorption

Multiphoton absorption mechanism

for small-wavelength, for example, excimer lasers:
λ = 248 nm (KrF)
λ = 193 nm (ArF)
λ = 157 nm (F2)

for lasers operating with short pulses:
nano (10 $^{-9}$ s), pico (10 -^{12}-s) or femtosecond (10 $^{-15}$)
(excimer or CO2 lasers and
Nd: YAG laser with a modulator factor Q-switch)

- when the energy quanta of laser radiation is high – occurs laser ablation
- athermal process - the temperature of the generated plasma is lower than in the case of long-term laser – allows deposition <u>on thermally sensitive substrates</u>

Ablation - a process in which high-energy laser radiation quanta produce lower bond energy between the particles, which allows the removal of atomic layers one-by-one

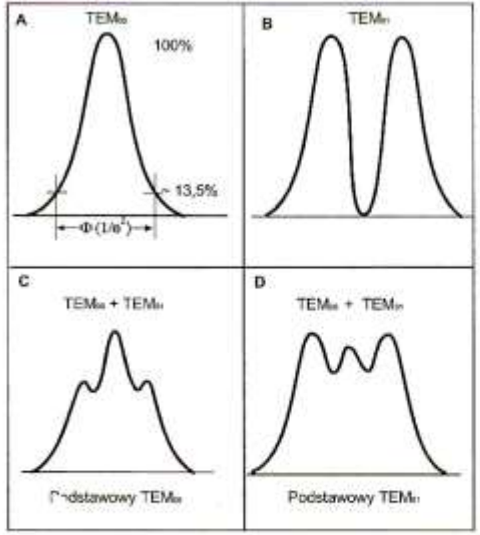
Classification of laser surface treatment

♦**heating**
↓
♦annealing
♦hardening

◘re-melting
↓
◘surface enrichment
◘glassy layers
◘plating
◘re-melting hardening

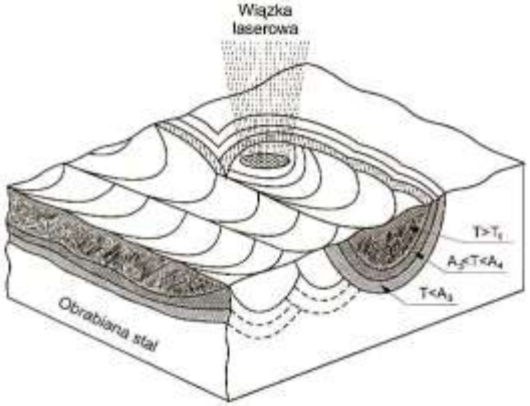
Δthermal shock
↓
Δimpact surface hardening

- Heating using laser radiation (Kus.2.1)

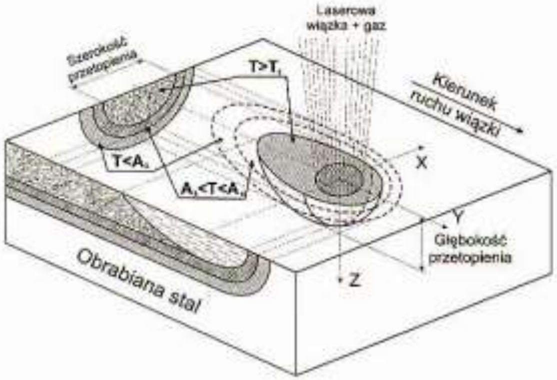


Rys. 2.1. Schematyczne przedstawienie rozkładów natężenia promieniowania laserowego w przekroju wiązki laserowej; a – o modzie podstawowym TEM_{00}, b, c, d – wielomodowej.

- Laser heat treatment (Kus.2.2 , 2.3)



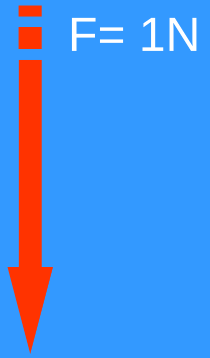
Schemat obróbki za pomocą lasera o działaniu impulsowym (TEM_{00}).

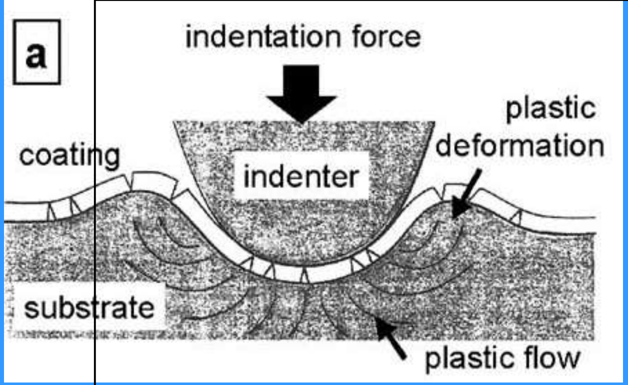


Schemat obróbki za pomocą lasera o działaniu ciągłym (TEM_{00}).

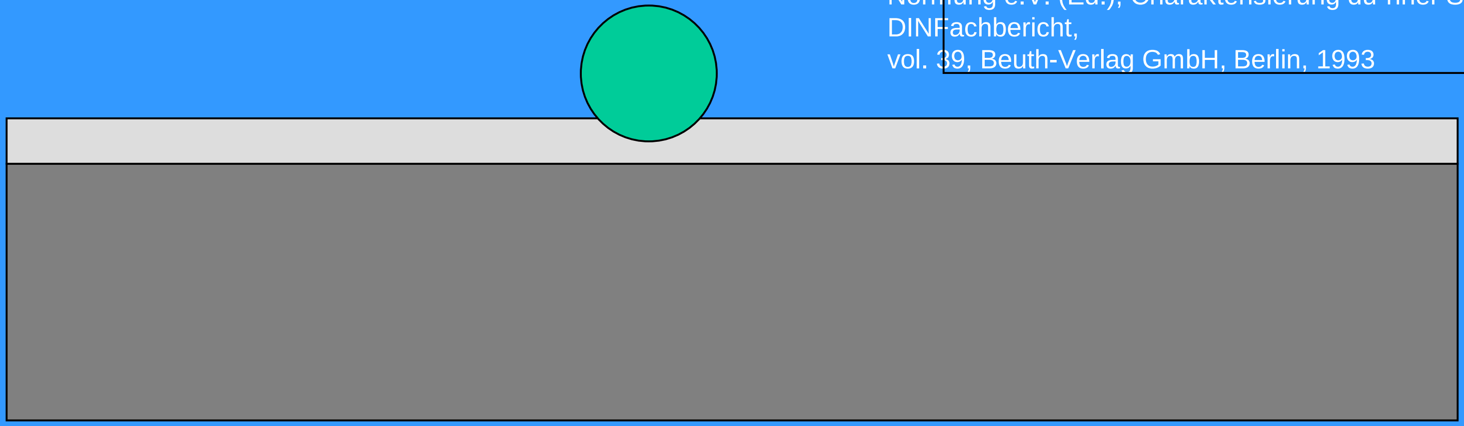
Wear test

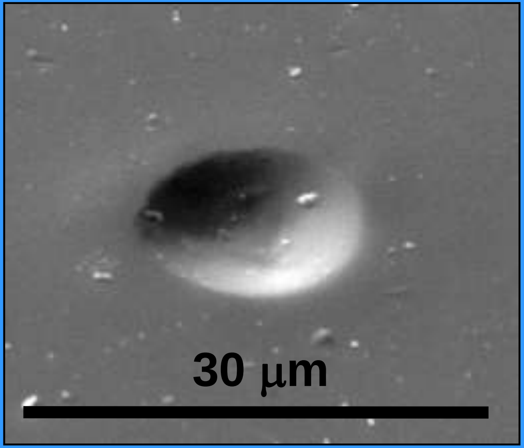
(ball pushed into the coating)





H. Jehn, G. Reiners, N. Siegel, in: DIN Deutsches Institut fu¨r Normung e.V. (Ed.), Charakterisierung du¨nner Schichten, DINFachbericht,
vol. 39, Beuth-Verlag GmbH, Berlin, 1993

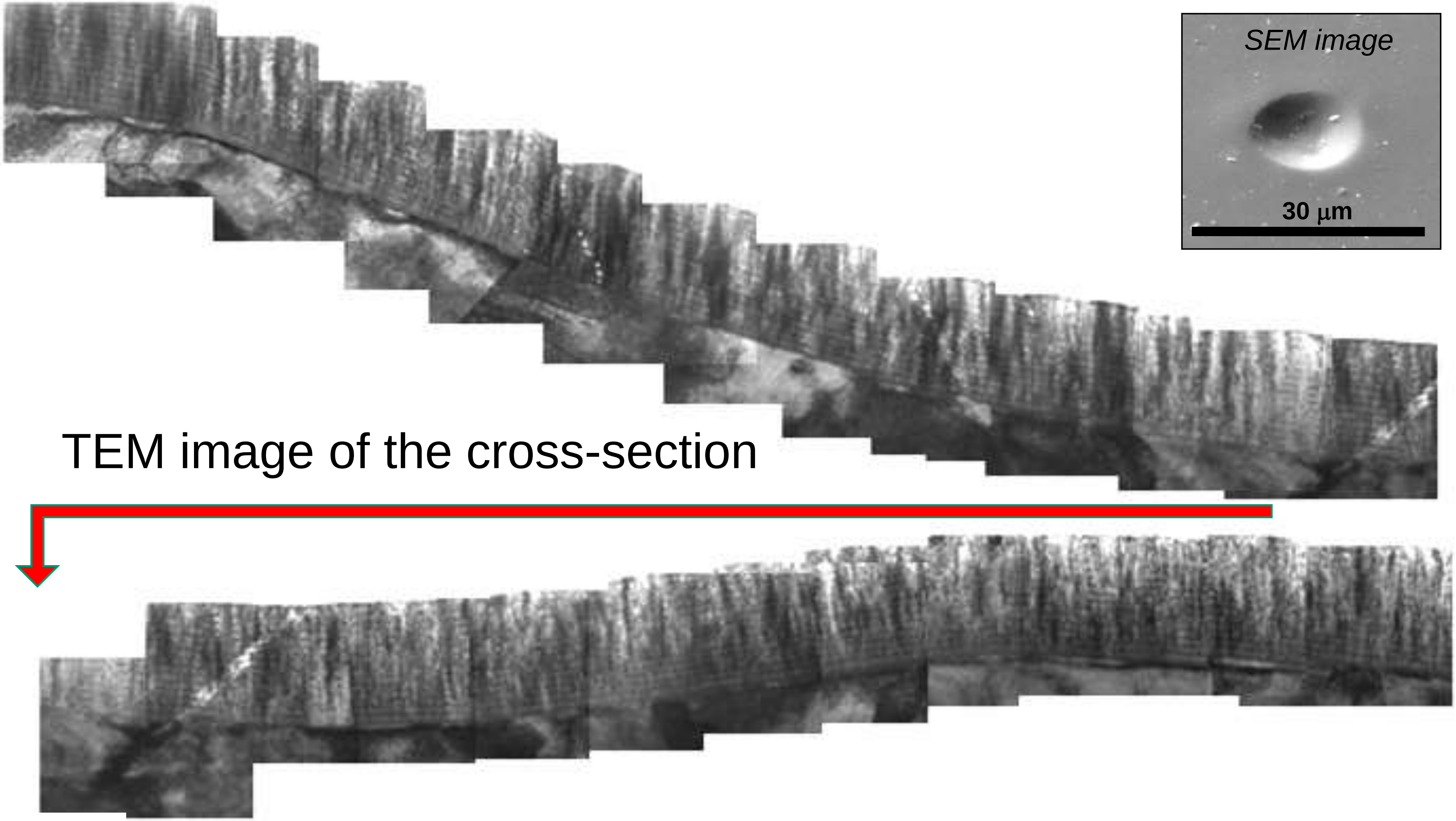




SEM image of the coating surface after mechanical test

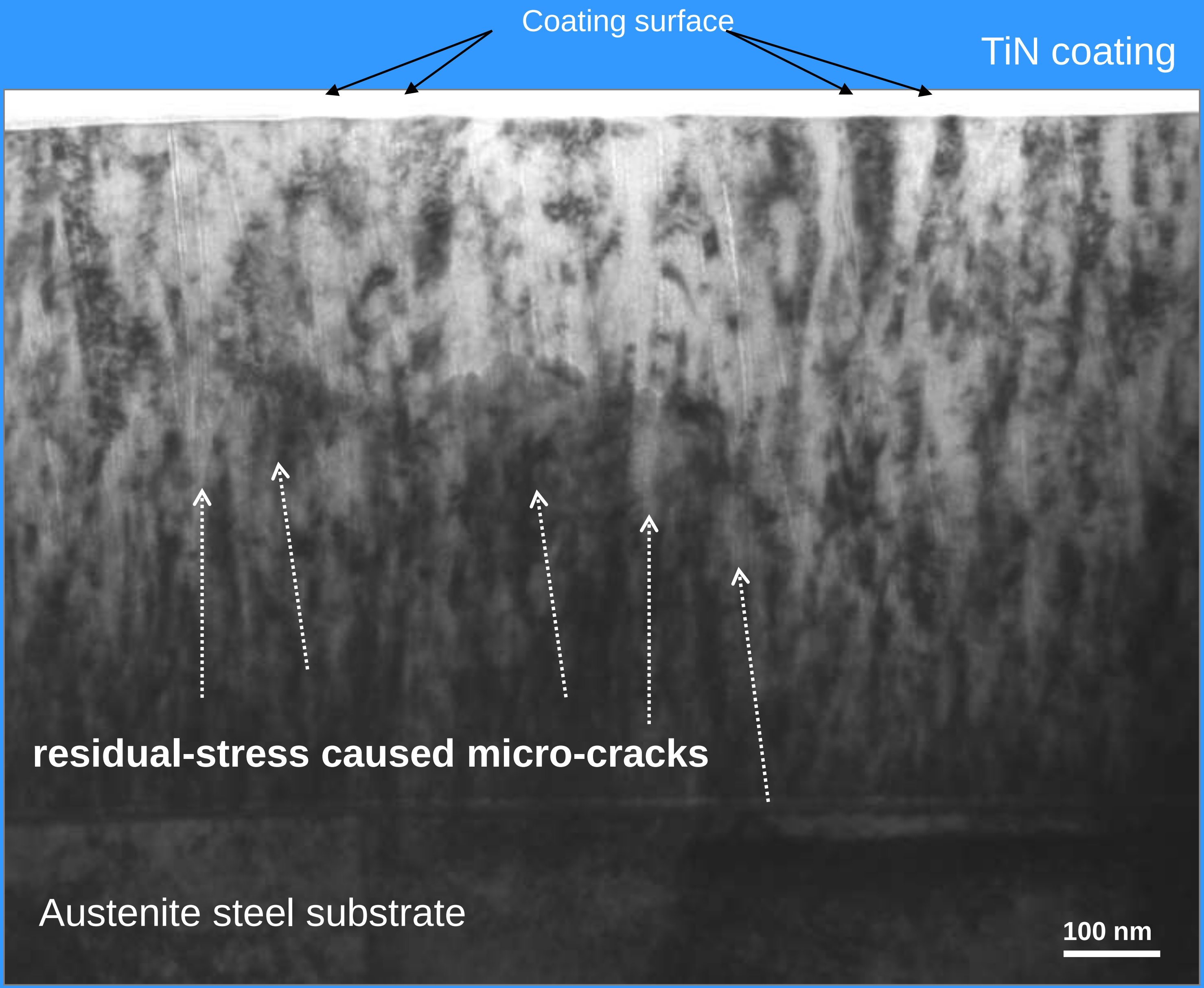
32 layered Ti/TiN coating

Cross- section of the place where penetrator was pushed into the coating



TEM image of the cross-section

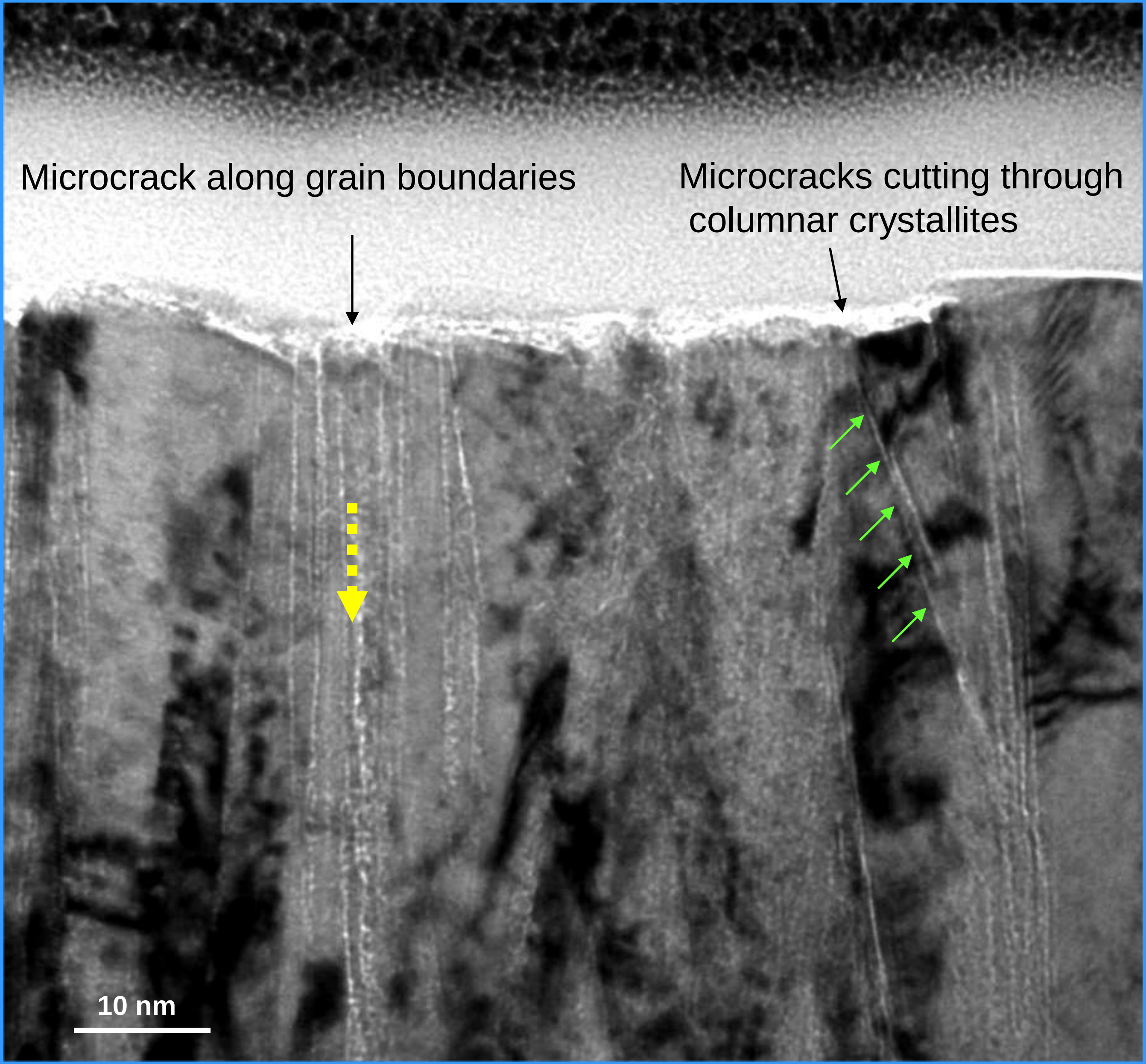
I. as-deposited mono-layer coating



TEM image of the cross-section

Single layered coating- low loading (0.25N)

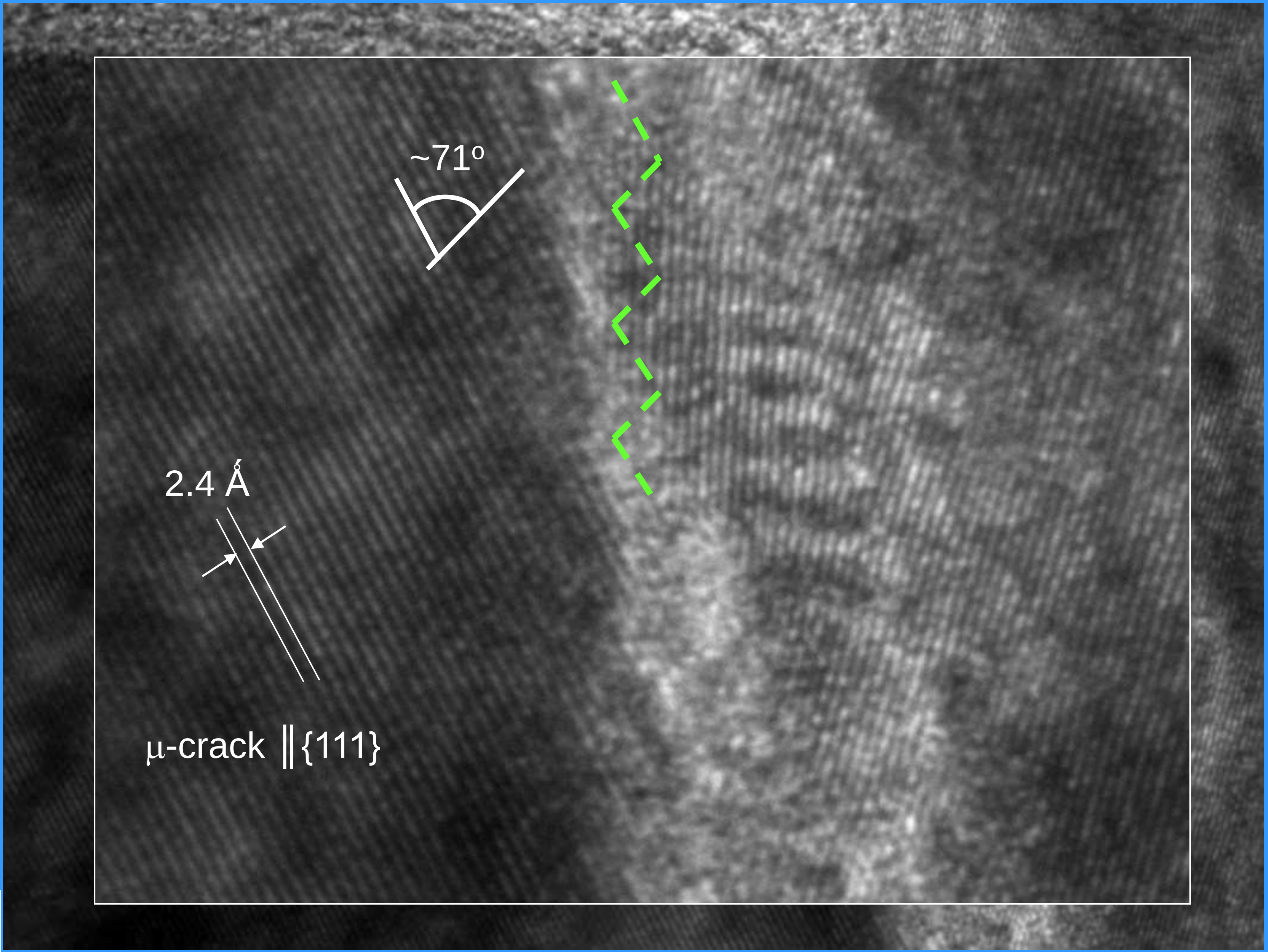
TiN coating



Microcrack along grain boundaries

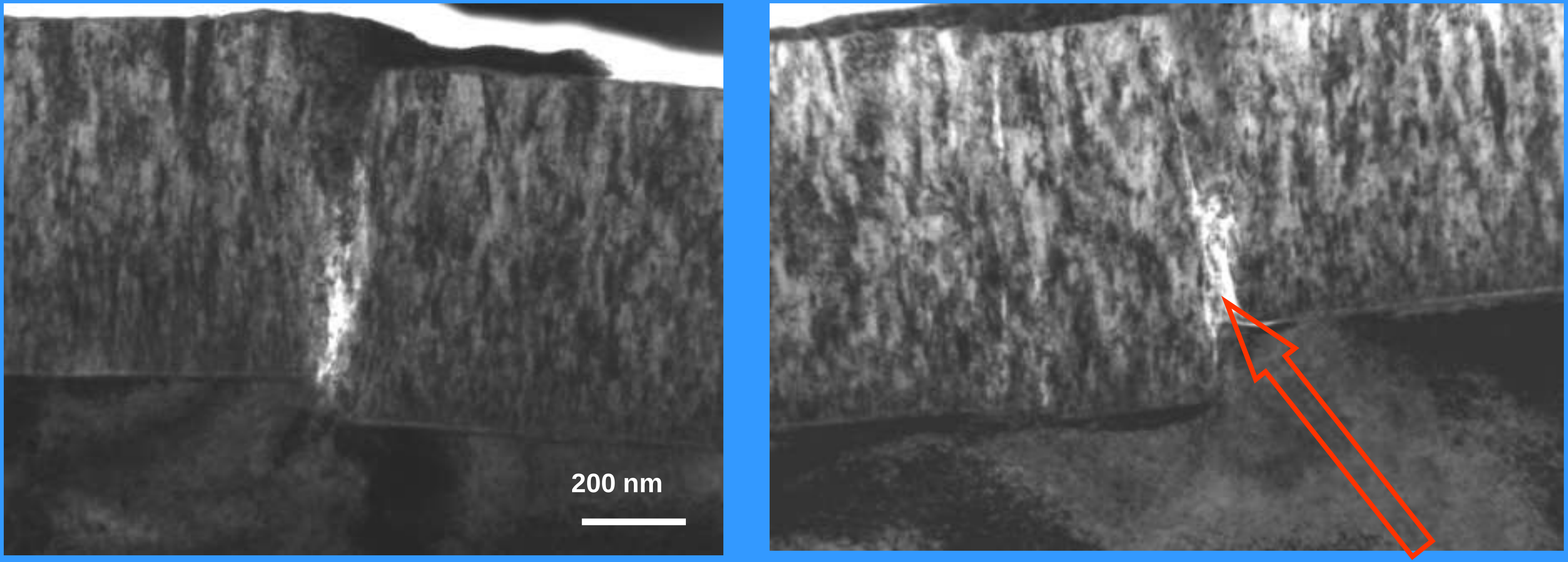
Microcracks cutting through columnar crystallites

TEM image of the cross-section



HREM image of the crack at the cross-section

Single layered coating- high loading (1N)

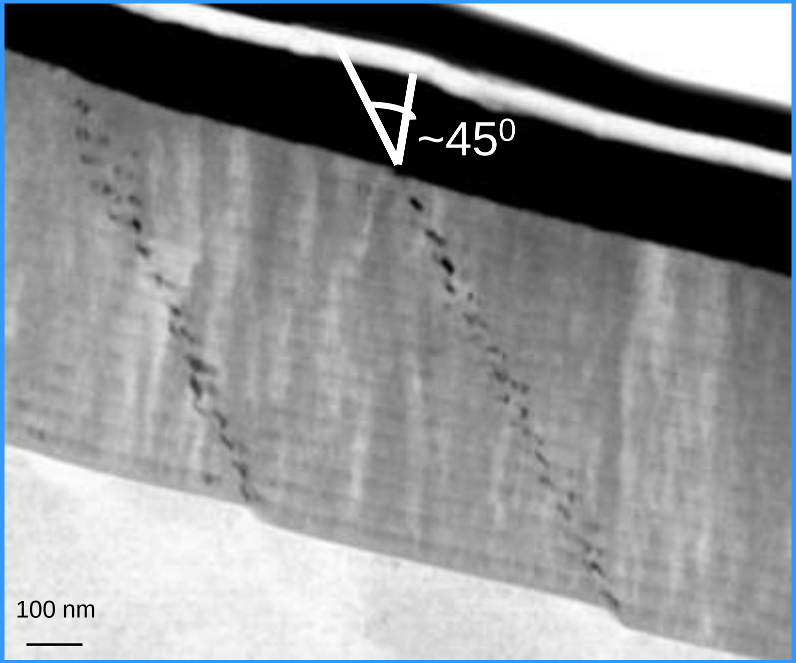


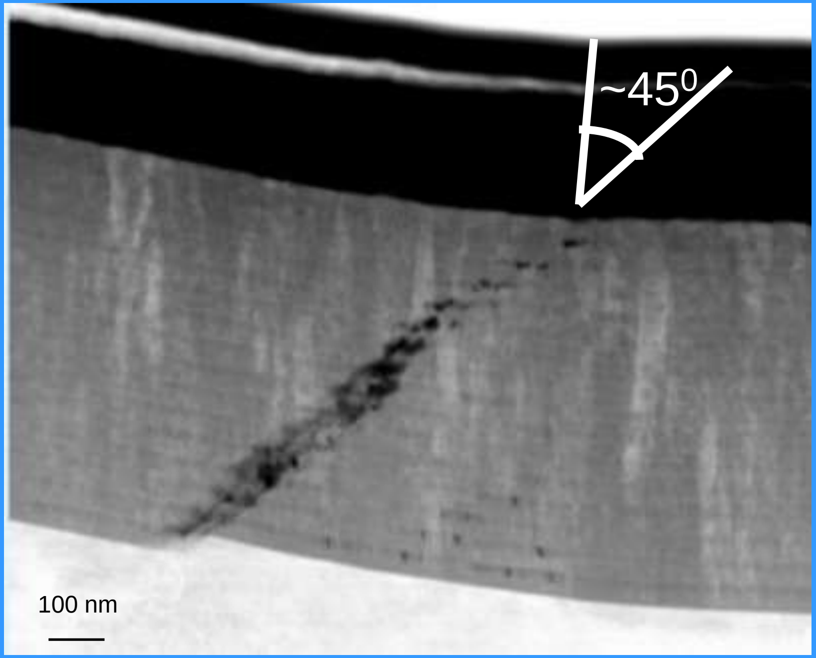
Area endangered by corrosion

Substrate has a contact with outside environment

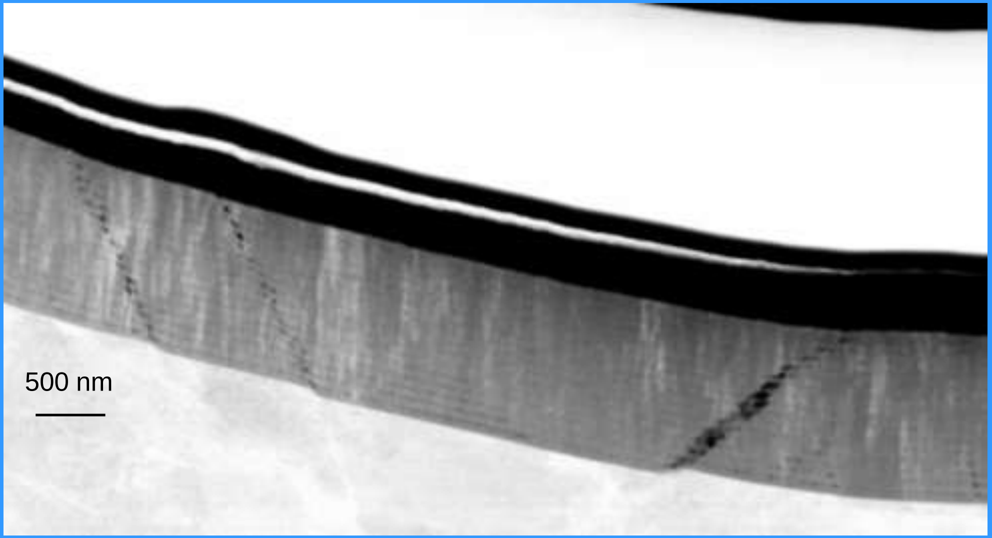
TEM image of the cross-section

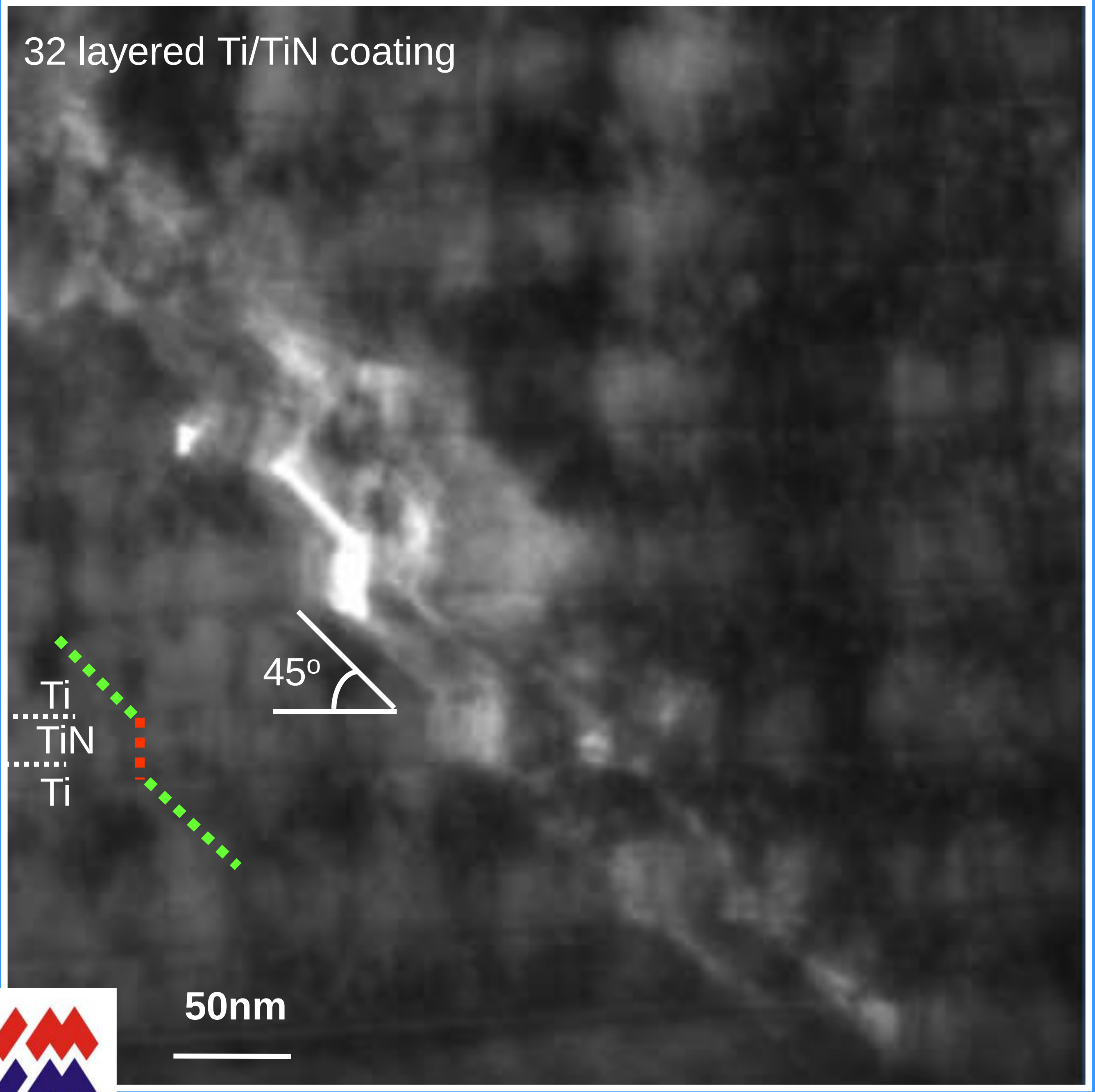
32 layered Ti/TiN coating ratio 1:1

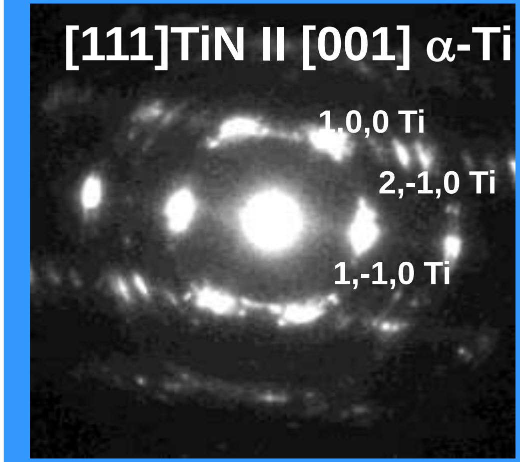




STEM images of cracks propagating across the coating under applied load





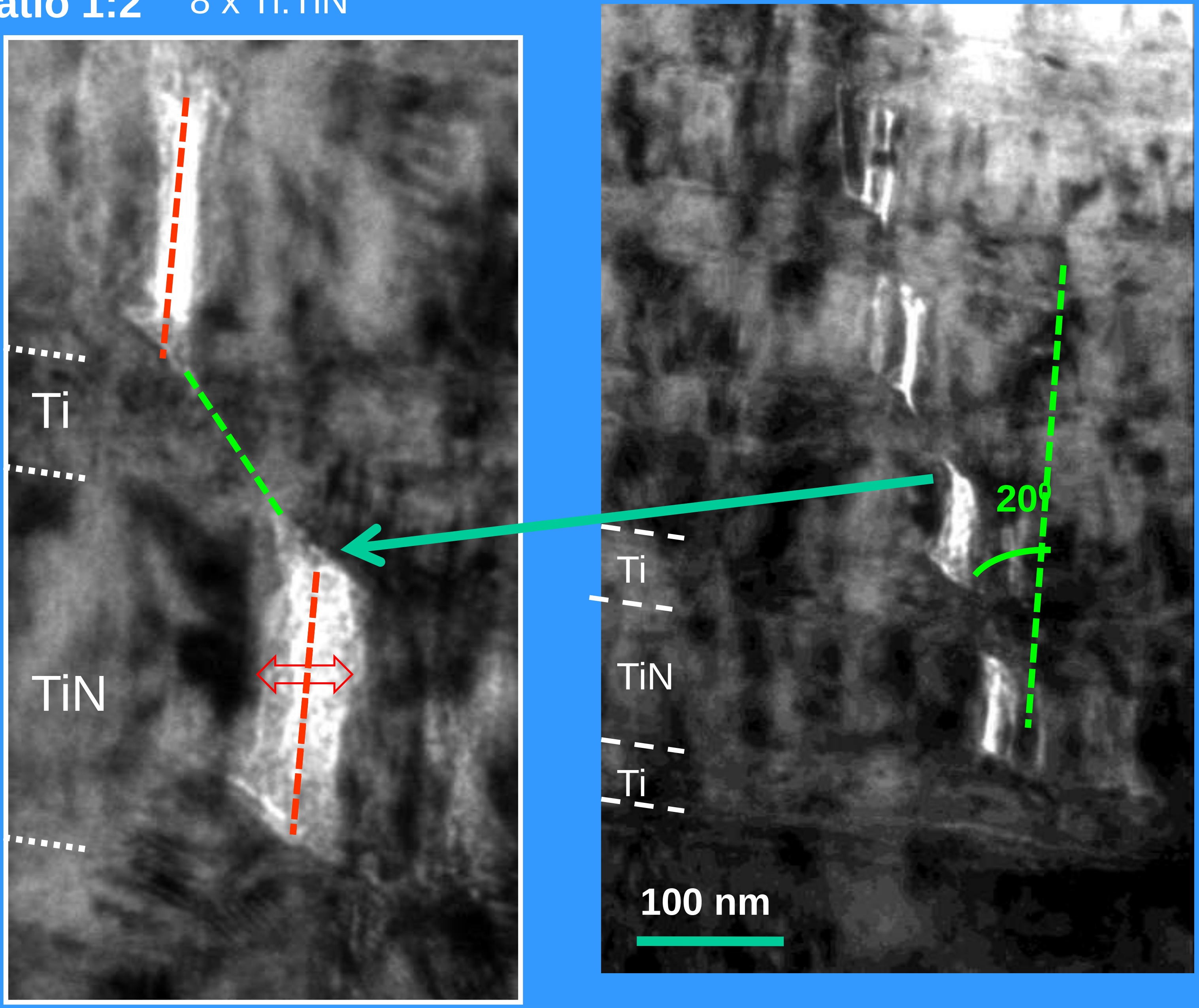


Zone [001]

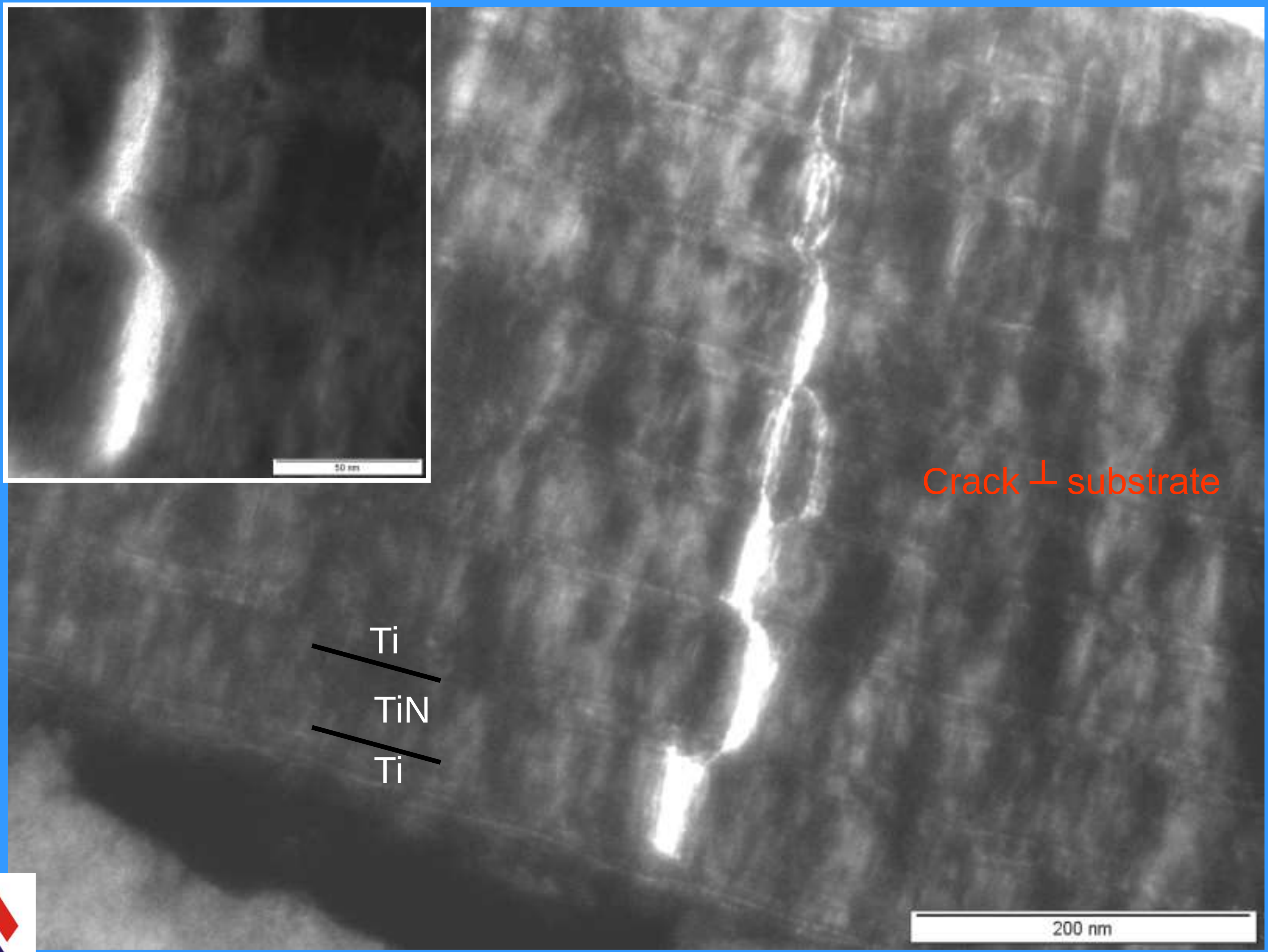
Local plastic deformation
(slip systems)
/cracking

TEM image of the cross-section

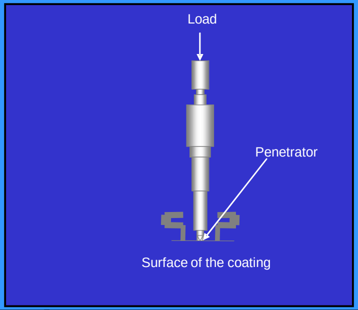
Ratio 1:2 8 x Ti:TiN



Ratio 1:4 8 x Ti:TiN

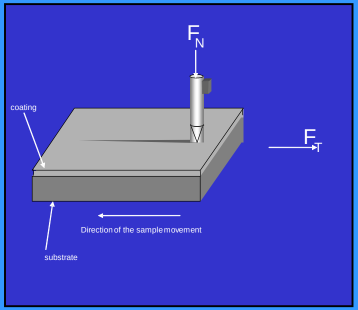


Analysis of mechanical properties



hardness

Type of penetrator: Vickers 136^0
load : 0.02- 30N

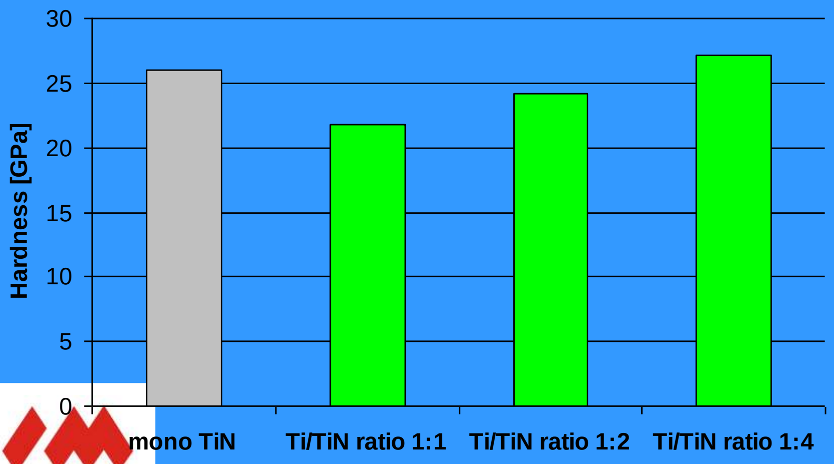


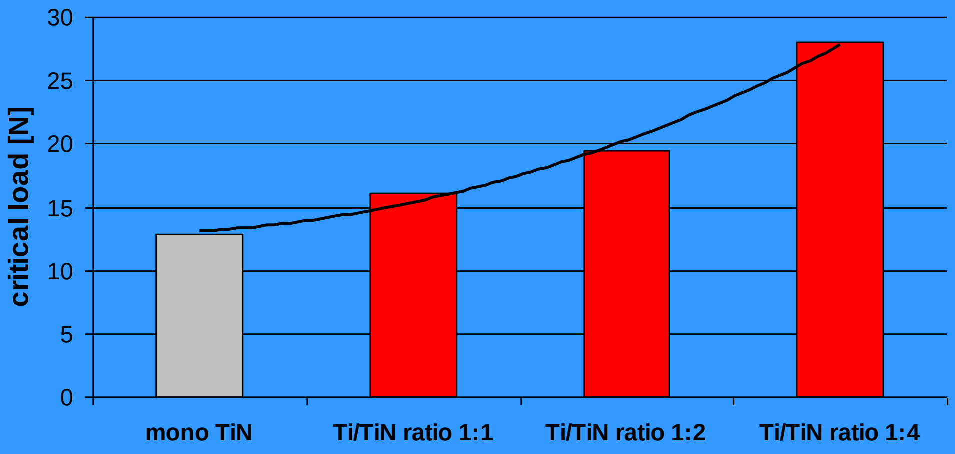
scratch

Type of penetrator: Rockwell 120^0
load : 0.05- 30N
speed : 0.4- 20mm/min
length of scratch : up to 20 mm

H [GPa]	Number of layers		Hardness	
8x(Ti+TiN)		E	10mN	deviation
TiN- mono			**26**	1.40
ratio 1-1	16	247	21.74	1.40
ratio 1-2	16	255	24.14	1.90
ratio 1-4	16	263	27.12	2.10

	Lc1 [N]	Lc2 [N]
TiN- mono	5,1	12,8
8x ratio 1-1	7,2	16,1
8x ratio 1-2	7	19,5
8x ratio 1-4	7	28

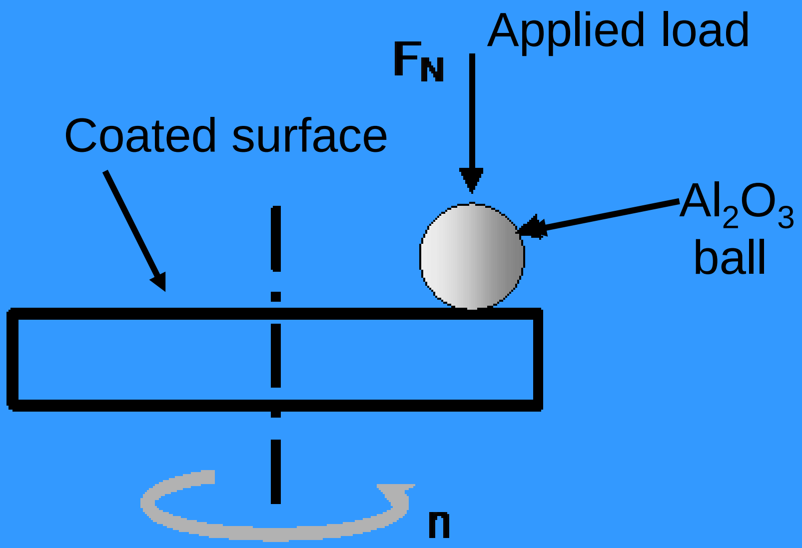


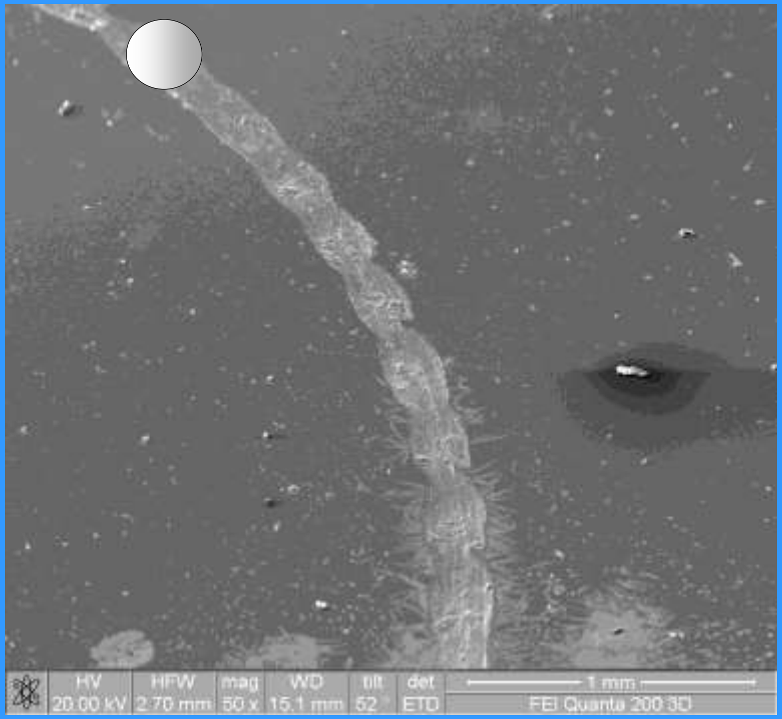


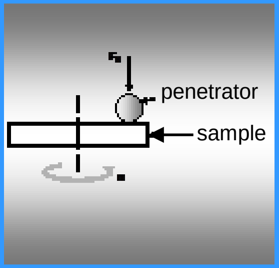
J.F.Archard,
J. Appl. Phys.24(1953)981

Wear - $V_w = K(S*N/H)$

V_w– amount of the removed material, S– distance, N– load, H– hardness, K– wear coefficient

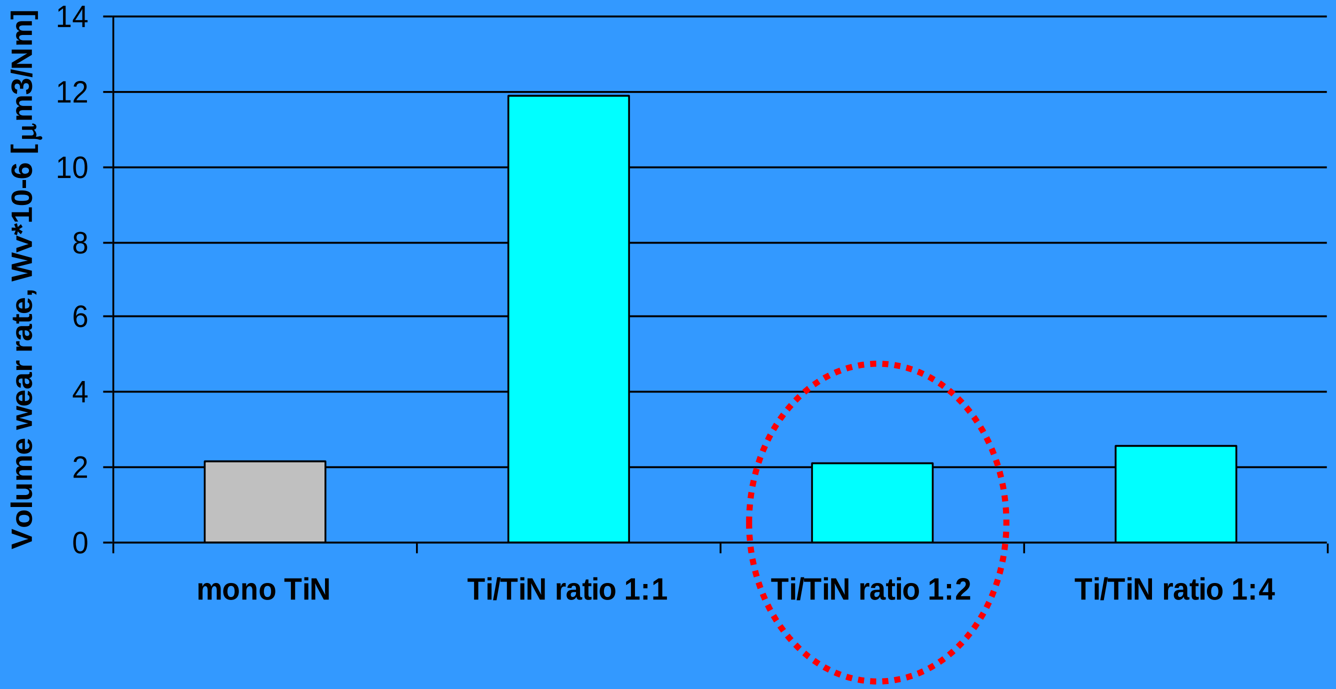


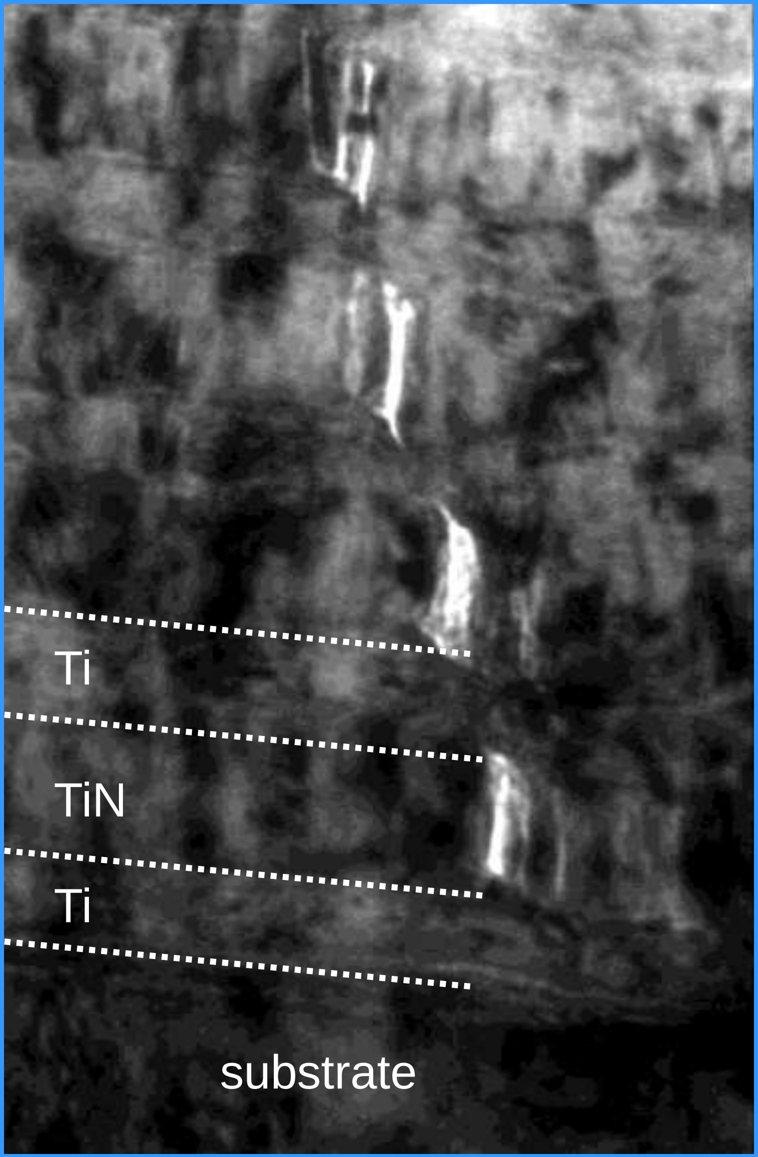




wear

	Wv*10^-6[µm^3/(N*m)]	Deviation.
TiN- mono	2,17	0,6
Ti/TiN-1:1	11,9	2,5
Ti/TiN-1:2	2,115	0,4
Ti/TiN-1:4	2,55	1,02





Conclusions

-As deposited single layered (TiN) coatings were characterised by vertical cracking caused by residual stress. Under the applied load, cracks at grain boundaries open fast leading to coating fragmentation exposing substrate.

- The multilayer TiN/Ti coatings deform both by brittle cracking of ceramic and plastic deformation of metalic layers. The TiN/Ti multilayer hardness and wear was at the level of TiN till the ceramic phase dominated.

- The deformation and wear of multilayer TiN/Ti multilayer coatings proceeds keeping contnuity of metalic layers and therefore protecting substrate (keeping corrosion at bay).

Friction elements

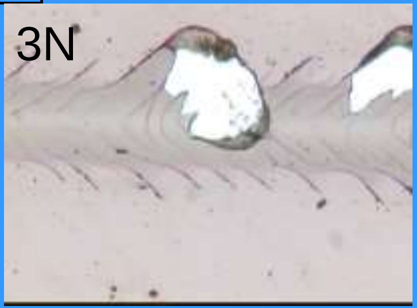
Tribology

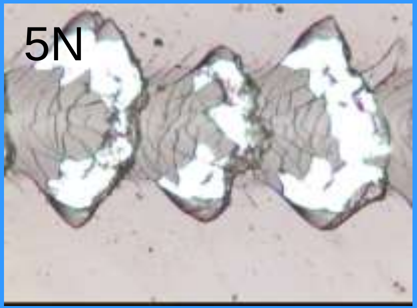
DLC		10mN		
	hmax [nm]	HV	HiT [GPa]	E [GPa]
Mean	**150**	**1190**	**12539,1**	**177**
Deviat	**8**	**44,0**	**463,9**	**10**

TiN		10mN		
	hmax [nm]	HV	HiT [GPa]	E [GPa]
Mean	**126**	**1410**	**14865,6**	**273**
Deviat	**8**	**62,6**	**659,3**	**22**

10mN

DLC





Rockwell
200 μm
0.01-30N

TiN

Powłoka	Wskaźnik zużycia	Współczynnik tarcia
DLC	18,11	0,09
TIN	8,86	0,2

Ball-on-disc

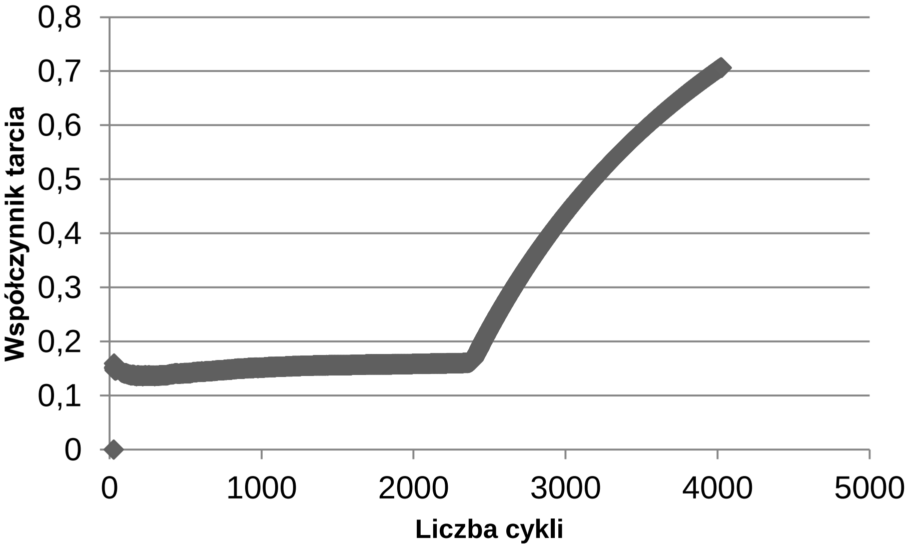
ISO 20808:2004

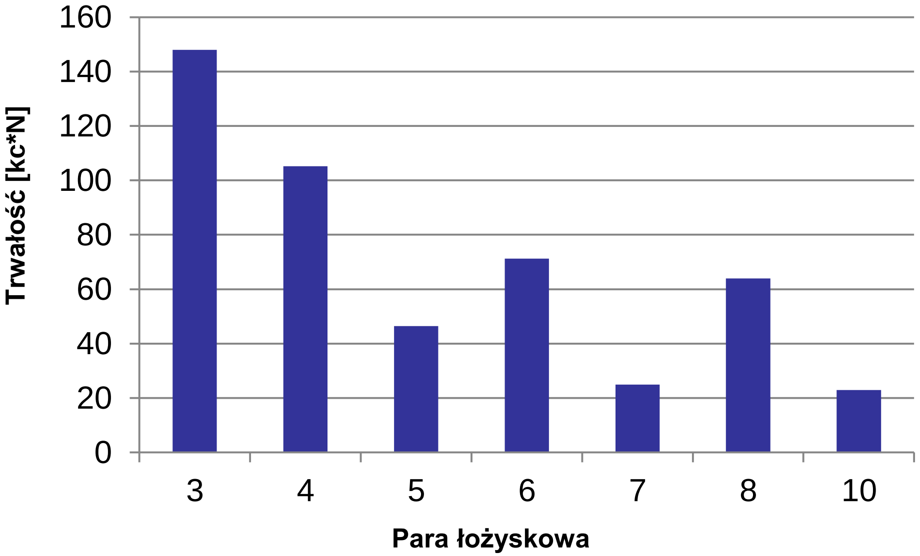
Tribology

Para	Fric. Coeff.				
Force >	1N	3N	5N	8N	12N
Para 3	0,11	0,11	0,11	0,12	0,15
Para 4	0,08	0,11	0,12	0,13	0,14
Para 5	0,07	0,07	0,14		
Para 6	0,13	0,12	0,14	0,2	
Para 7	0,12	0,14	0,17		
Para 8	0,1	0,12	0,15	0,17	
Para 10	0,12	0,1			

-Friction coefficient uder load 1N, rotation 150rot/min; test 20000 cycle

- Load sequence: 3N-5000cclei, 5N-5000cycle, 8N-5000cycle and 12N-5000cycle

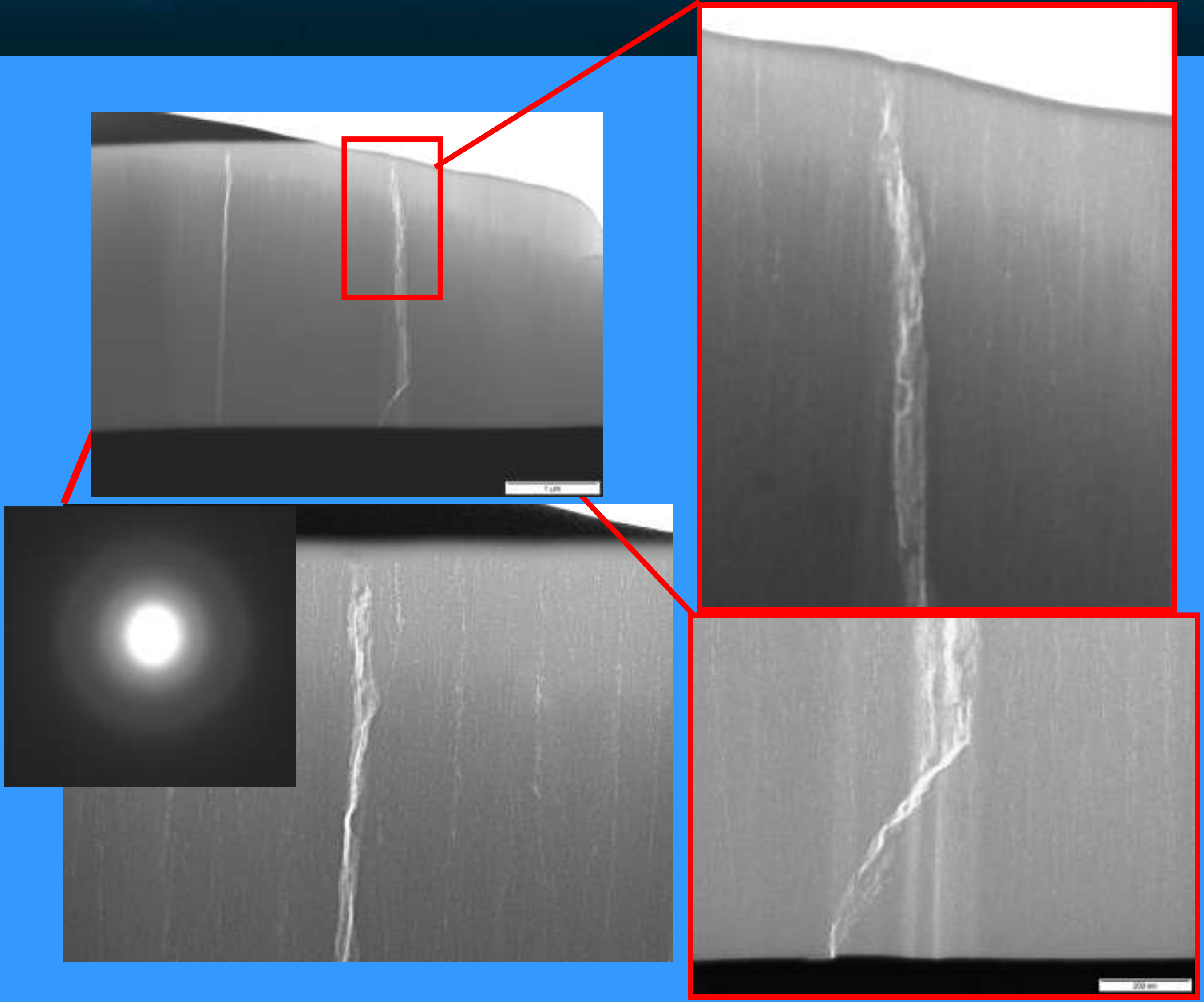




TEM

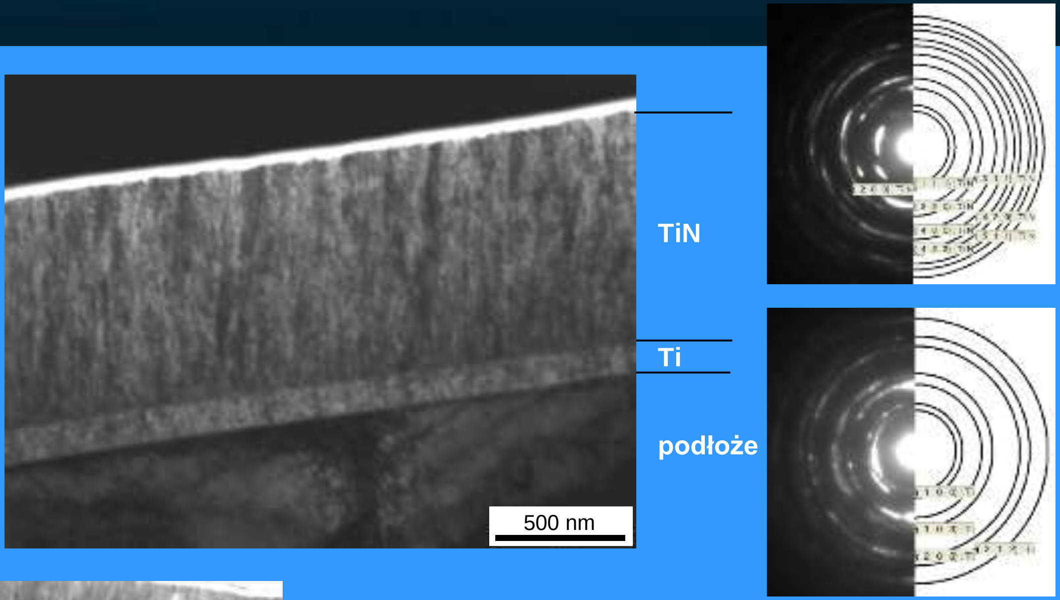
Friction elements

Amorphous carbon coating
Test- 1N/ 2000 cykli

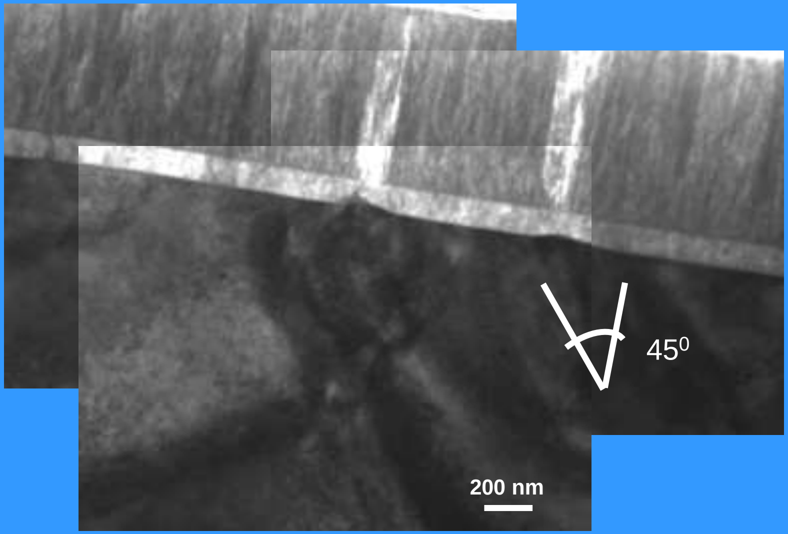


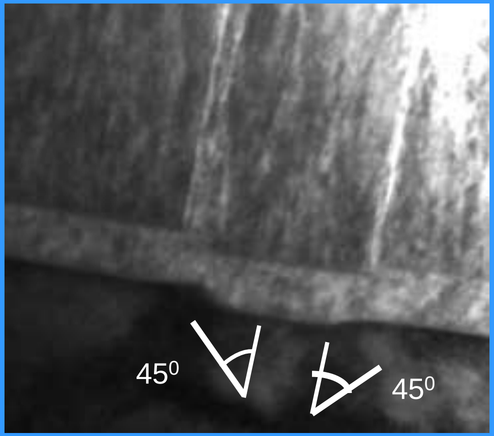
TEM

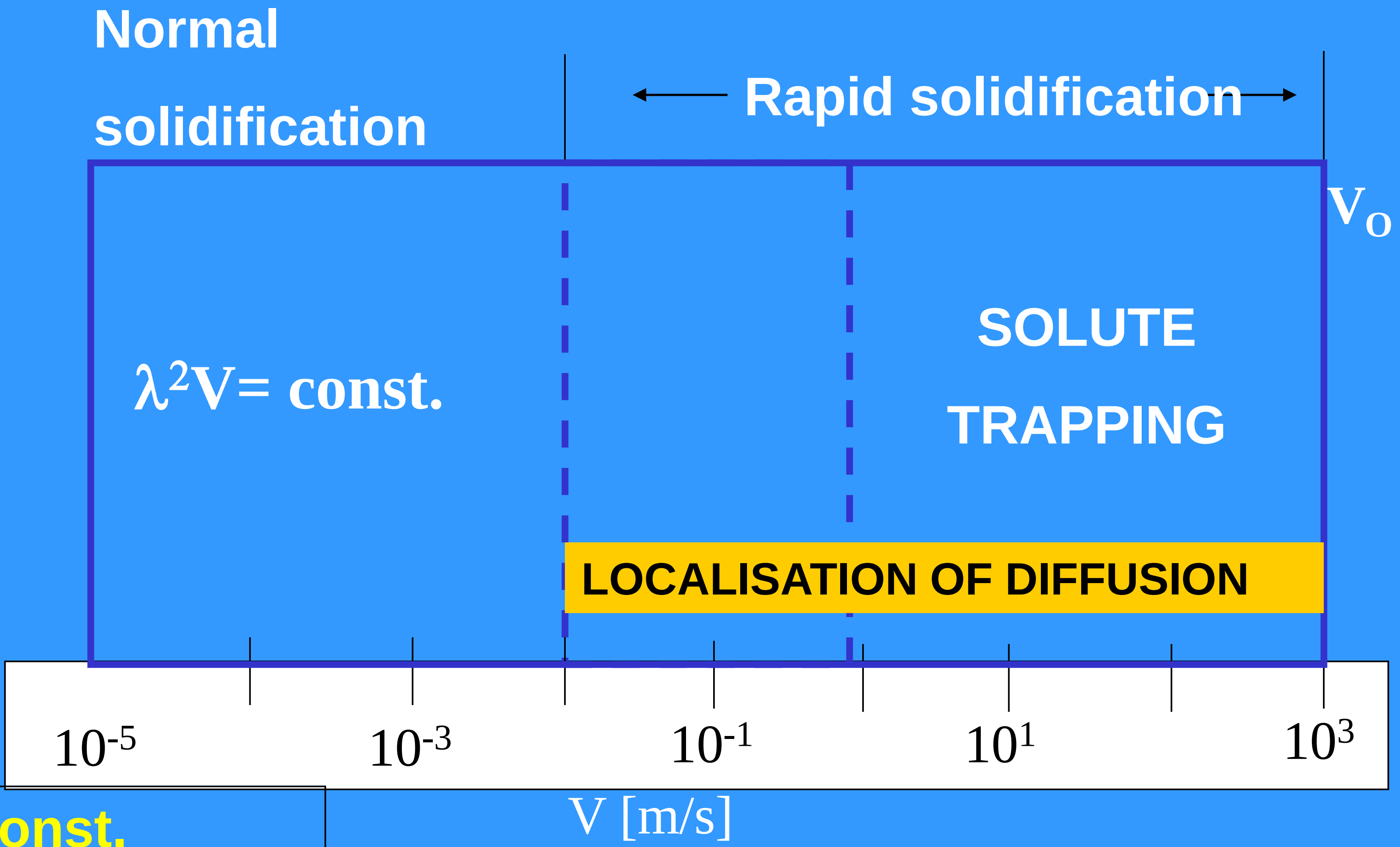
Friction elements



TiN coating
Test- 0,25N/ 20000 cykli







Normal solidification

← Rapid solidification →

V_O

$\lambda^2 V$= const.

SOLUTE TRAPPING

LOCALISATION OF DIFFUSION

10^{-5} 10^{-3} 10^{-1} 10^{1} 10^{3}

V [m/s]

d^2V= const.

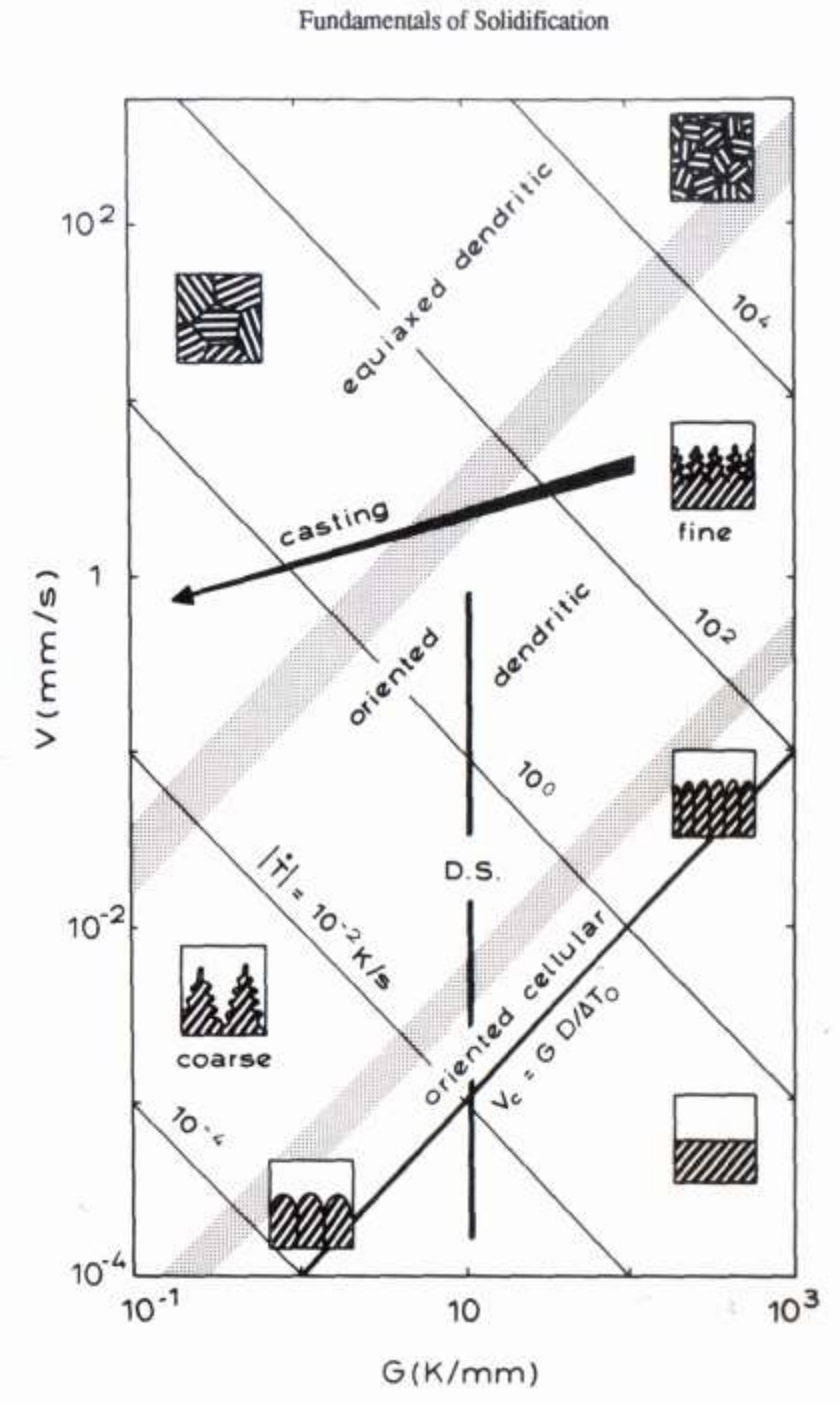
d- length of microstructure

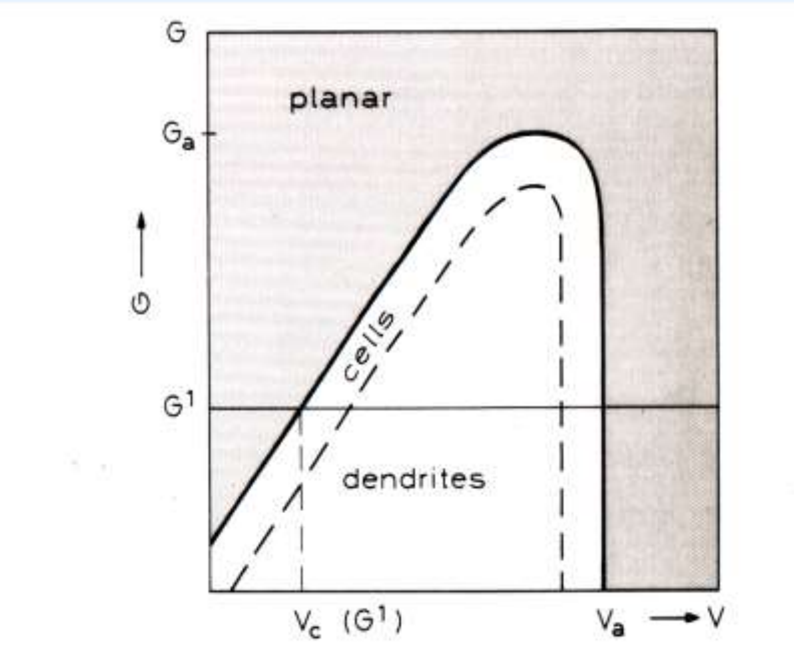
V- growth velocity

d represents either λ or R

λ–eutectic spacing

R- dendrite tip radius





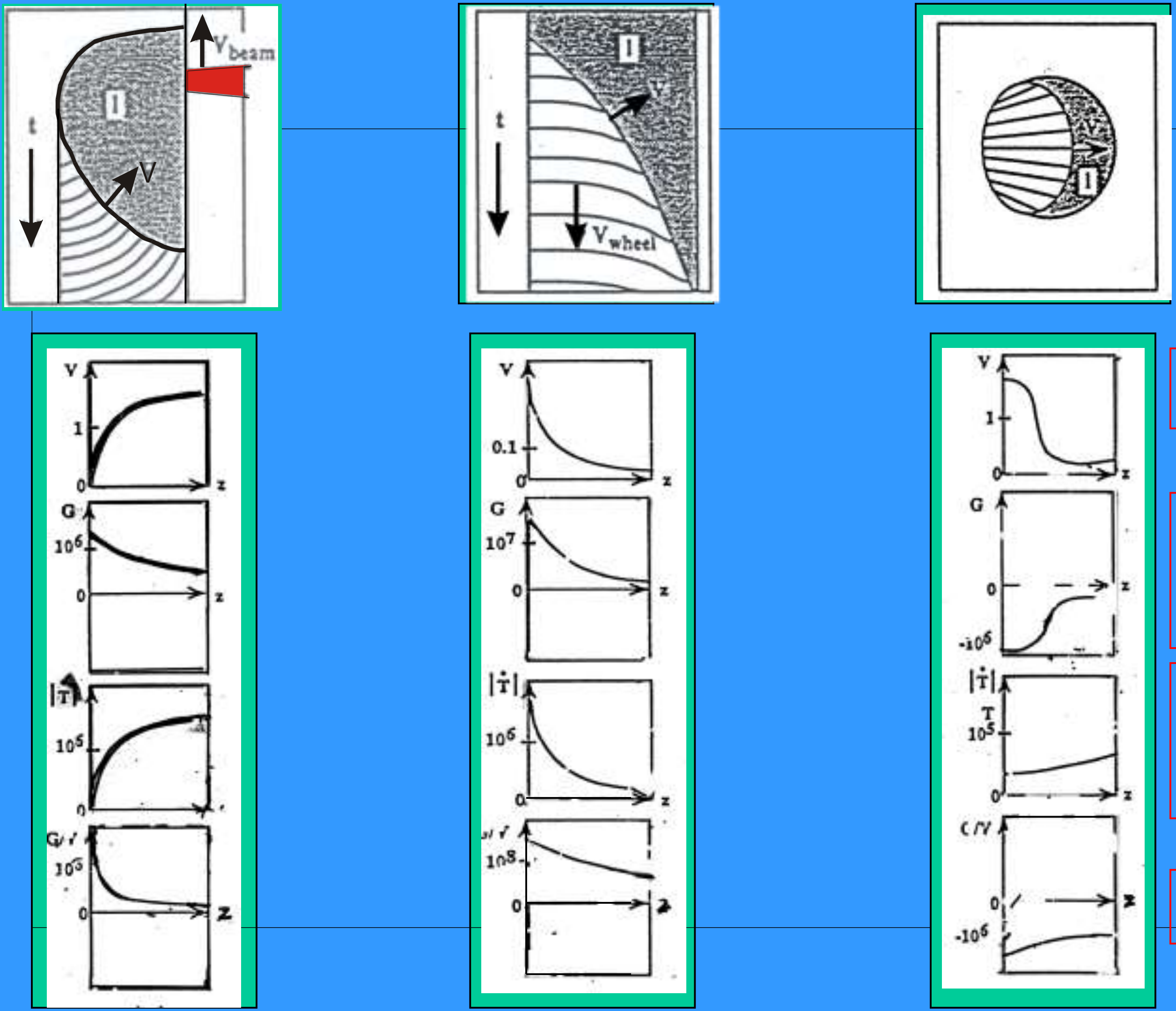
W. Kurz, D. J. Fisher, Fundamentals of Solidification;

TRANS. TECH. PUBL. 1992

Rapid solidification types

a. Laser surface remelting
b. Casting on rotation roller (melt spinning –chips)
c. Atomization (powder)

laser treatment **melt spinning** **atomization**



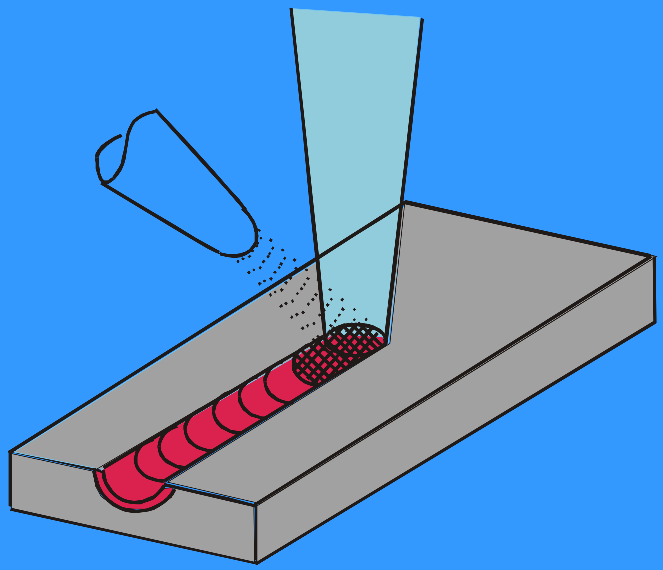
velocity (V)

temperature gradient (G)

cooling rate ($\dot{T}$)

G/V ratio

- **Laser Modification**
  - Nd:YAG
  - CO_2
  - Diode laser



Cross-section of the laser remelted zone

(Pau 7.5)

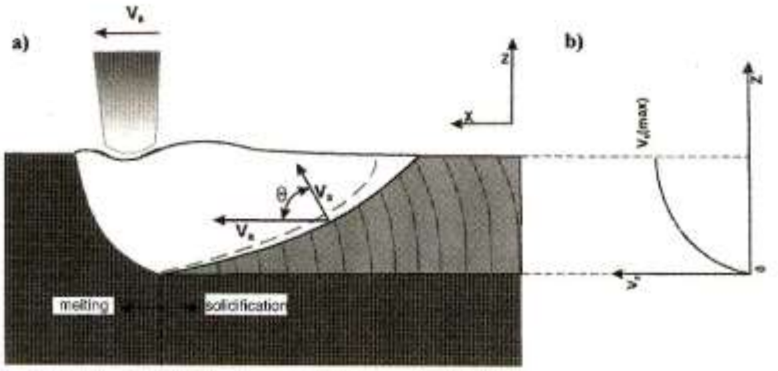
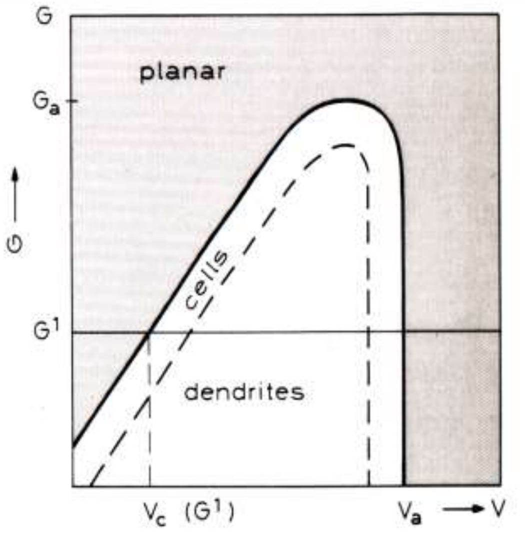


Figure 7.5: Scheme of longitudinal cross-section of laser track: (a) local solidification rate $V_s = V_B \cos T$ and (b) variation of solidification rate with respect to axis z.

Change range of the stable morphology (flate) of the interphase boarder

(Pau 7.6)



Costitutional supercooling (Przechłodzenie stężeniowe) (Pau 7.7)

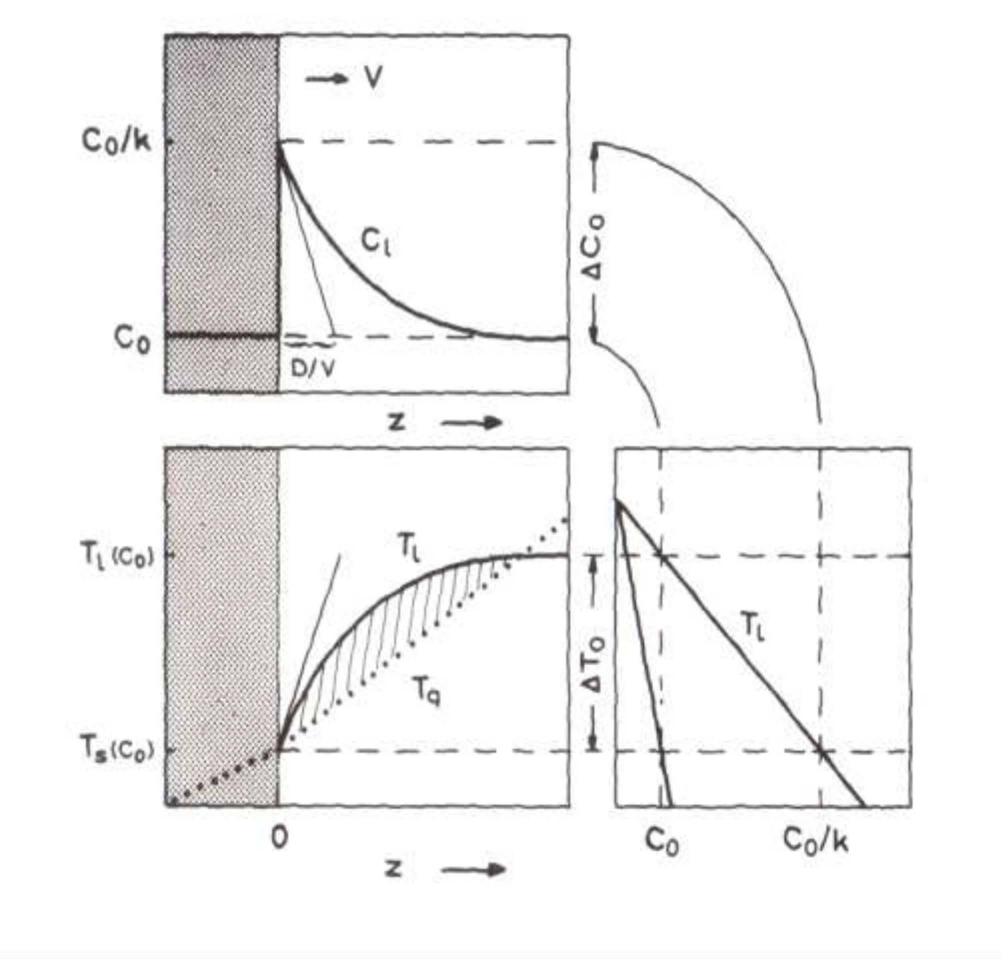
Local solidification equilibrium temperature (Lokalna równowagowa temperatura krystalizacji):

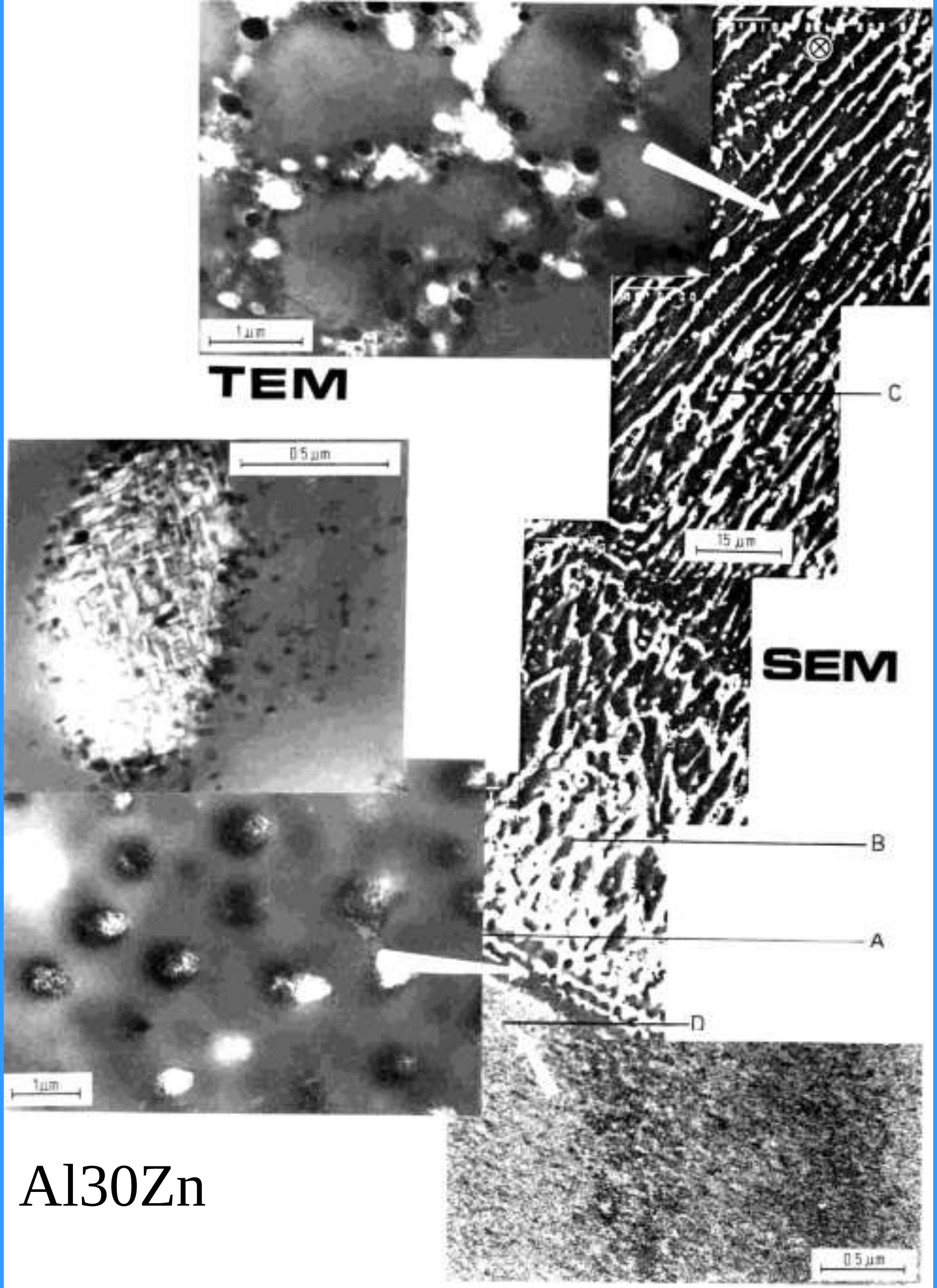
$T_1\ (C_0) - T_1 = m\ (C_0 - C_1\ )$

wher: $T_1\ (C_0)$ liquidus temperature for the initial content

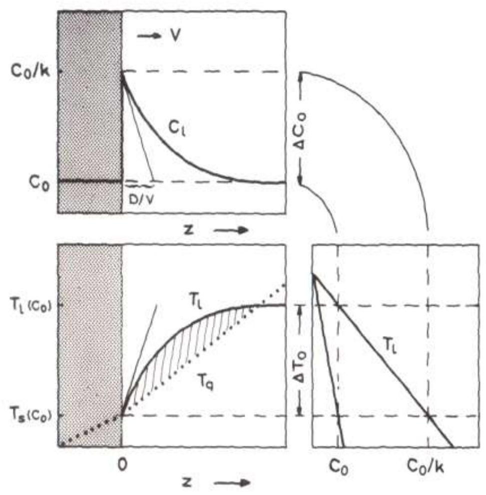
Temperature gradient:

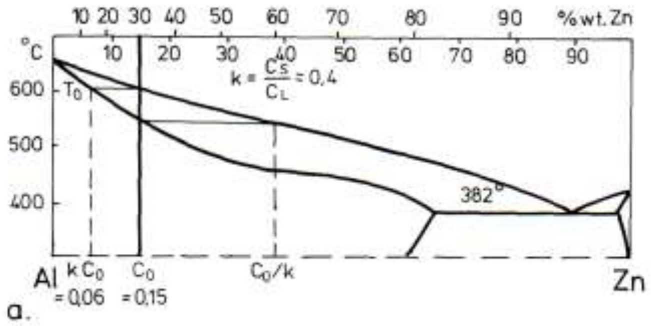
$G = (dT_q/dz)_{z=0}$

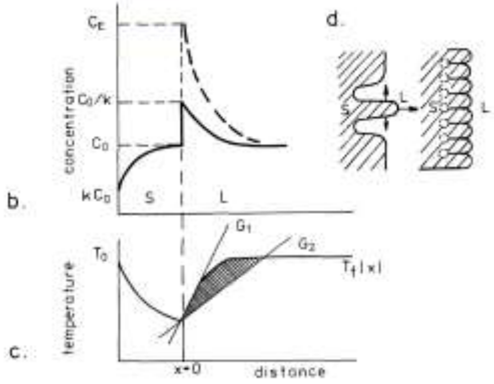



1 µm
TEM
0.5 µm
15 µm
SEM
C
B
A
D
1µm
0.5 µm

Al30Zn


→ V
C0/k
CL
ΔC0
C0
D/V
z →
TL(C0)
TL
Tq
ΔT0
TS(C0)
0
z →
C0
C0/k


10 20 30 40 50 60 70 80 90 %wt.Zn
°C
10 20 30 40 50 60 70 80 90
k = CS/CL = 0,4
600
T0
500
400
382°
Al
kC0 = 0,06
C0 = 0,15
C0/k
Zn
a.


CE
C0/k
C0
kC0
concentration
S
L
b.
d.
S
L
S
L
T0
G1
G2
Tf(x)
temperature
c.
x=0
distance

16. Szybkie laserowe protypowanie

Laser prototyping

- **Proces hybrydowy**

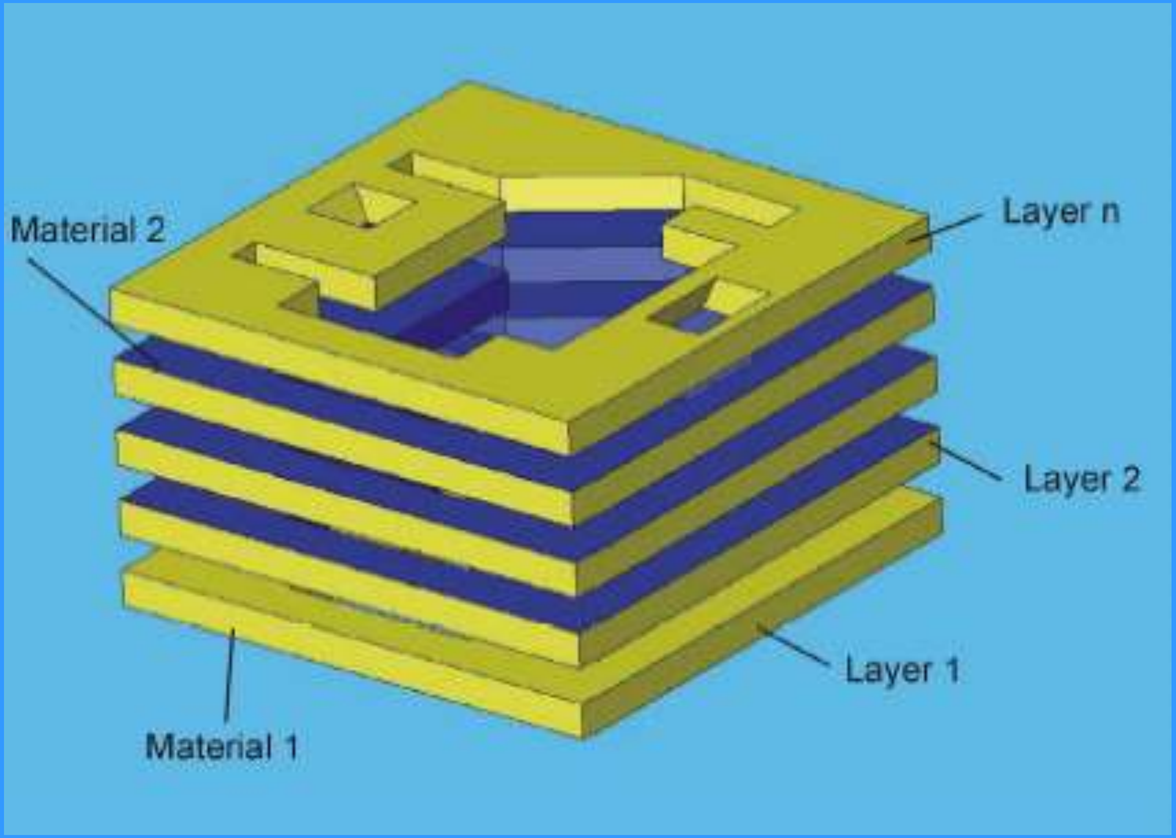
Laserowe natapianie + szybka obróbka nagniataniem

Hybrid manufacturing process

Laser cladding + high speed milling

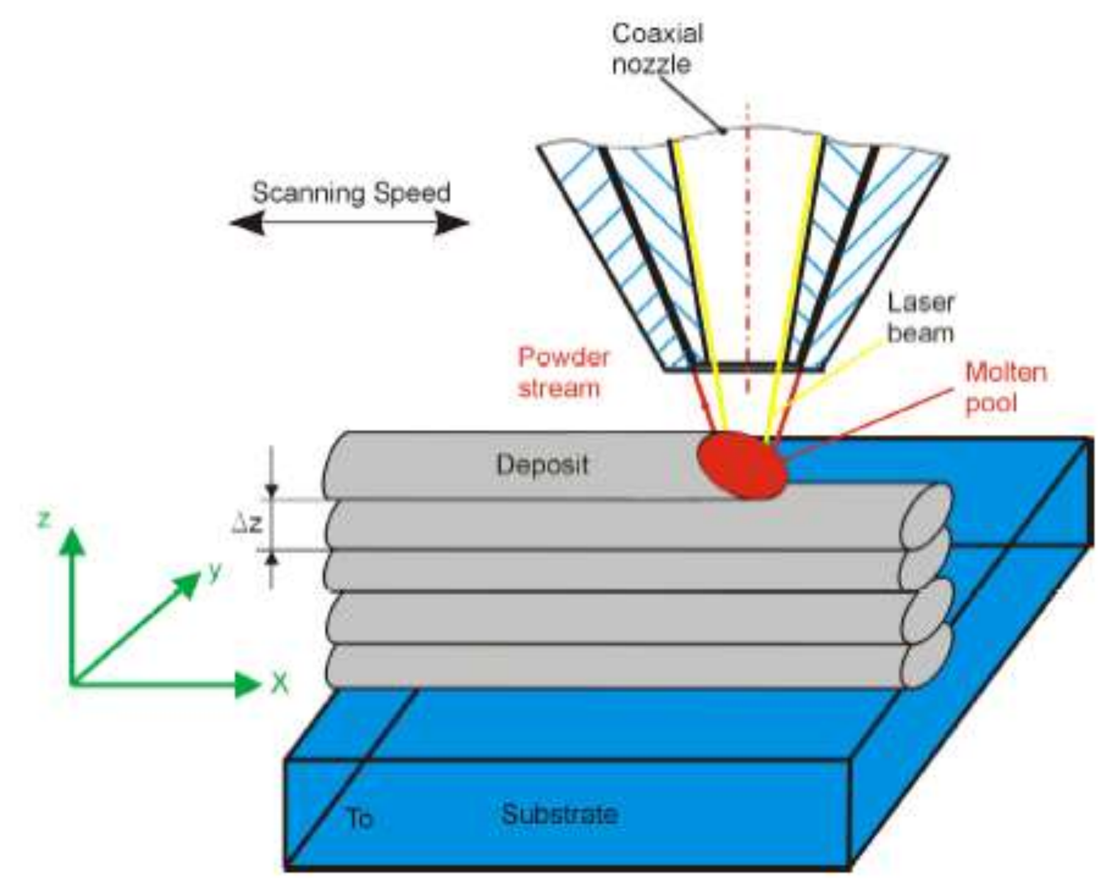
The Hybrid Concept

Combination of different metals within one part.

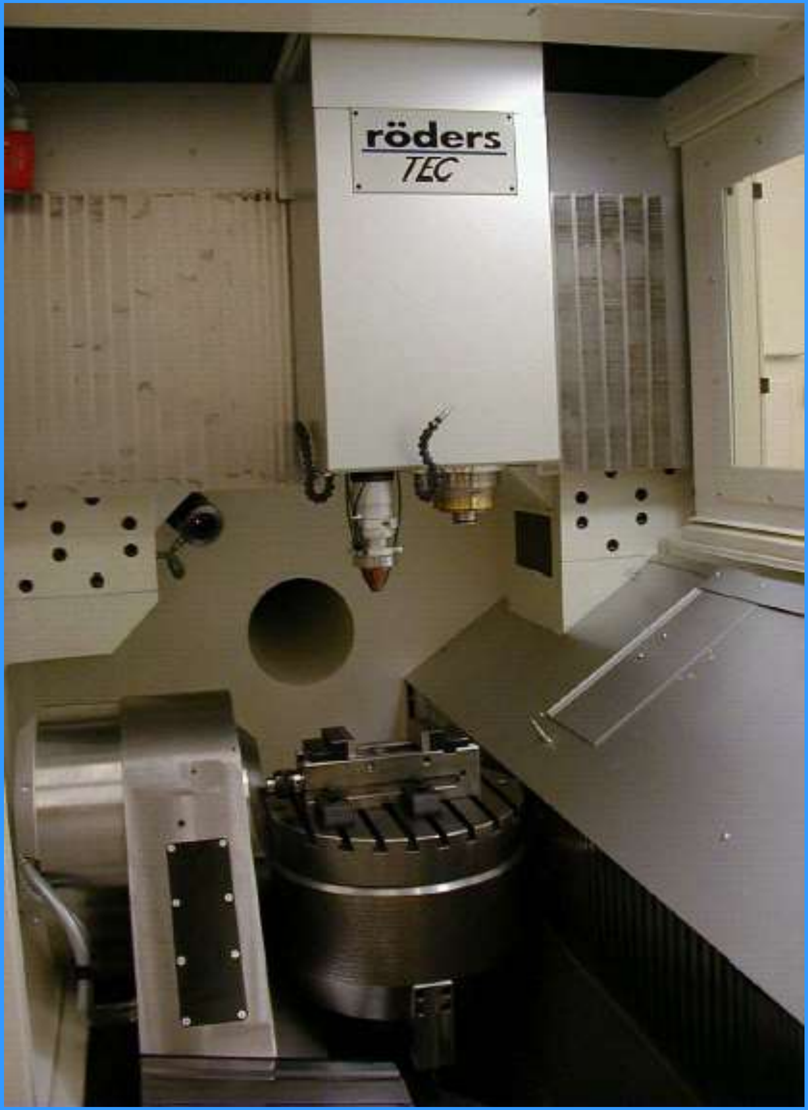


Introduction

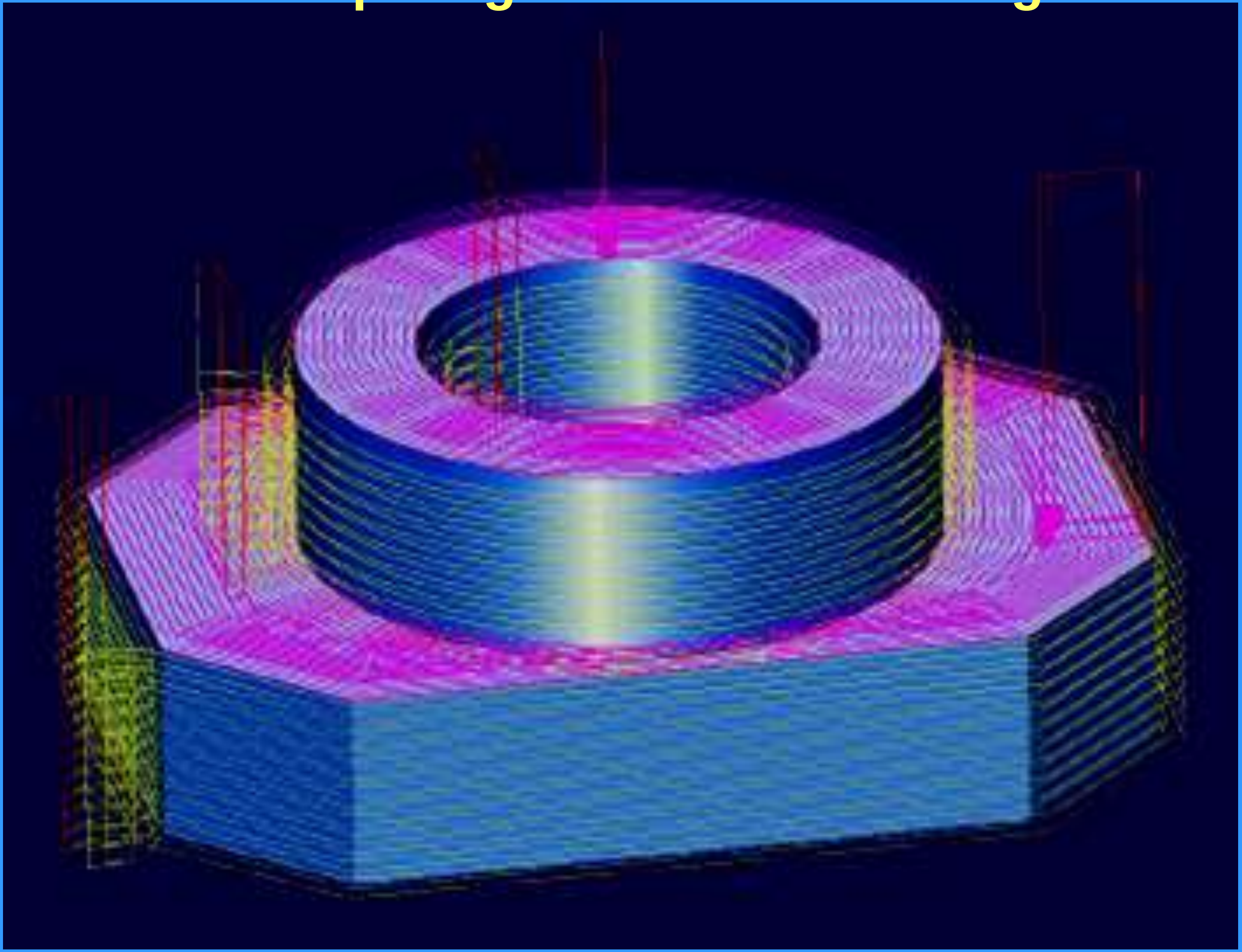
Schematic representation of the laser cladding process



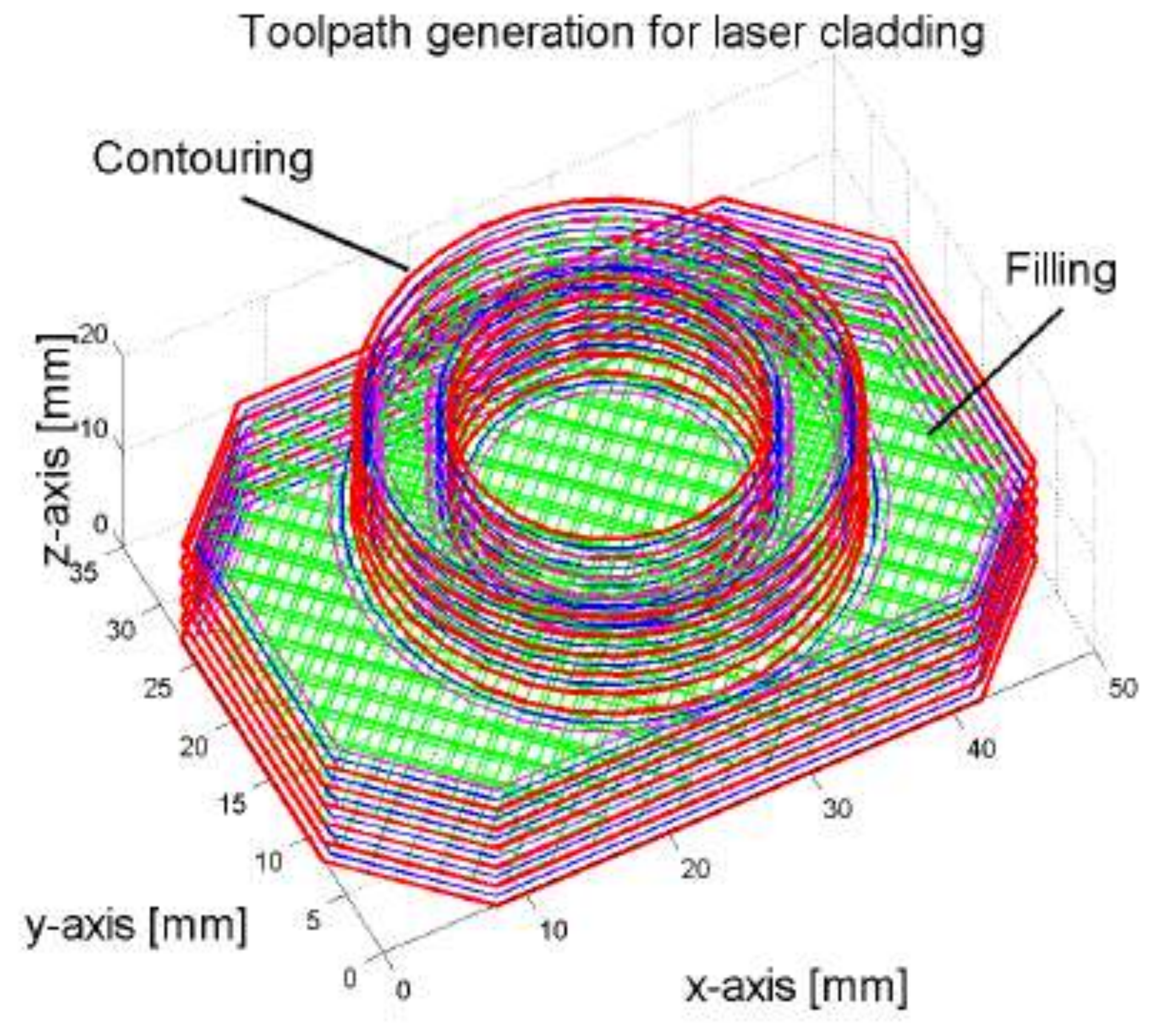
HSC milling machine combined with a Nd:YAG laser cladding nozzle.



Tool path generation for milling



Tool path generation for LC



Wineglass fabricated by 5-axis LC

11. Magnetron discharge plasma processes

Physical vapor deposition from the gas phase:

- evaporation
- sputtering
- spraying or ion-spraying, ion-plating

Sputtering sources

- diode sputtering system
- conventional magnetron
- unbalanced magnetron
- low-pressure magnetron
- magnetron-assisted ionization with electron beam or microwave discharge rf (13.56 MHz)
- ionized magnetron
- high-power, high-speed magnetron
- magnetron sputtering system with a closed box,
- dual magnetron

- Diode sputtering system

The substrate is immersed in the anode plasma

- Conventional magnetron

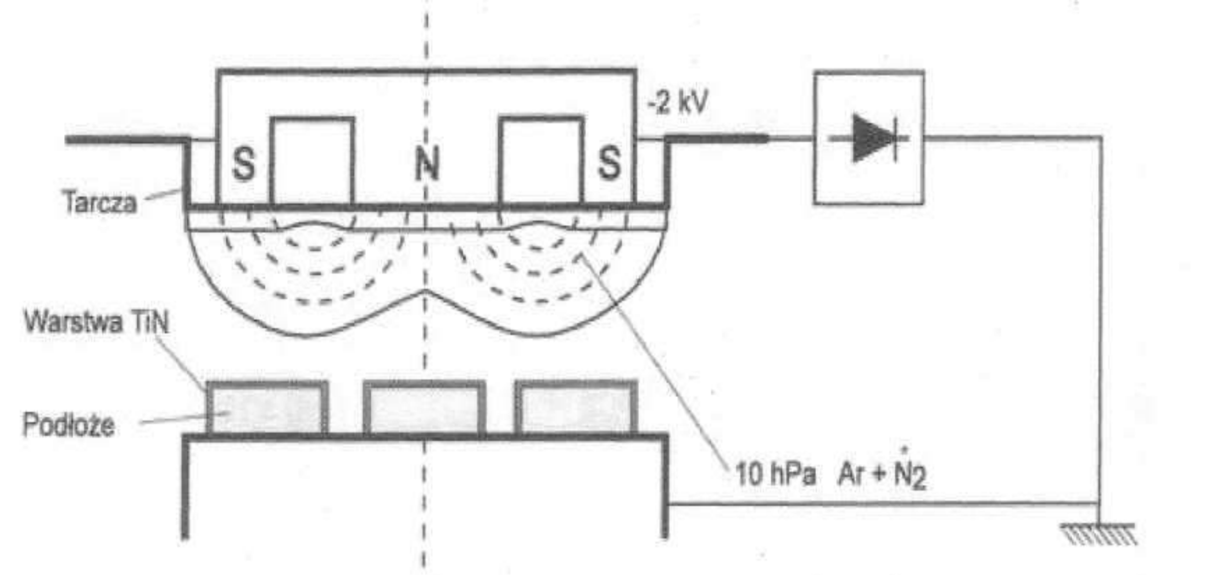
The magnetic field is applied to keep the glow discharge near the cathode (target) subjected to sputtering;

magnetic circuit is located outside the sputtered cathode to form over it semi-elliptic channel magnetic field

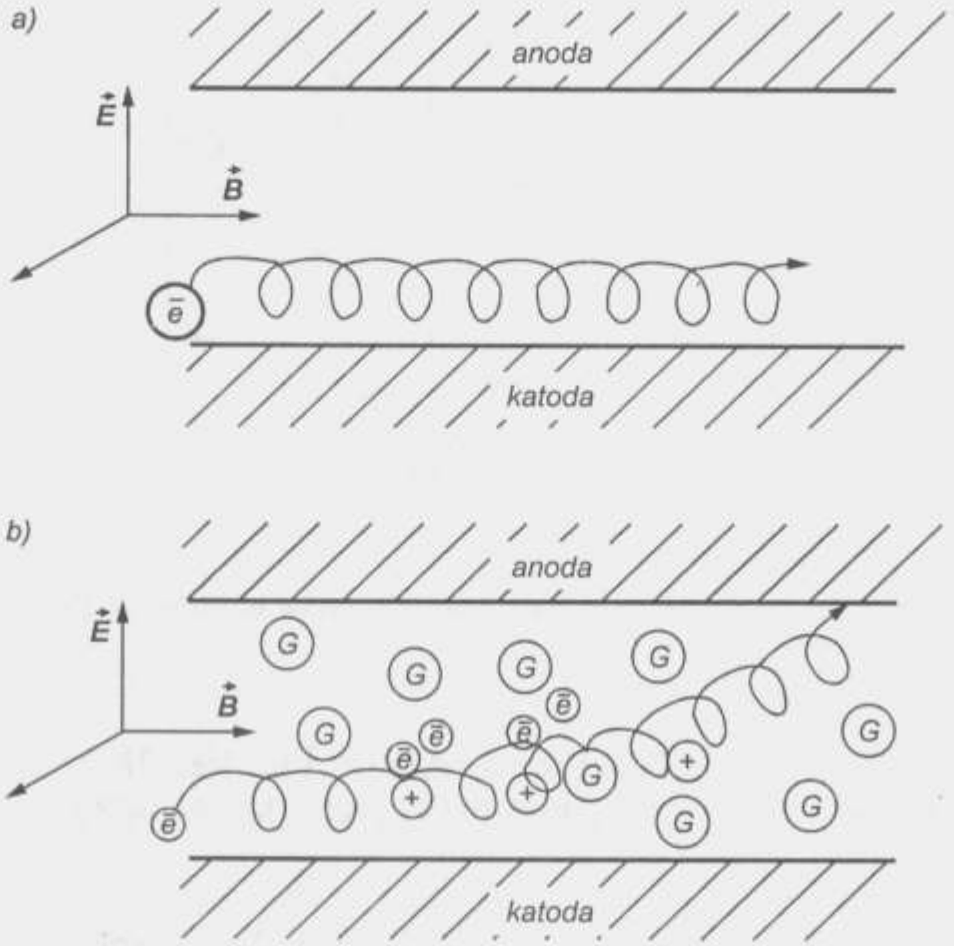
- Unbalanced magnetron

Because of the very important near the plasma confinement shield, the substrate is located in a low density plasma, the system is achieved by using an additional external magnetic circuit, the advantage is the possibility of continuous control over the field shield (s) and maintain a constant voltage at the glow discharge operating the target (ii)

Sputtering in the magnetic field, i.e. magnetron sputtering, extends the free path of electrons, so that you can have a density of ion current 10 - l00 times more than a simple sputtering, together with decreasing the pressure in the reaction environment (enclosure). Schematic diagram of the deposition of coatings using magnetron sputtering is shown below.



Schematic diagram of the magnetron sputtering



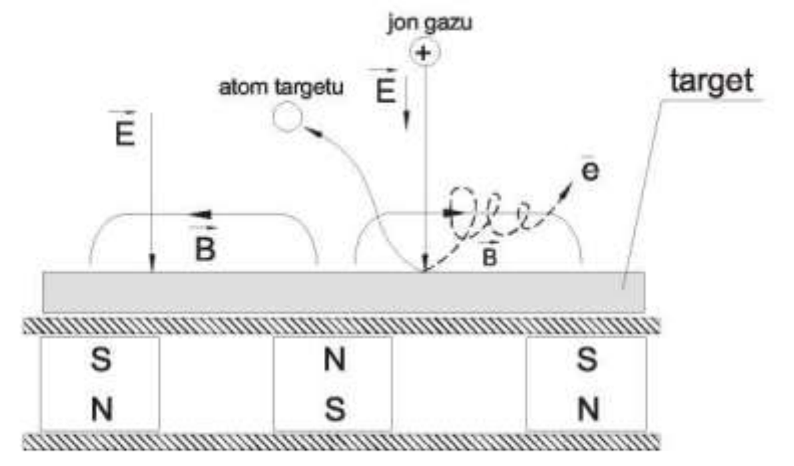
Ruch elektronu w skrzyżowanych polach ***E*** i ***B***: a) tor elektronu w gazie silnie rozrzedzonym (brak zderzeń), b) tor zakłócony zderzeniami z cząsteczkami gazu, powielanie elektronów

The movement of electrons in crossed E and B fields

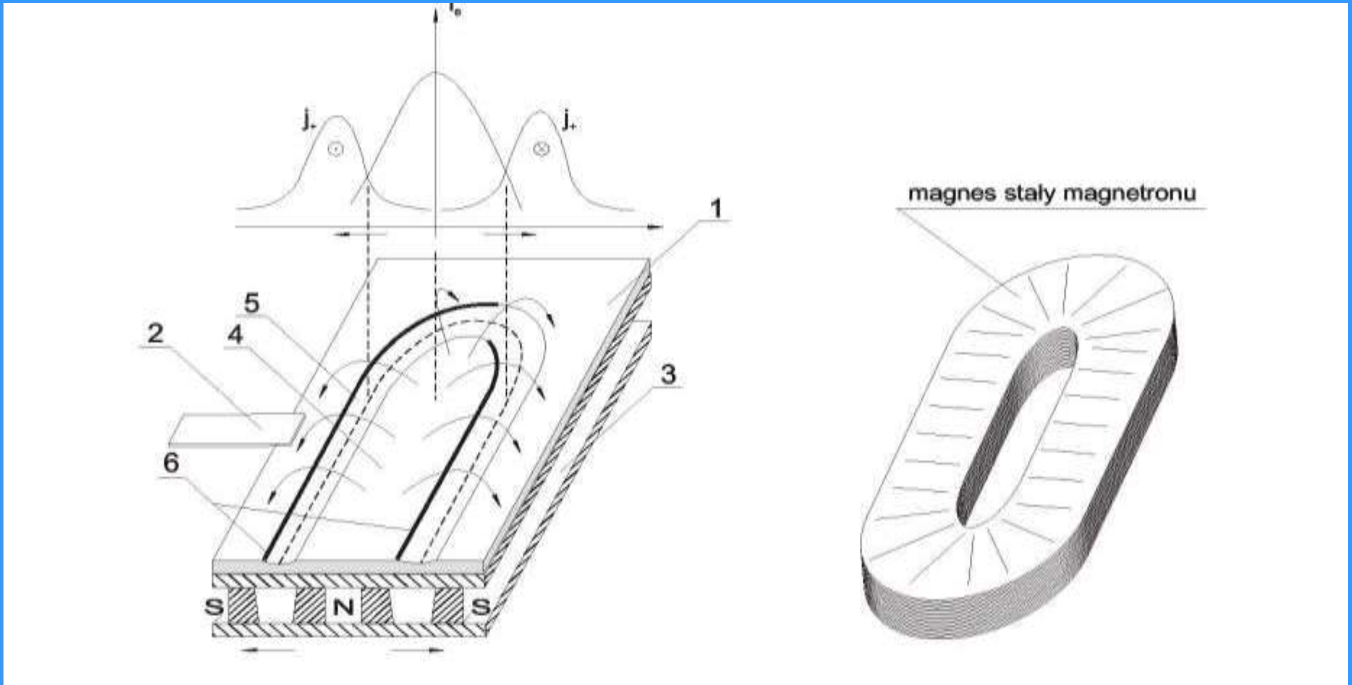
a. path of the electron in a highly rarefied (diluted)) gas (no collisions)

b disturbed path by collisions with gas particles (drift), duplication of electrons

Inhomogeneous magnetic field of the permanent magnet bends the path of the knocked electron from the target surface by ion bombardment and it runs tangentially along the lines of the magnetic field at the surface. The spiral motion (drift) of the electron increases the probability of collisions and thus strengthen the ionization. This reinforcement provides an increase in sputtering rate



The movement of electrons in crossed E and B fields

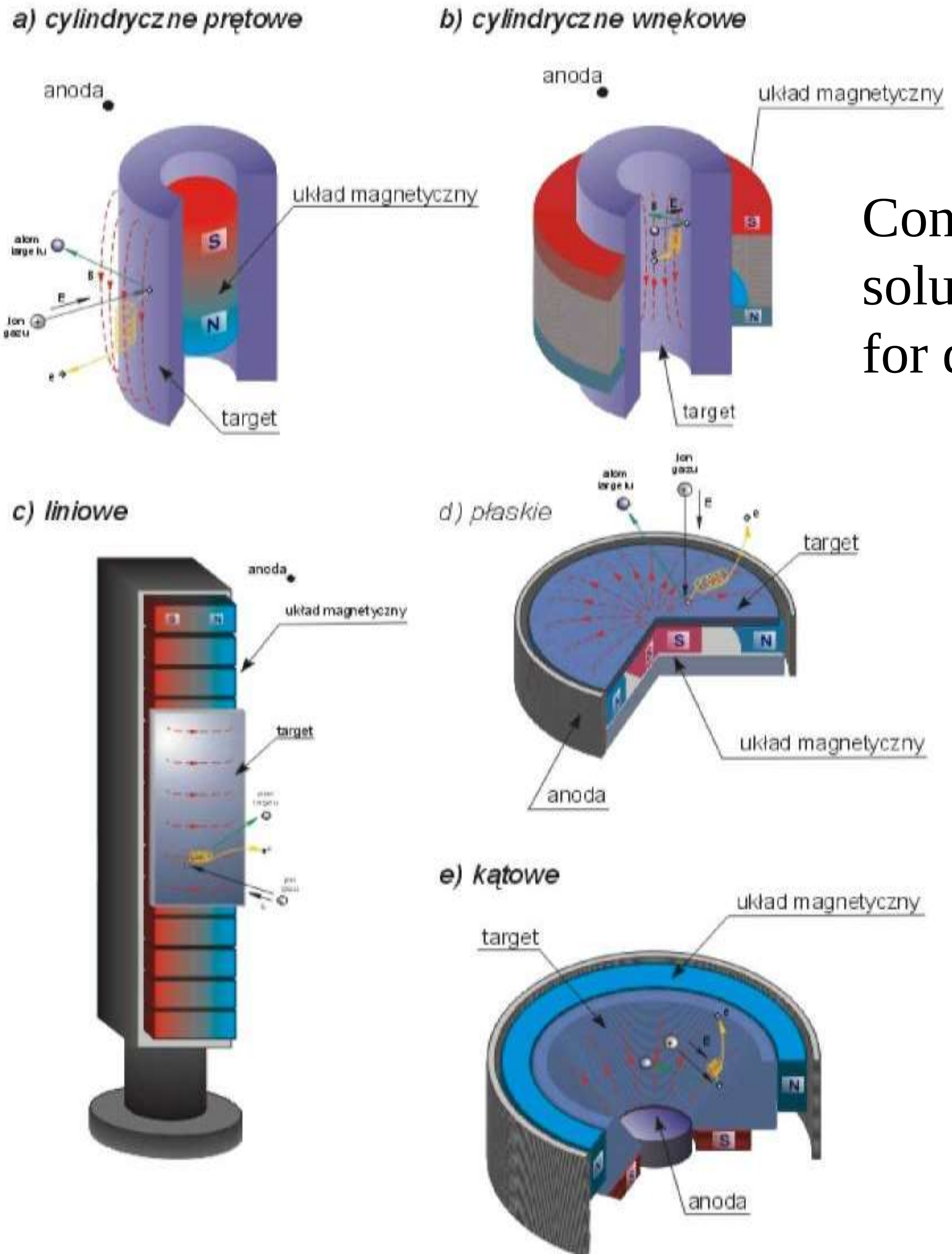


Magnetron source diagram (cross section) and permanent magnet

1 - target-cathode, 2 - anode
3 - pole shoe, 4 - space center
5 - space erosion, 6 - shoulder with a layer of secluded

1 - target-katoda , 2 - anoda
3 - nabiegunniki, 4 - przestrzeń środkowa
5 - przestrzeń erozyjna, 6 - pobocze z warstwą ustronną

Configuration of magnetic systems solutions
for different types of magnetrons



Rozwiązania konfiguracji układów magnetycznych do różnych typów magnetronów

Schemes (Pau 3.1)

(a) diode sputtering system

(b) conventional magnetron

(c) unbalanced magnetron

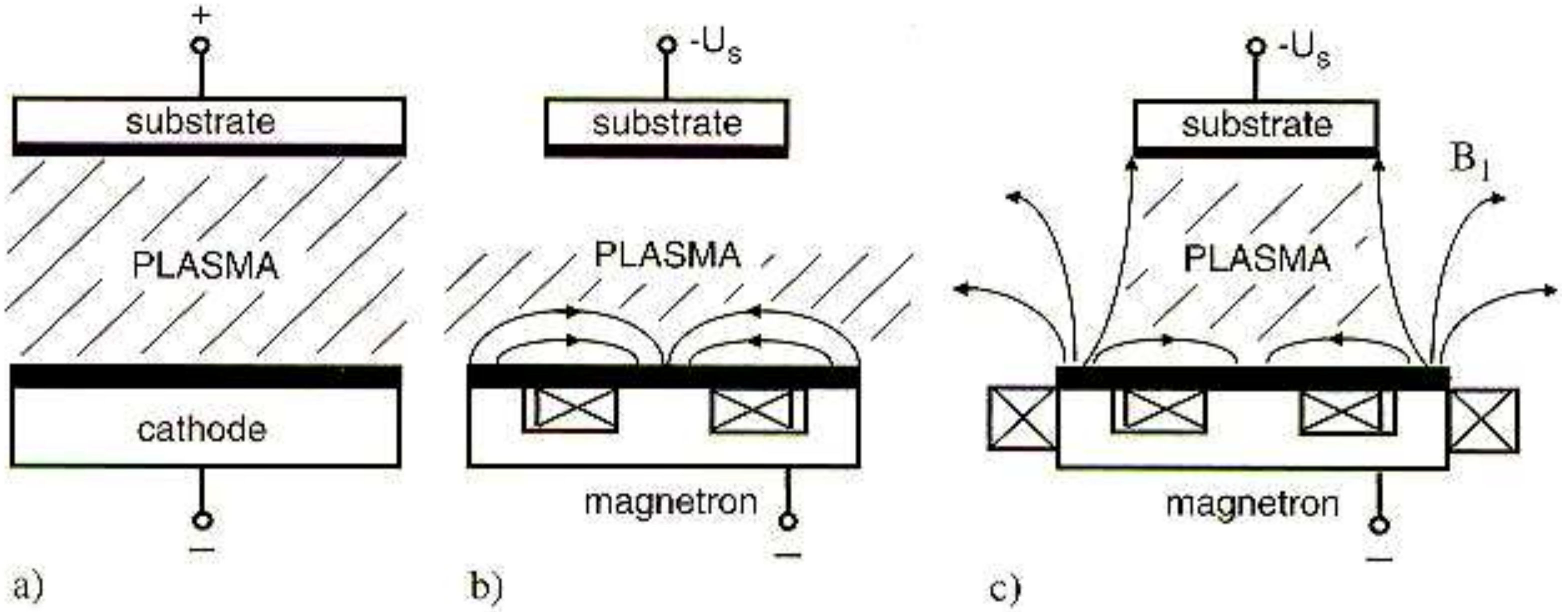


Figure 3.1: Comparison of (a) diode sputtering system with (b) CM and (c) UM.

- Low-pressure magnetron

  The main problem when sputtering at low pressure is the loss of charged particles from the discharge; to improve plasma confinement , the provision of auxiliary ionization of sputtered gas is used

The principle of low-pressure sputtering (Pau 3.2)

- (a) improving the plasma confinement
- (b) additional ionization

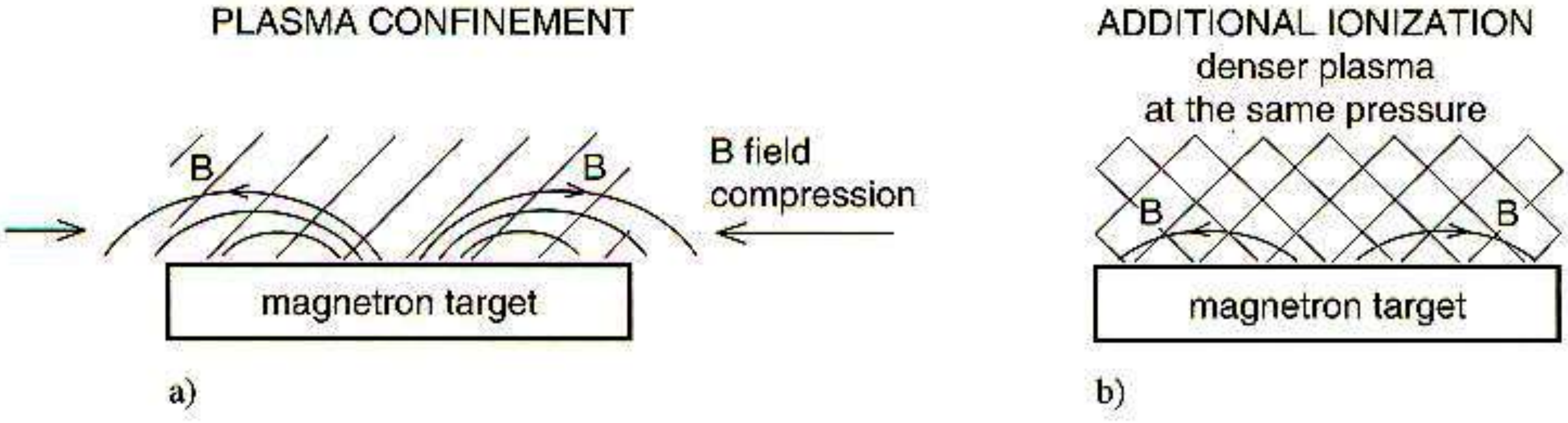


Figure 3.2: The basic principles of low-pressure sputtering discharge based on (a) the improvement of plasma confinement and (b) the additional ionization of magnetron discharge.

- Magnetron-assisted ionization with electron beam or microwave discharge rf (13.56 MHz)

Loss of charged particles can be compensated by additional ionization of the gas sputtering

- Magnetron with additional gas ionization (Pau 3.4)

a. conventional magnetron with an electron beam from a hot cathode

b. conventional magnetron with an arc source of hollow cathode

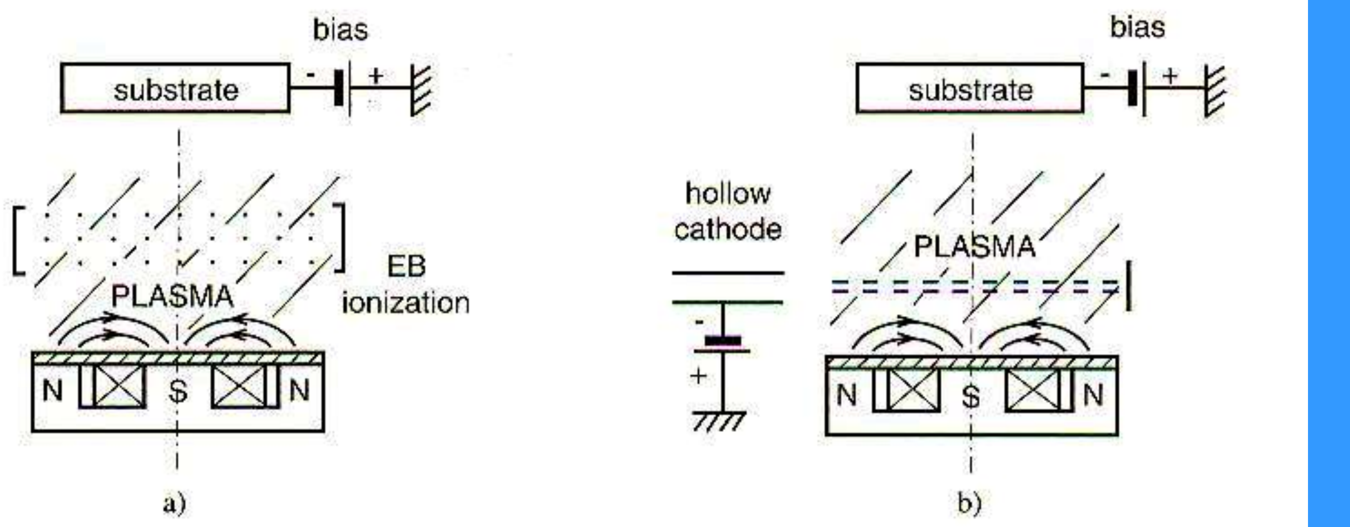


Figure 3.4: Magnetron with additional gas ionization (a) CM with the hot cathode electron beam and (b) CM with the hollow cathode arc electron source.

- Ionizing magnetron

During the magnetron discharge Ar + ions are mainly present, ionization of sputtered atoms is small about .1% or less, but very important for the application (to improve the deposition uniformity in narrow gaps) coil are used between the magnetron and the ground

The principle of the ionizing magnetron (Pau 3.5)

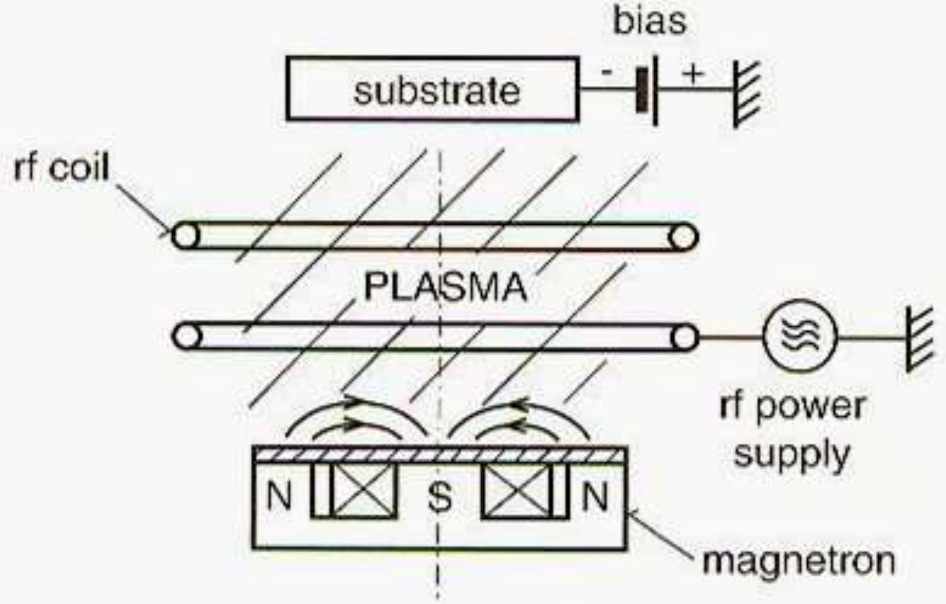


Figure 3.5: Schematic principle of IM.

- Magnetron sputtering system with a closed box
- Dual magnetron

Excellent trapped plasma during magnetron discharge is the basic assumption for the optimization of processes in advanced magnetron; systems with one or more magnetrons operating in the closed configuration are used

System Diagram with four magnetrons in a closed configuration (Pau 3.7)

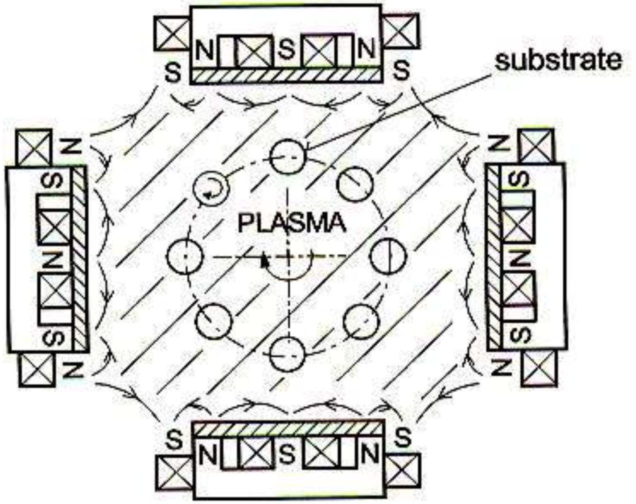


Figure 3.7: Schematic diagram of the sputtering machine with four magnetrons in a closed **B** field configuration.

Depending on the parameters of the sputtering the following process are distinguished:

- Not-reactive sputtering at constant current (dc) or frequency (rf)

2. Reactive sputtering
3. Argon ion-assisted sputtering
4. Low-pressure sputtering
5. Pulsed dc or rf sputtering
6. High-rate sputtering
7. Self-sputtering
8. Sputtered material ions assisted sputtering
9. Pulsed bias voltage sputtering (bias)
10. Low-energy bias sputtering

Processes 1-4 are used

Processes 5-10 in preparation for the implementation

- High-power, high-rate magnetron

Typical magnetrons have powers ranging from a few W/cm^2 to 10 W/cm^2, the reason for the development of high power magnetrons is:

- increase of deposition rate and shorten the process time
- alternative technologies to replace fast but toxic galvanic methods
- improvement of ionization of sputtered material
- elimination of gas formed in the process of sputtering

Argon is typically used in sputtering

Due to the level of gas pressure p_{Ar} magnetrons are divided into four groups:

1. Conventional sputtering p_{Ar} of ≥ 0.1 Pa
2. Low-pressure sputtering $p_{Ar} \leq 0.1$ Pa
3. Quick sputtering with $p_{Ar} > p_0 \approx 10\text{-}3$ Pa
4. Self-sputtering at $p_{Ar} = 0$

12. Surface modification by ion impact

- Surface modification of materials by plasma immersion and ion implantation (Plasma Immersion Ion Implantation PIII)
- The impact of ions on the surface of materials

PIII – used to modify the surface of semiconductor, metal, insulator, the material is immersed in the plasma at a given potential (negative potential - pulse)

Depending on the source of the plasma:

gas (GPIII)

solid - metal (MPIII) - or cathode sputtering process

Diagram of gas system GPIII (Pal 4.1)

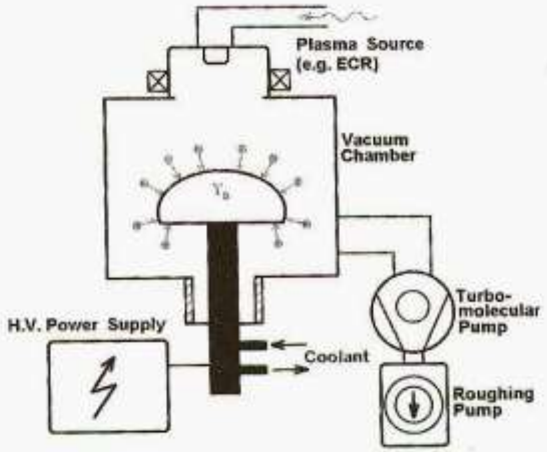


Figure 4.1: Schematic of the GPIII (reproduced with permission from Gunzel).

System diagram assisted by sputtering MPIII (Pal 4.5)

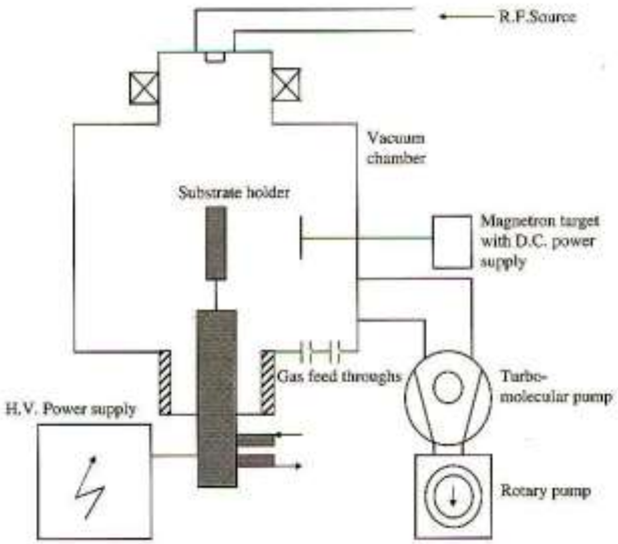


Figure 4.5: Schematics of the sputter-assisted MPIII [25].

The difference for plasma immersion (PIII) - the higher the energy, the occurrence arc controls the maximum energy

Energy source for ion implantation -

need to ionization of the gas or vapor using electrons with an energy of 100-200 eV (reduced pressure)

The principle of the process:

ions accelerated to high speed electrically hit the surface (they are implanted), and the goal is to improve the properties: electrical, tribological, corrosion, etc.

The system consists of:

ion source

high-voltage source

Application: for metals and alloys (mainly nitrogen ion implantation),

ceramics, polymers

Ion interaction with the surface

As a result of the impact of energetistic particles or atoms with the target occurs a number of processes (Pau 10.1)

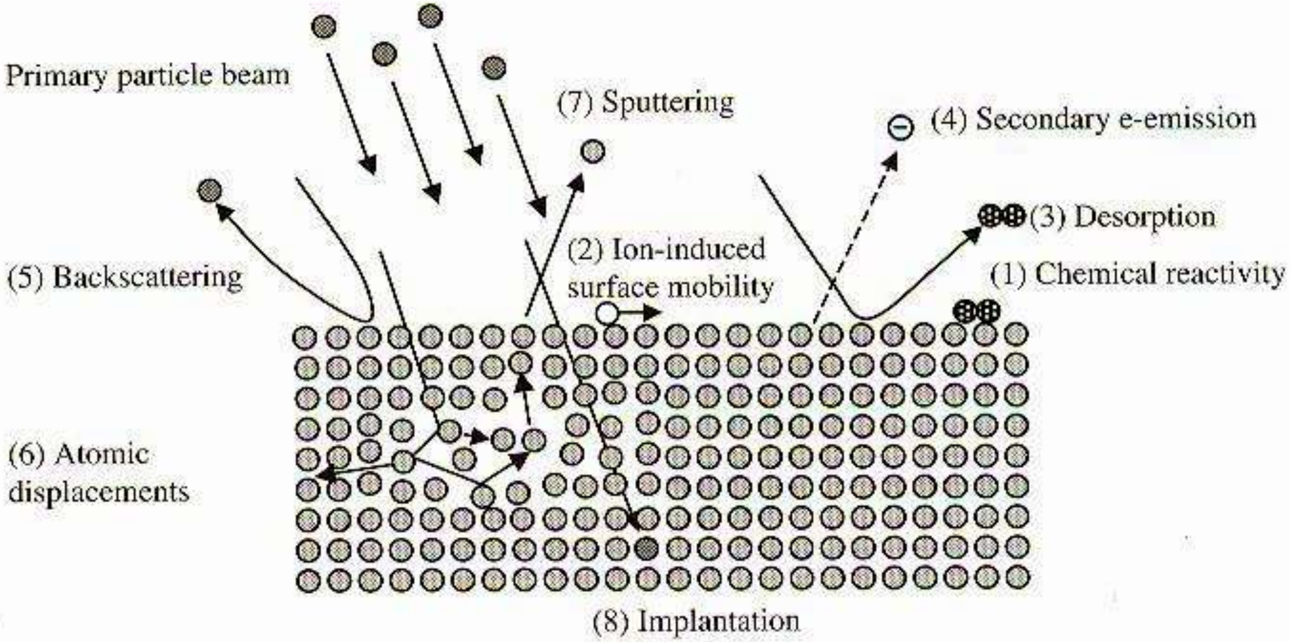


Figure 10.1: Scheme of ion-bombardment effects occurring at the surface and near-surface region of a solid (incoming ions = ●, chemical and adsorbed species = ⊕⊕, material atoms = ◎).

Sorting of effects of energetistic particle interaction with surface depending on the energy (Pau 10.2)

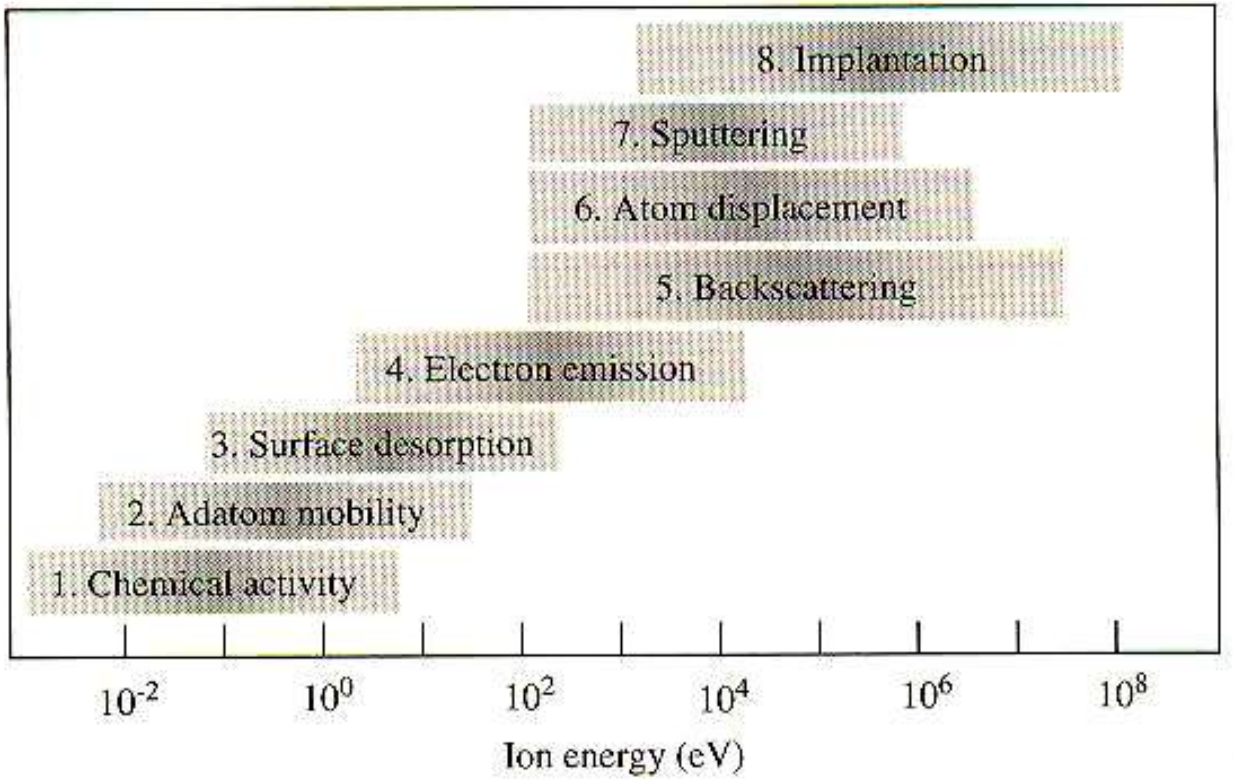


Figure 10.2: The different effects displayed in Fig. 10.1 sorted by their energy range.

13. Surface modification by plasma ion implantation

Selected ions are accelerated electrically to a high speed and driven or implanted into the workpiece to increase the properties (electrical, tribological, anti-corrosion)

The implantation system should have:

- Ion source
- High-voltage system
- Chamber to protect against electric punch

In addition: isotope separator system, vacuum (10-6 mbar) and vacuum control

14. Surface modification with low-energy and high-current electron beam

- Sources with a wide aperture ≥ 50cm2
- Low energy to about 40eV
- Large currents up to 50kA

by microsecond electron beam effects on matter

Effects caused by heat transfer:

-re-solidification

-controlled evaporation

-cleaning surfaces

-alloying under non-equilibrium conditions

15. Laser surface modification by melting

Rapid solidification → microstructure

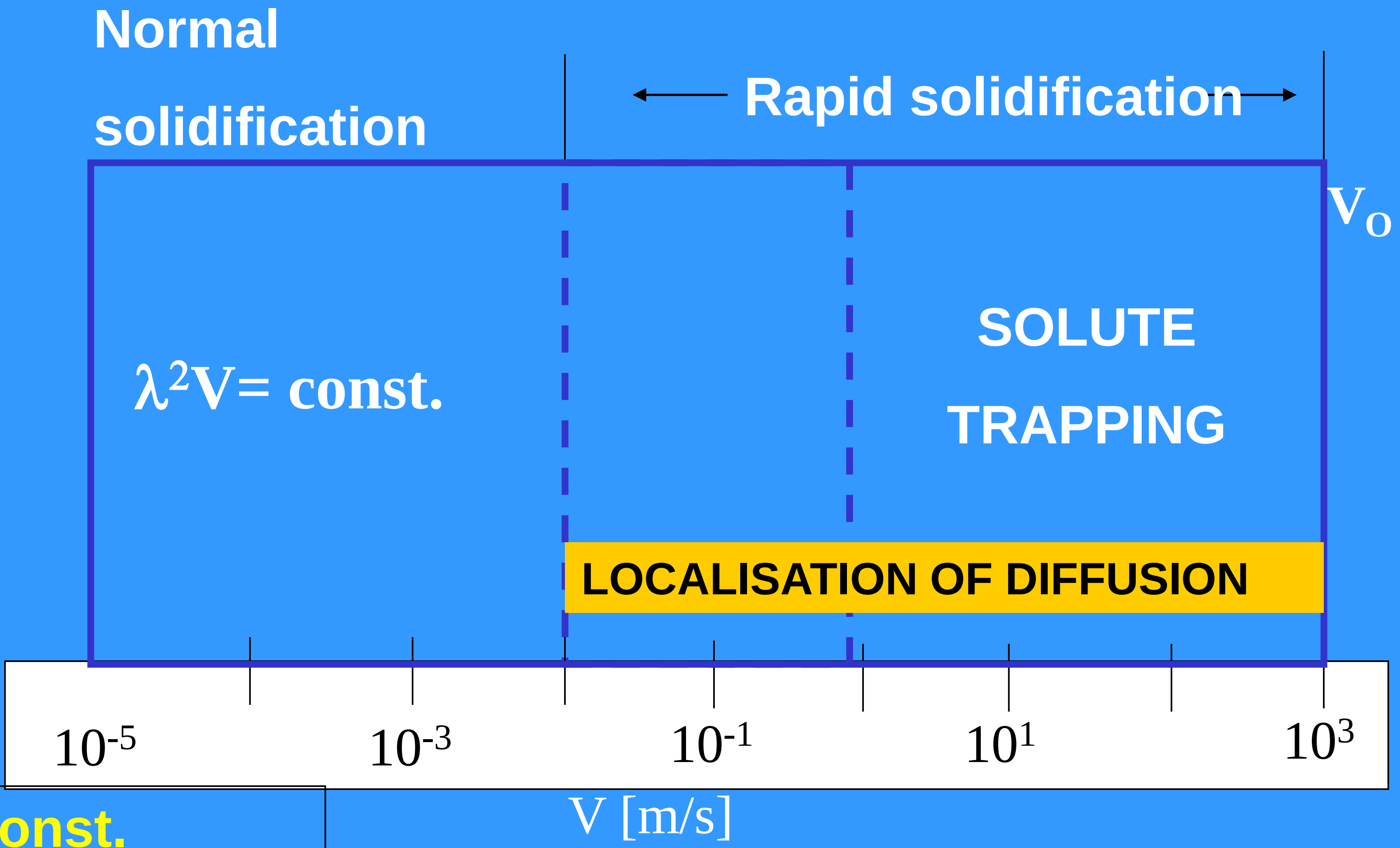
Location diffusion in the grain boundaries and width

The limited scope of collisions between atoms

15. Laserowa modyfikacja powierzchni poprzez przetopienie

Szybka krystalizacja → mikrostruktura

- Lokalizacja dyfuzji w obszarze ziaren i szerokości granic
- Ograniczony zakres kolizji pomiędzy atomami



Normal solidification

← Rapid solidification →

V_O

$\lambda^2 V = \text{const.}$

SOLUTE TRAPPING

LOCALISATION OF DIFFUSION

d^2V= const.

d- length of microstructure

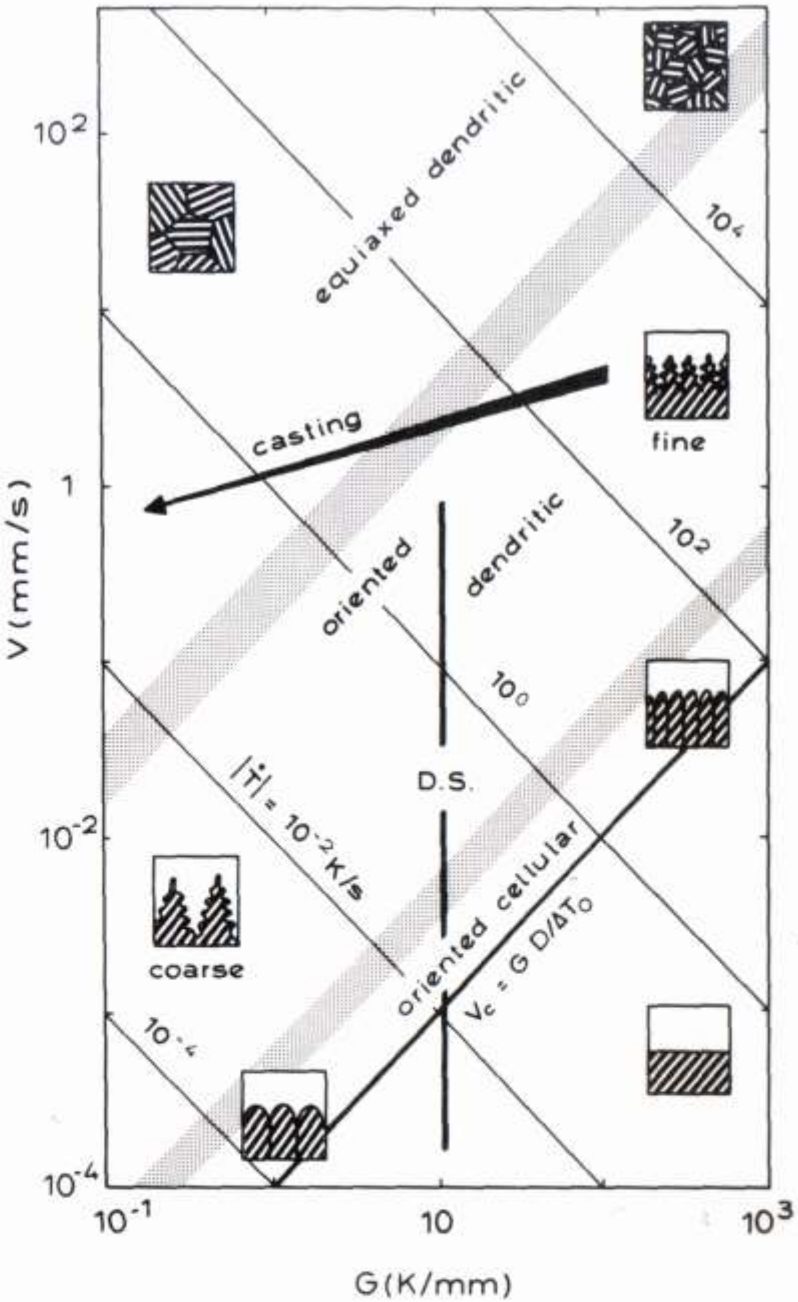
V- growth velocity

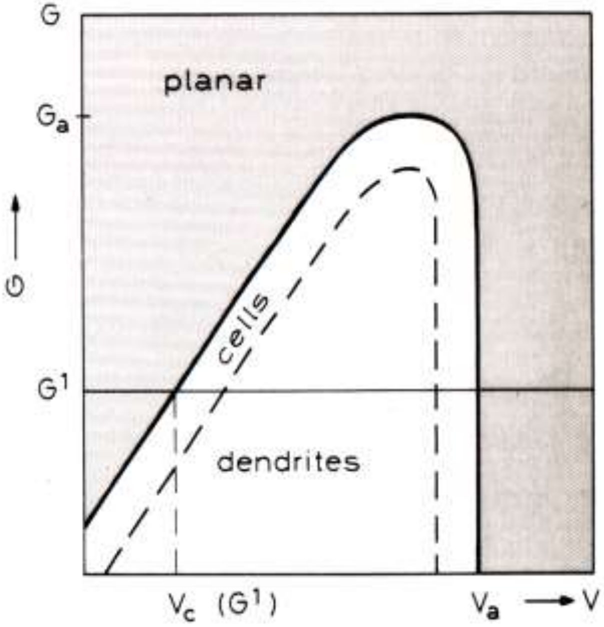
d represents either λ or R

λ–eutectic spacing

R- dendrite tip radius

Fundamentals of Solidification





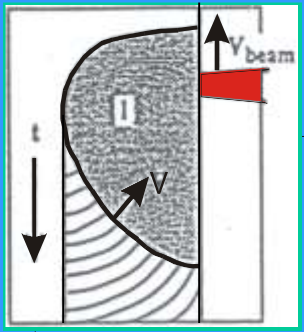
W. Kurz, D. J. Fisher, Fundamentals of Solidification;

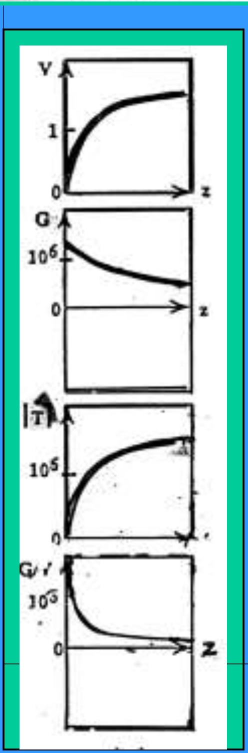
TRANS. TECH. PUBL. 1992

Rapid solidification types

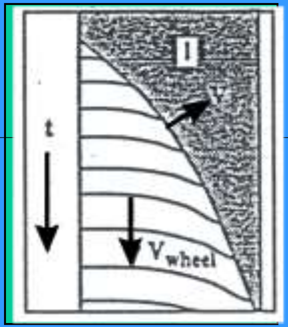
a. Laser surface remelting
b. Casting on rotation roller (melt spinning –chips)
c. Atomization (powder)

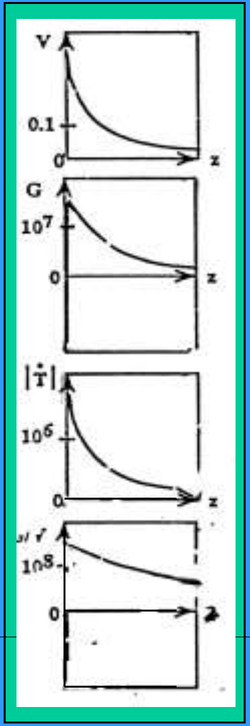
laser treatment



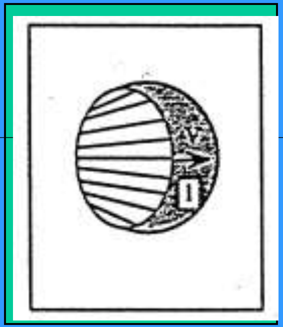


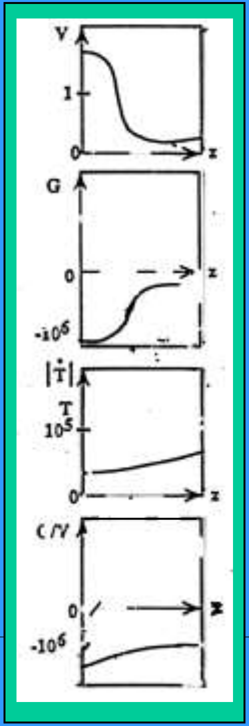
melt spinning





atomization





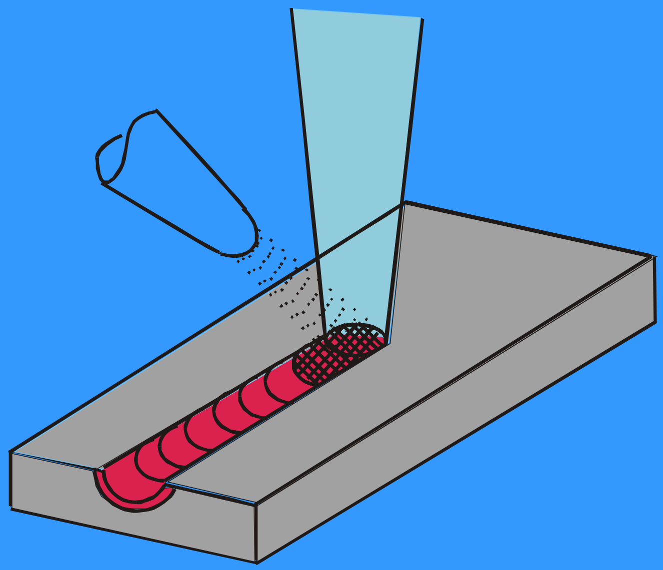
velocity (V)

temperature gradient (G)

cooling rate ($\dot{T}$)

G/V ratio

- **Laser Modification**
    - Nd:YAG
    - CO$_2$
    - Diode laser



Cross-section of the laser remelted zone

(Pau 7.5)

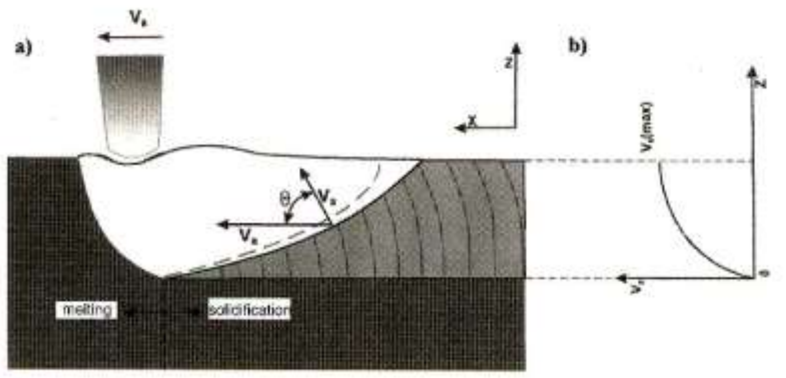
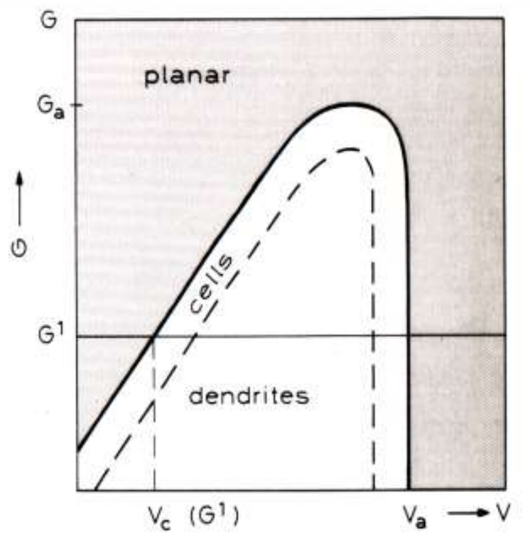


Figure 7.5: Scheme of longitudinal cross-section of laser track: (a) local solidification rate $V_s = V_B \cos T$ and (b) variation of solidification rate with respect to axis z.

Change range of the stable morphology (flate) of the interphase boarder

(Pau 7.6)



Costitutional supercooling (Przechłodzenie stężeniowe) (Pau 7.7)

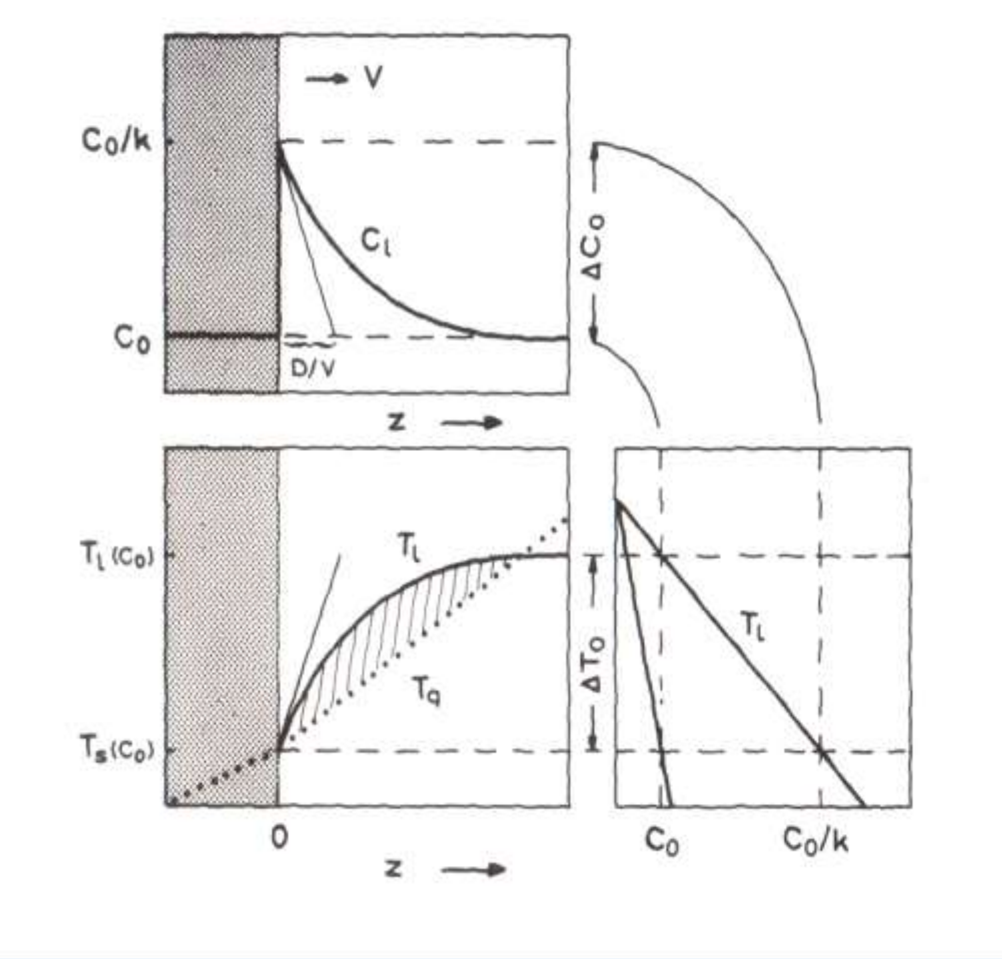
Local solidification equilibrium temperature (Lokalna równowagowa temperatura krystalizacji):

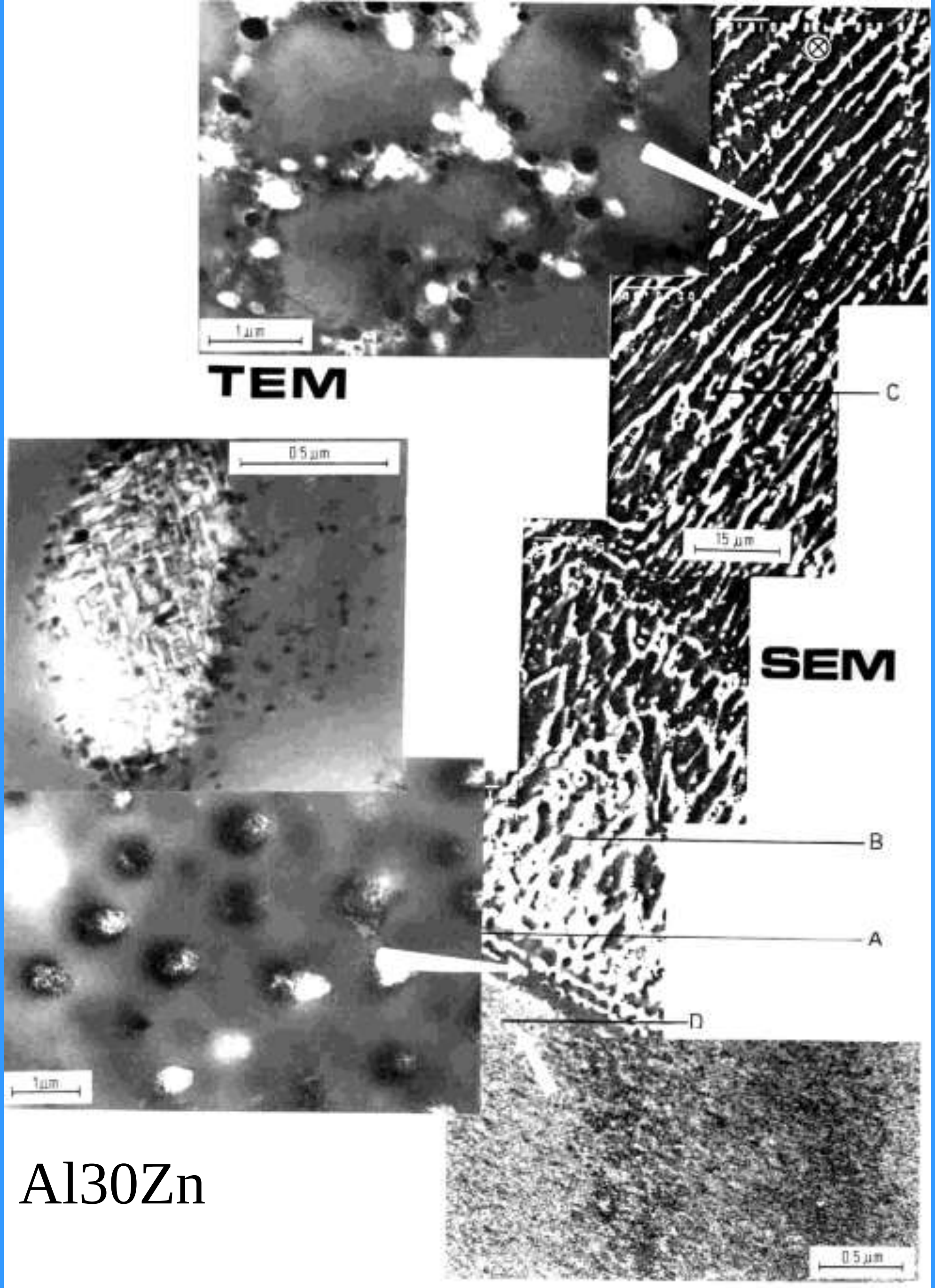
$T_1 (C_0) – T_1 = m (C_0 – C_1)$

wher: $T_1 (C_0)$ liquidus temperature for the initial content

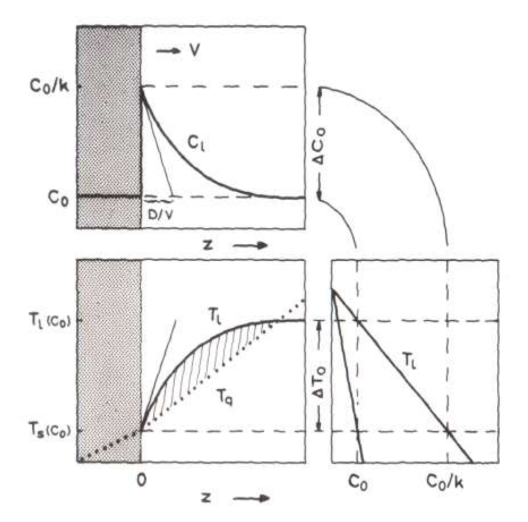
Temperature gradient:

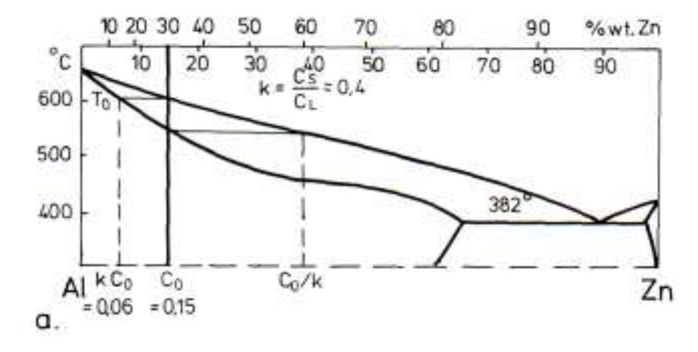
$G = (dT_q/dz)_{z=0}$

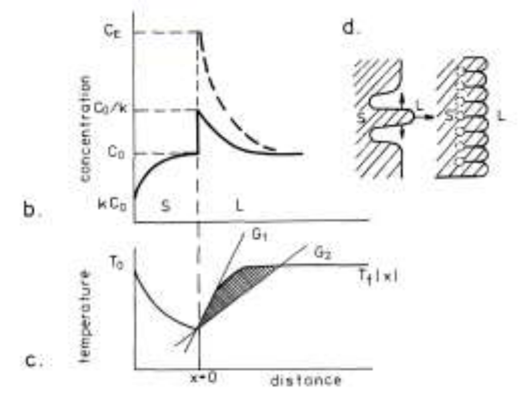



TEM
SEM
1 µm
0.5 µm
15 µm
C
B
A
D
1µm
0.5 µm

Al30Zn


V
C_0/k
C_L
ΔC_0
C_0
D/V
z
$T_L(C_0)$
T_L
T_q
ΔT_0
$T_s(C_0)$
0
z
C_0
C_0/k


10 20 30 40 50 60 70 80 90 %wt. Zn
10 20 30 40 50 60 70 80 90
°C
600
500
400
T_0
$k = \frac{C_S}{C_L} = 0{,}4$
382°
Al
$kC_0 = 0{,}06$
$C_0 = 0{,}15$
C_0/k
Zn
a.


C_E
C_0/k
C_0
kC_0
concentration
S
L
b.
d.
S
L
S
L
G_1
G_2
T_0
$T_f(x)$
temperature
c.
x=0
distance

16. Szybkie laserowe protypowanie

Laser prototyping

- **Proces hybrydowy**

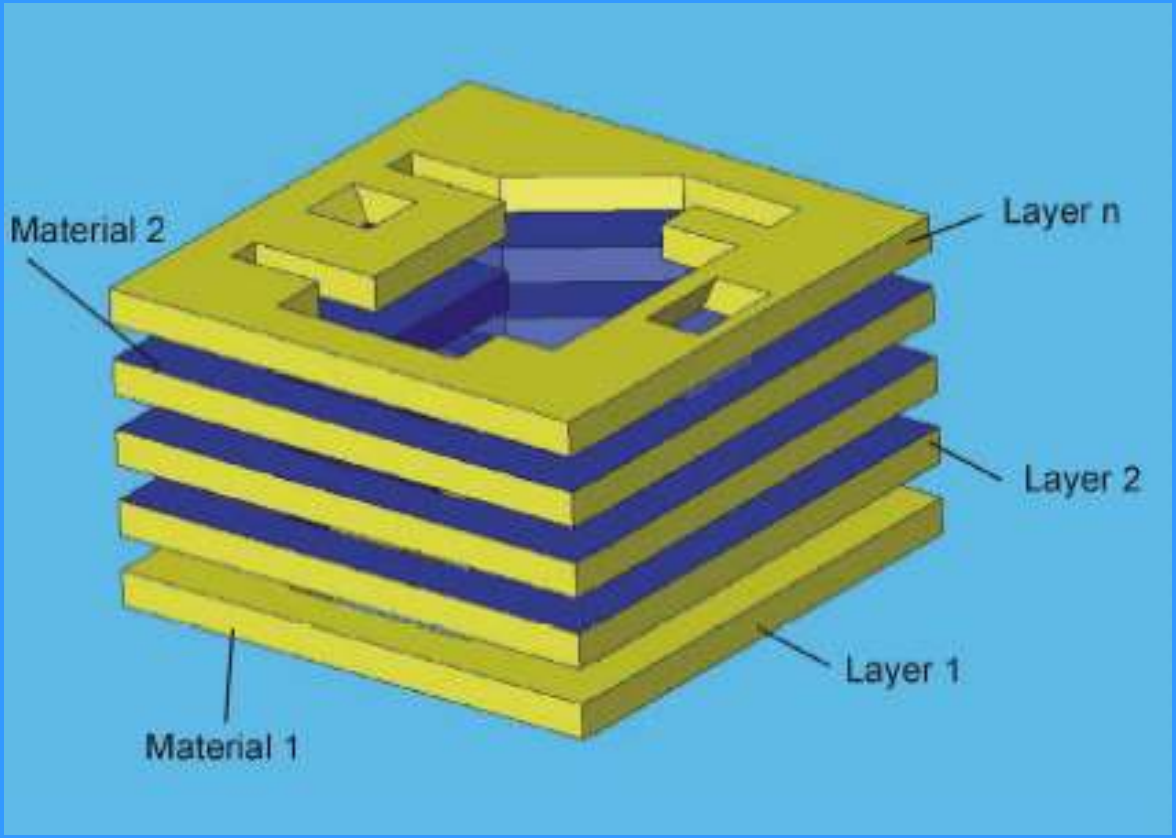
Laserowe natapianie + szybka obróbka nagniataniem

Hybrid manufacturing process

Laser cladding + high speed milling

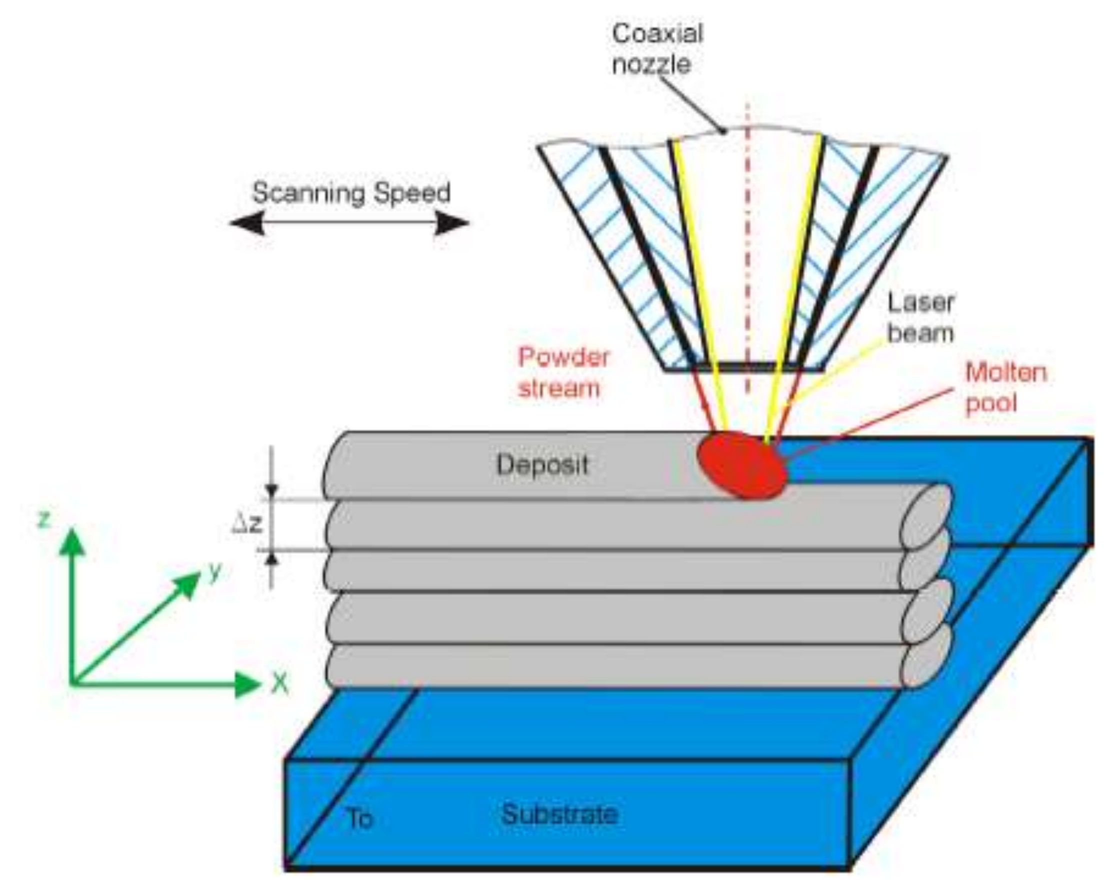
The Hybrid Concept

Combination of different metals within one part.

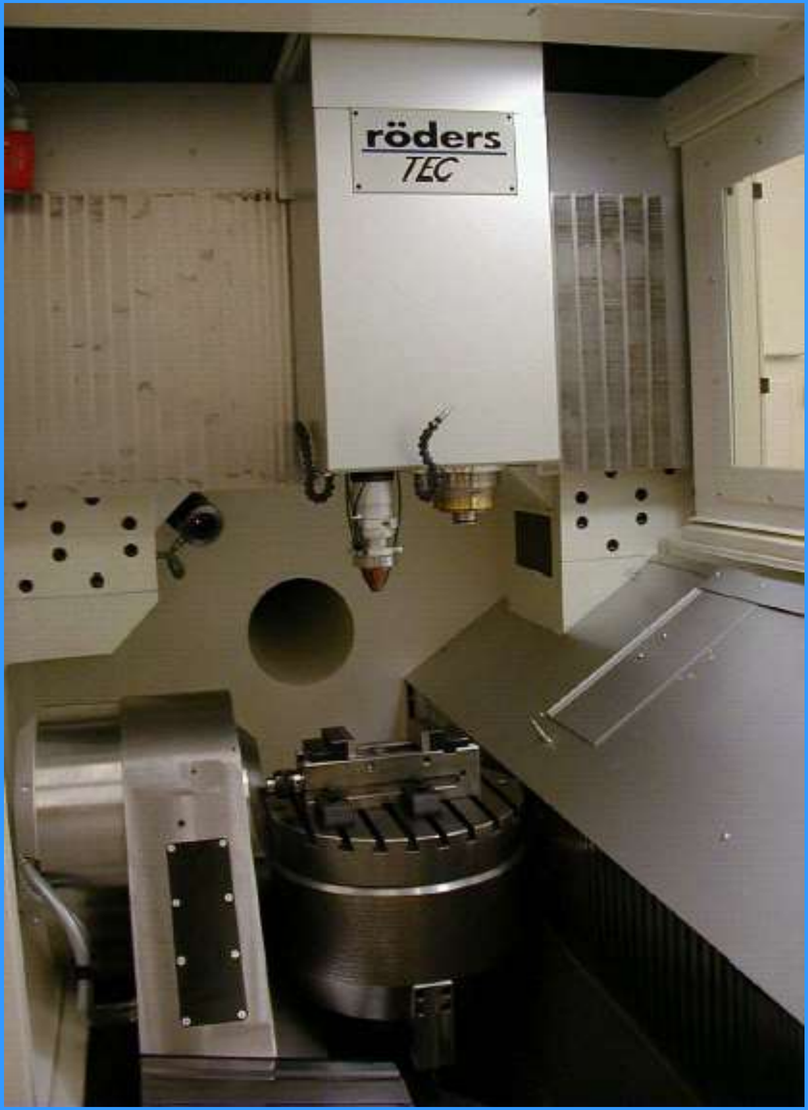


Introduction

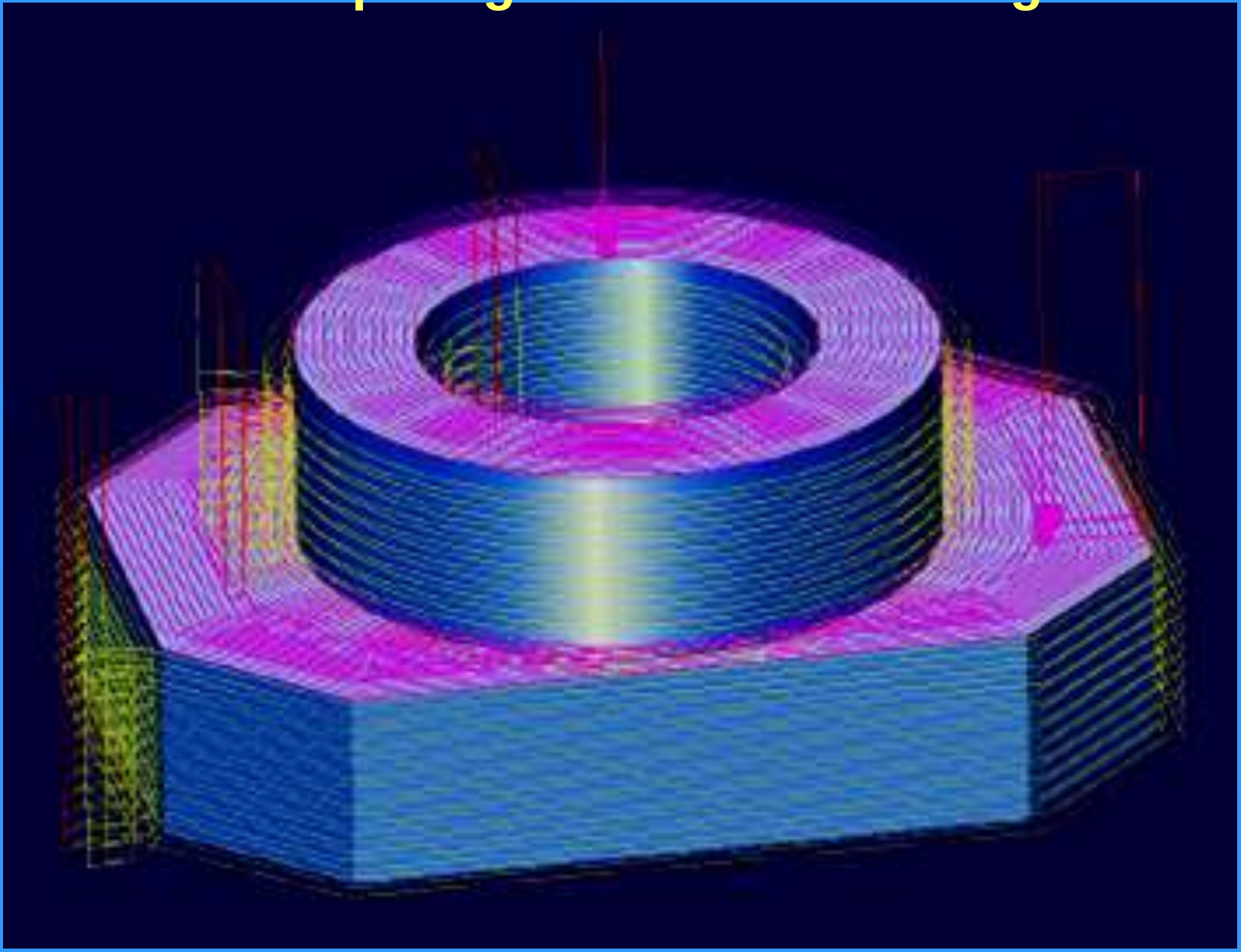
Schematic representation of the laser cladding process



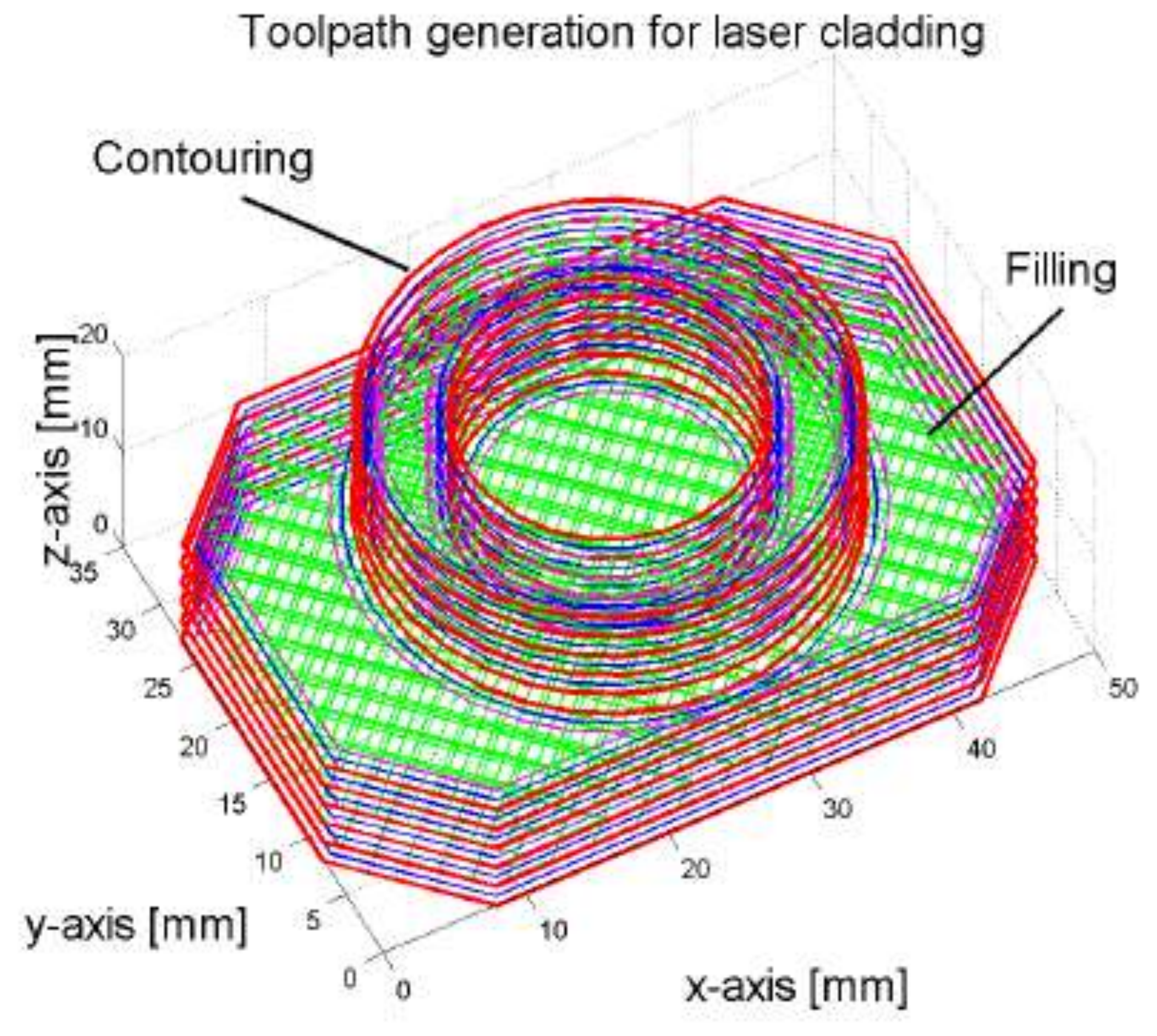
HSC milling machine combined with a Nd:YAG laser cladding nozzle.



Tool path generation for milling



Tool path generation for LC



Wineglass fabricated by 5-axis LC

17. Pulsed laser deposition with application of laser ablation

PLD method (pulsed laser deposition)

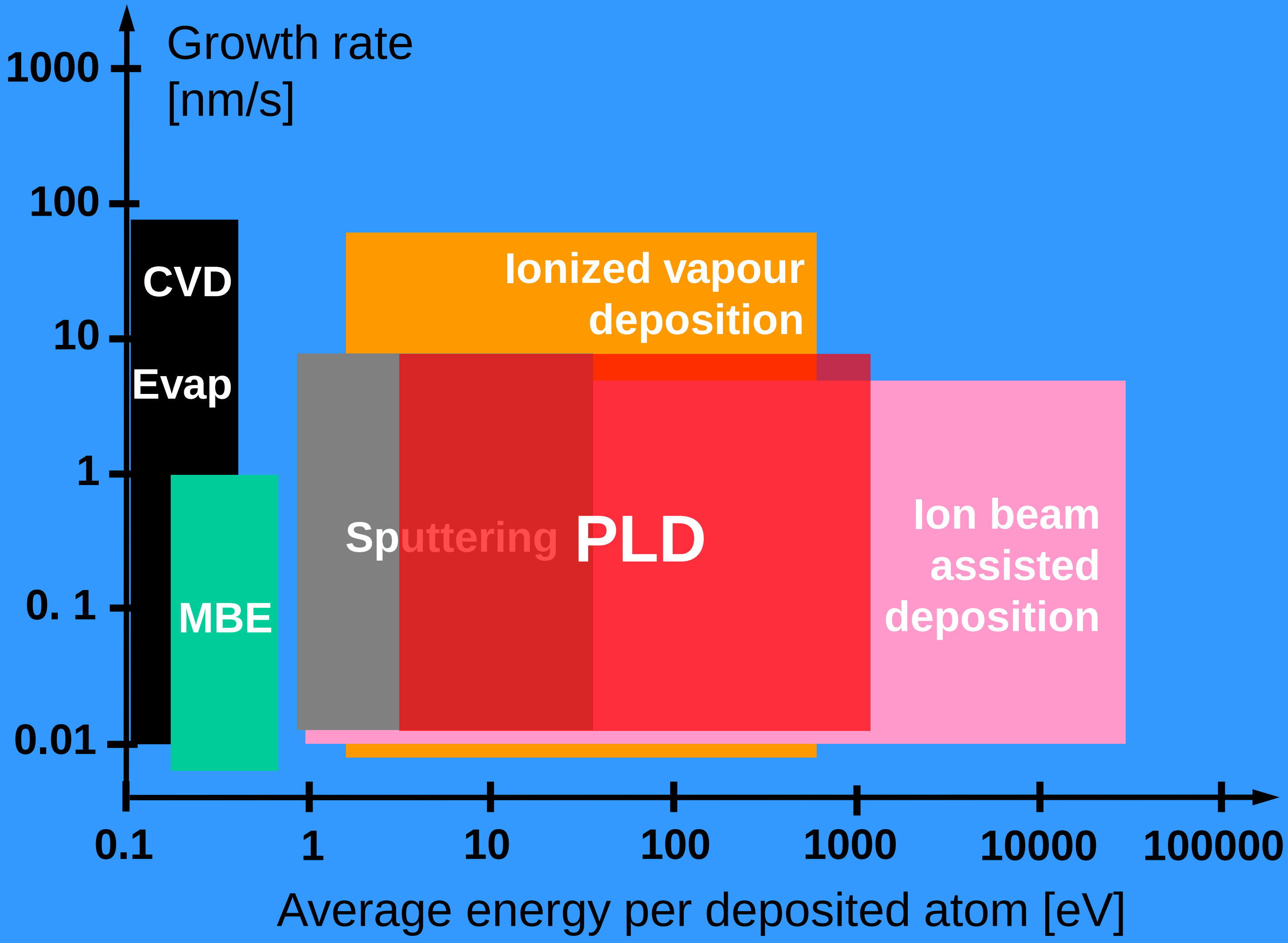
Ablation - a process in which high-energy laser radiation quanta produce lower bond energy between the particles, which allows the removal of atomic layers one by one

17. Osadzanie laserem impulsowym z wykorzystaniem ablacji laserowej

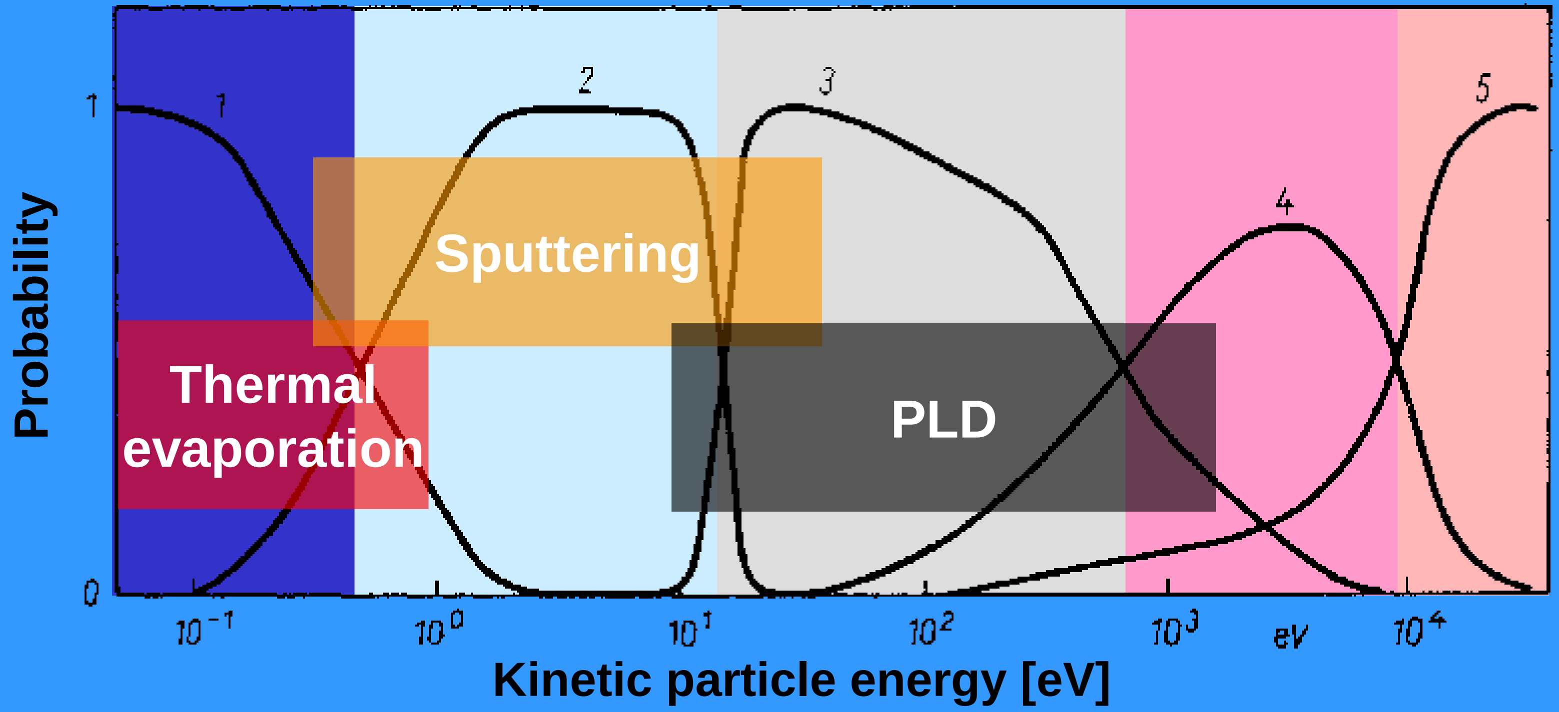
Metoda PLD (pulsed laser deposition)

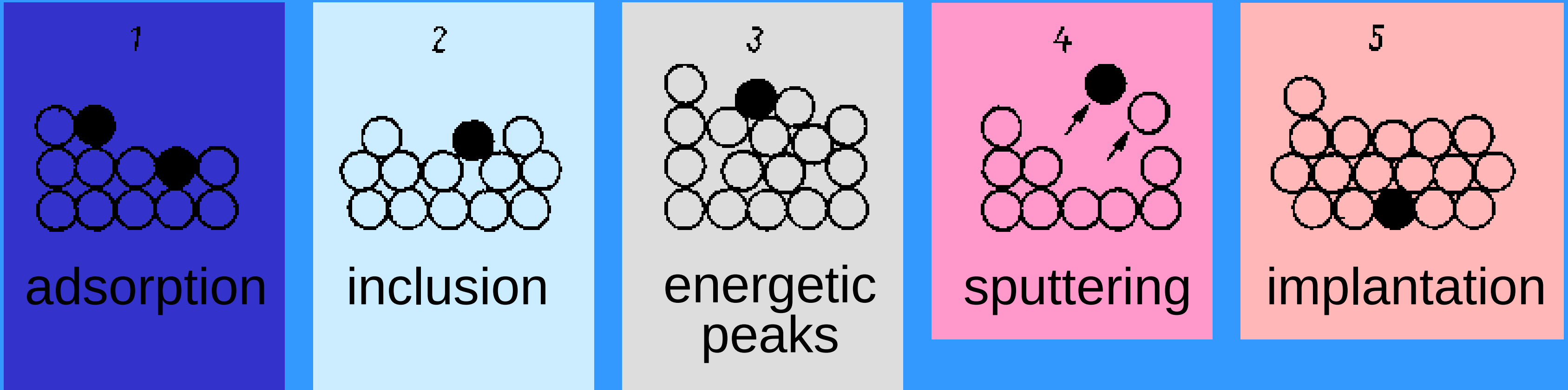
Ablacja – proces, w którym wysokoenergetyczne kwanty promieniowania laserowego wywołują obniżenie energii wiązań pomiędzy cząstkami, co umożliwia zdejmowanie warstw atomowych jedna po drugiej

Vapour energy

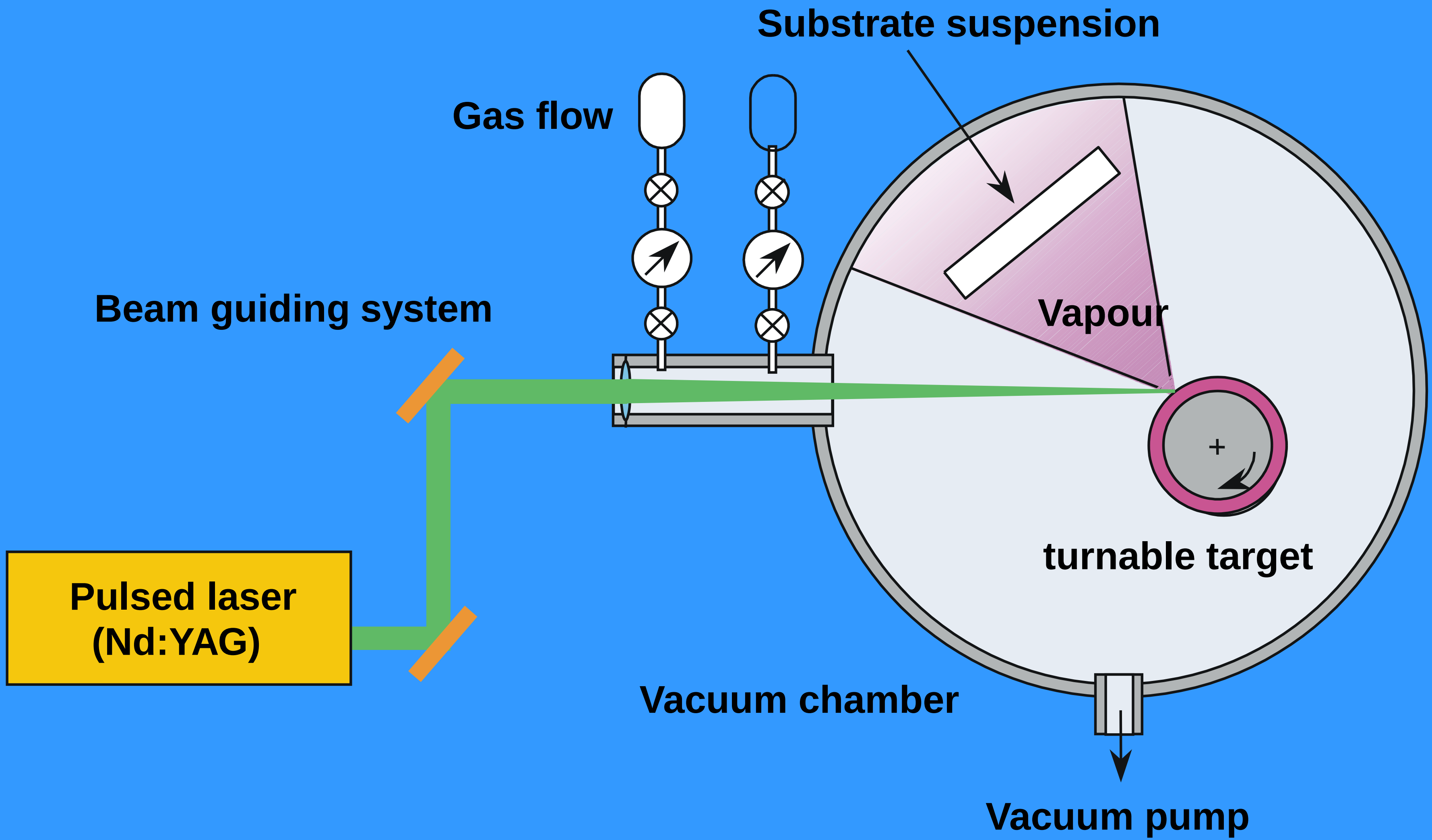


Energetic aspects in thin film growth





Pulsed Laser Deposition



Substrate suspension

Gas flow

Beam guiding system

Vapour

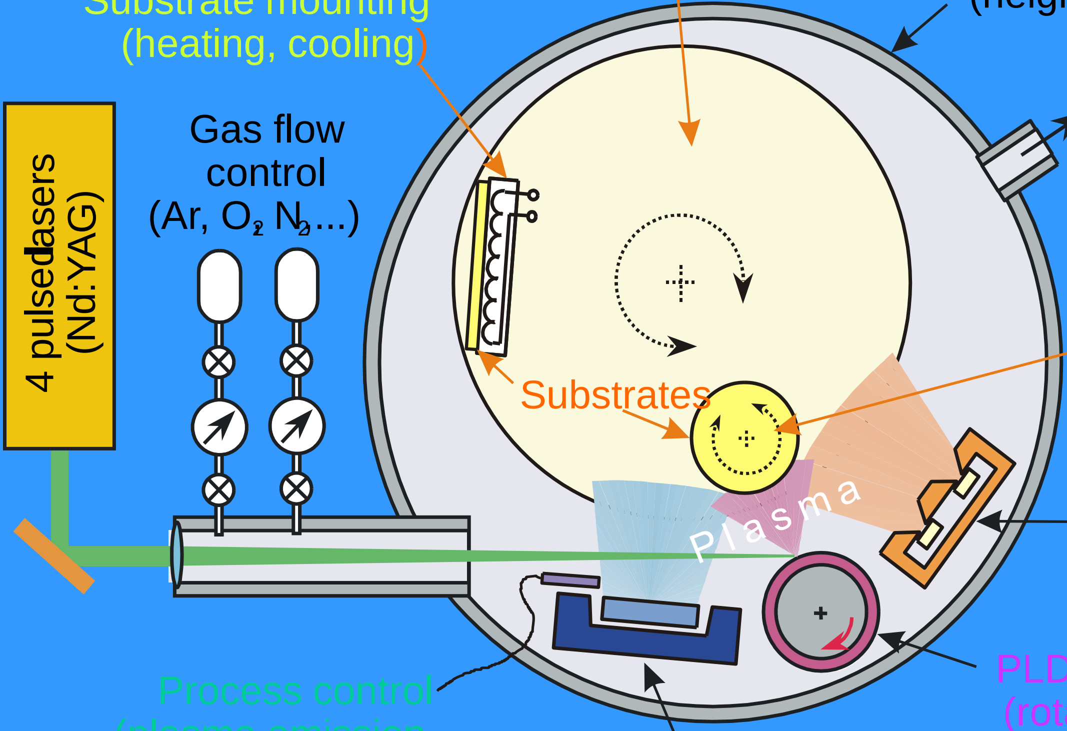
Pulsed laser
(Nd:YAG)

turnable target

Vacuum chamber

Vacuum pump

HybridPLD coating system



Rotary table (Ø 560 mm)
for substrate movement

Vacuum chamber
(height 650 mm)

Substrate mounting
(heating, cooling)

Vacuum
pump

Gas flow
control
(Ar, O_2, N_2...)

Substrate
rotation

Substrates

ALS linear
ion source

PLD evaporator
(rotating target)

Process control
(plasma emission,
gas analytics,
optical plasma spectroscopy,
Raman spectroscopy,
Quartz oscillator,
Temperature, etc.)

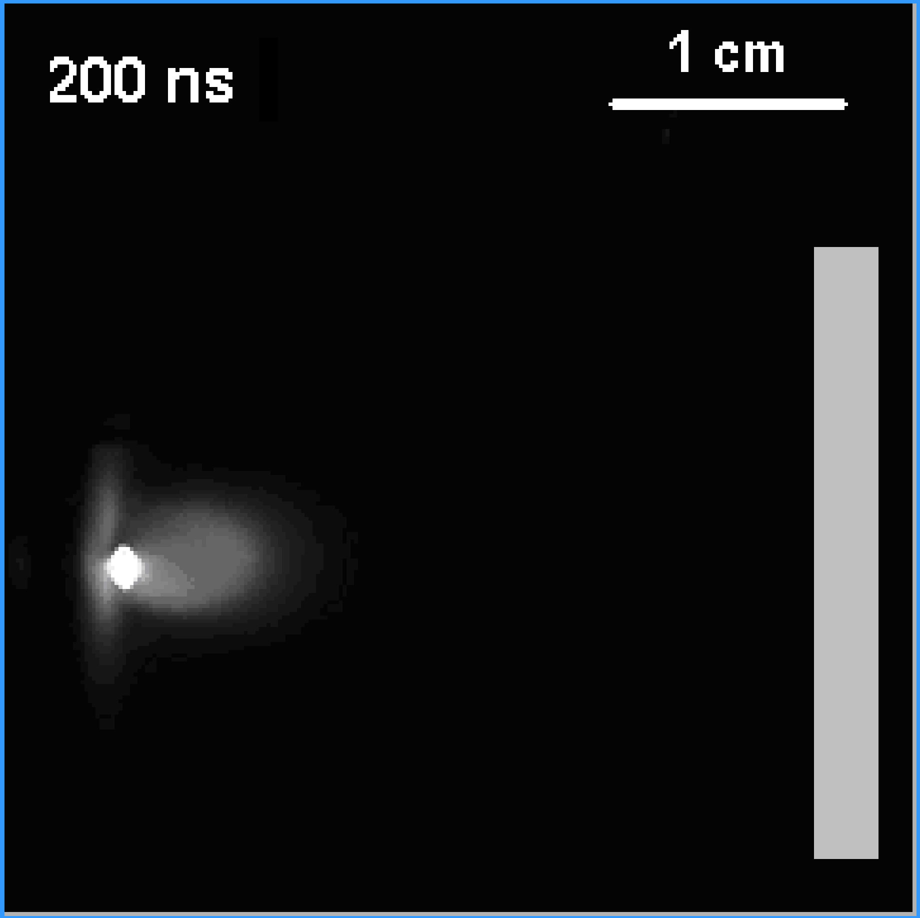
Magnetron sputter sources
(RF, MF pulsed DC)
& bias voltage supply

J.M.Lackner, W.Waldhauser, Galvanotechnik 96, p. 2208-2216, 2005

CHAMBER ENVIRONMENT INTERACTION ON THE SHAPE OF THE PLASMA FLOW

Titanium target ablation in the vacuum
10^{-5}mbar (10^{-3} Pa)

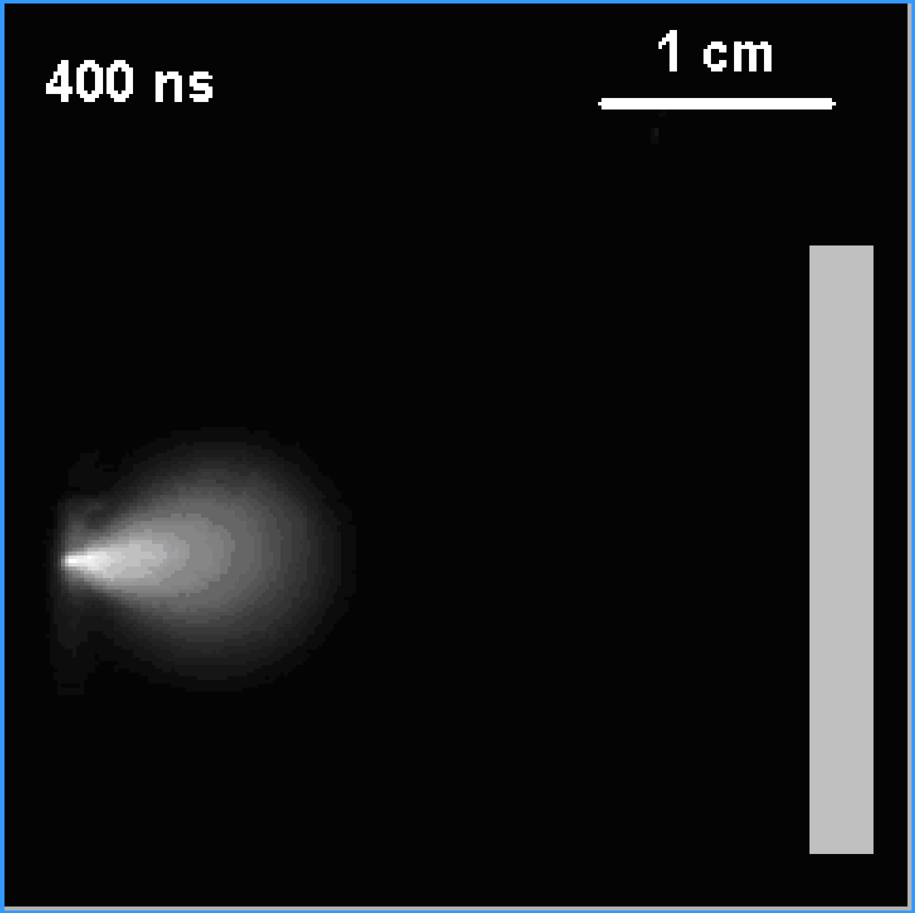
Plasma plum flow as a function of time (CCD registration)



CHAMBER ENVIRONMENT INTERACTION ON THE SHAPE OF THE PLASMA FLOW

Titanium target ablation in 5 Pa (5x10^{-2}mbar) pressure

Plasma plum flow as a function of time (CCD registration)



Advantages of PLD

1. high local temperatures on target surface
   ➔ **large number of coatings materials**
2. short laser pulses
   ➔ **congruent evaporation of the target material**
3. evaporation in vacuum without the use of crucibles
   ➔ **high purity of coatings**
4. high kinetic energies of the vaporised particles
   ➔ **improved adhesion, extremely fine structure**
5. very low substrate temperatures possible
   ➔ **coating of temperature sensitive parts**

J.M.Lackner; Surface & Coatings Technology 200, p. 1439-1444, 2005

Physico-chemical processes in transit of evaporated stream

- The energy of particles striking the passage of ionized particles and recombination is mainly a change in the dynamics along a plume axis
- Distribution of particles in the plume has a strong maximum along its axis
- As ablation occurs in the vacuum forming of agglomerates occurs which composition is depending on the energy and could be compatible with a target chemical content
- As ablation occurs in the gas core particle dissociation occurs, leading to a reaction between the atoms
- During expansion of the gas plume a collision occurs between atoms, leading to the incorporation of foreign particles and formation of agglomerates with the composition compatible with the target stoichiometry

Procesy fizyko-chemiczne podczas transportu odparowanej strugi

(i) Energia uderzających cząstek po przelocie i rekombinacji cząstek zjonizowanych wiąże się głównie ze zmianą ich dynamiki wzdłuż osi strugi

(ii) Rozkład cząstek w strudze posiada silne maksimum względem osi strugi

(iii) Gdy ablacja zachodzi w próżni to tworzące się aglomeraty w przypadku tarczy wieloskładnikowej w zależności od warunków energetycznych posiadają skład kompatybilny z tarczą

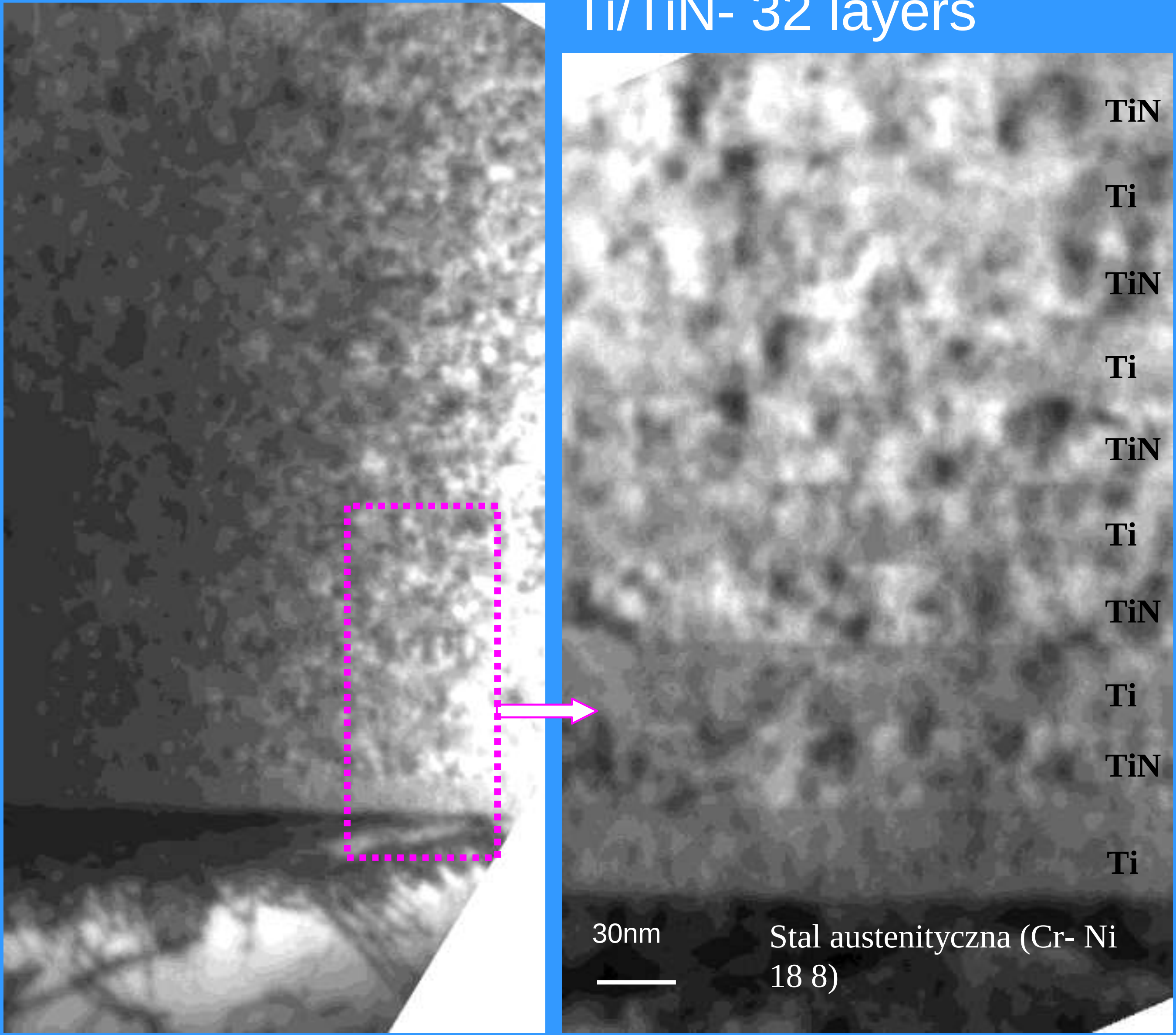
(iv) Gdy ablacja zachodzi w gazie zachodzi dysocjacja cząstek podstawowych prowadzący do reakcji pomiędzy atomami

(v) Podczas ekspansji strugi w gazie dochodzi do kolizji pomiędzy atomami prowadząc do włączenia obcych cząstek i utworzenia aglomeratów których skład jest kompatybilny ze stechiometrią tarczy

TEM examination on cross-section

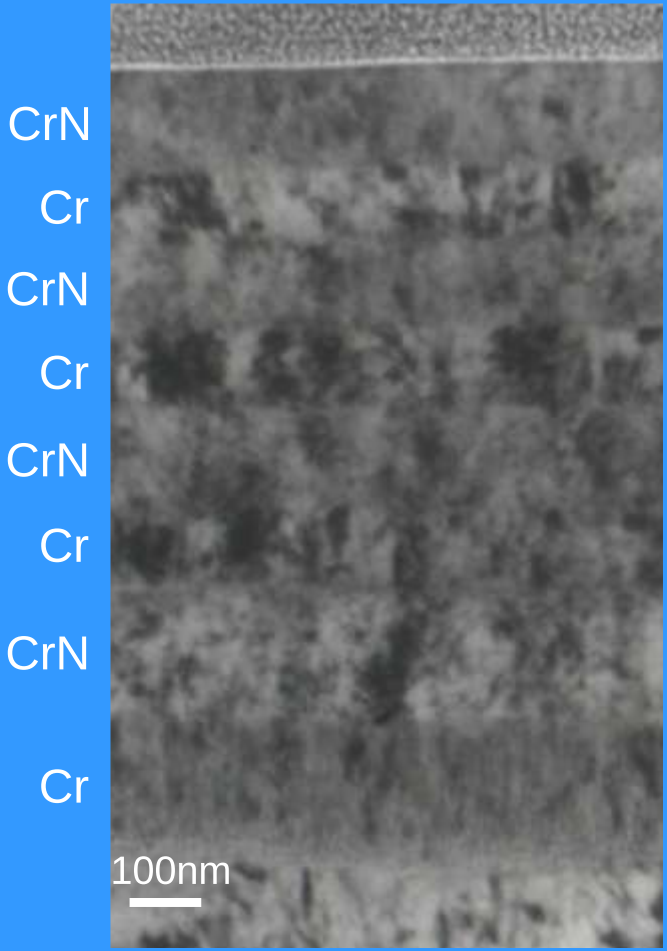
Multilayer system

Ti/TiN- 32 layers



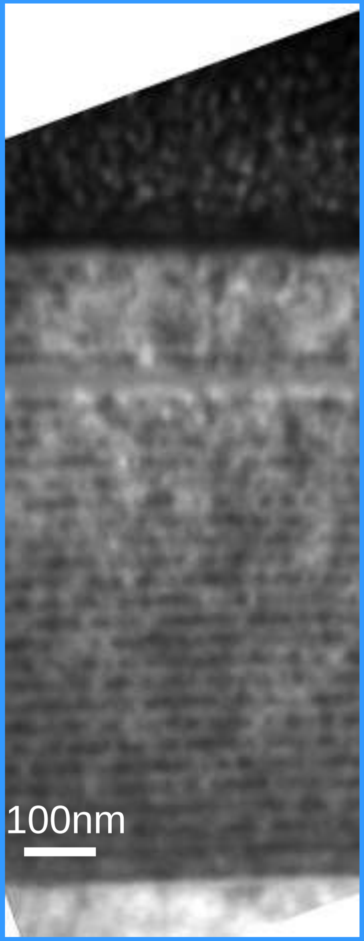
Cr/CrN

8- layers

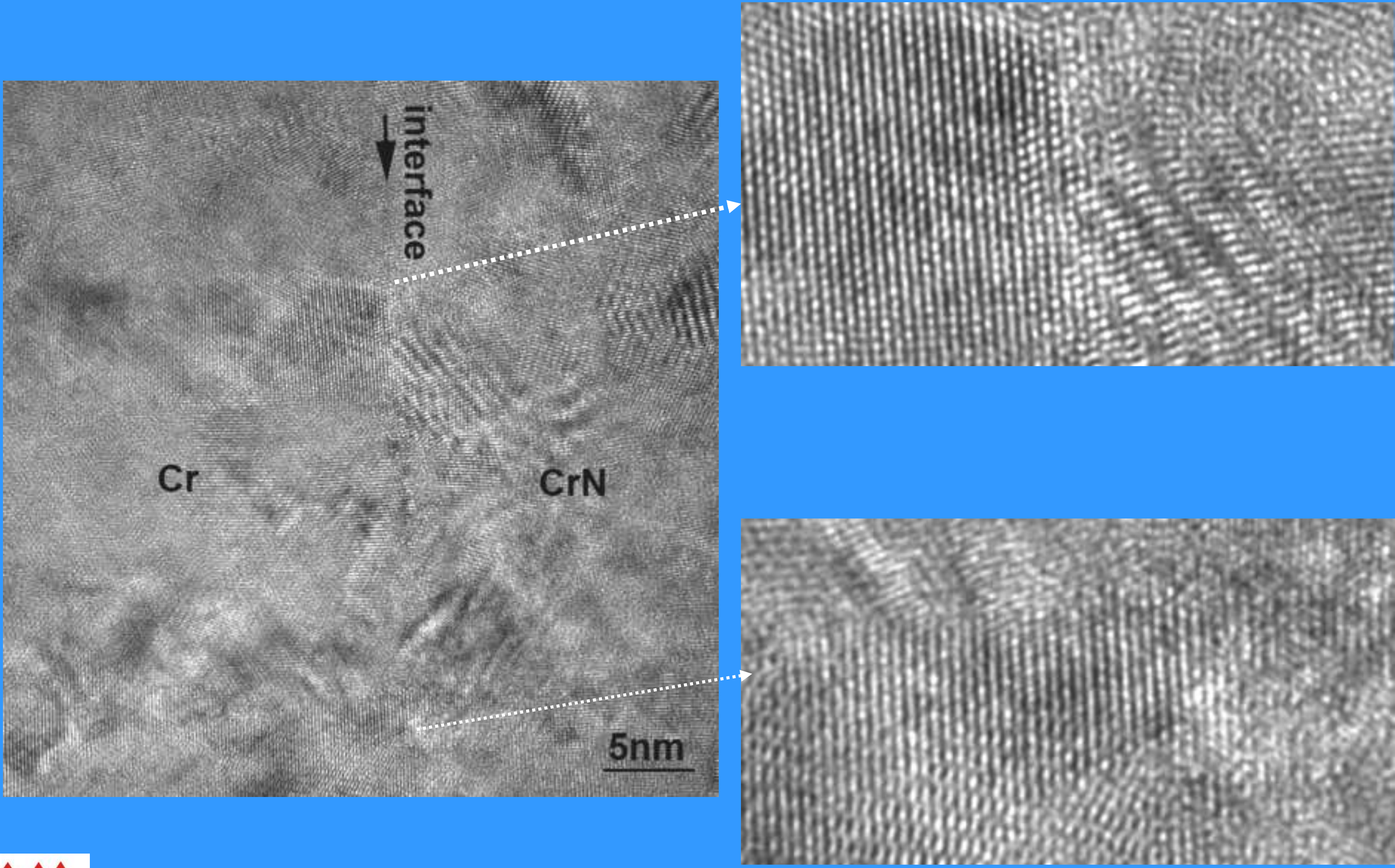


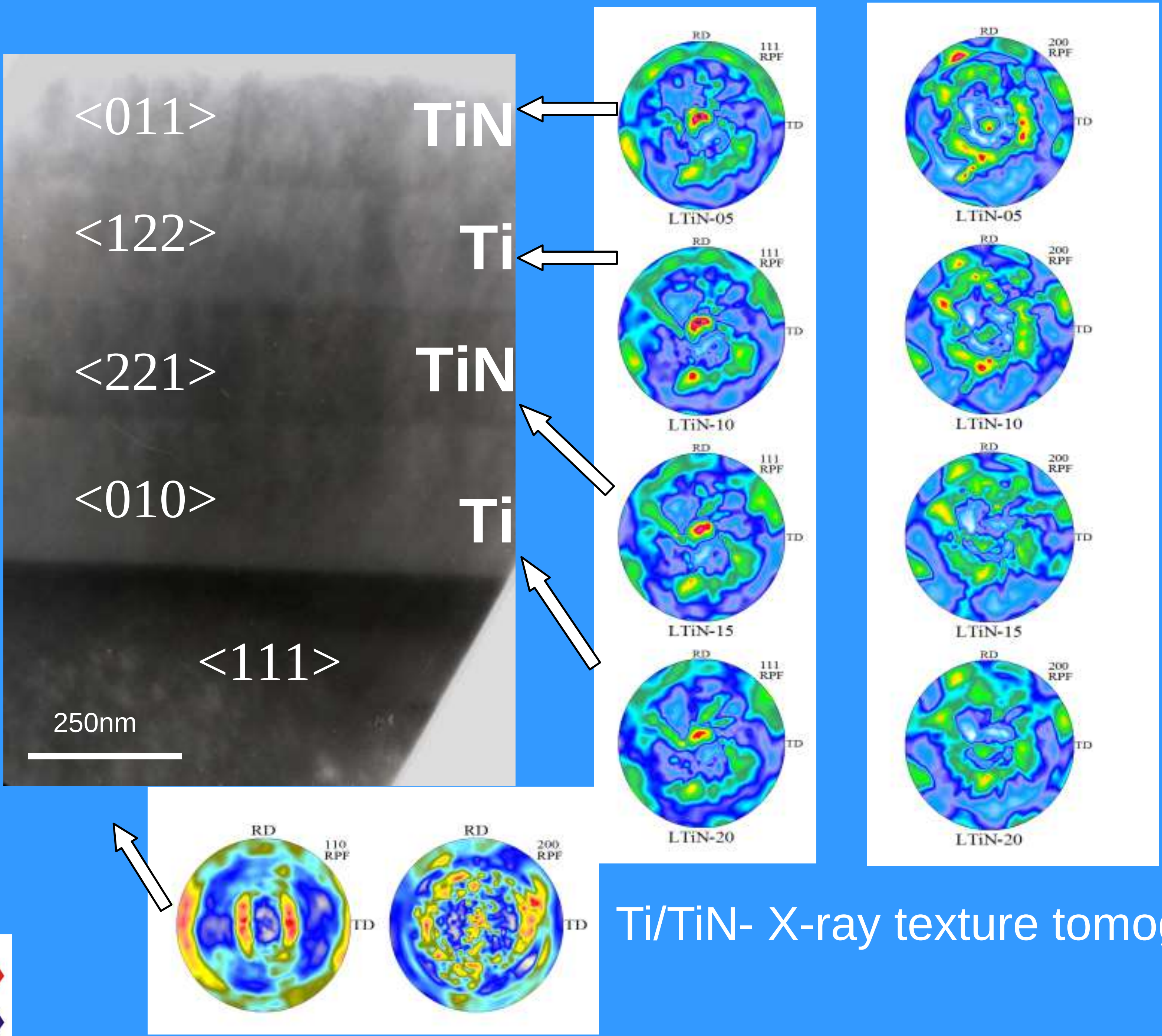
32- layers

64- layers

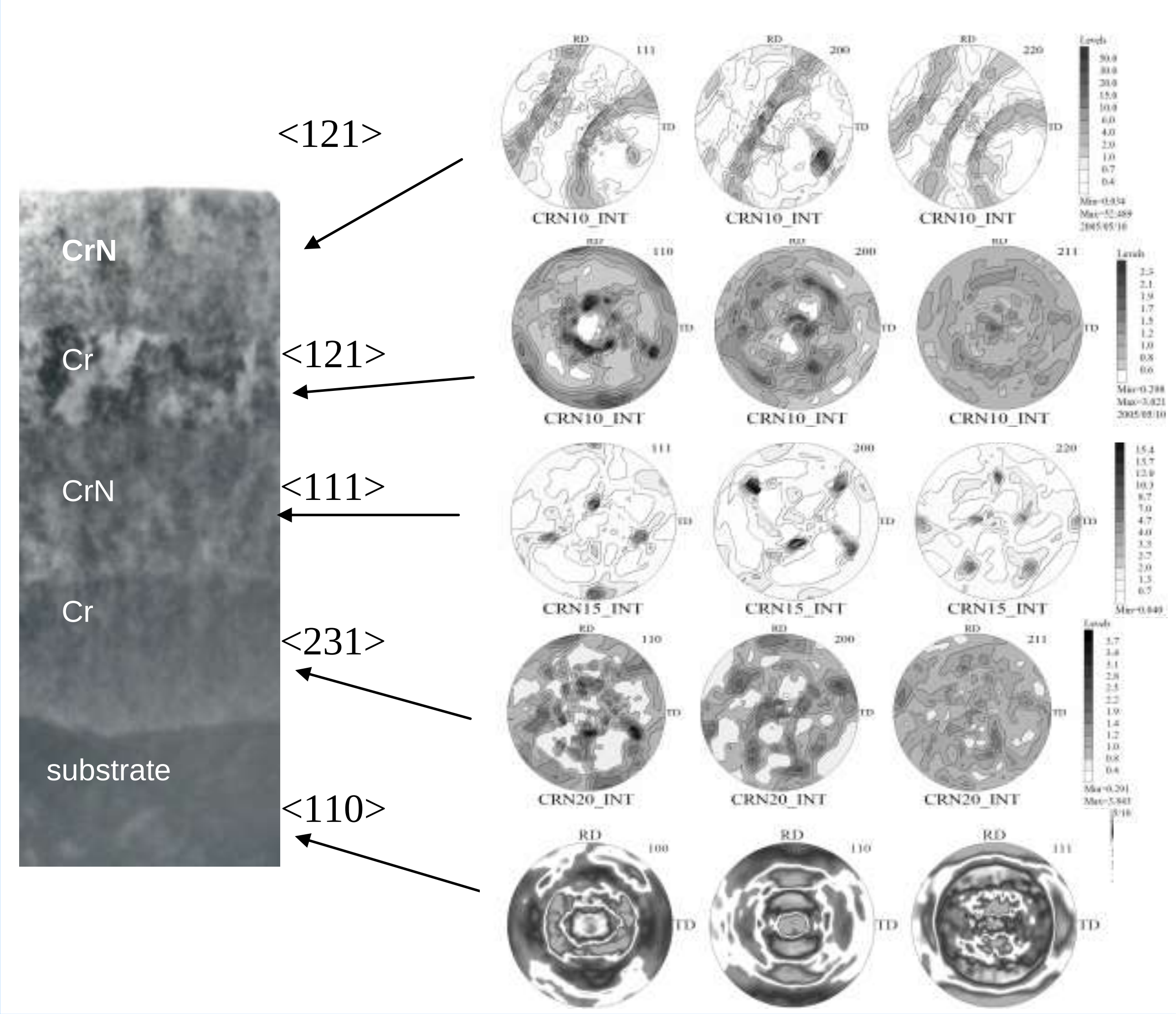


Cr/CrN- 8 layers (HRTEM)



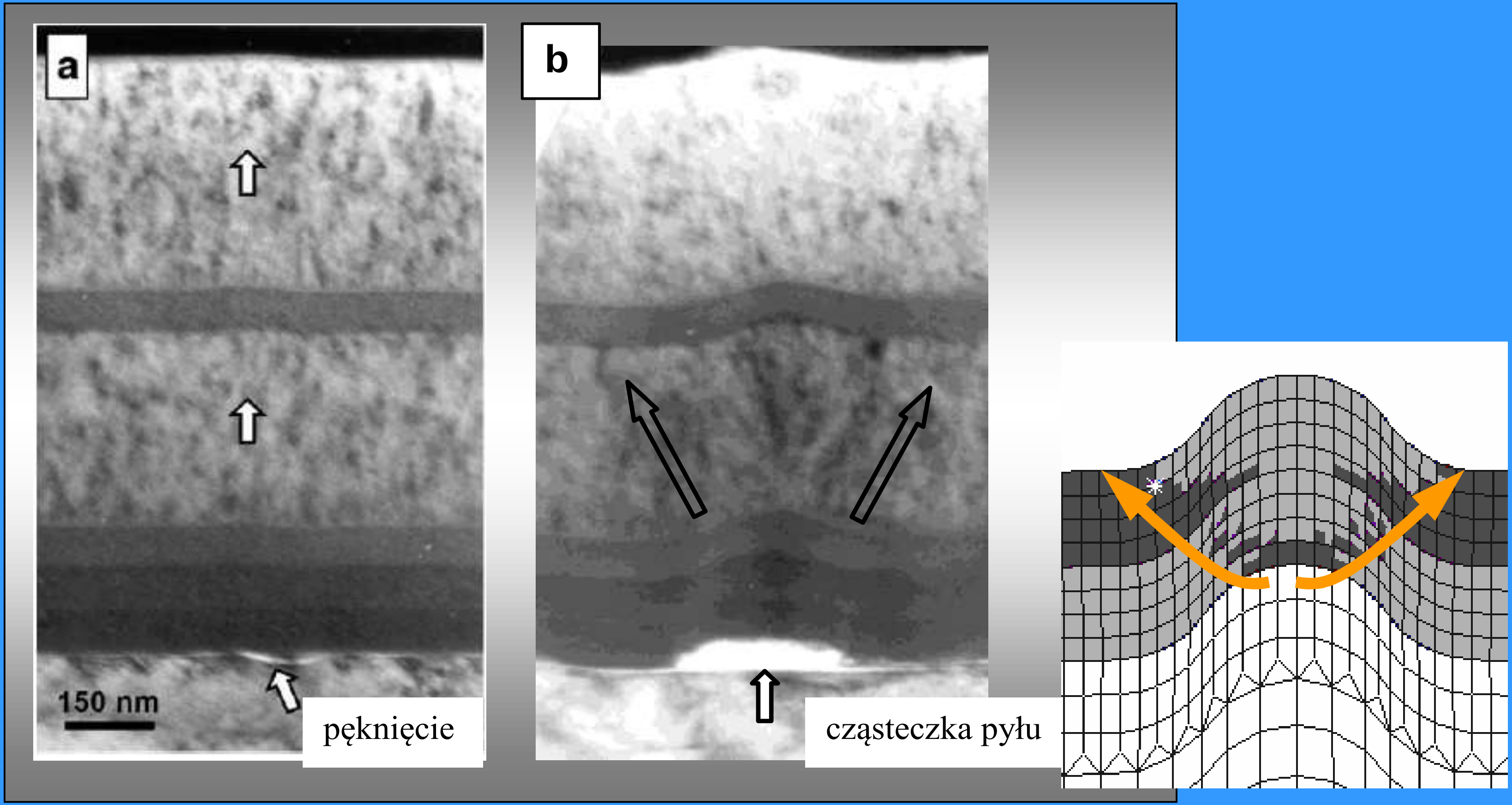


Ti/TiN- X-ray texture tomography

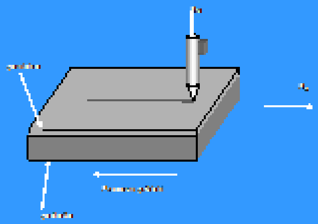


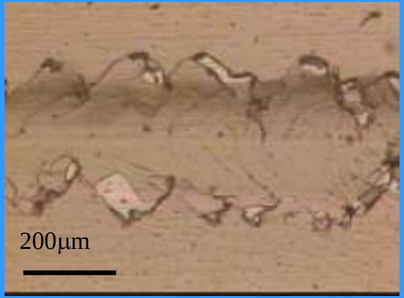
Cr/CrN- X-ray texture tomography

Cr/CrN- 4 layers (defect)



0.86%





Kierunek przesuwania się penetratora

L_c=3N

18. Surface cleaning with the use of laser ablation

The main mechanisms responsible for ablation:

- spraying collision
- thermal spraying
- spraying electron
- spraying delamination
- spraying hydrodynamic

Renovation works of art using pulsed laser - selective removal of the surface layer of dirt with minimal interference in areas immediately adjacent to it

18a. Nanomaterials and nanotechnologies

1 nm = 10^{-9}m

Główka szpilki /head of pin/	1 000 000 nm
Włos ludzki /human hair/	50 000 – 80 000 nm
Komórki /cells/	5 000 – 200 000 nm
Proteiny /proteins/	3 -20 nm
Łańcuchy DNA (średnica) DNA chains	2 nm
Wirusy /viruses/	10 – 200 nm
Molecule against viruses Molekuły leków zwalczających wirusy	5 nm
Hydrogen atom Atom wodoru	**0.1 nm**

Def. **/Narodowa Strategia dla Polski 2006/**

Nanotechnology is the design and manufacture of the structure in which at least one dimension less than 100 nm and which have new properties resulting from nanosize

Richard P.Feyman

/meeting of the American Physical Society, California 1959/

„There's Plenty Room at the Bottom”

Def. /Narodowa Strategia dla Polski 2006/

Nanotechnologia to projektowanie i wytwarzanie struktur, w których przynajmniej jeden rozmiar jest poniżej 100 nm i które posiadają nowe właściwości wynikające z nanorozmiaru

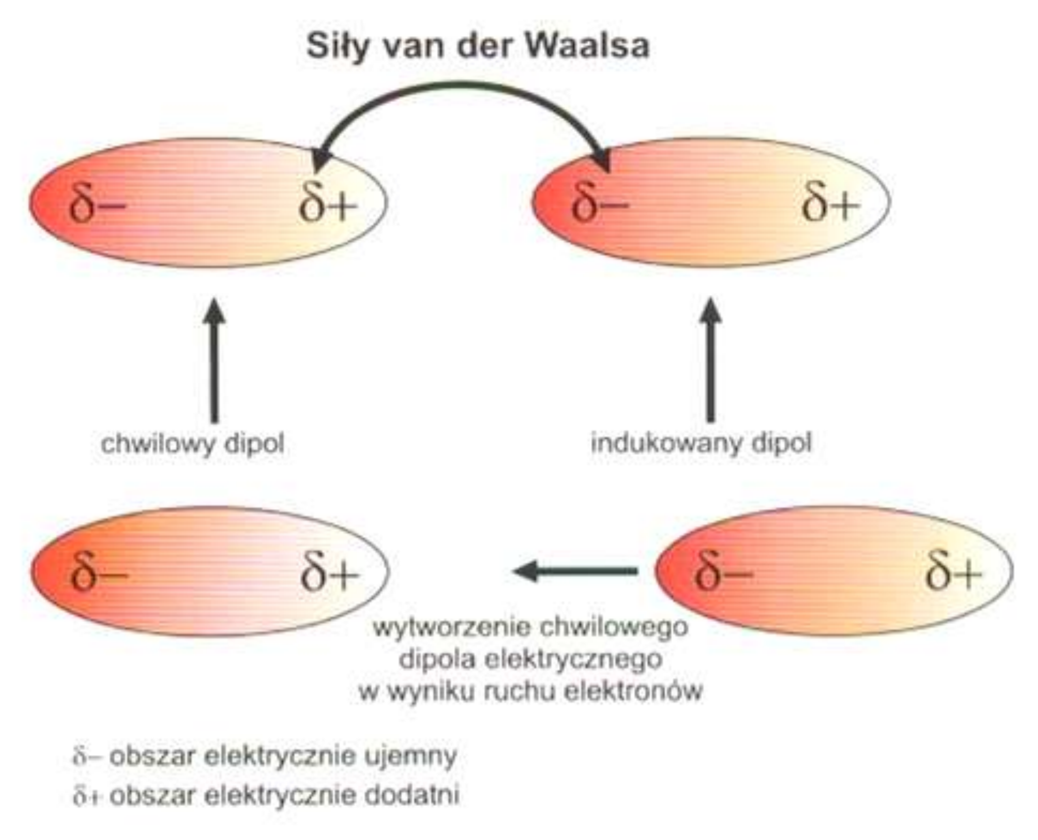
Richard P.Feyman

/spotkanie Amerykańskiego Towarzystwa Fizycznego, Kalifornia 1959/

„There‚s Plenty Room at the Bottom”

Nanomaterials is a field that takes a materials science-based approach to nanotechnology. It studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller than a one tenth of a micrometer in at least one dimension,[1] though this term is sometimes also used for materials smaller than one micrometer.

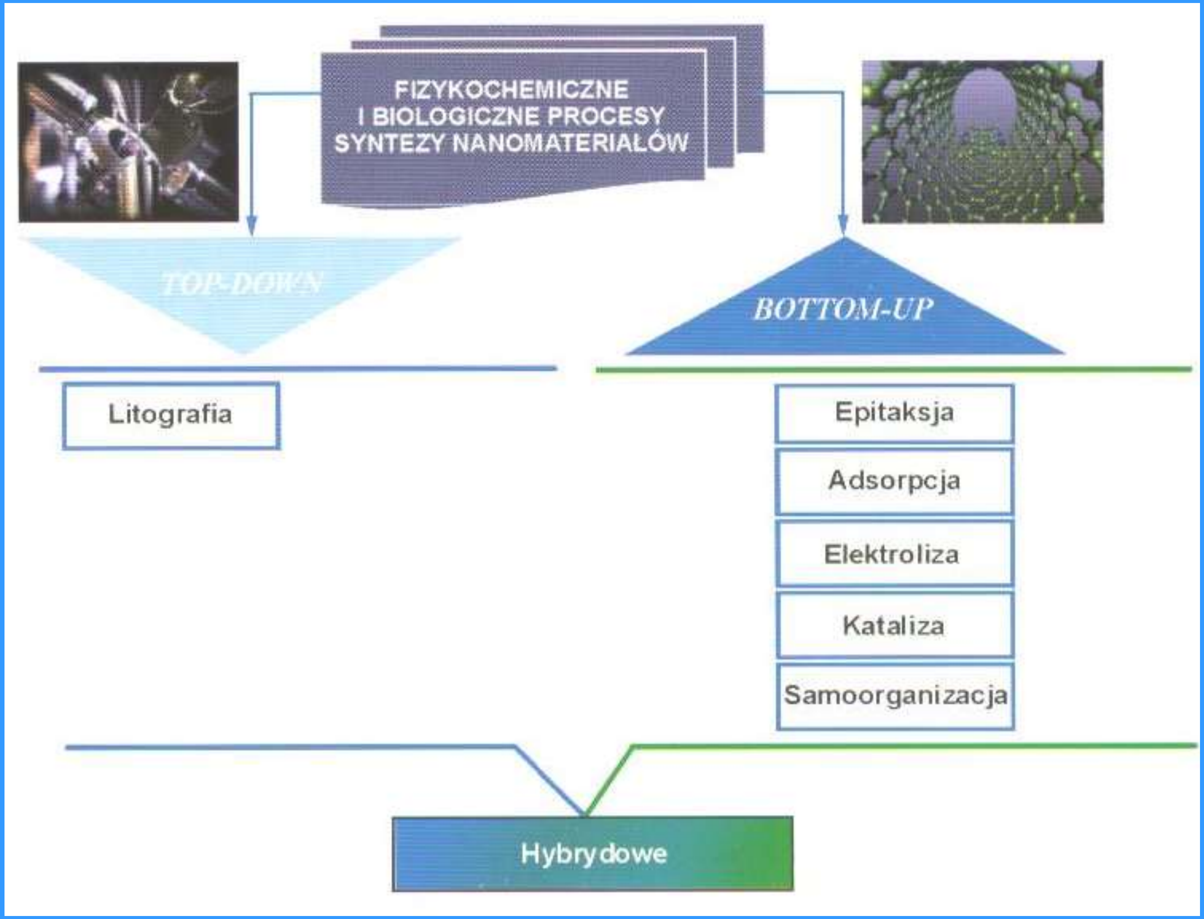
Phenomena in microscale (Maz.2.4)



van der Waals bonding

Processes of nanomaterial synthesis (Maz.2.13)

- -od dołu do góry (bottom-up)
- -od góry do dołu (top-down)
- -samoorganizacja (self-organization)



Klasyfikacja procesów syntezy nanomateriałów

Artificial superlattices

- **Low dimension structures** Nano-size structures / quantum dots, quantum wells, quantum wires
- **Carbon structures** Carbone structures / fullerenes, nanotubes and their modifications to other atoms, graphene/
- **Molecular and hipermolecular structures** Nanostructures and hiper-structures/dendrymers, molecular clusters, molecular connections/

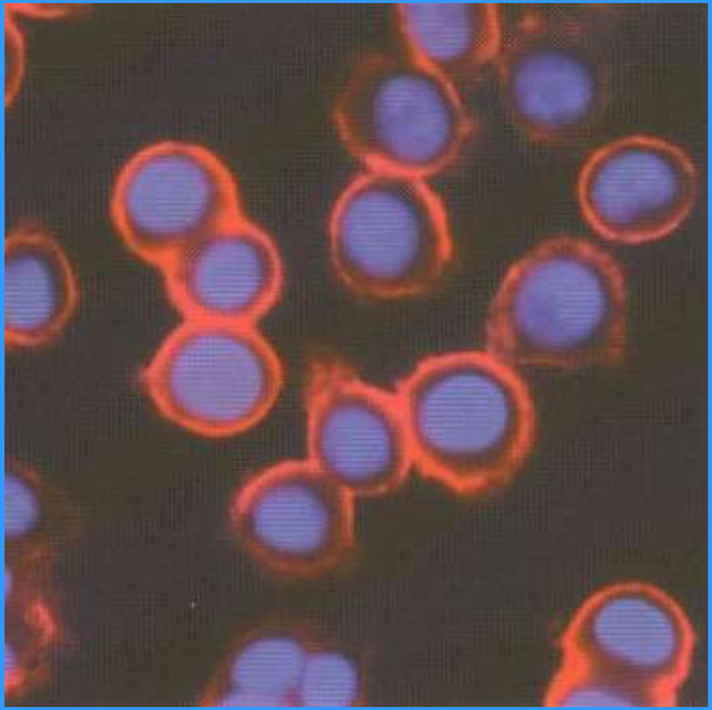
Dendrimers- repeatedly and very regularly branched polymers with a structure called "dense star”

Artificial superlattices

- **Low dimension structures** Struktury niskowymiarowe /kropki kwantowe, studnie kwantowe, druty kwantowe/
- **Carbon structures** Struktury węglowe /fulereny, nanorurki i ich modyfikacje innymi atomami, grafen/
- **Molecular and hipermolecular structures** Nanostruktury molekularne i nadmolekularne /dendrymery, warstwy molekularne, klastery,złącza molekularne/

Dendrymery- to wielokrotnie i bardzo regularnie rozgałęzione polimery posiadające strukturę zwaną „gęstą gwiazda”

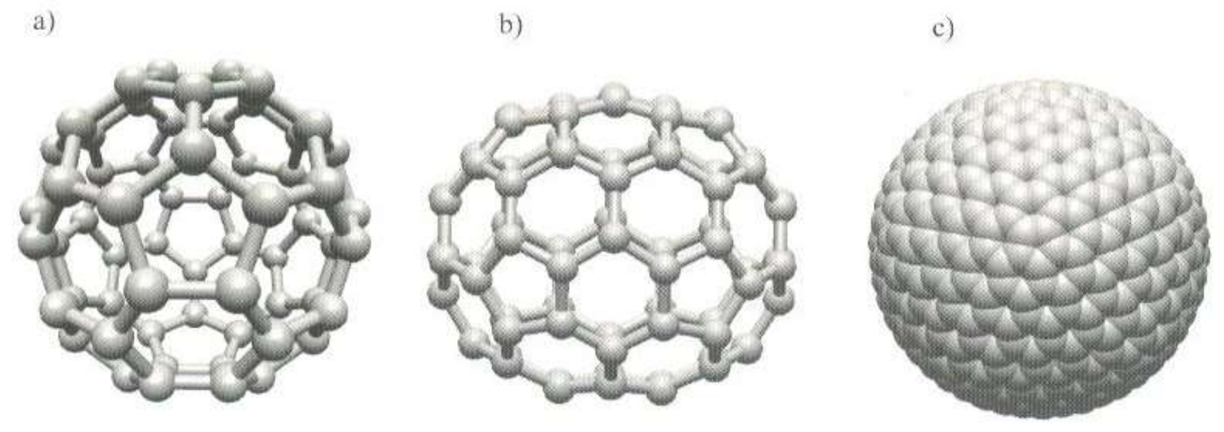
(Maz.2.36)



Tumor markers: red color corresponds to the quantum dots
on the surface of breast cancer cells,
and the cell nucleus is stained in blue

Markery nowotworów: czerwony kolor odpowiada kropkom kwantowym na powierzchni komórek raka piersi, natomiast jądro komórki jest zabarwione na niebiesko

(Maz.2.40)



Models of fullerenes
a) C60, b) C70, c) C500

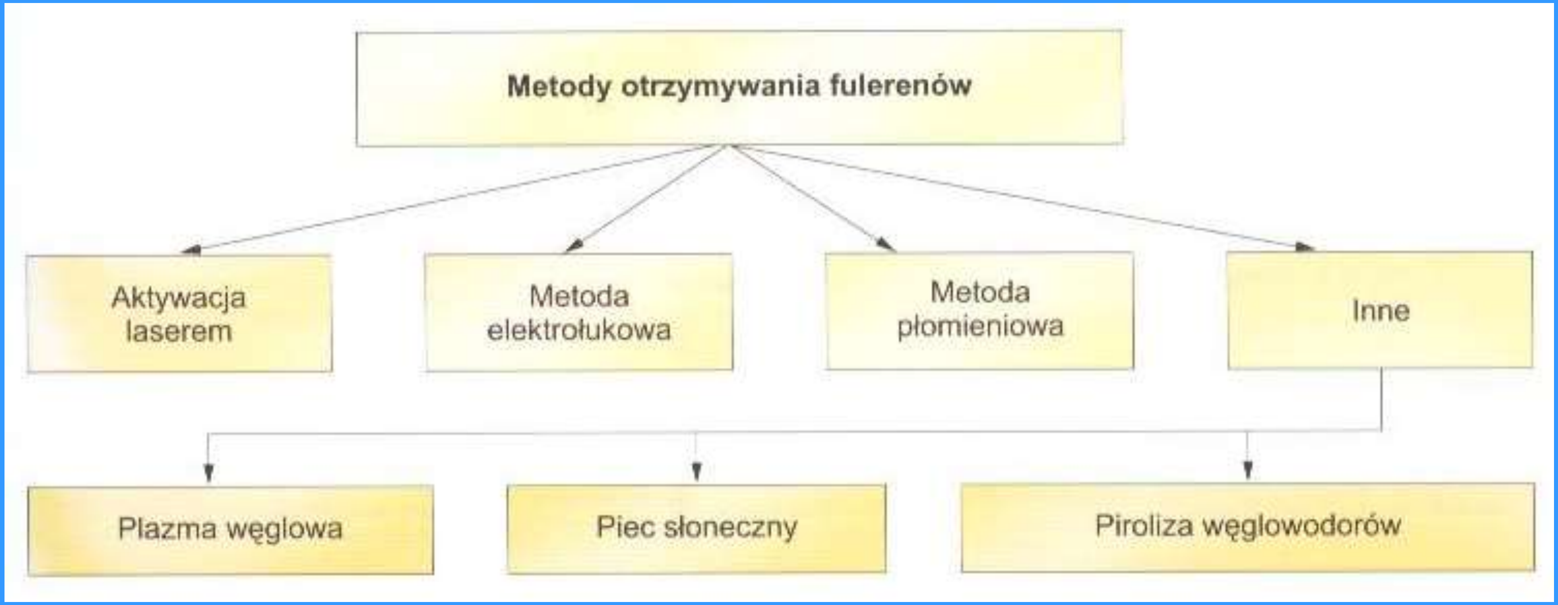
Modele fulerenów a) C_{60}, b) C_{70}, c) C_{500}

- **Buckminsterfullerene** is a spherical molecule with the formula C60. It was first prepared in 1985 by Harold Kroto, James Heath, Sean O'Brien, Robert Curl and Richard Smalley at Rice University.[1] Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of buckminsterfullerene and the related class of molecules, the fullerenes. The name is an homage to Richard Buckminster Fuller, whose geodesic domes it resembles. Buckminsterfullerene was the first fullerene molecule discovered and it is also the most common in terms of natural occurrence, as it can be found in small quantities in soot.[2][3][4]
- Buckminsterfullerene is the largest matter to have been shown to exhibit wave–particle duality.[5]

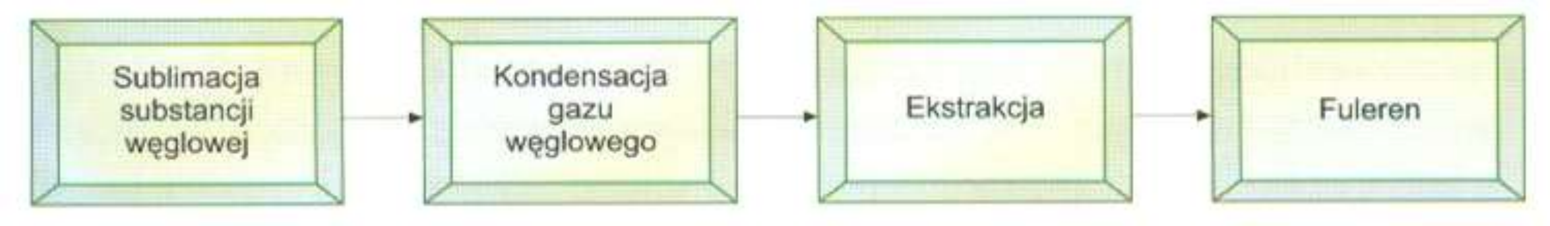
(Montreal Expo 67 – USA exposition in pavilion design by Buckminster Fuller)

Fulerene fabrication

(Maz.2.41) (Maz.2.42)



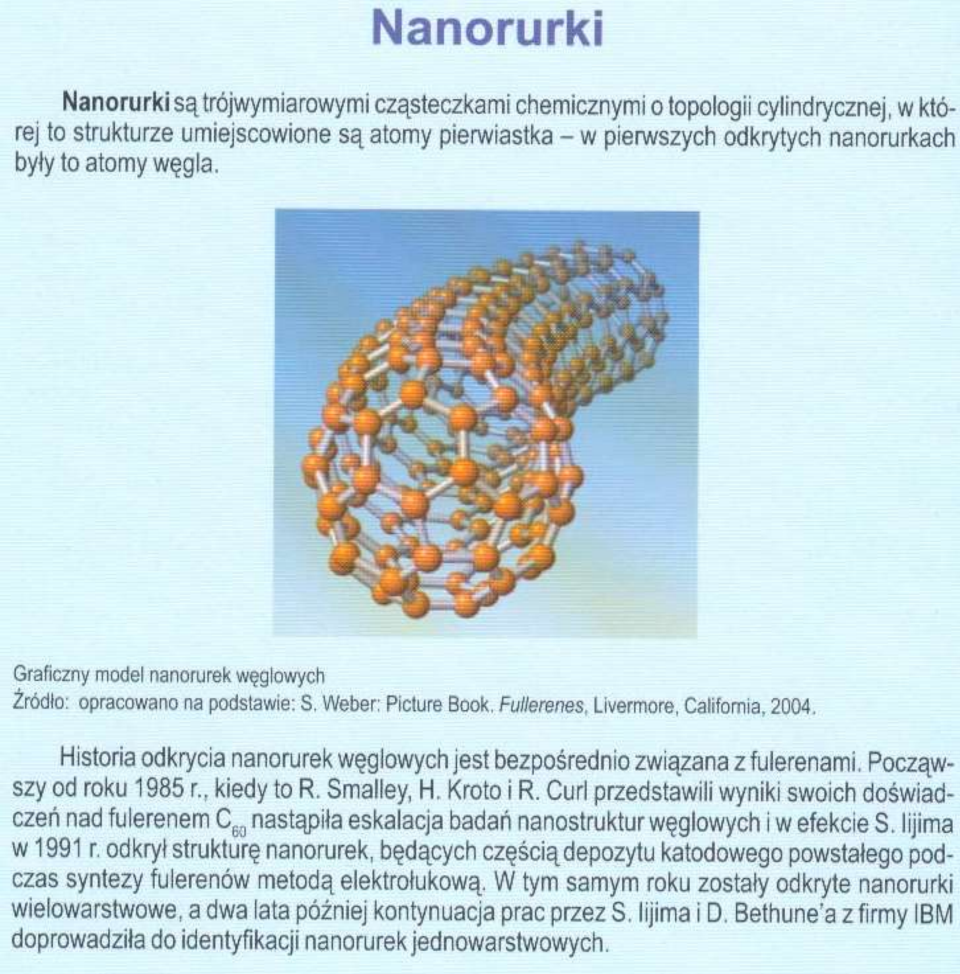
Metody wytwarzania fulerenów



Schemat procesu otrzymywania fulerenów

(Maz. str.246)

Nanotubes

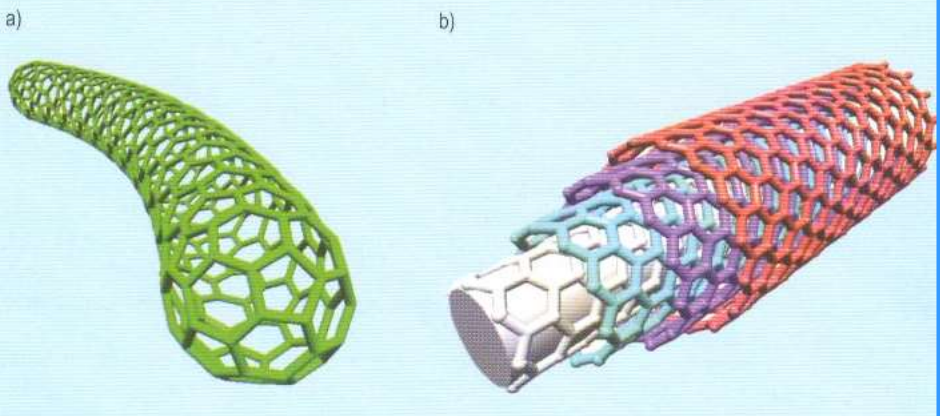


Nanorurki

Nanorurki są trójwymiarowymi cząsteczkami chemicznymi o topologii cylindrycznej, w której to strukturze umiejscowione są atomy pierwiastka – w pierwszych odkrytych nanorurkach były to atomy węgla.

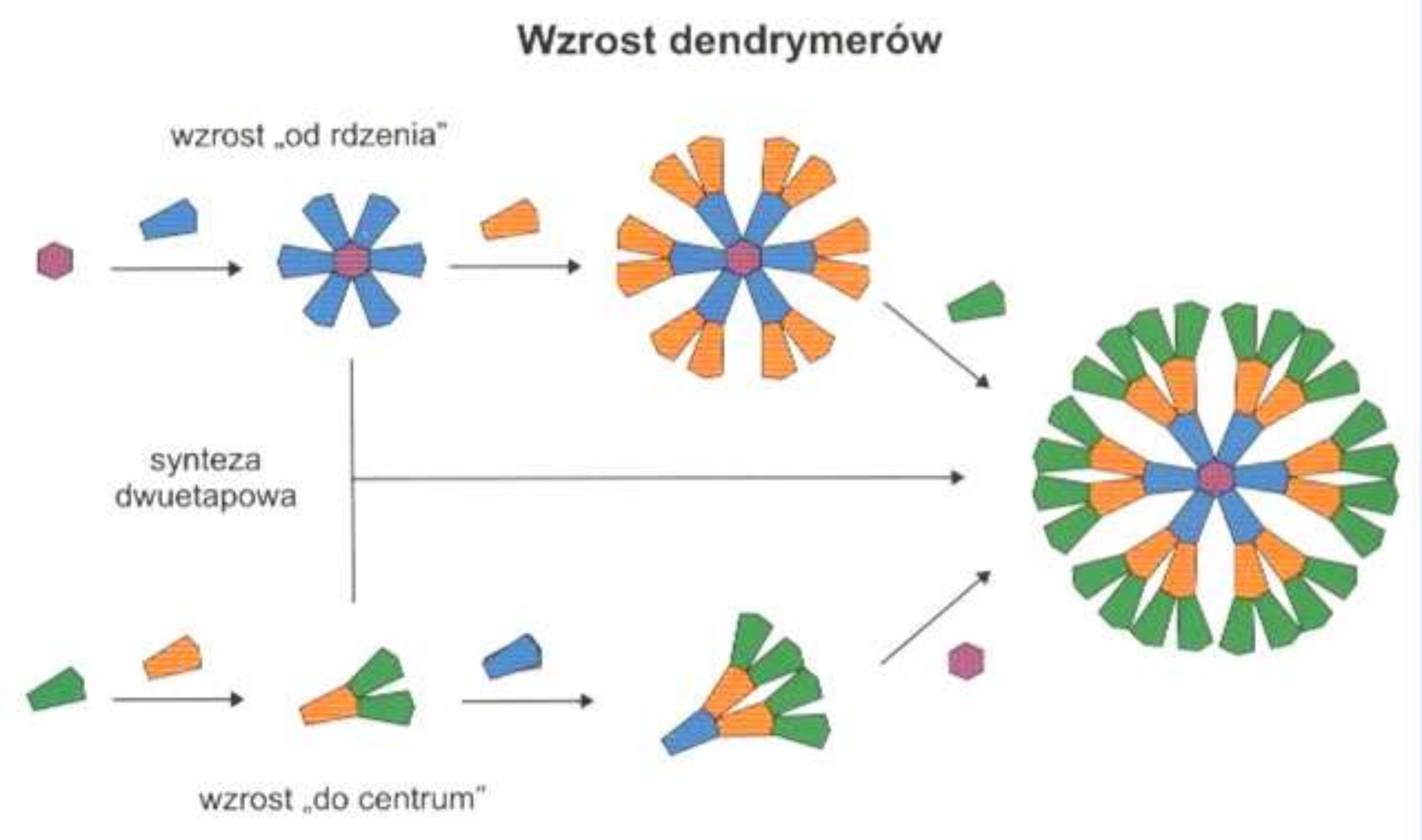
Graficzny model nanorurek węglowych
Źródło: opracowano na podstawie: S. Weber: Picture Book. *Fullerenes*, Livermore, California, 2004.

Historia odkrycia nanorurek węglowych jest bezpośrednio związana z fulerenami. Począwszy od roku 1985 r., kiedy to R. Smalley, H. Kroto i R. Curl przedstawili wyniki swoich doświadczeń nad fulerenem C_{60} nastąpiła eskalacja badań nanostruktur węglowych i w efekcie S. Iijima w 1991 r. odkrył strukturę nanorurek, będących częścią depozytu katodowego powstałego podczas syntezy fulerenów metodą elektrołukową. W tym samym roku zostały odkryte nanorurki wielowarstwowe, a dwa lata później kontynuacja prac przez S. Iijima i D. Bethune'a z firmy IBM doprowadziła do identyfikacji nanorurek jednowarstwowych.



Nanorurki: a) jednowarstwowe, b) wielowarstwowe
Źródło: opracowano z wykorzystaniem programu NanotubeModelerver.1.3.8 firmyJCrystalSoft.

(Maz.2.52) Dendrimer growth



Uproszczony schemat powstawania dendrymeru

Graphene

Flat monolayer of carbon atoms packed in the structure of the 2D honeycomb,

the basic building block for all sizes of graphite materials.

It can be:

- curled up in 0D-fullerenes
- rolled in 2D - nanotubes
- arranged in a stack in 3D - Graphite

Grafen (ang.graphene)

Płaska ***monowarstwa*** atomów węgla upakowana w strukturę 2D typu plastra miodu; podstawowy blok budowlany dla materiałów grafitowych wszystkich rozmiarów.

Może byś: zwinięty w OD –fulereny

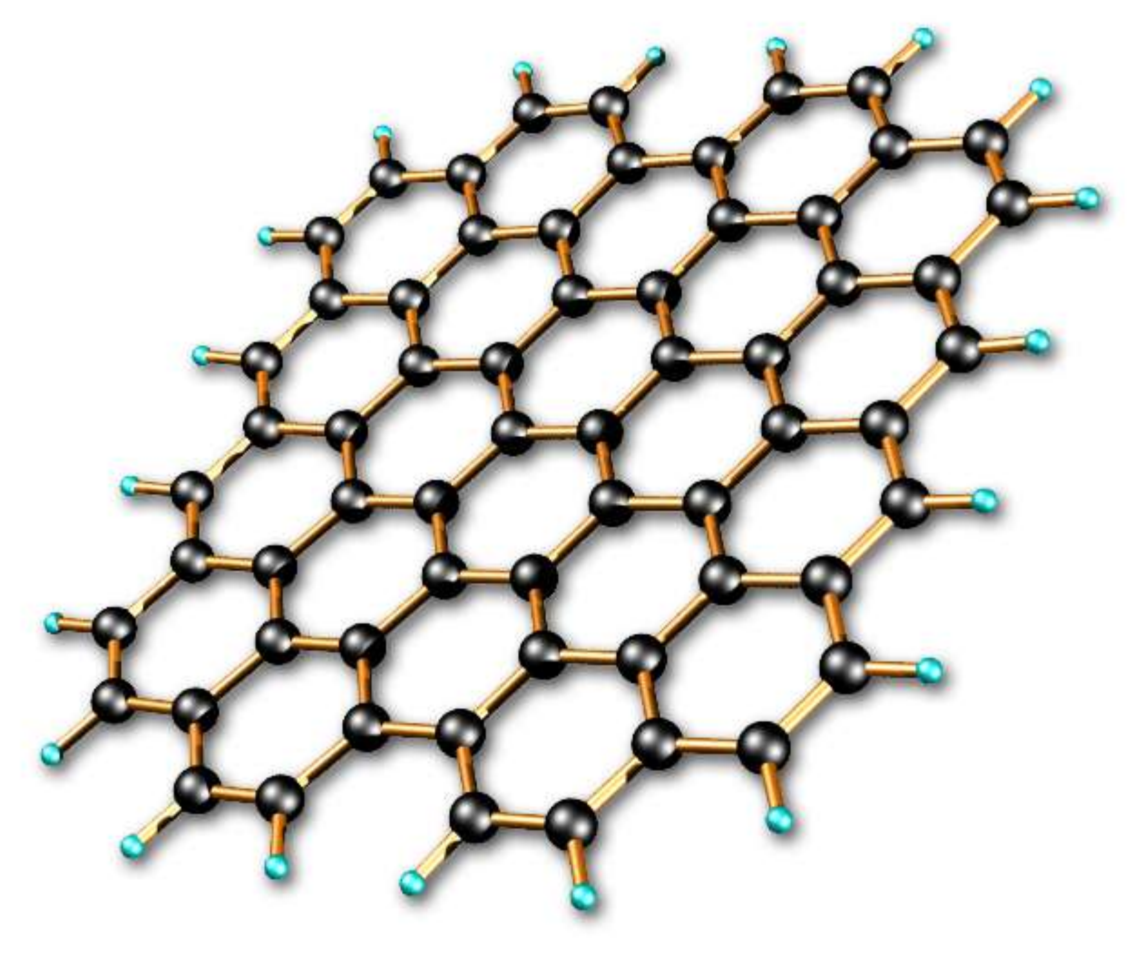
zrolowany w 2D – nanorurki

ułożony w stosie w 3D – grafit

Brak podstawowej przerwy energetycznej w strukturze elektronowej

Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.[1] The term *graphene* was coined as a combination of graphite and the suffix -ene by Hanns-Peter Boehm,[2] who described single-layer carbon foils in 1962.[3] Graphene is most easily visualized as an atomic-scale chicken wire made of carbon atoms and their bonds. The crystalline or "flake" form of graphite consists of many graphene sheets stacked together.

Absence of a fundamental energy gap in its electronic structure



Graphene structure

Graphene

methods of preparation

laboratory (A.Geim, K.Novoselov) tixo

- thermal decomposition of silicon carbide, silicon sublimation from SiC plate (at > 1600degC)

- epitaxial CVD (ITME) evaporation of silicon from SiC by laminar flow of argon, propane C3 H8 (diffusion coefficient different for silicon and propane in argon at > 1600degC

Grafen

Metody wytwarzania

Laboratoryjna (A.Geima, K.Novoselova) tixo

- rozkładu termicznego SiC ;sublimacja krzemu z płytki SiC (temp. >1600^{0}C)
- epitaksjalna CVD (ITME) odparowanie krzemu z SiC przy laminarnym przepływie argonu + propan C_3 H_8 (różny wsp.dyfuzji krzemu i propanu w argonie)

Structural nanomaterials

Nanomateriały strukturalne

- **Nano-powders** Nanoproszki
  - -**chemical methods** metody chemiczne
  - -**dispersive mechanical methods**

dyspersyjne metody mechaniczne (mielenie, wibracje, tarcie)

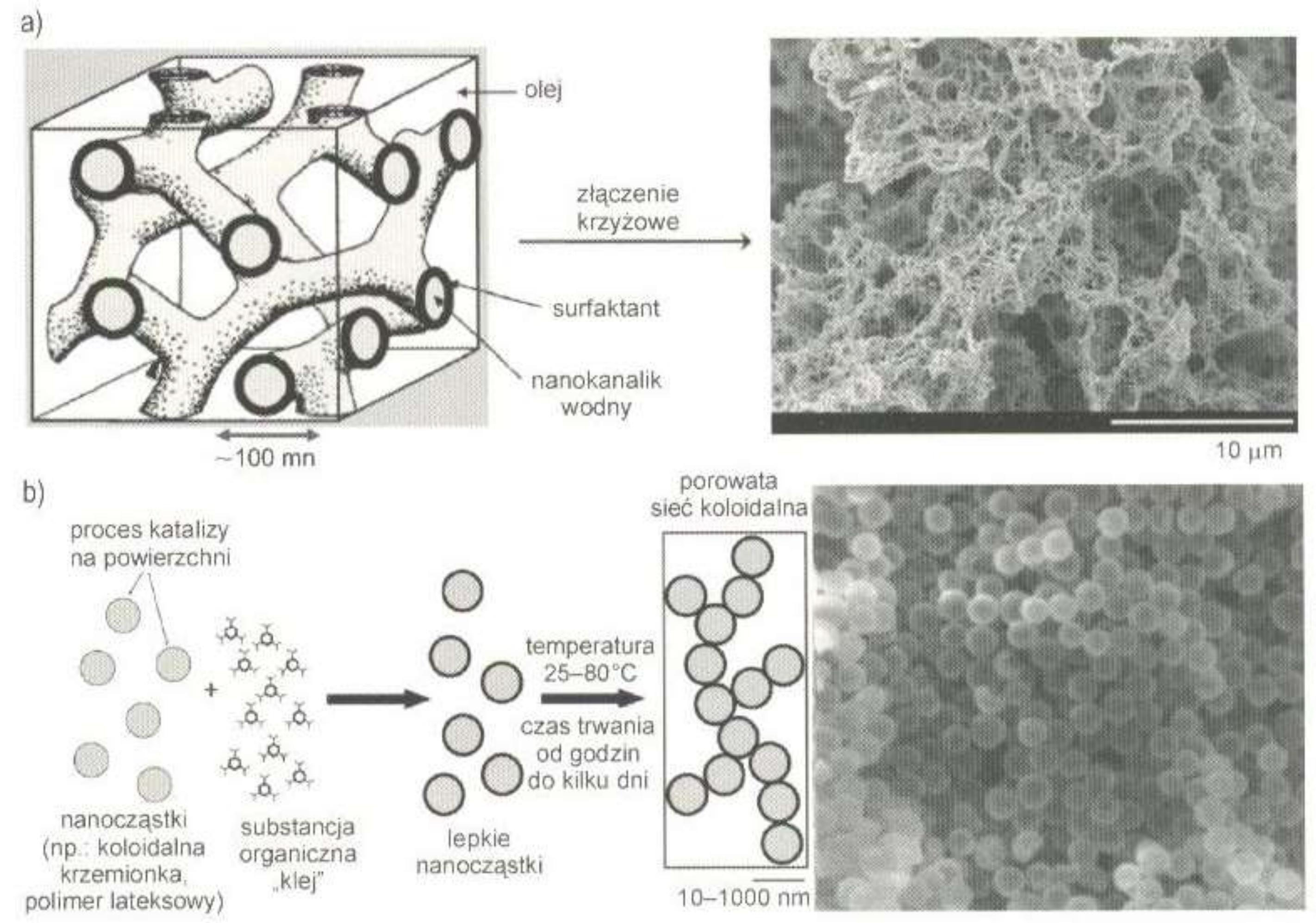
  - -**vacuum methods** metody próżniowe
- **Nano-fibers** Nanowłókna
  - -electrospining elektroprzędzenie
  - -mechanical - sprying of alloys

    mechaniczne (wydmuchiwanie stopu)
  - -chemical chemiczne

Nanomateriały strukturalne

- Nanoproszki
  - -metody chemiczne
  - -dyspersyjne metody mechaniczne (mielenie, wibracje, tarcie)
  - -metody próżniowe
- Nanowłókna
  - -elektroprzędzenie
  - -mechaniczne (wydmuchiwanie stopu)
  - -chemiczne

- **Porous nanomaterials** (Maz.2.72)



Przykłady przestrzennej struktury materiałów nanoporowatych: a) struktura porowata nieregularna, b) struktura zbudowana z kulistych nanocząstek o średnicy < 200 nm i odległości pomiędzy nanocząstkami większej niż 500 nm

- **Nano-metals**

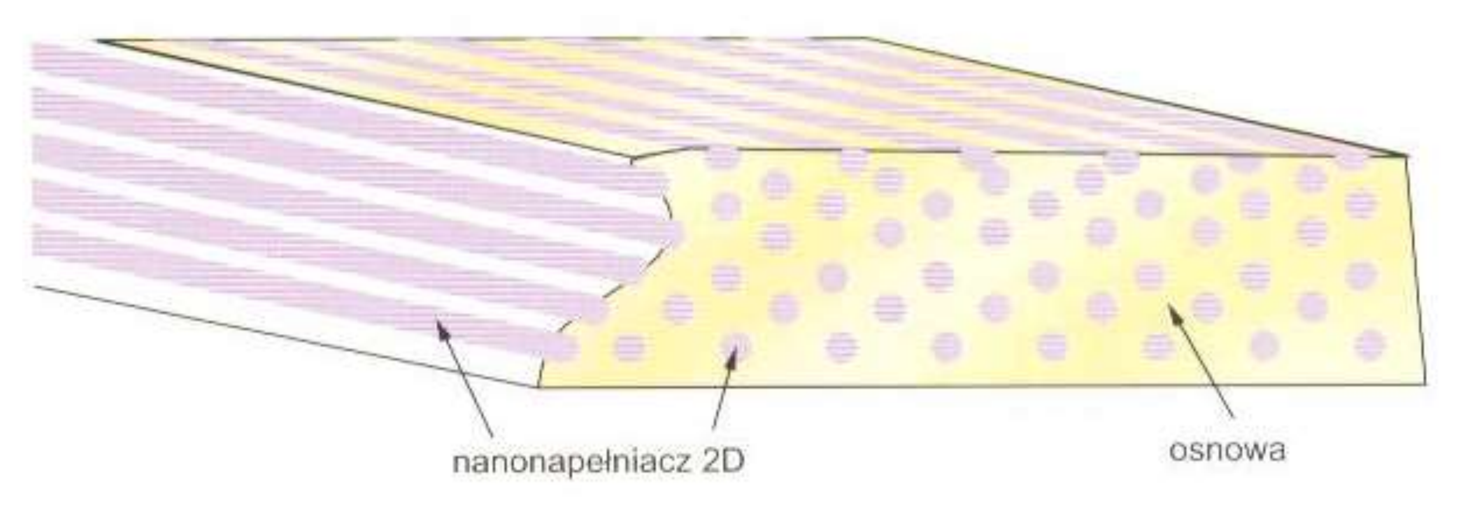
SPD – severe plastic deformation

ECAP –przeciskanie przez kanał kątowy /equal angular pressing/

HPT –skręcanie /high pressure torsion/

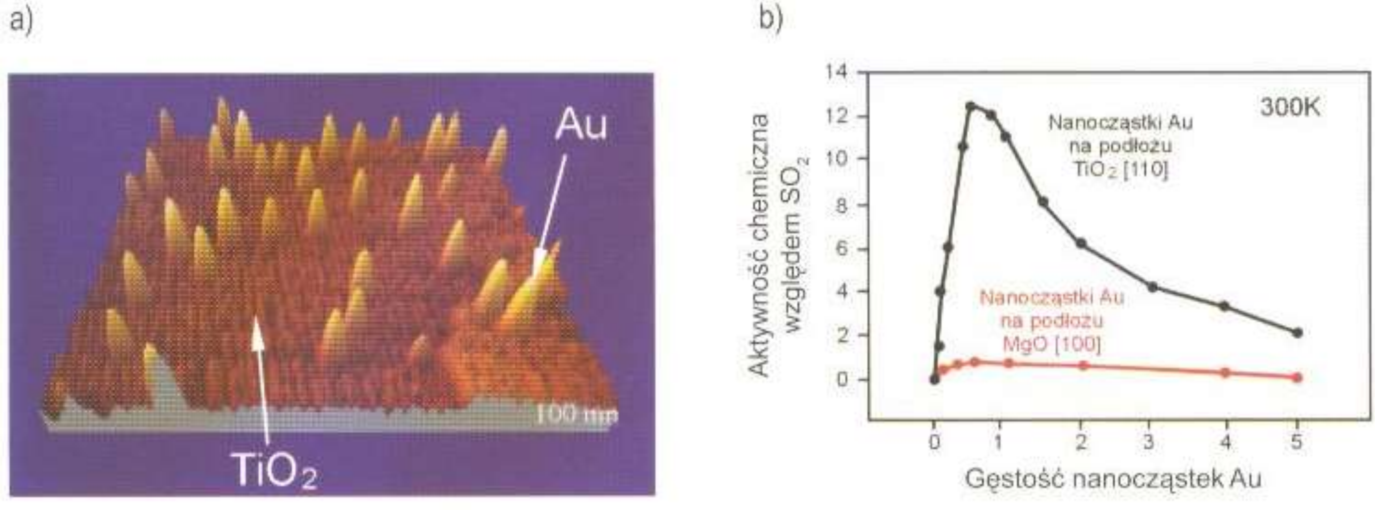
ARP –walcowanie akumulacyjne /accumulative roll bonding/

- **Nano-composites** (Maz.2.78)/reinforcement powders, fibers/



Model of nanostructure 2D

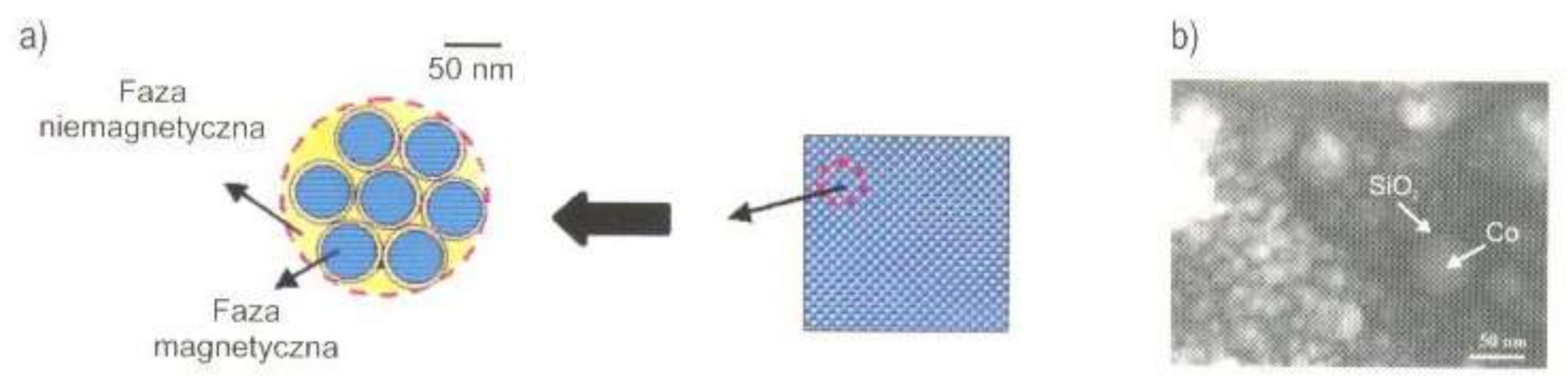
- **Functional nanomaterials**
- **Catalitic nanomaterials** (Maz.2.80)



Struktura powierzchni katalizatora nano-Au: a) topologia powierzchni; b) zależność aktywności chemicznej od podłoża

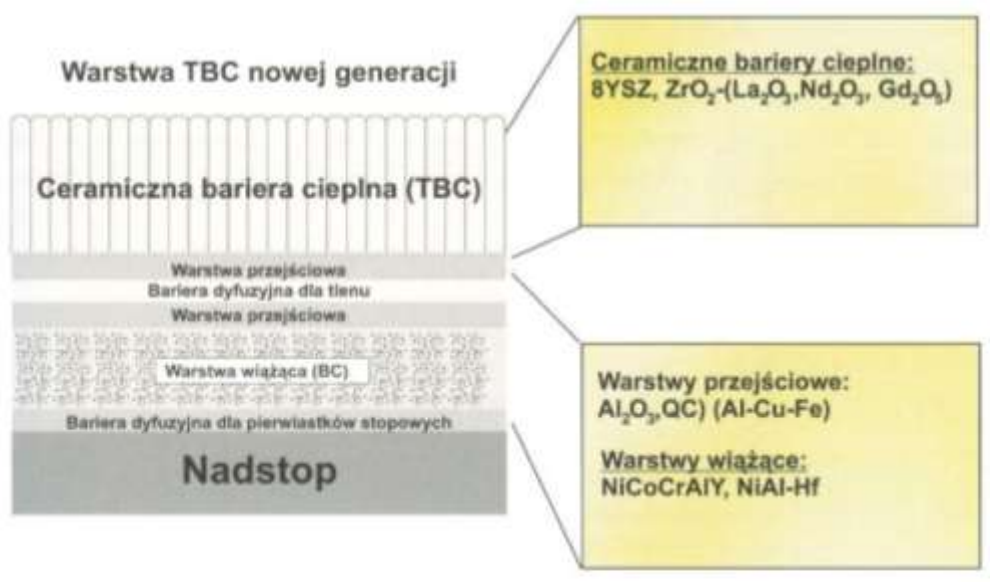
- **Electronic nanomaterials**
- **Magnetic nanomaterials**

- **Nanolayers and nanocoatings**(Maz.2.82)



Kompozyt jako nanomateriał magnetyczny: a) schemat budowy nanokompozytu magnetycznego; b) obraz struktury nanomateriału magnetycznego z tunelowego mikroskopu elektronowego

- **Thermal barier coatings** (Maz.2.88)



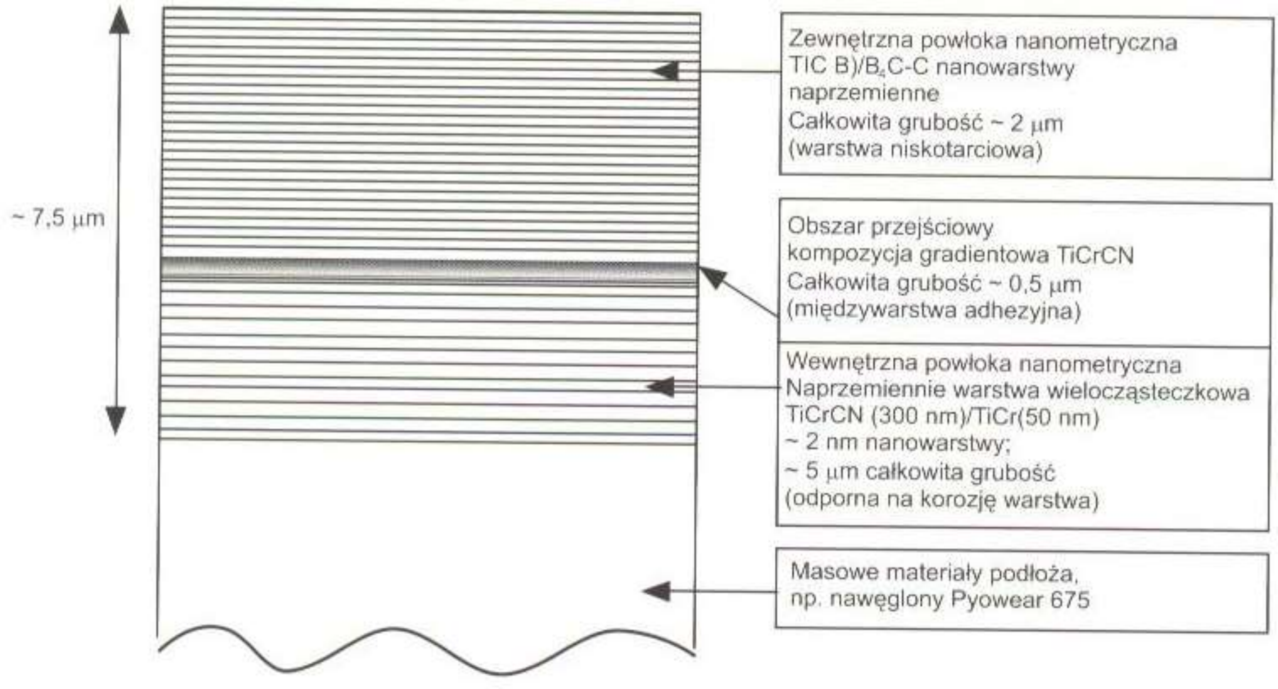
Ceramiczne bariery cieplne:
8YSZ, ZrO_2-(La_2O_3,Nd_2O_3, Gd_2O_3)

Warstwy przejściowe:
Al_2O_3,QC) (Al-Cu-Fe)

Warstwy wiążące:
NiCoCrAlY, NiAl-Hf

Schemat powłoki ochronnej z barierą cieplną

- **Antiwear coatings** (Maz.2.92)



Zewnętrzna powłoka nanometryczna
TIC B)/B_4C-C nanowarstwy
naprzemienne
Całkowita grubość ~ 2 μm
(warstwa niskotarciowa)

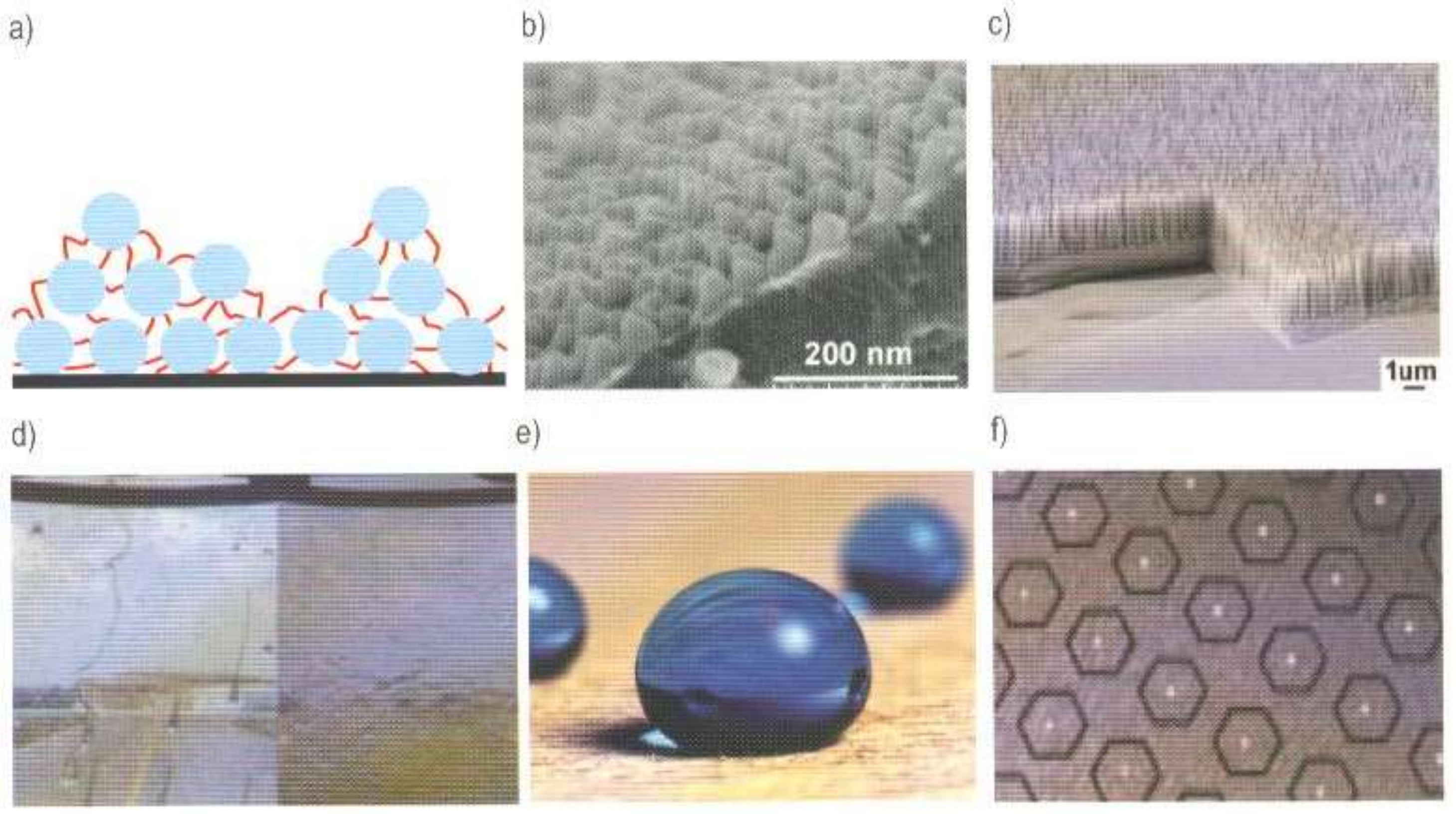
Obszar przejściowy
kompozycja gradientowa TiCrCN
Całkowita grubość ~ 0,5 μm
(międzywarstwa adhezyjna)

Wewnętrzna powłoka nanometryczna
Naprzemiennie warstwa wielocząsteczkowa
TiCrCN (300 nm)/TiCr(50 nm)
~ 2 nm nanowarstwy;
~ 5 μm całkowita grubość
(odporna na korozję warstwa)

Masowe materiały podłoża,
np. nawęglony Pyowear 675

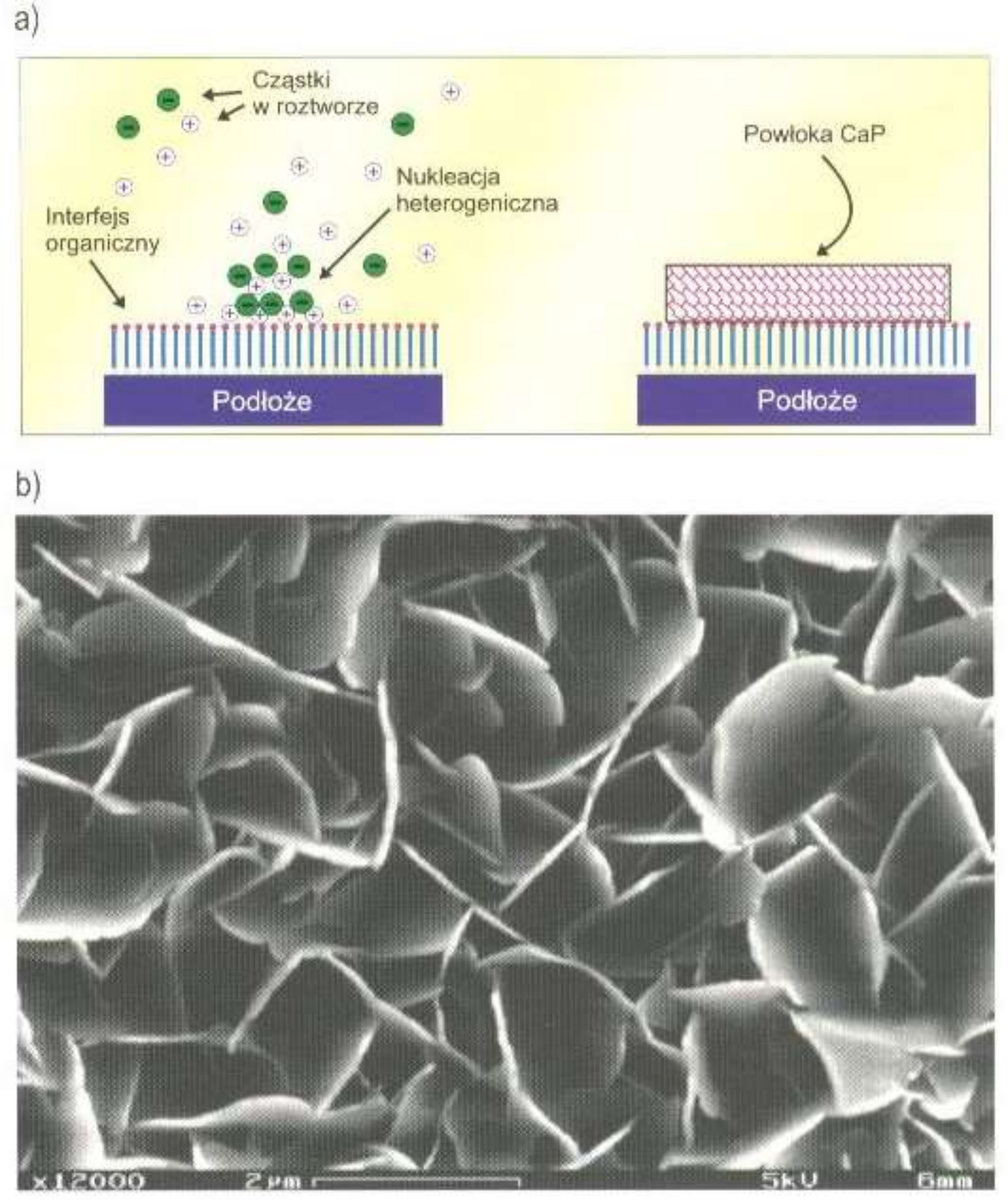
Schemat wielowarstwowej nanostrukturalnej powłoki przeciwzużyciowej zaprojektowanej do zastosowania na kołach zębatych w przemyśle lotniczym

- **Hydrophobic coatings** (Maz.2.95)



Przykłady nanostrukturalnych powłok hydrofobowych i ich zastosowań

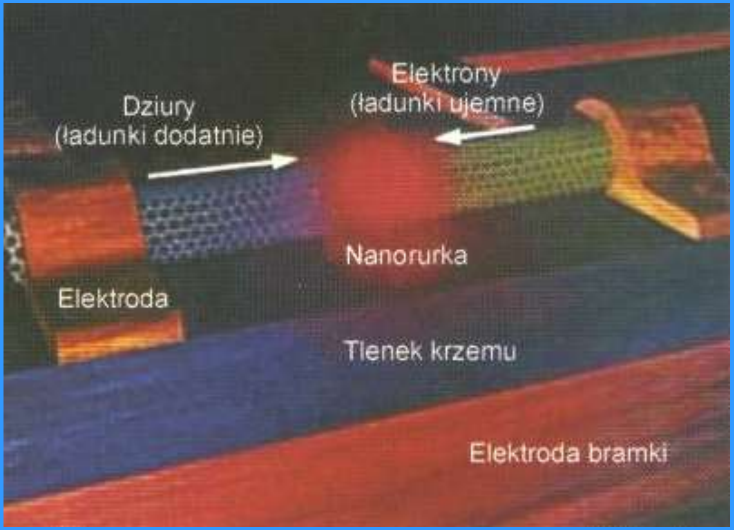
• Biocompatibile coatings (Maz.2.96)



Powłoka CaP wytworzona z wykorzystaniem biomimetycznego procesu osadzania SIM: a) schemat procesu osadzania, b) obraz mikroskopu SEM powierzchni powłoki

Devices in nano-scale

- Photonic nano-devices (Maz.2.99)

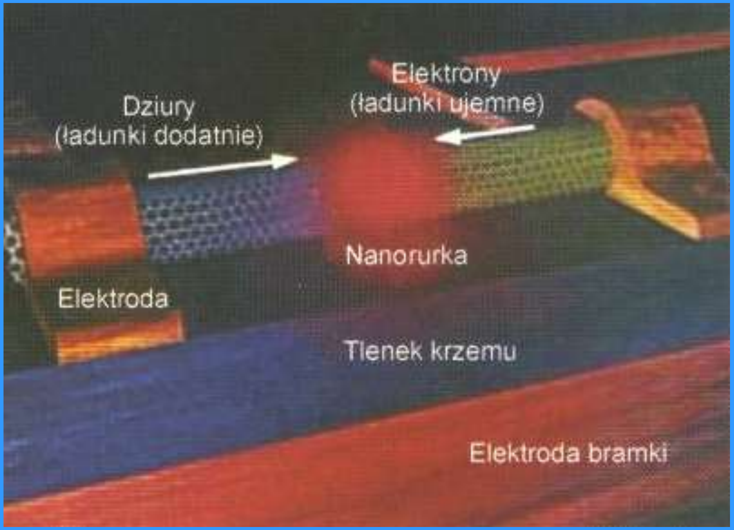


The principle of operation of the light source using carbon nanotubes

- Nano-sensors and biosensors
- Nano-elements prone and moving
- Nano-drive
- Nano-machines and nano-robots
- Nano-manipulatorof particles and molecules
- Nano-source power, nano-generator
- Nano-filters active

Urządzenia w nanoskali

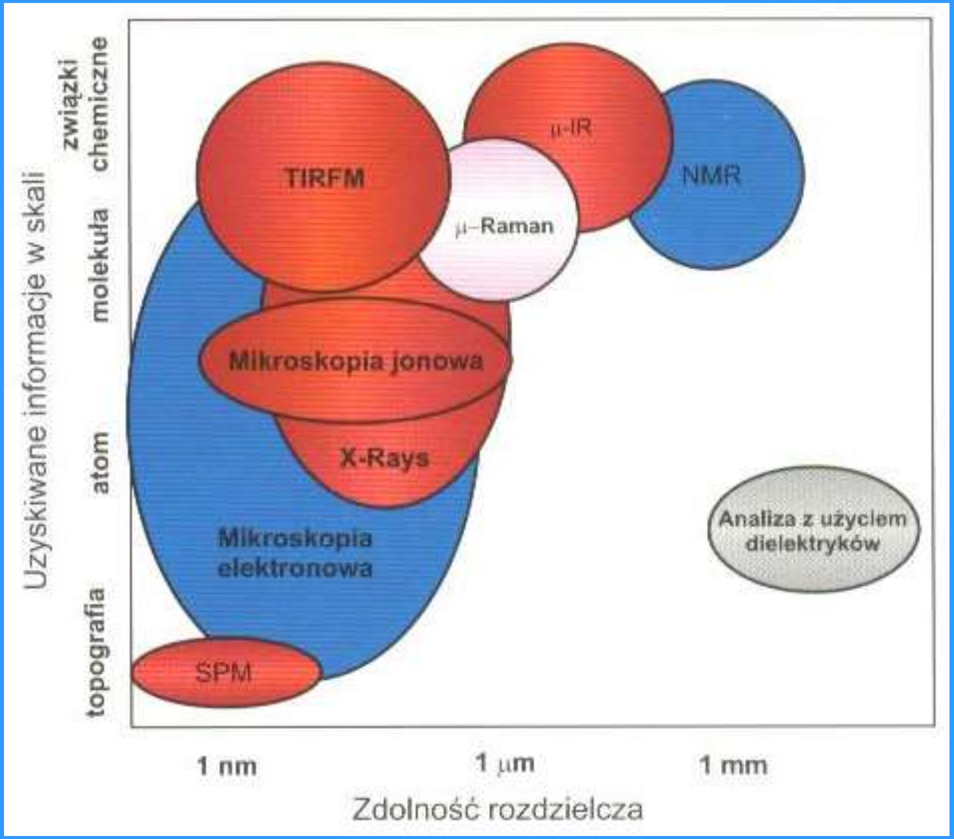
- Nanourządzenia fotoniczne (Maz.2.99)



Zasada działania źródła światła z wykorzystaniem nanorurki węglowej

- Nanosensory i biosensory
- Nanoelementy podatne i ruchome
- Nanonapędy
- Nanomaszyny i nanoroboty
- Nanomanipulatory cząstek i molekuł
- Nanoźródła zasilania, nanogeneratory
- Nanofiltry aktywne

Nanodiagnostic and nanometrology (Maz.2.129)



SPM-Scaning Probe Microscopy;

TIRFM-Total Internal Reflection Fluorescence Microscope

FIM-Field Ion Microscope

μ-IR-Infrared Radiation; NMR-Nuclear Magnetic Resonanse

Nanotechnology

processes and devices

- Synthesis of nanoparticles and crystallites
- Production nanometals
- Production of composites
- Preparation of surface nanostructures
- Production of semiconductor nanostructures
- Design and manufacture of process equipment
- Advanced universal components / plasma sources, ion sources, vacuum systems, microwave systems, distributed control systems /

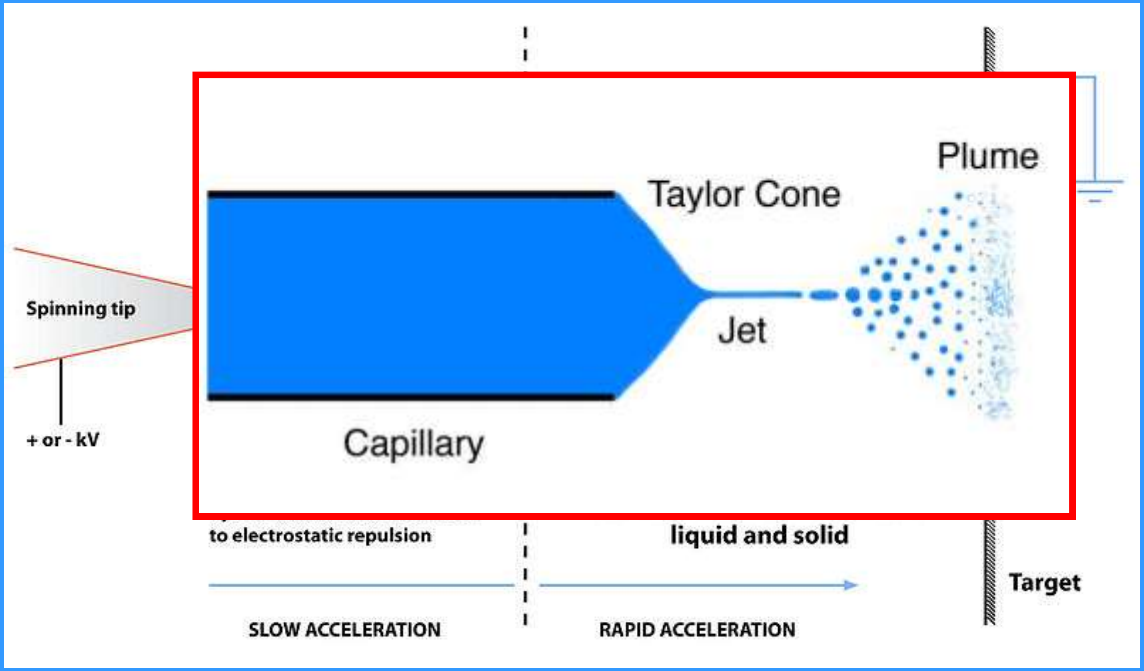
Nanotechnologie

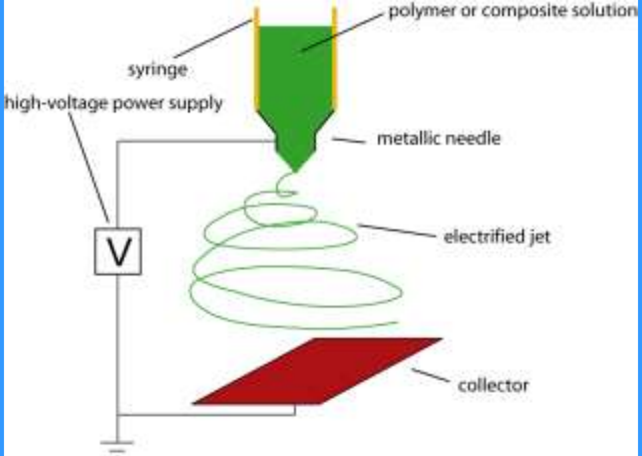
procesy i urządzenia

- Synteza nanocząstek i krystalitów
- Produkcja nanometali
- Produkcja kompozytów
- Wytwarzanie nanostruktur powierzchniowych
- Produkcja nanostruktur półprzewodnikowych
- Projektowanie i wytwarzanie urządzeń technologicznych
- Zaawansowane podzespoły uniwersalne /źródła plazmy, źródła jonów, układy próżniowe, układy mikrofalowe, rozproszone systemy sterowania/

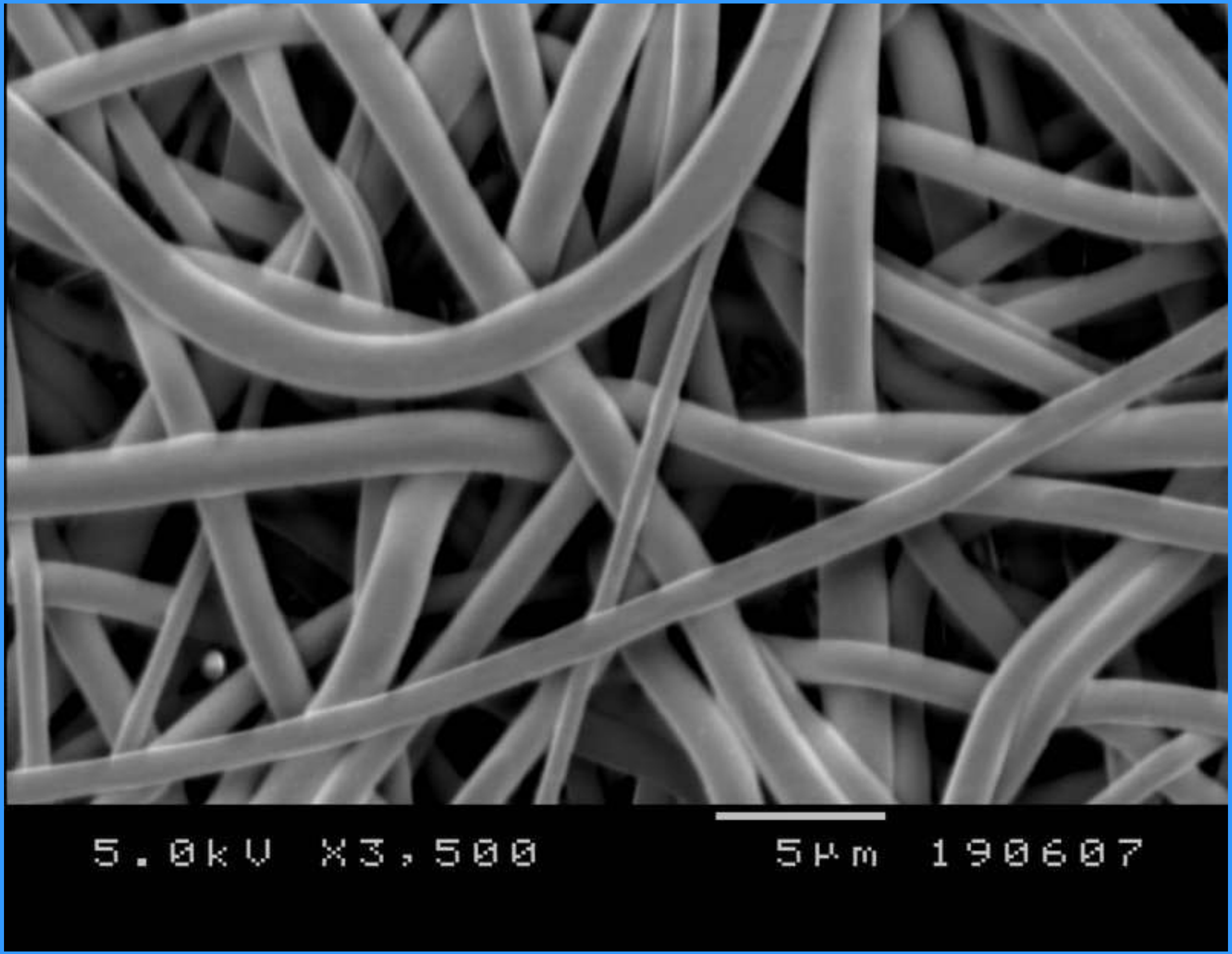
Electrospinning

Tissue precursors – Electrospinning technology





Tissue precursors - electrospinning

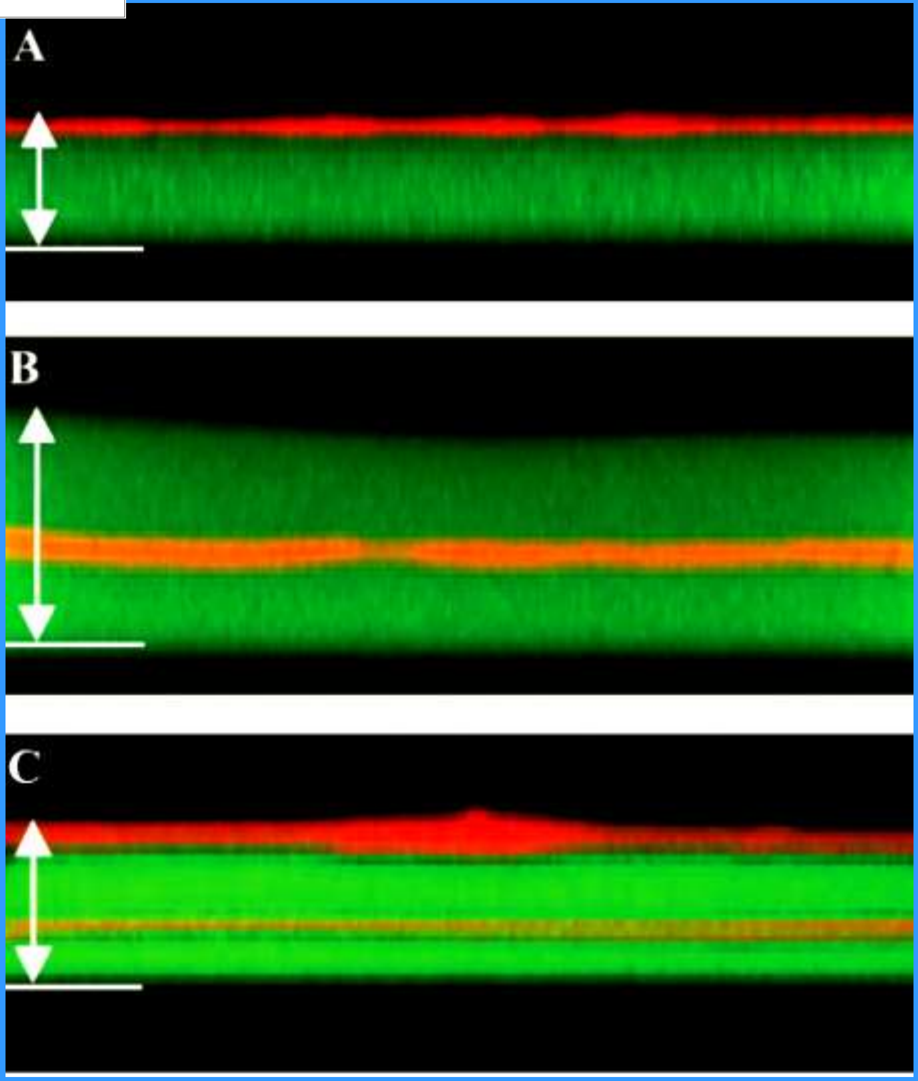


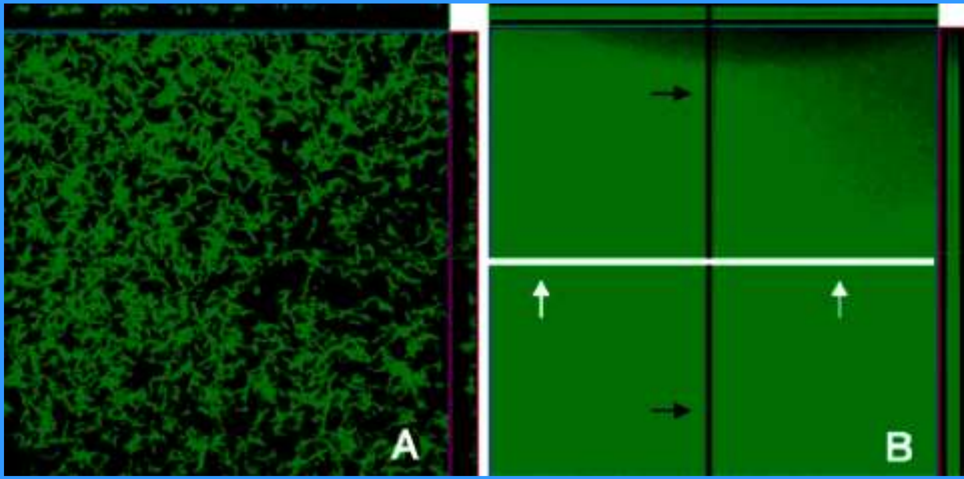
Center for Biomedical Engineering and Physics;
Medical University Viena AKH Austria,
Centrum Materiałów Węglowych i Polimerowych PAN Zabrze

Polyelectrolites

PLL/HA

poly-L-lysine/hyaluronic acid



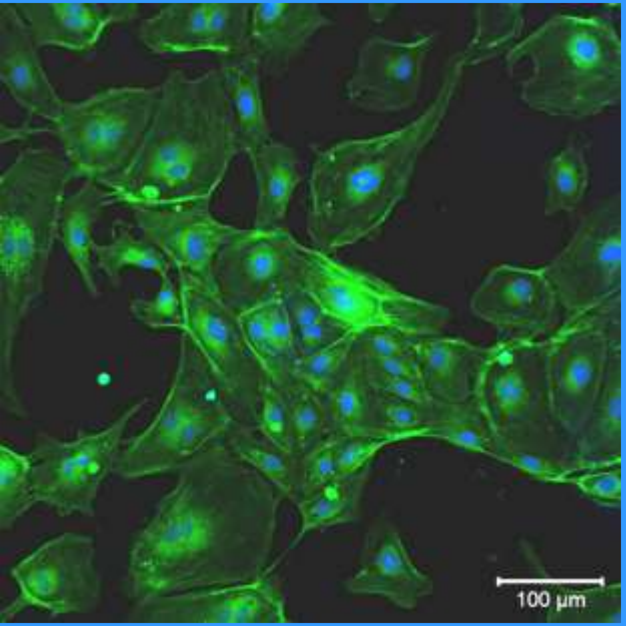


•Ludovic Richert, Fouzia Boulmedais, Philippe Lavalle, Jerome Mutterer, Emmanuelle Ferreux, Gero Decher, Pierre Schaaf, Jean-Claude Voegel and Catherine Picart; Improvement of Stability and Cell Adhesion Properties of Polyelectrolyte Multilayer Films by Chemical Cross-Linking; Biomacromolecules (2004), 5,284-294

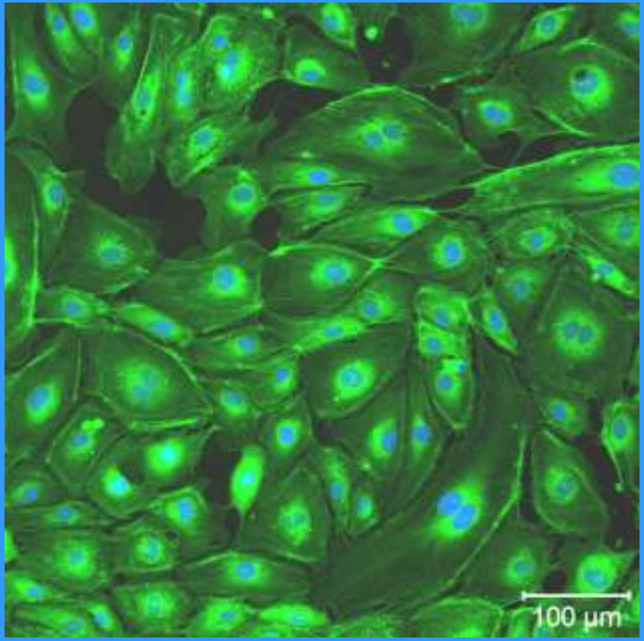
C. Picart, J. Mutterer, L. Richert, Y. Luo, G. D. Prestwich, P. Schaaf, J.C. Voegel, and P. Lavalle Molecular basis for the explanation of the exponential growth of polyelectrolyte multilayers; PNAS October 1, (2002) vol. 99 no. 20 p 12531–12535

Cell answer

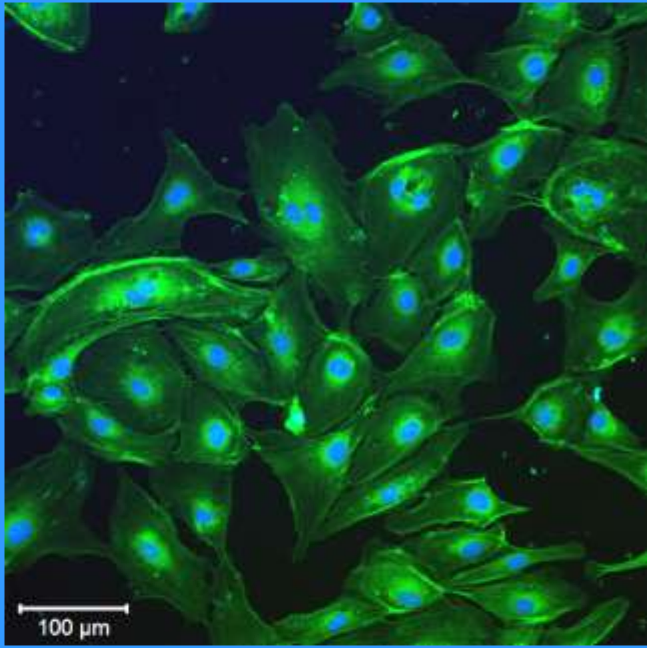
12 (PLL-HA) cross +PLL+ fibronectin + HUVEC



200 mM

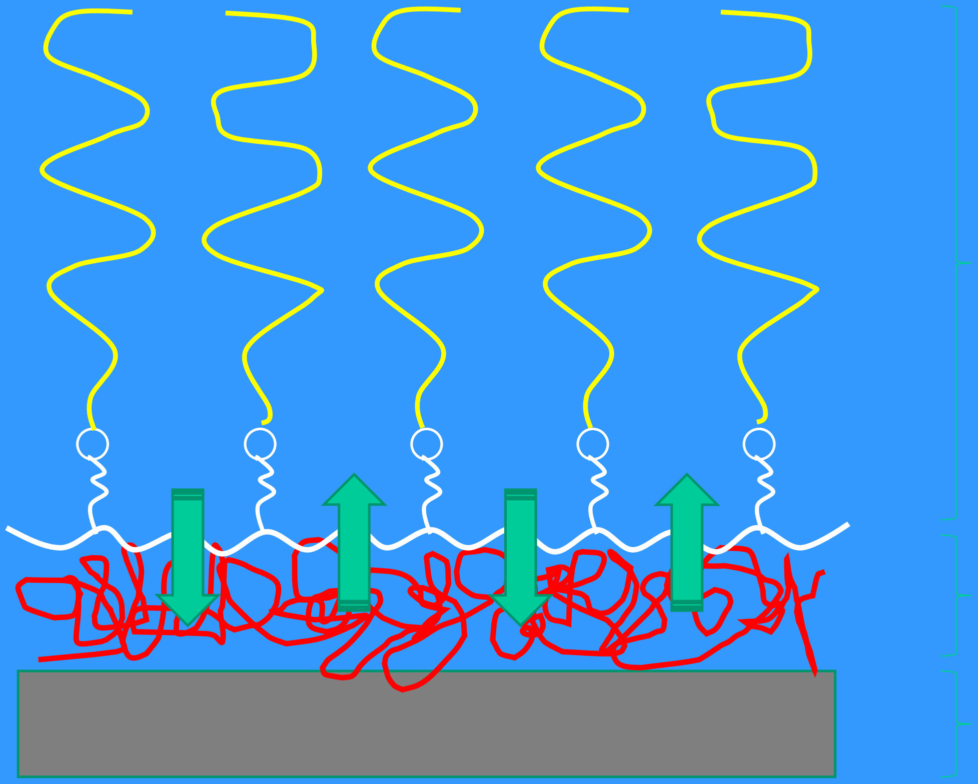


400 mM



800 mM

Proposition



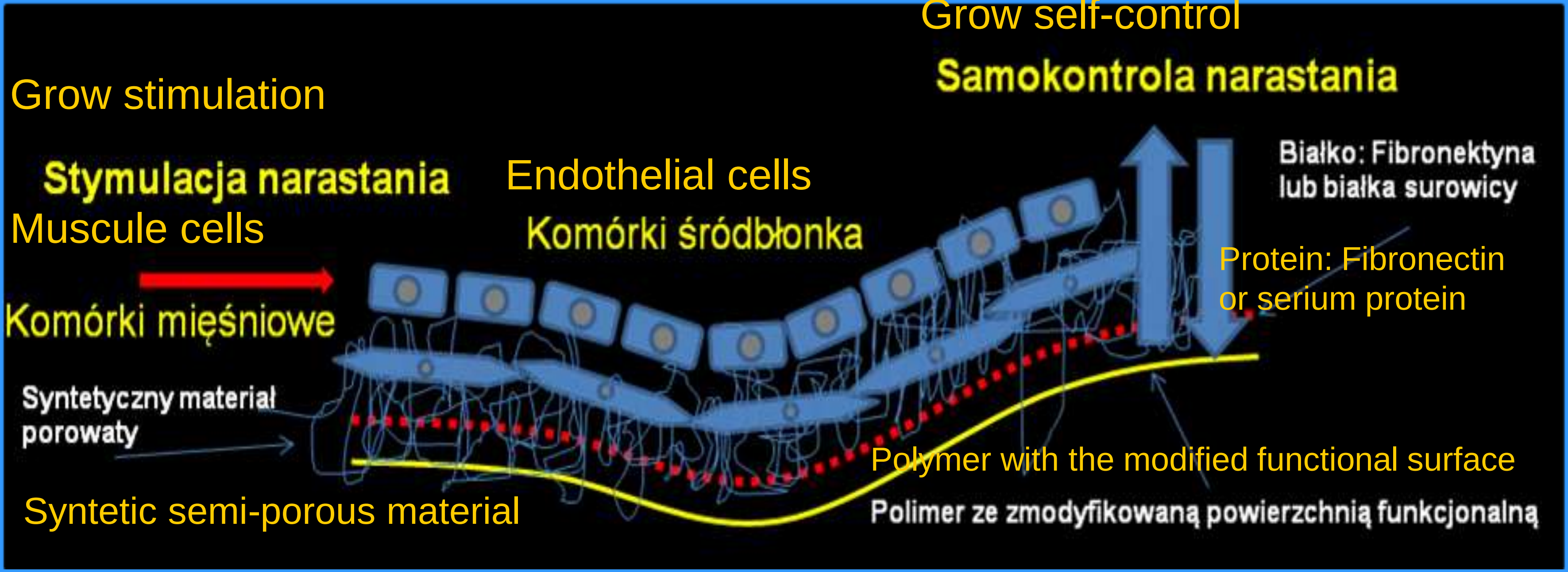
Antythrombogenic function

Porous coatings

Substrate with ceramic/metallic coatings

Sara Morgenthaler, Christian Zink, Brigitte Städler, Janos Vörös, Seunghwan Lee, Nicholas D. Spencer,a and Samuele G. P. Tosatti; Poly L-lysine-grafted-poly„ethylene glycol-based surface-chemical gradients. Preparation, characterization, and first applications; Biointerphases 1„4, American Vacuum Society December 2006

Architecture of semi-porous coating



Grow self-control

Grow stimulation

Endothelial cells

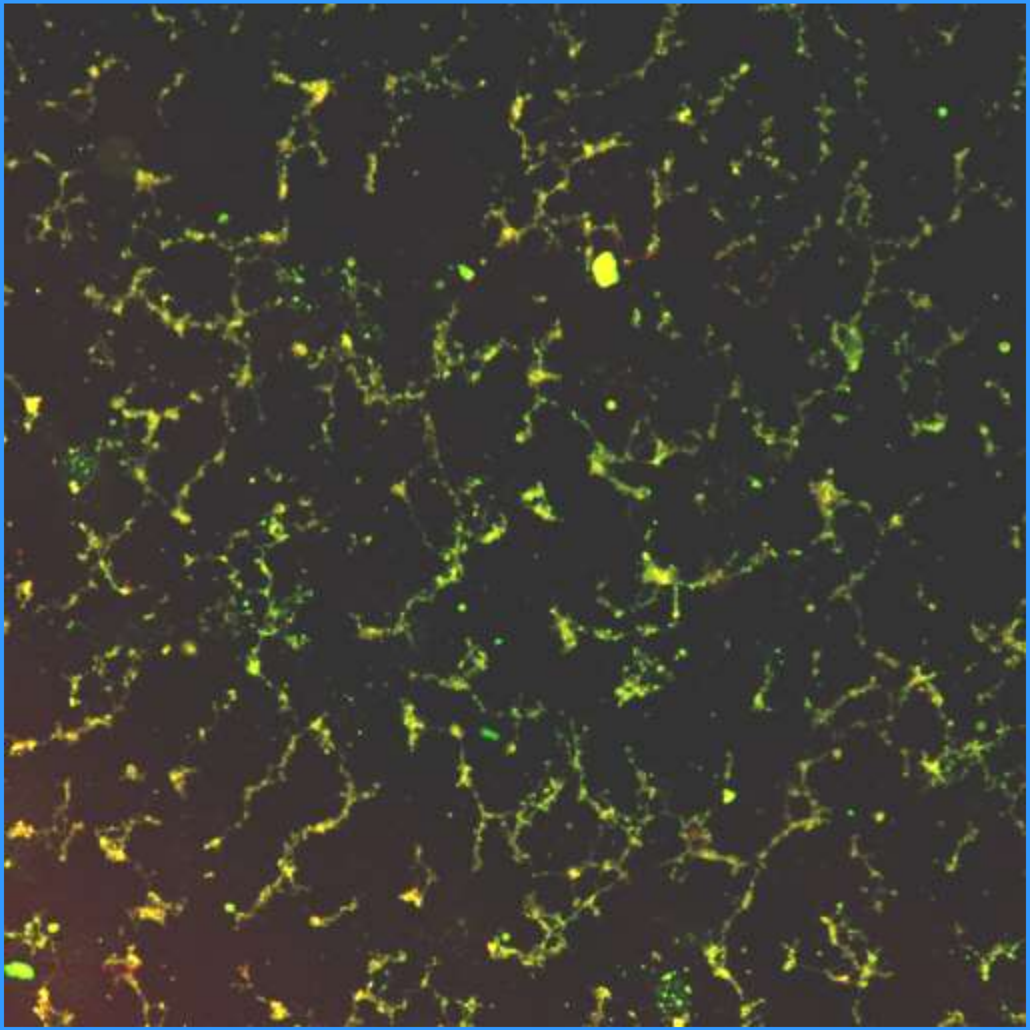
Muscule cells

Protein: Fibronectin
or serium protein

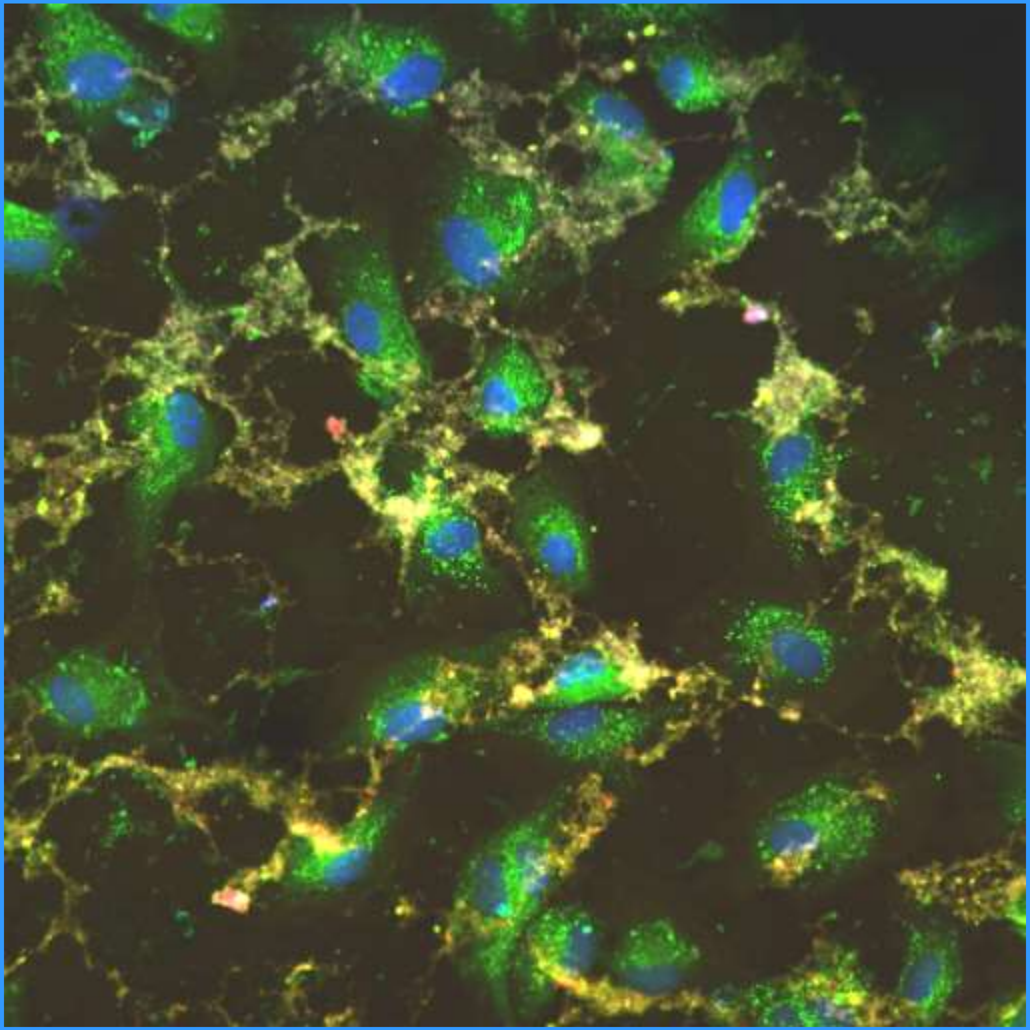
Polymer with the modified functional surface

Syntetic semi-porous material

Surface CLSM PEG (poly-ethylene-glycol)



CLSM PEG+RGD (protein domains)+HUVEC



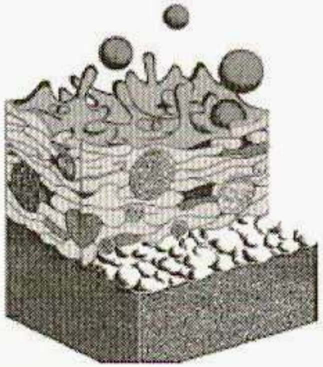
19. Surface modification using thermal plasma

Thermal Plasma

is created during the discharge at a direct-current (dc) or is generated using a radio frequency (RF) at atmospheric pressure and reduced pressure (between 10 and 50 kPa); is used widely in surface engineering

Deposition using plasma (plasma spray);

metallic and non-metallic particles are embedded in the liquid or the semi-liquid state on substrate (Pau 9.1)



Sketch of the coating structure with splats, un-melted particles, voids, pores.

Following plasma spraying systems are distinguished:

- direct current (DC) system
- at radio frequency (RF)
- in an electric arc (the base is part of an electrical circuit)
- two-wire system (arc between two wires with continuous traverse)

Layout of the direct-current system (Pau 9.2)

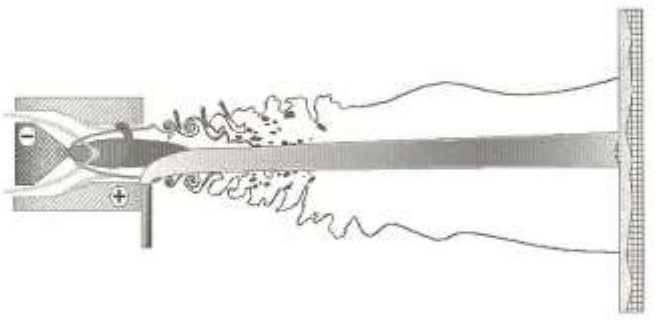


Figure 9.2: Sketch of the d.c. plasma-spraying process.

Layout of two-wire system (Pau 9.5)

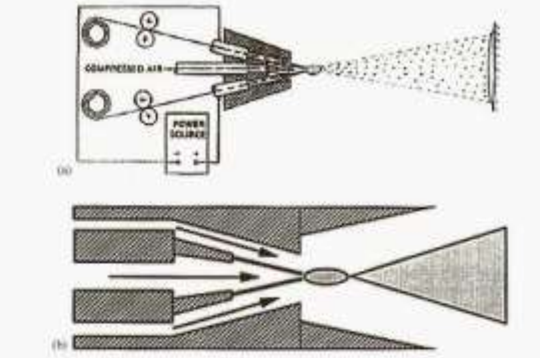
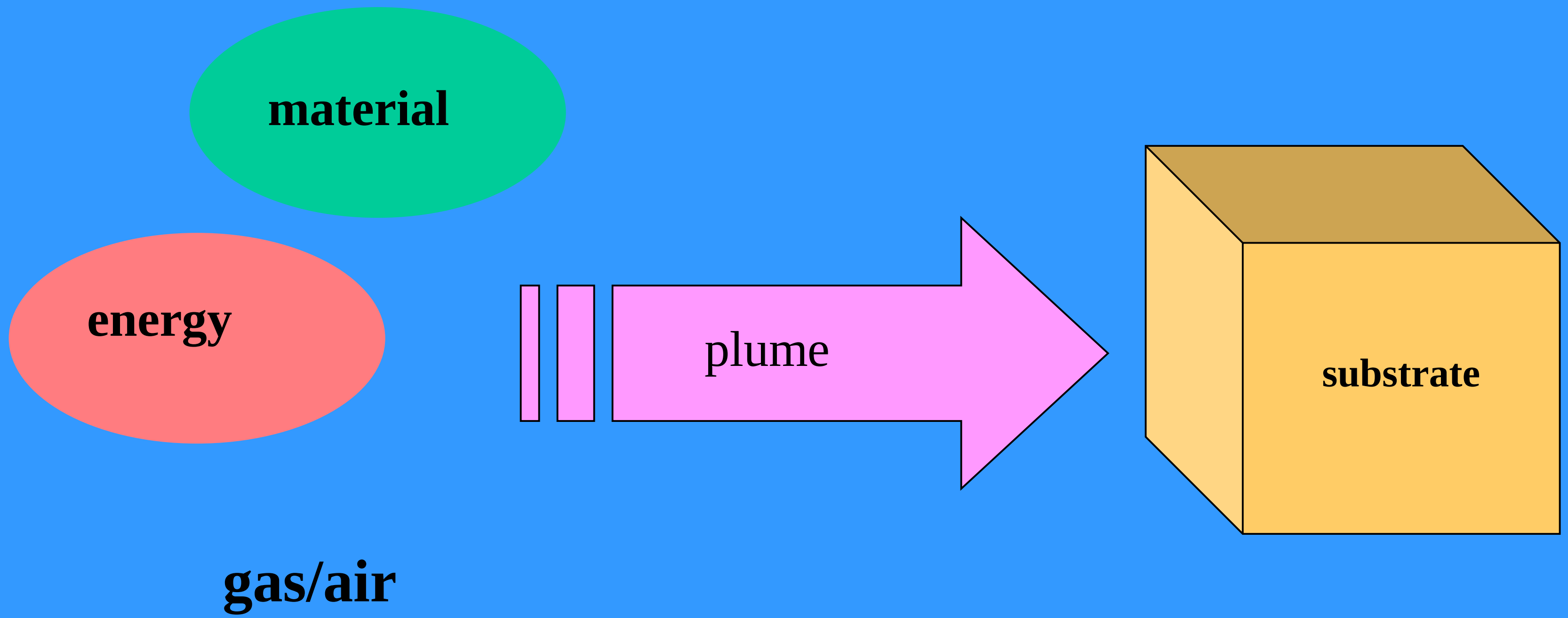


Figure 9.5: (a) Sketch of the wire-arc spraying process and (b) primary and secondary atomization gas in wire-arc spraying.

The first application of plasma spraying techniques - focused on corrosion protection of steel plates by the hot-dip zinckify - was developed on early in the twentieth century by Schoop

Scheme of plasma spray process



material

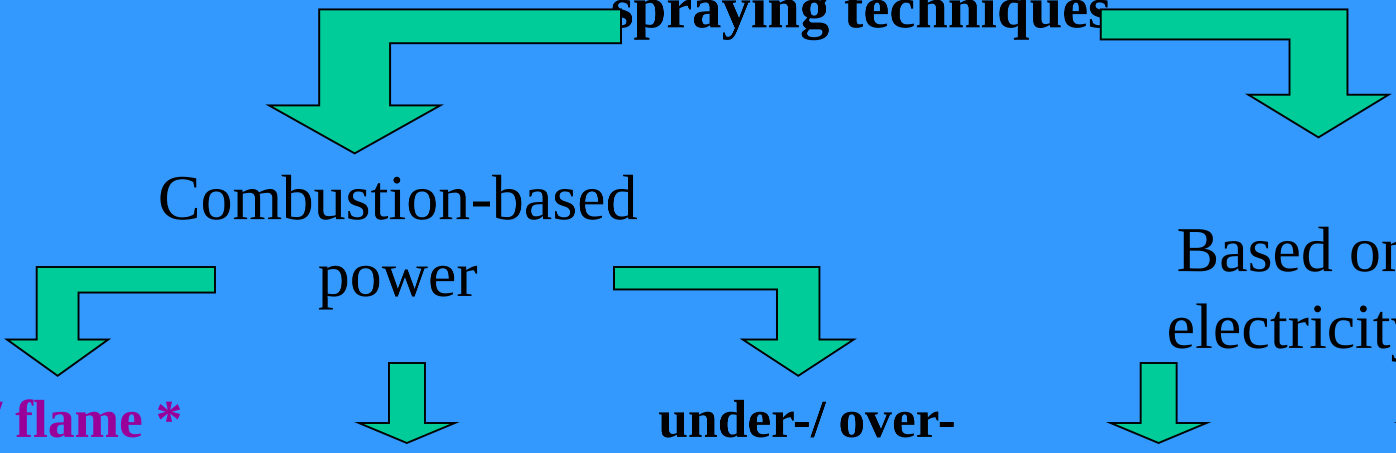
energy

plume

substrate

gas/air

Division of plasma spraying techniques



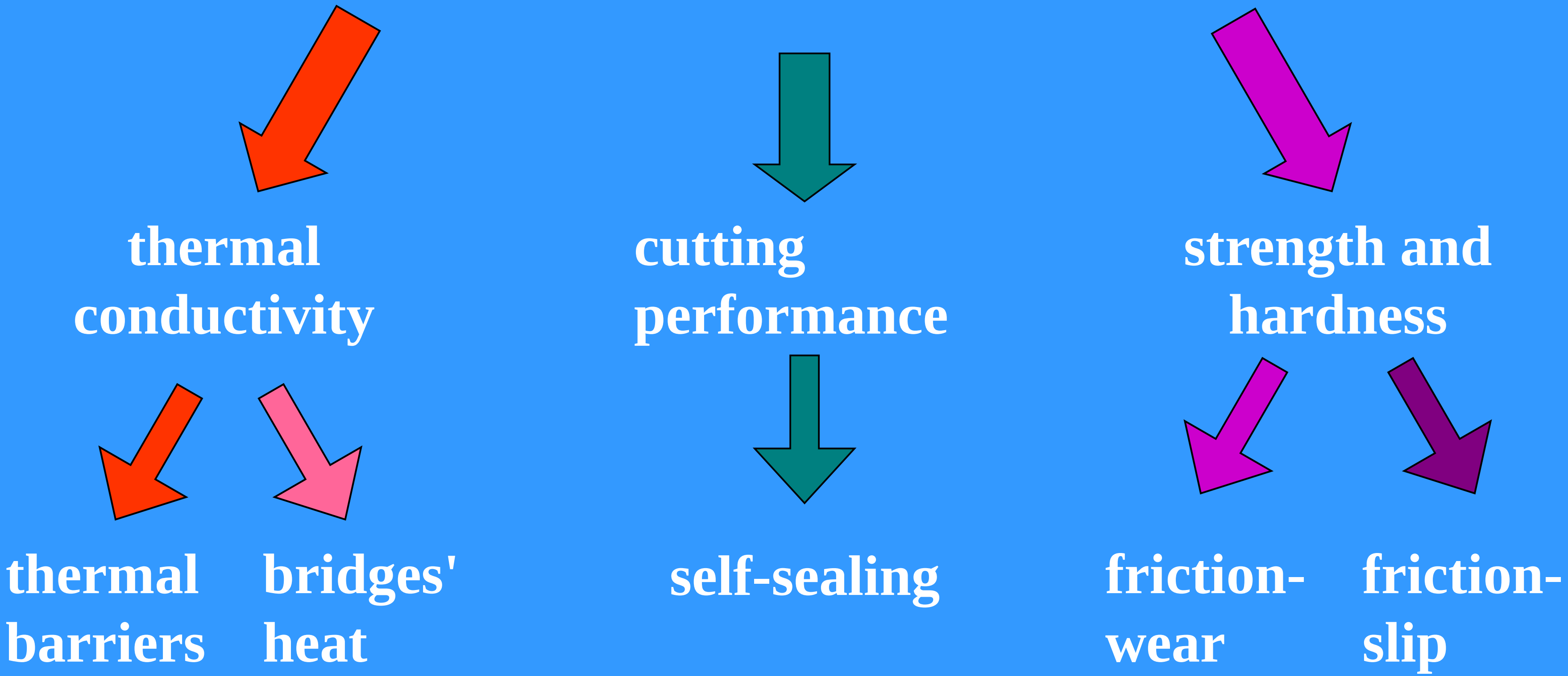
Combustion-based power

Based on electricity

	fire / flame *	detonation	under-/ over-sound	arc *	plasma*
T[ºC]	~ 3 000	~ 3000	~ 3 000	~ 4 000	5 000 - 25 000
V [m/s]	40 - 100	~ 2000	400 - 1000 - 1600	50 - 150	80 - 300

** sometimes the information is added on the "pressure"*

Classification of plasma sprayed layers for their properties and application



thermal conductivity

- thermal barriers
- bridges' heat

cutting performance

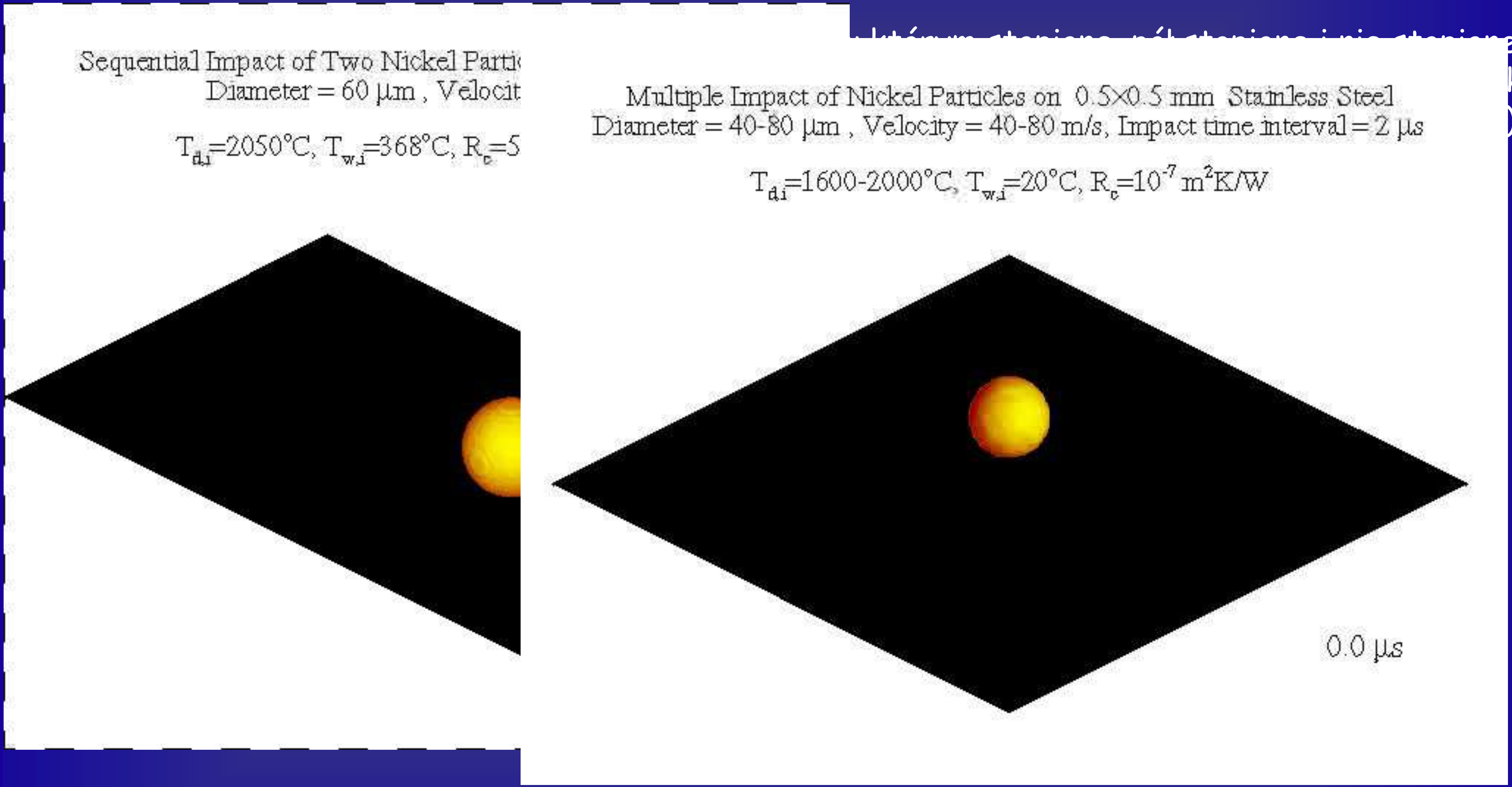
- self-sealing

strength and hardness

- friction-wear
- friction-slip

Thermal spraying coatings

którym stopiona, półstopiona i nie stopione



Thermal spraying coatings

Thermal spraying coatings can be characterized by:

- high resistance to abrasion, high temperature and corrosion

- thermal parameters set (Thermal Barrier Coatings - thermally insulating coating)

- biocompatibility (Hydroxyapatite - NATR. plasma, amorphous 30 - 200 um)

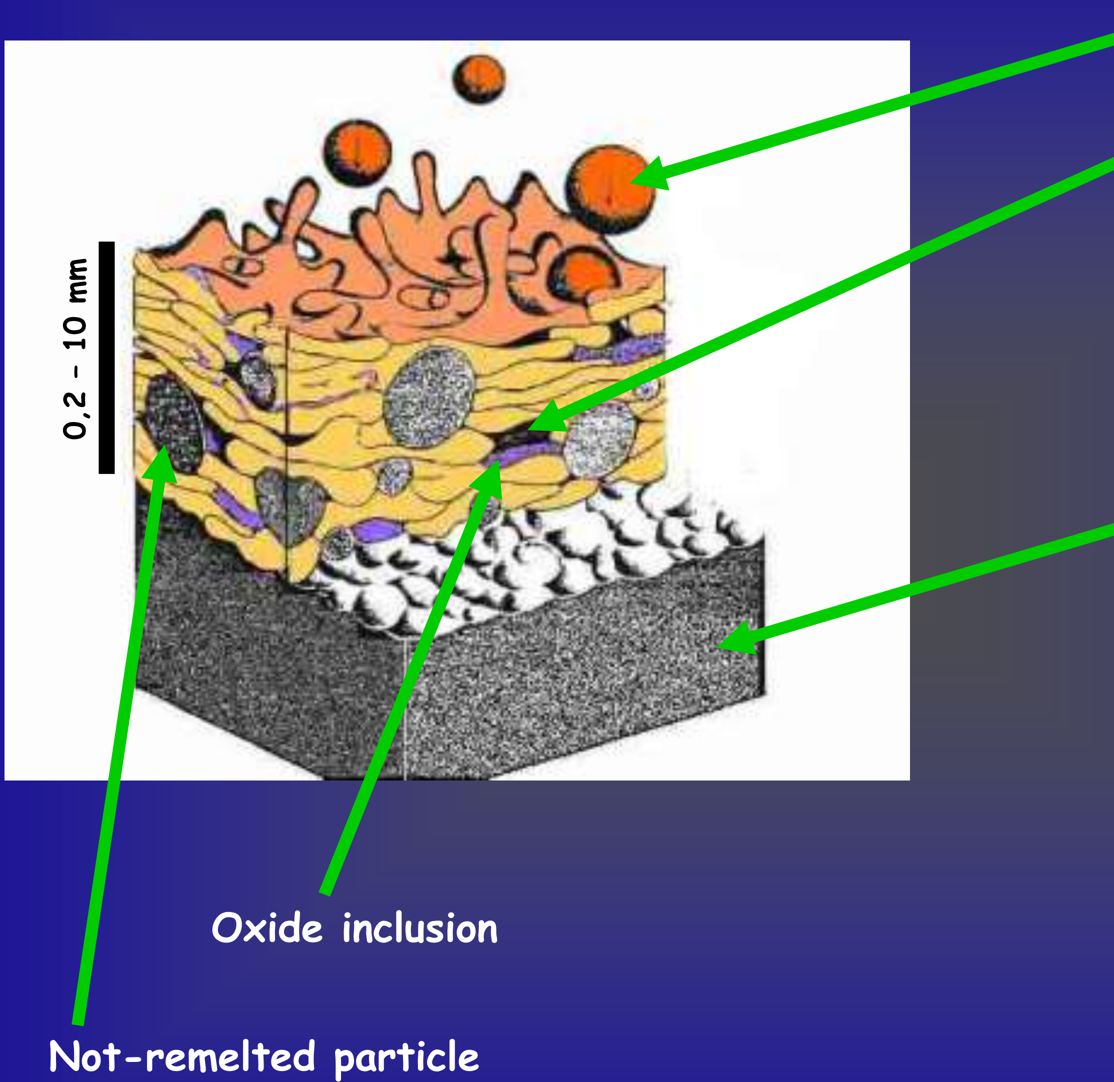
In addition are obtained:

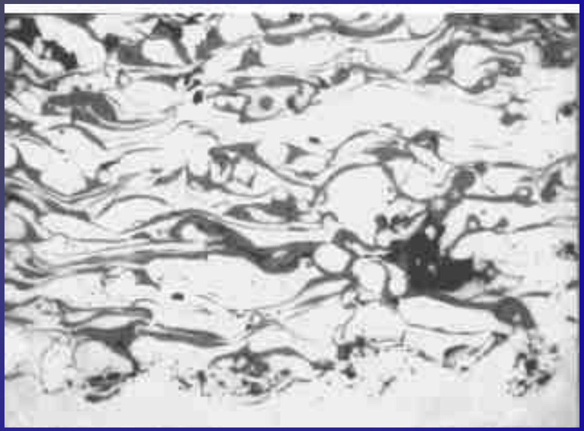
layer of ion guides in the cells (Solid Oxygen Fuel Cells).
electrodes and dense membranes)

regeneration of used machinery parts, chemical equipment, decorative coatings

You can spray multilayers (eg in order to reduce the difference of coefficients thermal expansion of the substrate and the applied layer), and to obtain graded materials (FGM Functionally Graded Material) with a gradient composition, particle size, porosity.

Thermal spraying coatings




Typical surface morphology

Thermal spraying coatings

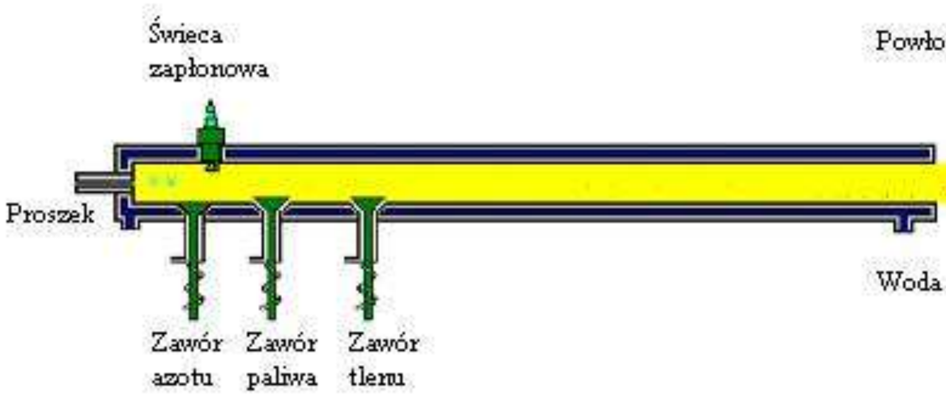
Comparison of spraying methods

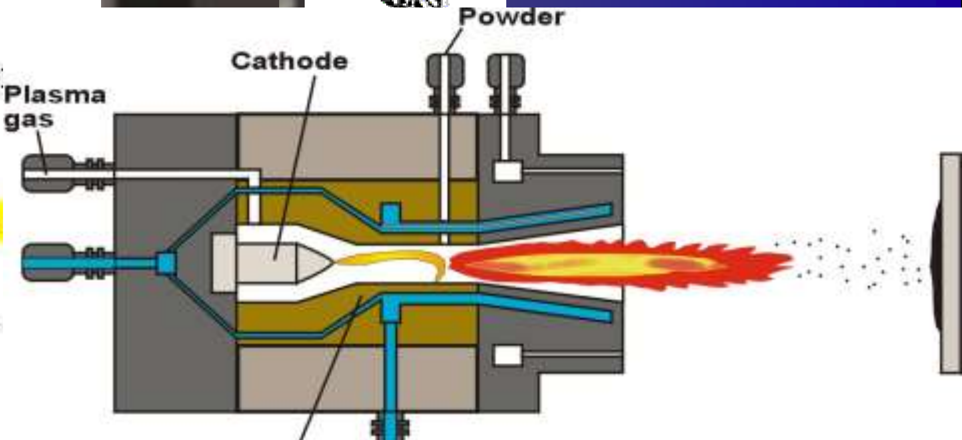
	Szybkość cząstek [m/s] Particle speed	Adhezja [Mpa] Ahesion	Zawartość tlenków [%] Oxides concentration	Porowatość [%] Porosity	Prędkość nanoszenia [kg/h] Deposition rate	Typowa grubość powłoki [mm] Typical coating thickness
Płomieniowe Flame	40	<8	10 - 15	10 - 15	1 - 10	0,2 - 10
Łukowe Arc	100	10 - 30	10 - 20	5 - 10	6 -60	0,2 - 10
Plazmowe Plasma	200 -300	20 -70	1 - 3	5 - 10	1 - 5	0,2 - 2
HVOF	600 - 1000	>70	1 - 2	1 - 2	1 - 5	0,2 - 2
Detonacyjne Detonation	800 - 1000	>70	0,1	0,1 - 1	1 – 2,5	bd

Thermal spraying coatings

Comparison of spraying methods

	Szybkość cząstek [m/s] Particle speed	Adhezja [Mpa] Ahesion	Zawartość tlenków [%] Oxides concentration	Porowatość [%] Porosity	Prędkość nanoszenia [kg/h] Deposition rate	Typowa grubość powłoki [mm] Typical coating thickness
Płomieniowe Flame	40	<8	10 - 15	10 - 15	1 - 10	0,2 - 10
Łukowe Arc	100	10 - 30	10 - 20	5 - 10	6 -60	0,2 - 10
Plazmowe Plasma	200 -300	20 -70	1 - 3	5 - 10	1 - 5	0,2 - 2
HVOF	600 - 1000	>70	1 - 2	1 - 2	1 - 5	0,2 - 2
Detonacyjne Detonation	800 1000	>70	0,1	0,1 1	1 - 2,5	bd



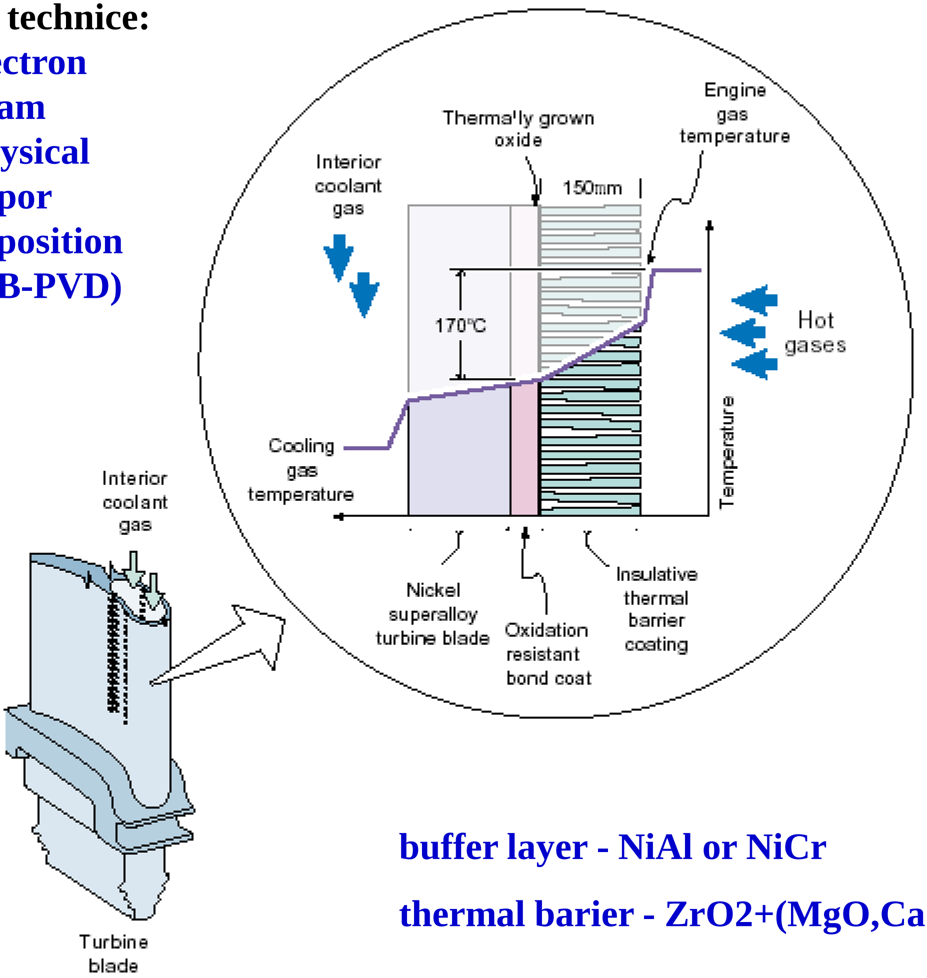


<u>Charakterystyka uzyskiwanych powłok</u>:

- możliwość nanoszenia warstw metali (Ti), stopów (NiCr), ceramiki (Al_2O_3), cermetów ($C_{\text{graf pokryty powierzchniowo Ni}}$) węglików ($Cr_2C_3$)
- nanoszone warstwy mogą być grube
- wiązanie warstwa - podłoże jest mechaniczne, adhezyjne lub dyfuzyjne (nie występuje nadtopienie powierzchni podłoża)
- możliwe jest natryskiwanie materiałów i podłoży metalurgicznie niezgodnych ($T_1>T_2$)
- tanio, łatwo i szybko nanoszone powłoki regenerujące części urządzeń są wytrzymałe (zwiększenie żywotności maszyn)

Warstwowe bariery termiczne

dotąd oparte na technice:
electron beam physical vapor deposition (EB-PVD)



buffer layer - NiAl or NiCr

thermal barier - ZrO2+(MgO,CaO)

Uszczelnienia - natryskiwanie plazmowe

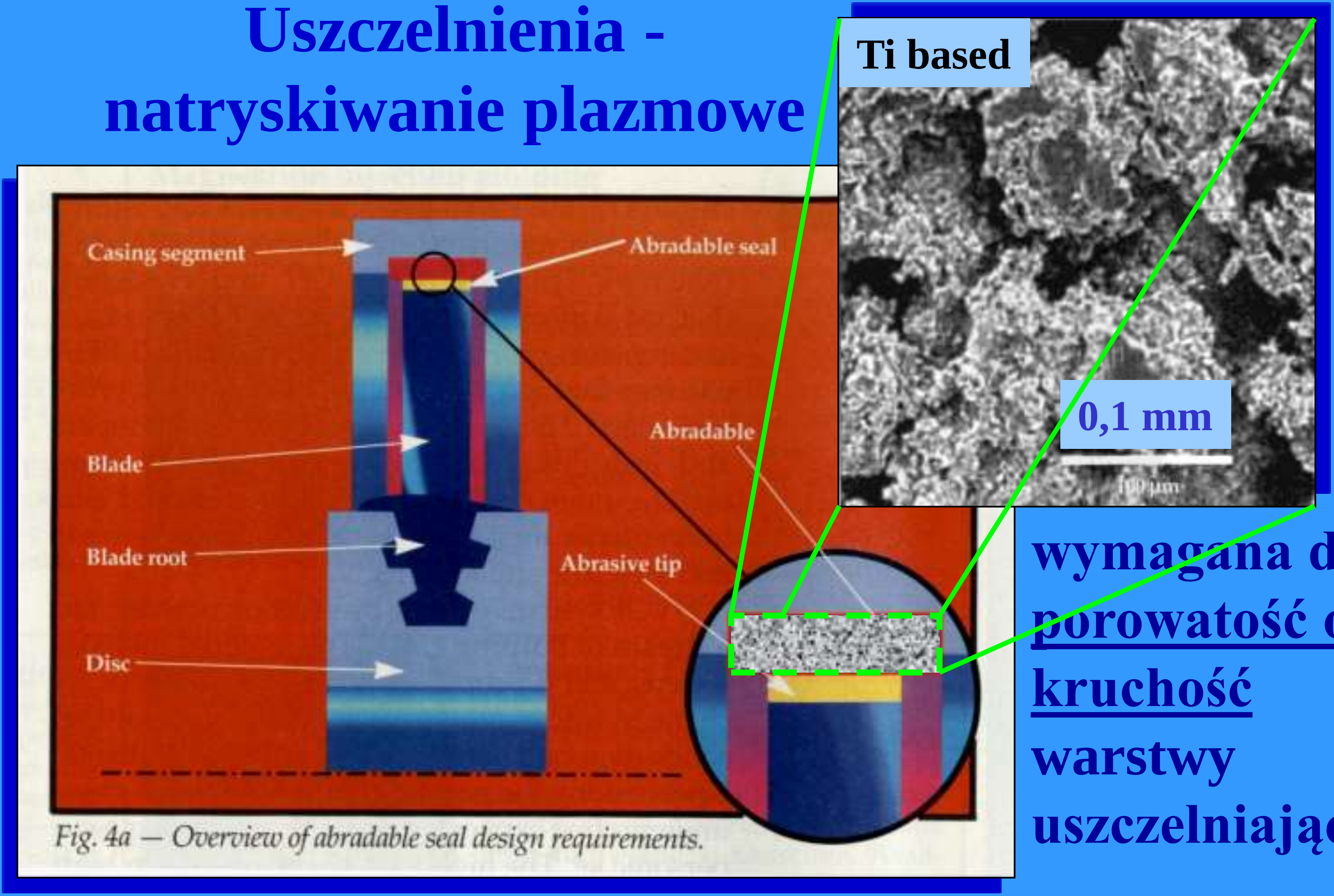
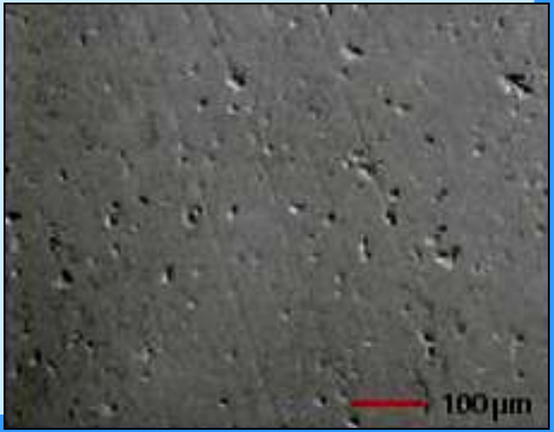


Fig. 4a — Overview of abradable seal design requirements.

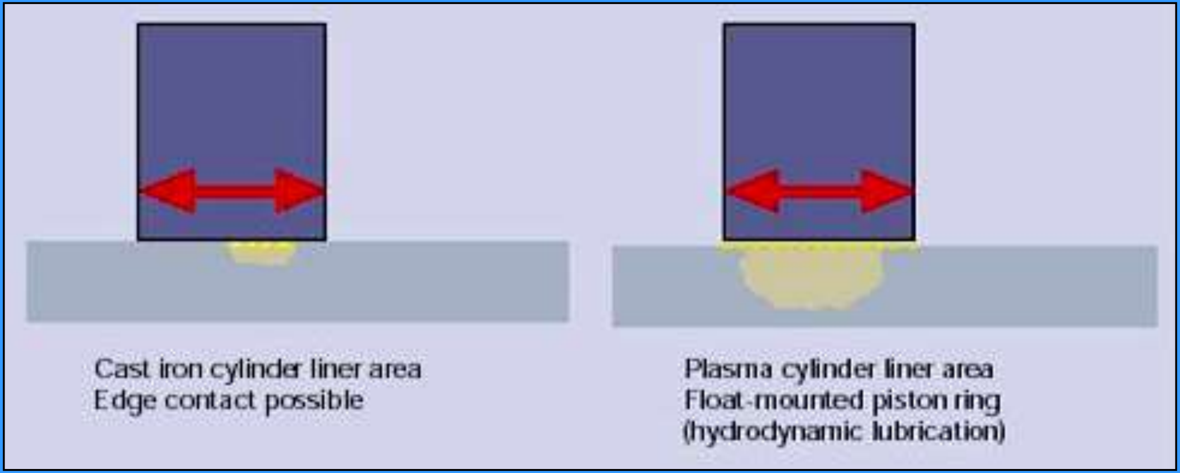
wymagana duża porowatość oraz kruchość warstwy uszczelniającej

koszt warstwy rekompensowany zwiększeniem żywotności/ sprawności układu napędowego

Tarcie - poślizg (sliding wear)

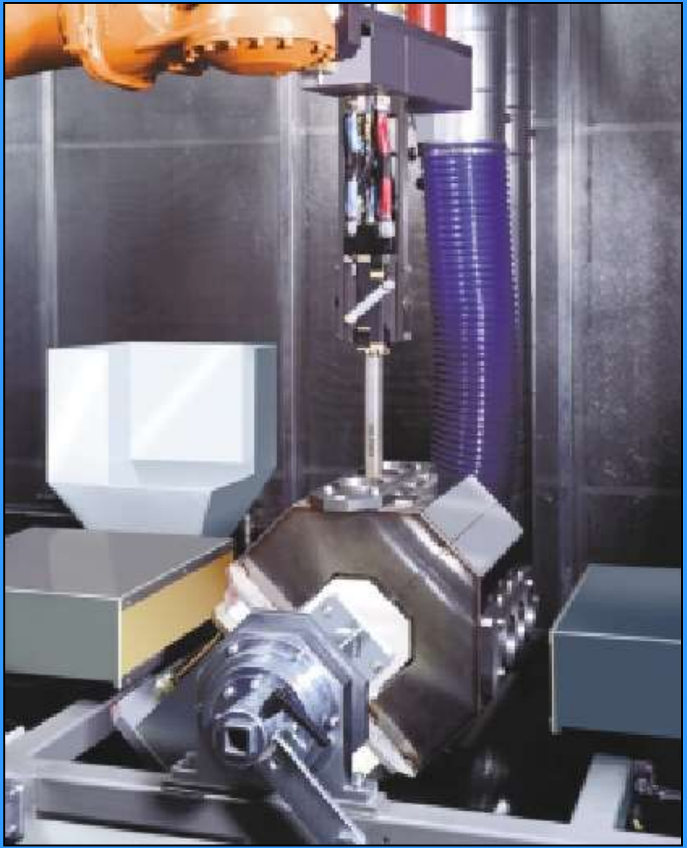


warstwa (Fe-based + Cr)
min. grub. ~ 150µm
podłoże AlSi



Cylinder bores of an engine block processed with a plasma sprayed coating:
1) after grit-blasting, 2) after plasma spray coating, 3) after honing

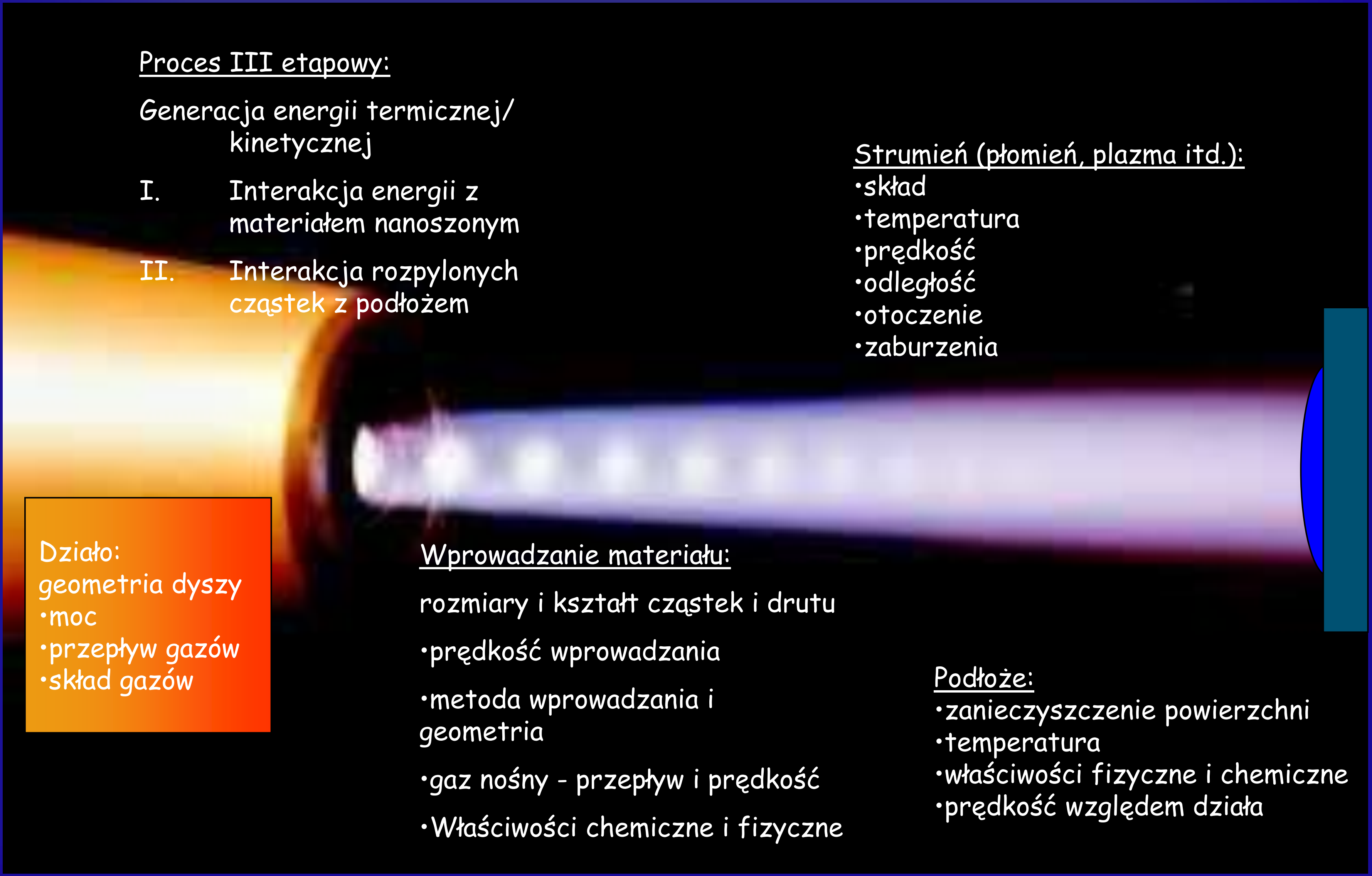
Tarcie - poślizg (c.d.)



Zalety silnika z „AlSi + natryskiwanie” natryskiwanych /w stosunku do żeliwa/:

- **tarcie zmniejszone o ~30%**
- **masa obniżona o ~1kg**

Podsumowanie



Proces III etapowy:

Generacja energii termicznej/kinetycznej

I. Interakcja energii z materiałem nanoszonym

II. Interakcja rozpylonych cząstek z podłożem

Strumień (płomień, plazma itd.):
- skład
- temperatura
- prędkość
- odległość
- otoczenie
- zaburzenia

Działo:
geometria dyszy
- moc
- przepływ gazów
- skład gazów

Wprowadzanie materiału:

rozmiary i kształt cząstek i drutu

- prędkość wprowadzania
- metoda wprowadzania i geometria
- gaz nośny - przepływ i prędkość
- Właściwości chemiczne i fizyczne

Podłoże:
- zanieczyszczenie powierzchni
- temperatura
- właściwości fizyczne i chemiczne
- prędkość względem działa

20. Arc evaporation

Arc discharging (Arcing) - an electrical discharge with a relatively high current at relatively low voltage, characterized by a collective mechanism of electron emission cathode

Arcing is used for surface modification and synthesis of thin films

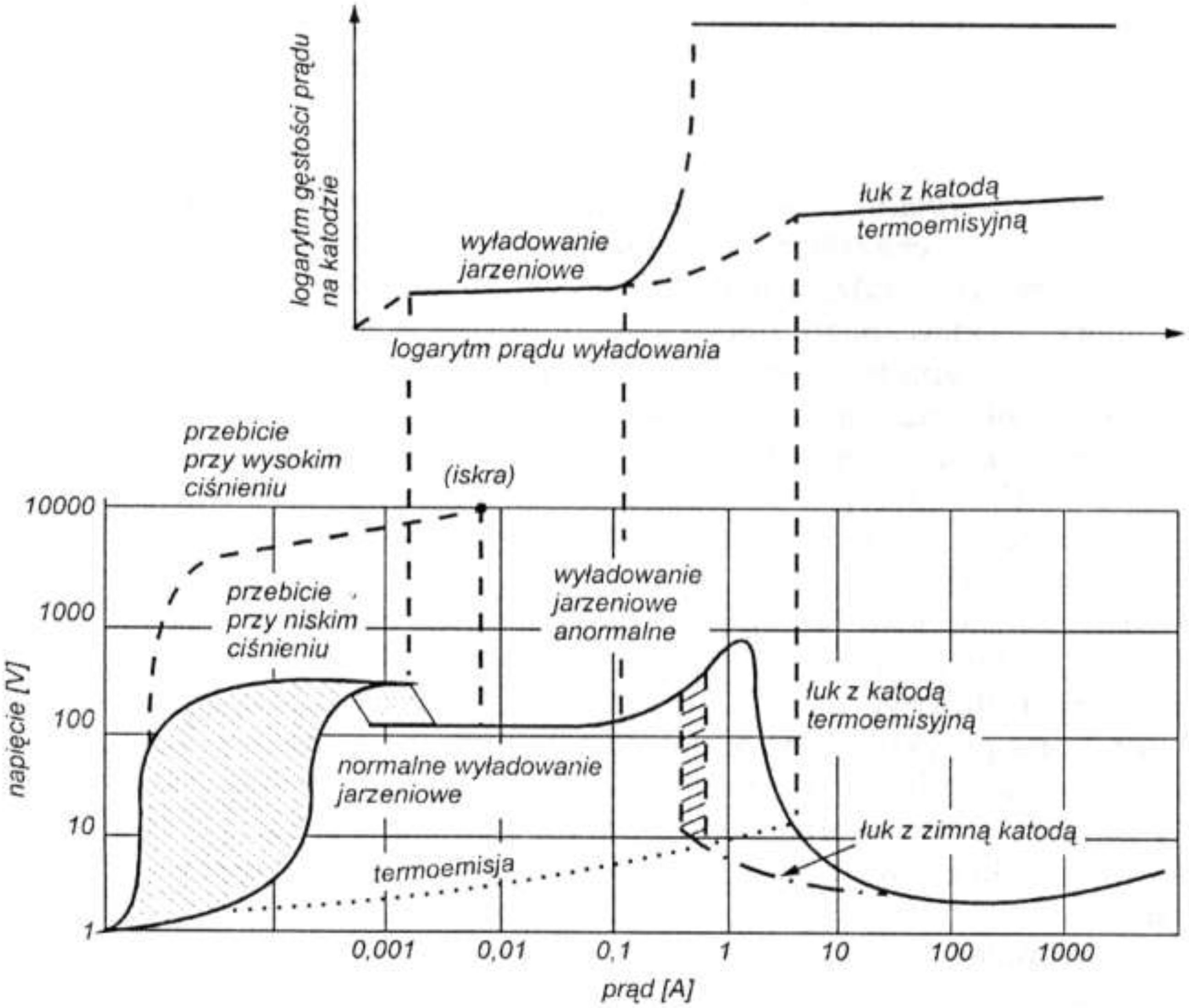
- Arcing
- Glow discharge radio frequency of 13.56 MHz (RF)
- Microwave discharge of 2.45 GHz (MW)

20. Odparowanie łukowe

Wyładowanie łukowe – wyładowanie elektryczne o stosunkowo wysokim prądzie przy względnie niskim napięciu, charakteryzuje się kolektywnym mechanizmem emisji elektronów z katody

Wyładowanie łukowe stosuje się do modyfikacji powierzchni i syntezy cienkich warstw

- Wyładowanie łukowe
- Wyładowanie jarzeniowe częstości radiowej RF 13.56 MHz
- Wyładowanie mikrofalowe MW 2.45 GHz



Charakterystyka napięciowo-prądowa wyładowania elektrycznego w gazie [41]

Voltage-current characteristics of electrical discharge in the gas

The structure of glow discharge

The cathode (-)

Aston darkroom

cathode glow

cathodic darkroom

glow negative (negative glow)

Faraday darkroom

positive glow

darkroom anodic

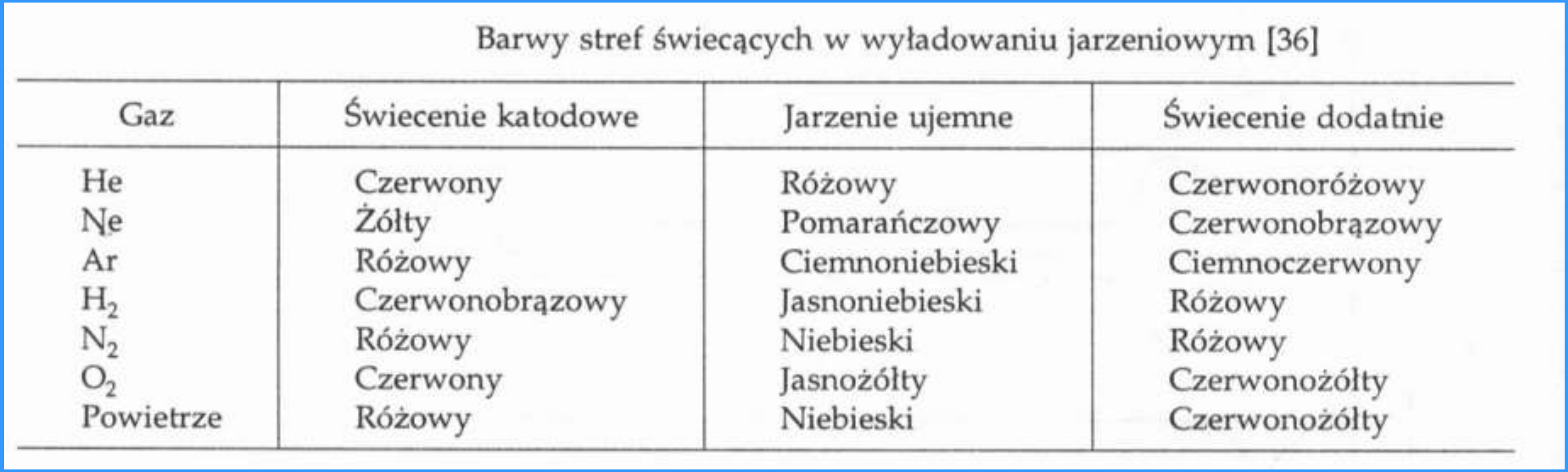
anode glow

The anode (+)

Struktura wyładowania jarzeniowego

KATODA (-)
ciemnia Astona
poświata katodowa
ciemnia katodowa
jarzenie ujemne (poświata ujemna)
ciemnia Faradaya
jarzenie dodatnie
ciemnia anodowa
jarzenie anodowe (poświata anodowa)
ANODA (+)

Color light-emitting zone in glow discharge



Barwy stref świecących w wyładowaniu jarzeniowym [36]

Gaz	Świecenie katodowe	Jarzenie ujemne	Świecenie dodatnie
He	Czerwony	Różowy	Czerwonoróżowy
Ne	Żółty	Pomarańczowy	Czerwonobrązowy
Ar	Różowy	Ciemnoniebieski	Ciemnoczerwony
H_2	Czerwonobrązowy	Jasnoniebieski	Różowy
N_2	Różowy	Niebieski	Różowy
O_2	Czerwony	Jasnożółty	Czerwonożółty
Powietrze	Różowy	Niebieski	Czerwonożółty

Coating of Tubes

First steps of
pre-treatment and film deposition
inside long tubes

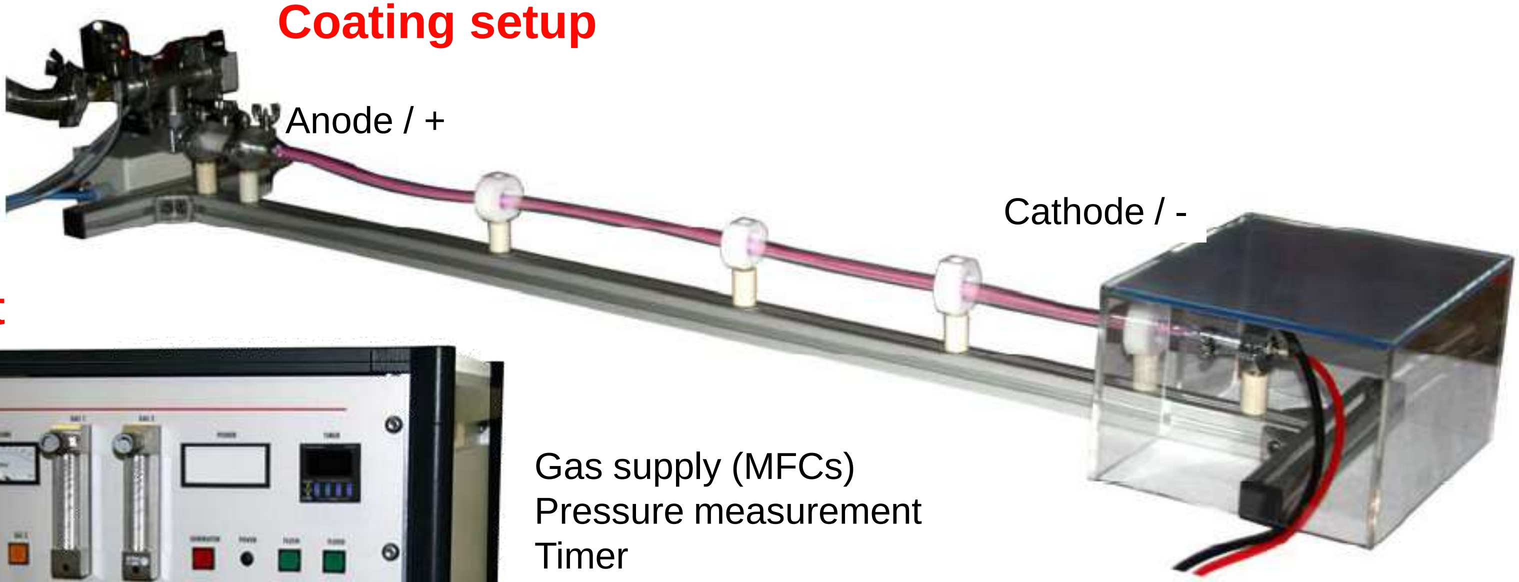
Background - Motivation

- **Problems in using traditional PVD/CVD coating techniques:**
  - **PVD: directed particle beam (plasma)**
    low deposition rate on surfaces parallel to directed beam
    in holes: Depth/diameter ratio high => very low rate
  - **CVD: deposition from gaseous precursor – easier coating in holes**
    traditional precursors require high temperatures
    only carbon / metal-organic precursors allow coating on polymers

- **Need for coating inside tube-shaped medical parts:**
  - **Direct contact to body fluids (blood, etc.)**
  - **Prevention of any harmful body reactions**

Coating system

Coating setup



Pump
Pump valve
Pressure gauge

Anode / +

Cathode / -

Gas / power supply
(control unit)

Control unit

Gas supply (MFCs)
Pressure measurement
Timer

HV Pulse Generator

Plasmastrom (ungeregelt)

Pulse width (5-20 ms range

Pulse frequency (20-550 Hz)

Supplier:
Diener Electronic GmbH

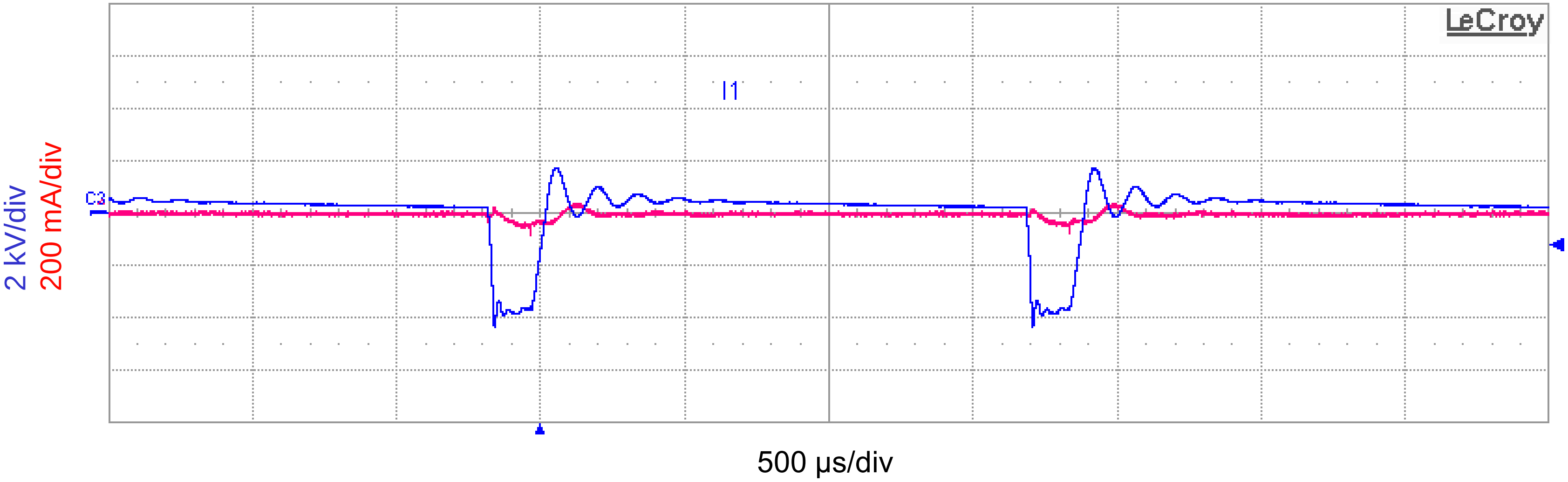
System specification

Power supply: 25 kV, 20-550 Hz pulsing, 5-20 ms pulse width

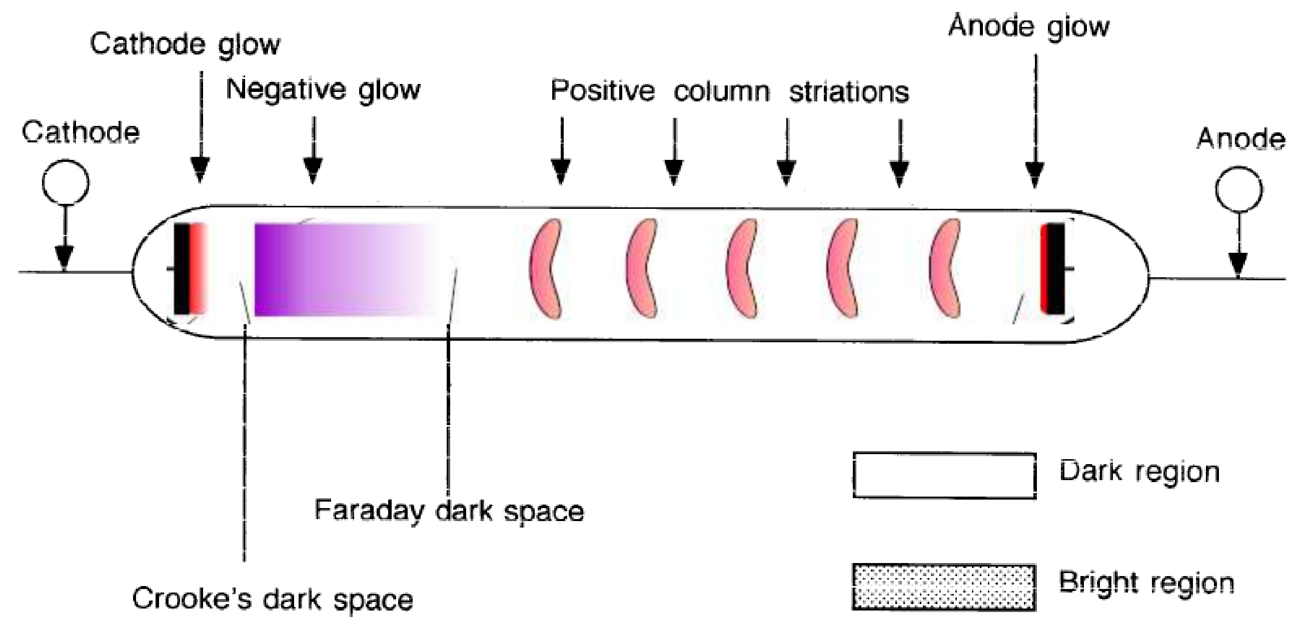
Gas supply: 0-40 sccm gas flow (nearly all gases useable)
dosing vapours by bubbler unit (e.g. HMDSO, metal-organics) and use of carrier gas

Vacuum conditions: working pressure: 0.2 – 1.4 mbar

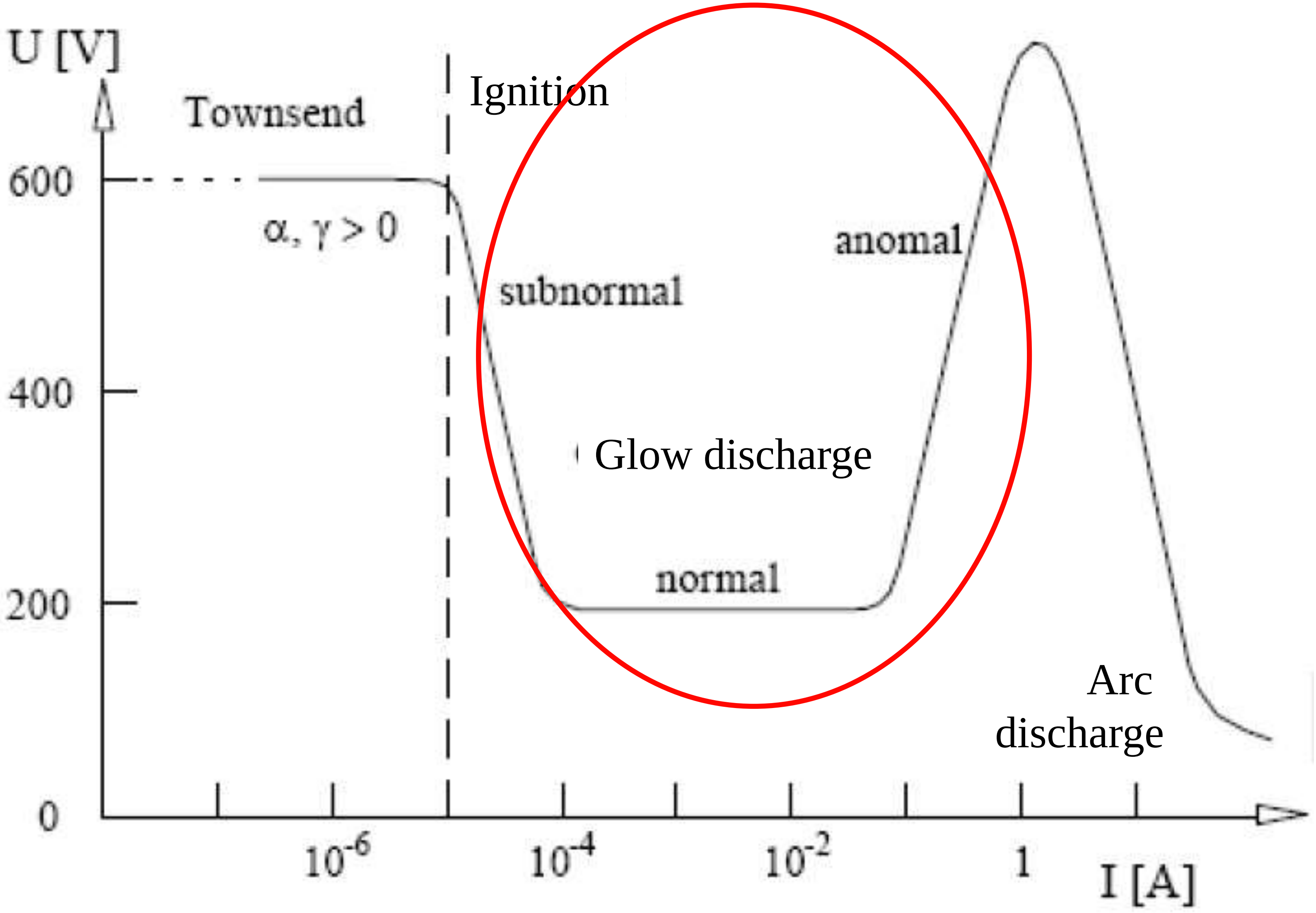
Pulse shape:



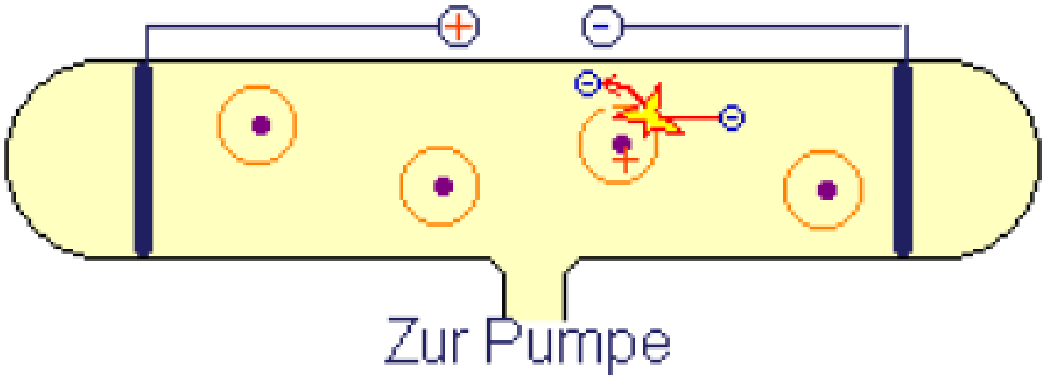
Operation / plasma emission

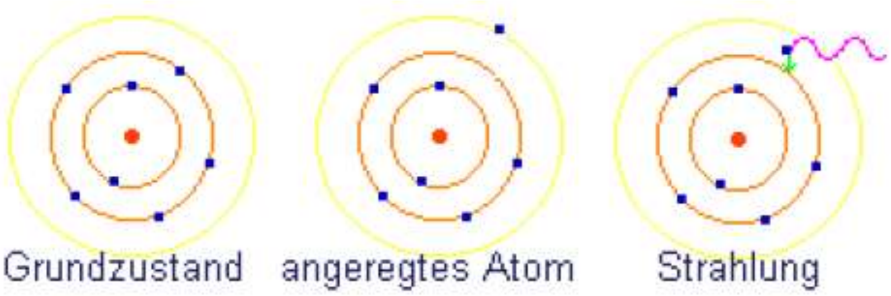


Background - Discharges



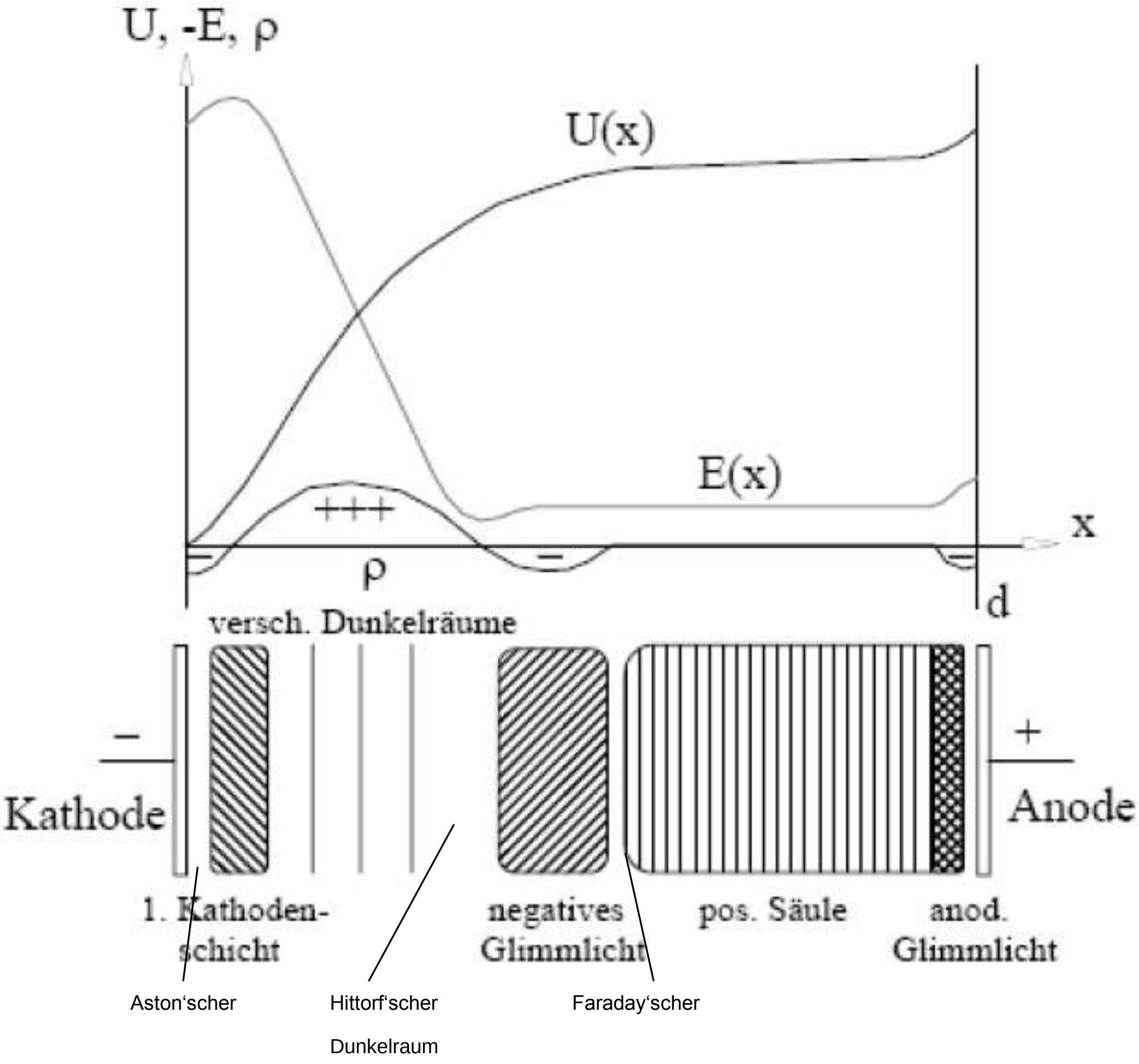
Background – discharge





Electrical conduction in gases – ionization and radiation phenomena

Background – Glow discharge

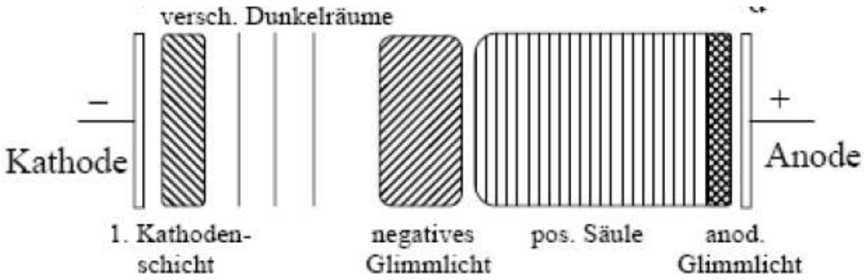


Aston'scher Dunkelraum:
Wenige Elektronen, zu langsam zur Anregung
Glimmhaut: Hohe Ionendichte, Elektronenenergie reicht zur *Anregung* (nicht ionisation)
Hittorf'scher (Crook'scher) Dunkelraum: Elektronen werden weiter beschleunigt bis zur Ionisationsenergie
Negative Säule (Glimmlicht): Ionisationsfront, Licht durch Rekombinationsstrahlung
Faraday'scher Dunkelraum:
Geringe Elektronenenergie als Folge inelastischer Stöße an der Ionisationsfront, freie Weglänge kurz, Feld klein und nicht zur Anregung ausreichend
Positive Säule:
Quasineutrales Plasma ($Zn_i = n_e$), kleines elektrisches Feld, Spannungsabfall durch elektrischen Widerstand
Anodenfall: Negative Raumladung

Background – Glow discharge

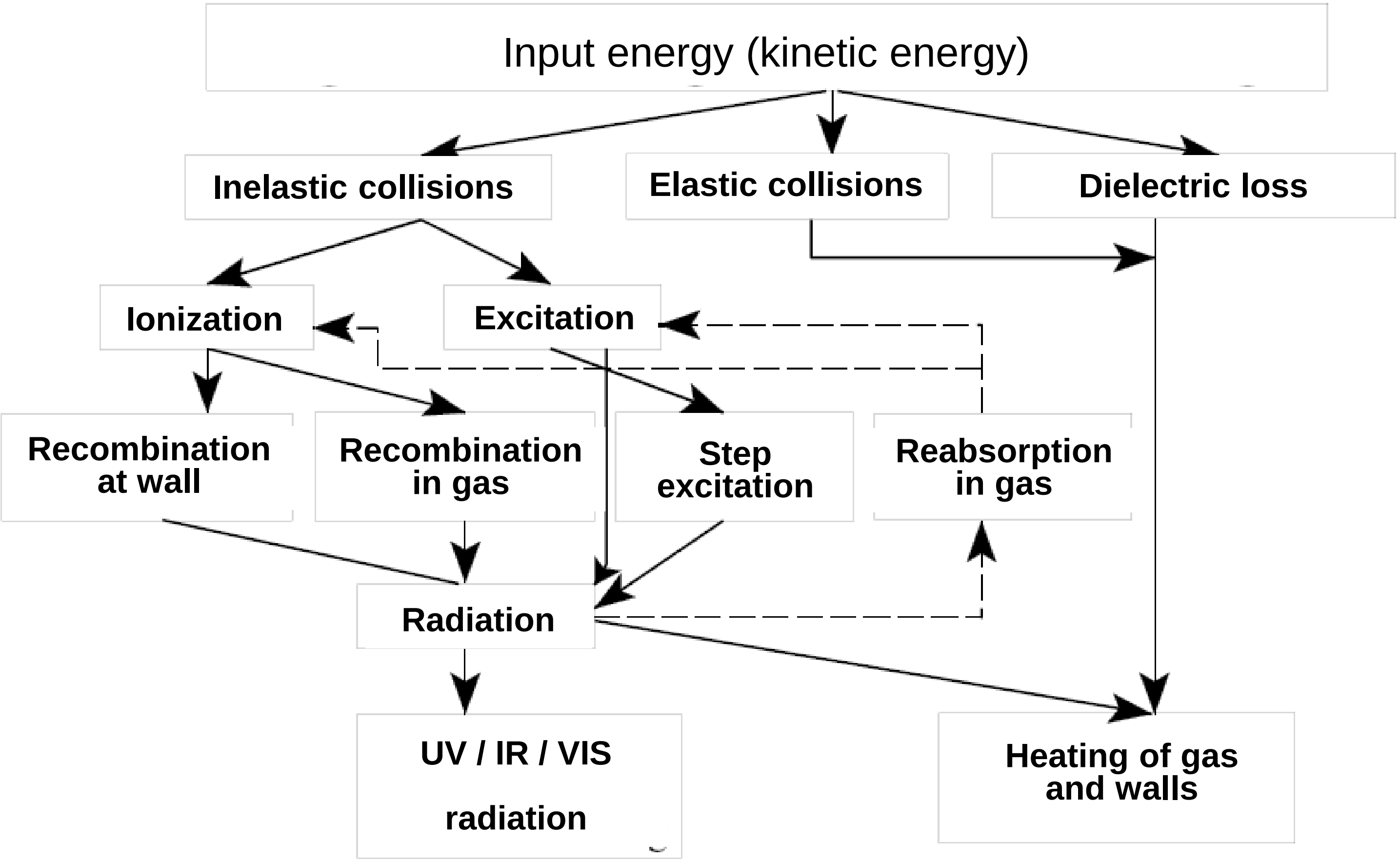
Kathode

Anode



Quelle: `http://w5jgv.com/rife`

Background – glow discharge



Input energy (kinetic energy)

Inelastic collisions

Elastic collisions

Dielectric loss

Ionization

Excitation

Recombination at wall

Recombination in gas

Step excitation

Reabsorption in gas

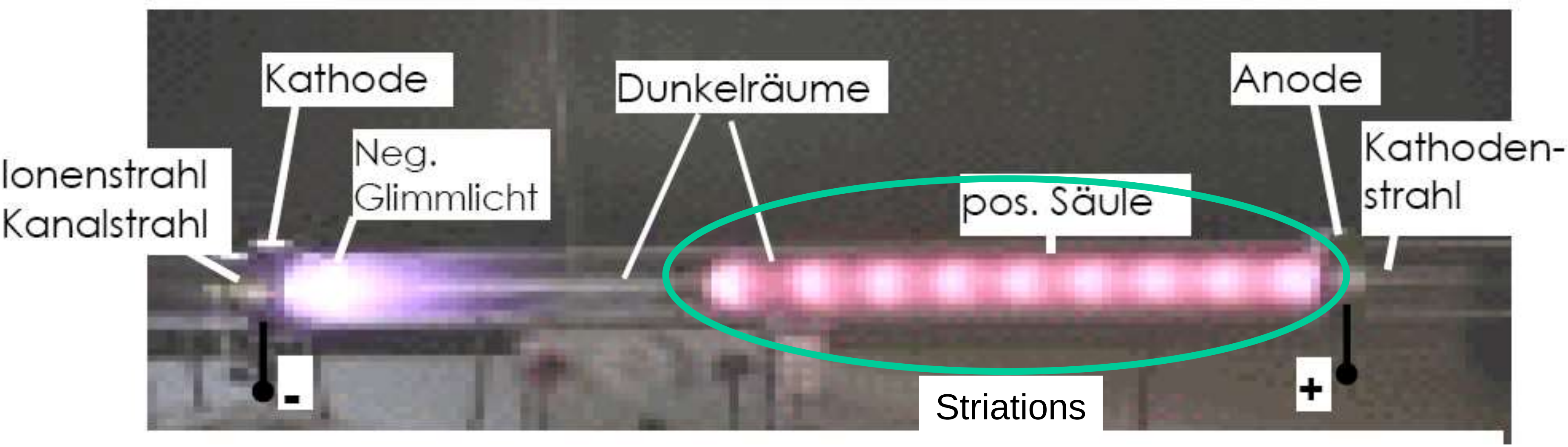
Radiation

UV / IR / VIS radiation

Heating of gas and walls

Energy conversation in positive column of glow discharge plasma

Background – glow discharge



21. Surface diagnostics methods

a. Spectroscopic methods of surface analysis

b. Structure diagnostics (AFM, SEM, TEM, Acoustic Microscopy SAM, Confocal Laser Microscopy CLSM)

c. Residual stress and methods of measurements

a. spectroscopic method of analysis of surface and thin film

Critical properties during deposition and surface modification

- Fizysorption and chemisorption
- Surface tension

Fizysorption → **van der Waalsa forces→ reversible**

Chemisorption →**atomic binding, polar, ionic chemical reaction →**
→often irreversible

Dependent properties of surface phenomena

Electrical properties	**Mechanical Properties**	**Kinetically controlled magnetic**	**Magnetic**
-heterojunction **-recombination processes** **-diffusion and subsidies** **-electromigration**	**-metal fatigue** **-adhesion** -adsorption -metal/ceramika -metal/polimer -hard layer -nitrides -carbides	-adsorption--segregation -catalysis -activation -poisoning -corrosion -sedimentation -growth	-height magneto-resistance -normal magnetic anisotropy

The study of solid surfaces

-structural studies

Optical microscopy (LM resolution 250nm)

Scanning electron microscopy SEM (10nm)

Transmission electron microscopy TEM (0.2nm)

Atomic force microscopy AFM (0.2nm)

Spectroscopy examines and explains the interaction between matter theory, which is a collection of atoms and molecules and electromagnetic radiation. These interactions cause a change in the internal energy according to the principle of conservation of energy expressed by the formula:

$$\boxed{E = h \cdot \nu = h \cdot \frac{c}{\lambda}}$$

where:

E - energy change

h - Planck's constant

υ-frequency

c - speed of light

λ-wavelength radiation

- test methods for electronic structure

Photoelectron spectrometry: PES,

Reverse photo-emission: IPES

Electron energy loss spectrometry: EELS,

United strictly surface: FES, INS, FIS

- study the dynamics of solid

Infrared Spectrometry: IRS, DS, FTS,

Light scattering: BS, RS,

Inelastic neutron scattering INS, ICNS, TF, NSE, IINS, QNS, CN, VNS,

Point-contact spectroscopy: PSC, TEF,

Electron energy loss spectroscopy: EELS

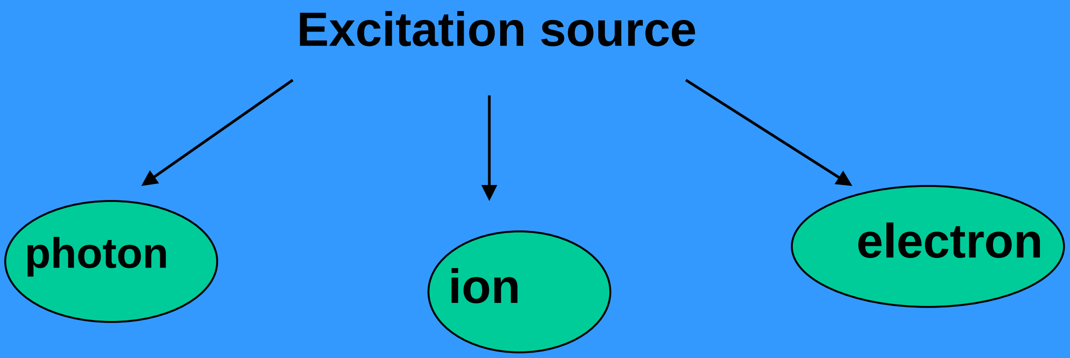
He atoms scattering: HAS

Inelastic X-ray scattering: IXS

Diagnostics of coatings based on electron spectroscopy and photospectroscopy

Information searching:

- chemical composition
- identification of the phases and their distribution in the sample
- characteristics of interphase boundaries



Excitation source

photon

ion

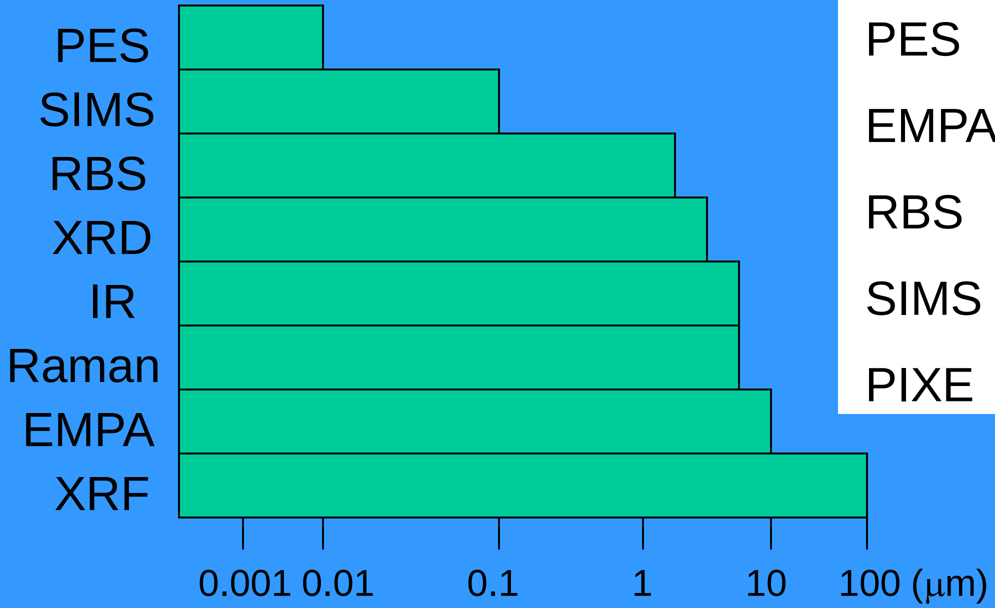
electron

Excitation source → Analysed signal ↓	optical	X-ray	electron	ions
Optical	IR, VIS, UV, PL, EL		UPS	
X-rays		XRF, XRD	XPS, XAES,SEM TEM, AES	
Electron		EMPA	LEED, EELS	
ions		PIXE	IAES	SIMS,RBS, NRA,ERDA

AES-Auger Electron Spectroscopy
EELS-electron energy loss spectroscopy
EL-ellipsometry
EMPA-electron microprobe analysis
ERDA-elastic recoildetection analysis
ESD-electron simulated desorption
LEED-low energy electron diffraction
IAES-ion-induced Auger electron spectroscopy
IR-infrared spectroscopy
XRD-X-ray diffraction analysis
VIS-visible absorption
XPS-X-ray photoelectron spectroscopy

NRA-nuclear radiation analysis
PIXE-particle-induced X-ray emission
PL-photoluminescence
PSD-photon stimulated desorption
RBS-Rutheford backscattering
SEM-scanning electron microscopy
SIMS-secondary ion mass spectrometry
UPS-ultrafiolet photoelectron spectroscopy
UV-ultrafiolet absorption
XRF-X-ray fluorescence
XAES-X-ray induced AES

Measuring depth and sensitivity of each method



Methods	limit od detection	range
AES	0,1-1 % at.	>He
PES	0,1-1 % at.	>H
EMPA	0,1 % at.	>Be
RBS	0,1 % at.	>C
SIMS	0,1-1000 ppm	all
PIXE	0,1-10 ppm	>Na

Methods for the surface analysis as a function: measured value and its detection

Measured value → Detection ↓	Photons IR-FTIR	Electrons EMPA	Particles	Fields
Photon	SERS,XRD XRF	BIS		
Electron	XPS-ESCA SEXAFS UPS, XANES	AES EELS LEED SEM RHEED		
Particles -ions -Neutrons -Atoms			ISS(ions) NAA(neutrons) RBS(ions) SIMS(jony)	AP
Fields -Force -Electric -Magnetic				AFM STM MFM

Methods for the analysis area as a function: collected information

Information	Methods	Vacuum
Analitycal	AES	UHV
	XRF	Normal vacuum up to atmosphere
	NAA	None
	RBS	Normal vacuum
	SERS	Atmosphere + liquid
	LAMMA	Normal vacuum
	GDS	None
	SIMS	UHV + gas
	XPS-ESCA	UHV

Information	**Method**	**Vacuum**
Morphology	SEM	Normal vacuum
	AFM	None
	STM	Normal vacuum up to atmosphere
Crystal structure	XRD	None
	LEED	UHV
	RHEED	UHV
-long range	STM	UHV
-close range	EXAFS	UHV
Electron structure	UPS	UHV
	EELS	UHV

Analytical methods:

• **An elementar surface analysis**	**AES**
With knowing of the elementar bounds	**ESCA**

• **Quantitative analysis**	**NAA, XRF**
• **Very small concentrations**	**SIMS, AP**
• **Fast in-depth analysis (destructive)**	**SIMS**
With many elements in the sample	**GDS**

• **Non-destructive in-depth analysis**	**RBS**
• **Knowledge of the surface morphology**	**SEM**
Atomically resolved	**STM**
At molecular scale	**AFM**

- **Knowledge of the crystal structure;**

ISS, LEED, RHEED, STM, GIXS

Analytical methods (cont.):

• Short-distance order	**EXAFS, SEXAFS**
• Cartography of elements	**SAM**
….*spatially resolved*	**XRF, SIMS**
• Knowledge of the electronic structure	**ARUPS, EELS**
• Work without UHV contraints	**GDL, XRD, AFM**
• ..and even with liquidus!	**STM, AFM**
• Investigating organic materials	**FTIR, XPS**

--

ARUPS: Angle resolved ultra violet photo electron spectroscopy

SAM: Scanning Auger microscopy

Chemical analysis (elements and bindings)

XRF lub EMPA; EXAFS lub SEXAFS (surface)

Analysis of the surface properties: ellipsometry, megneto-optical Kerr effect (MOKE)

The most effective methods of surface analysis:

- based on the emission of X-ray: XPS lub ESCA (electron spectroscopy for chemical analysis); AES; XRF
- based on the absorption of X-ray : SEXAFS
- based on electron : AES (range 1 to 2.5nm)
- based on ions: SIMS
- ellipsometry and Kerr optical effect
- measurements of the wetting contact angle
- Raman spectroscopy

Acronyms used in the analysis of the surface

AAS:	**Atomic absorption spectroscopy**
AES:	**Auger electron spectroscopy** **(lub: Atomic emission spectroscopy)**
AFM:	**Atomic force microscopy**
AFS:	**Atomic fluorescence spectroscopy**
AP:	**Atomic probe**
ATR:	**Attenuated total reflexion** **(osłabione odbicie całkowite)**
BET:	**Bruauer, Emmet, Teller**
BIS:	**Bremsstrahlung Isochronal Spectroscopy** **(lub: bioelectrical impedance spectroscopy)**
CP/MAR/NMR	**Cross polarization magic angle rotation NMR (nuclear magnetic resonanse)**

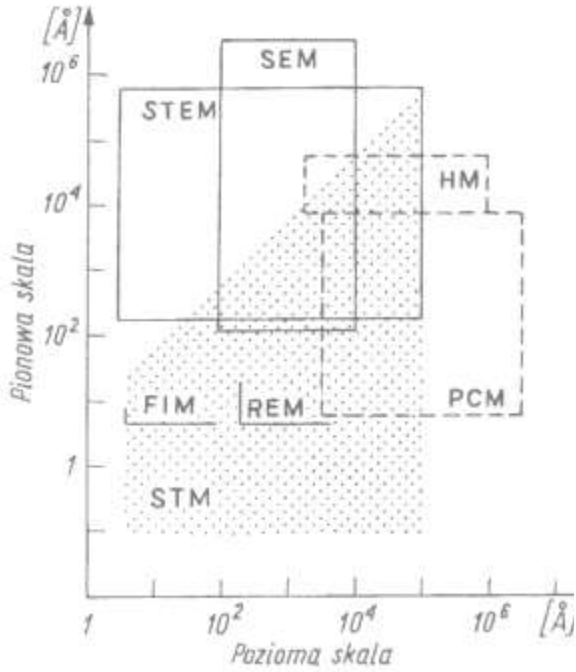
EBIC:	**Electron beam-induced current**
EDS:	**Energy-dispersive spectrometer**
EDX:	**Electron dispersion X-ray (spectroscopy)**
EELS:	**Electron energy loss spectroscopy**
EPMA:	**Electron probe microanalysis**
ESCA:	**Electron spectroscopy for chemical analysis**
(S)EXAFS:	**(Surface) Extended X-ray absorption fine structure**
FTIR:	**Frustrated total internal reflexion and Fourier transform infrared**
GDL:	**Glow discharge lamp**
GISAXS:	**Grazing incidence small angle X-ray scattering**
GIXS:	**Grazing incidence X-ray scattering**
IBAD:	**Ion-beam-assisted deposition**
IBS:	**Ion-beam sputtering**
ISS:	**Ion scattering spectroscopy**

LAMMA: **Laser assisted microprobe analysis**
LEED: **Low-energy electron diffraction**
MBE: **Molecular beam epitaxy**
MFM: **Magnetic force microscopy**
MOKE: **Magneto-optical Kerr effect**
NAA: **Neutron activation analysis**
NMR: **Nuclear magnetic resonanse**
PIXE: **Proton-induced X-ray emission**
RBS: **Rutheford backscattering**
SEM: **Scanning electron microscope**
SERS: **Surface-enhanced Raman spectroscopy**
SIMS: **Secondary ion mass spectroscopy**
(ToF)-SIMS: **Time-of-flight SIMS**

SNMS:	**Secondary neutral ion mass spectroscopy**
SNOM:	**Scanning near field optical microscopy**
STEM:	**Scanning transmission electron microscopy**
STM:	**Scanning tunneling microscopy**
TEM:	**Transmission electron microscopy**
(HR)TEM:	**High-resolution TEM**
UPS:	**Ultraviolet photoelectron spectroscopy**
WDS:	**Wavelenght-dispersive spectrometer**
XANES:	**X-ray absorption near edge structure**
XAS:	**X-ray absorption spectroscopy**
XPS:	**X-ray photoelectron spectroscopy**
XRD:	**X-ray diffraction**
XPF:	**X-ray fluorescence**

b. Structural diagnostics (AFM, SEM, TEM)

Electron microscopy



STEM - scanning, transmission electron microscope

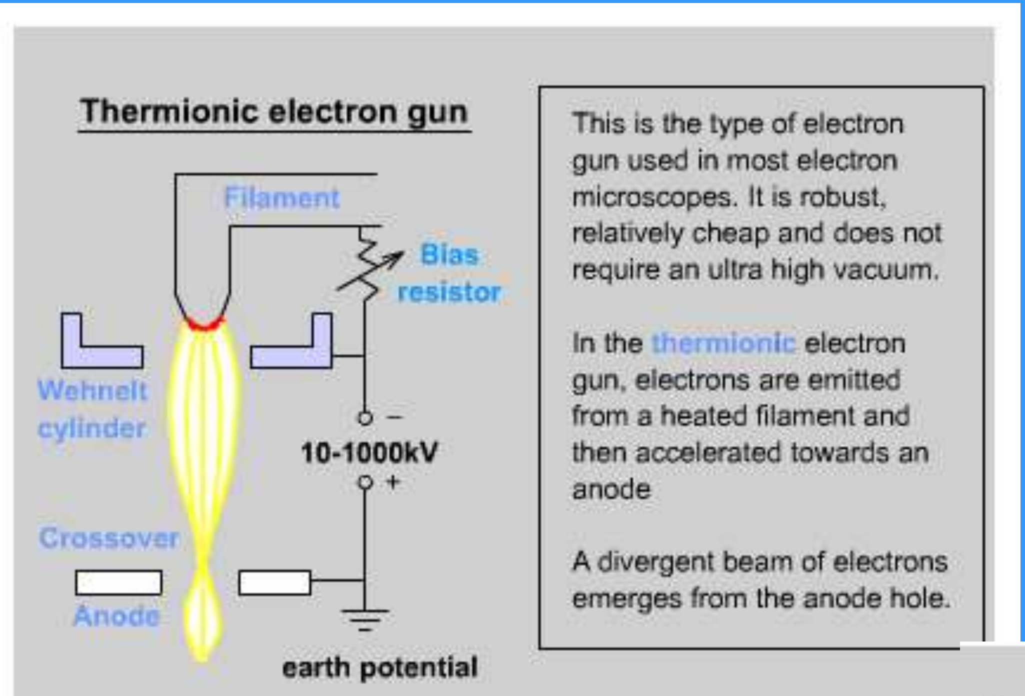
SEM - scanning electron microscope

FIM - field ion microscope

REM - reflective electron microscope

PCM - phase-contrast microscope

STM - scanning tunneling microscope

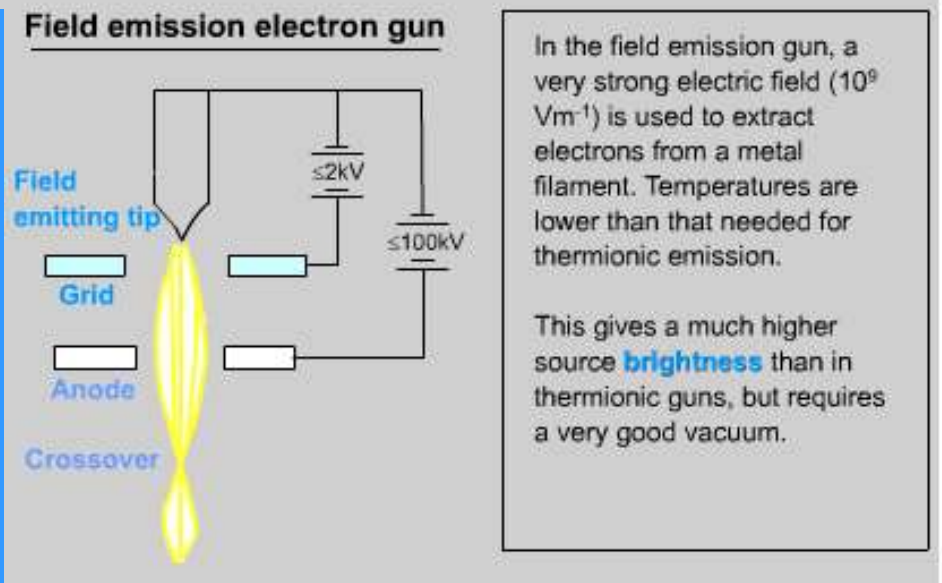


Thermionic electron gun

This is the type of electron gun used in most electron microscopes. It is robust, relatively cheap and does not require an ultra high vacuum.

In the thermionic electron gun, electrons are emitted from a heated filament and then accelerated towards an anode

A divergent beam of electrons emerges from the anode hole.



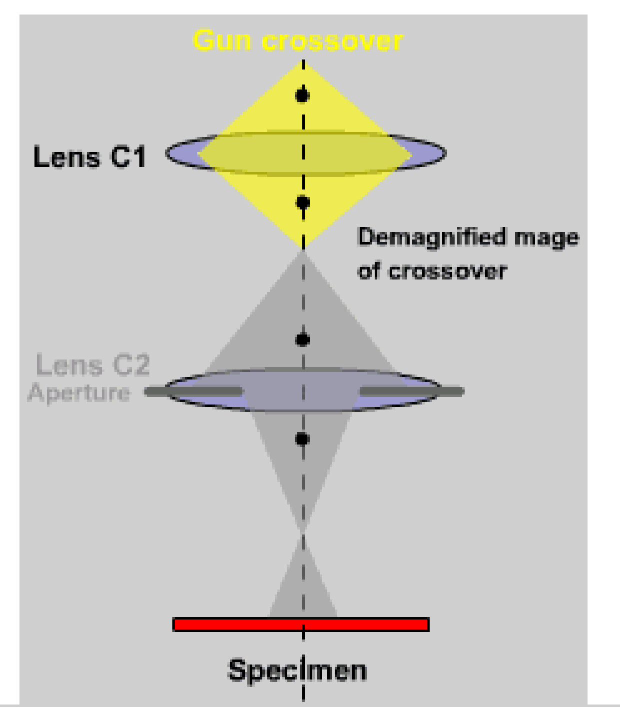
Field emission electron gun

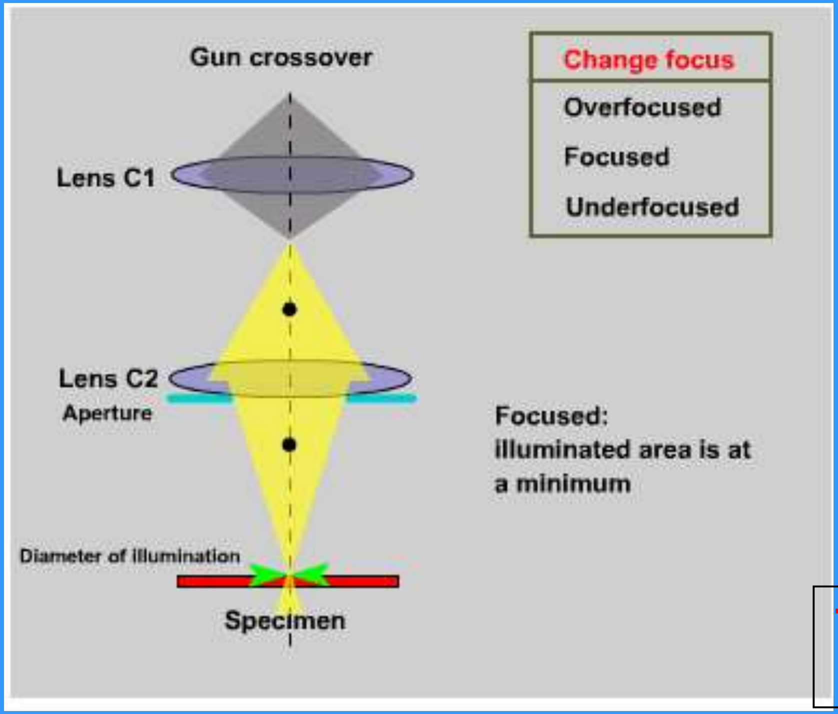
In the field emission gun, a very strong electric field (10^9 Vm^{-1}) is used to extract electrons from a metal filament. Temperatures are lower than that needed for thermionic emission.

This gives a much higher source brightness than in thermionic guns, but requires a very good vacuum.

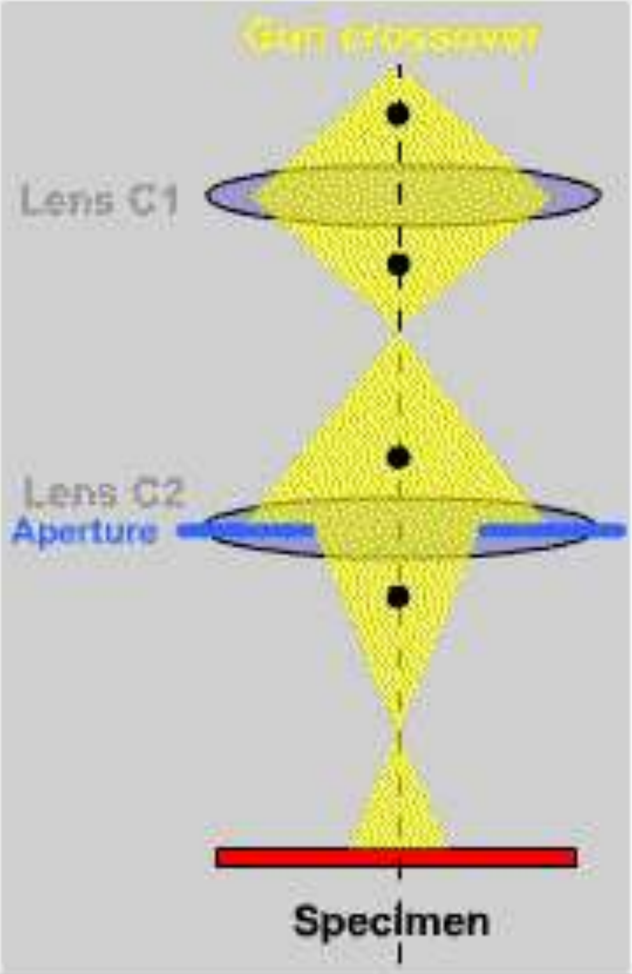
TEM
LAB

condensor lenses



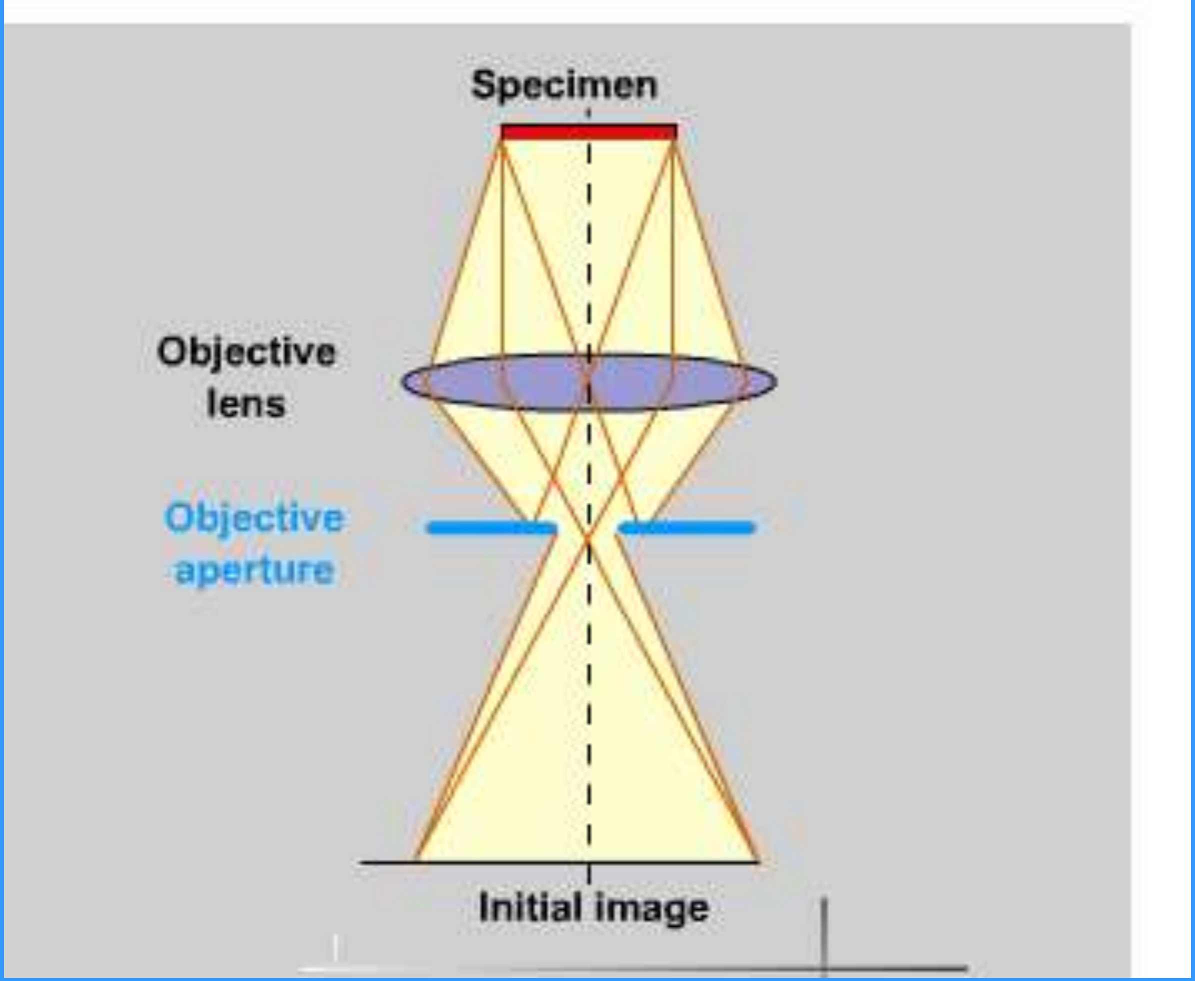


TEM
LAB

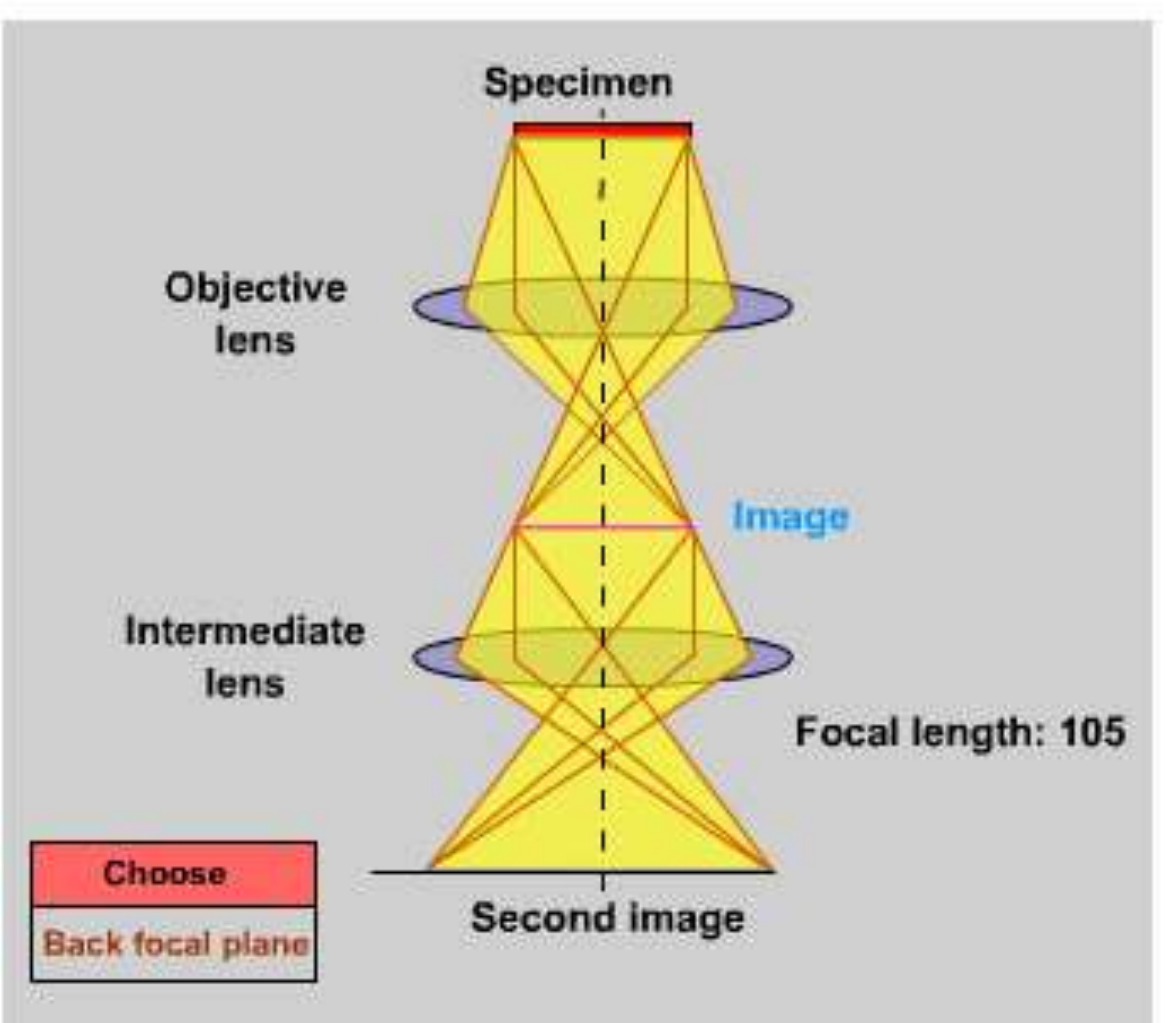


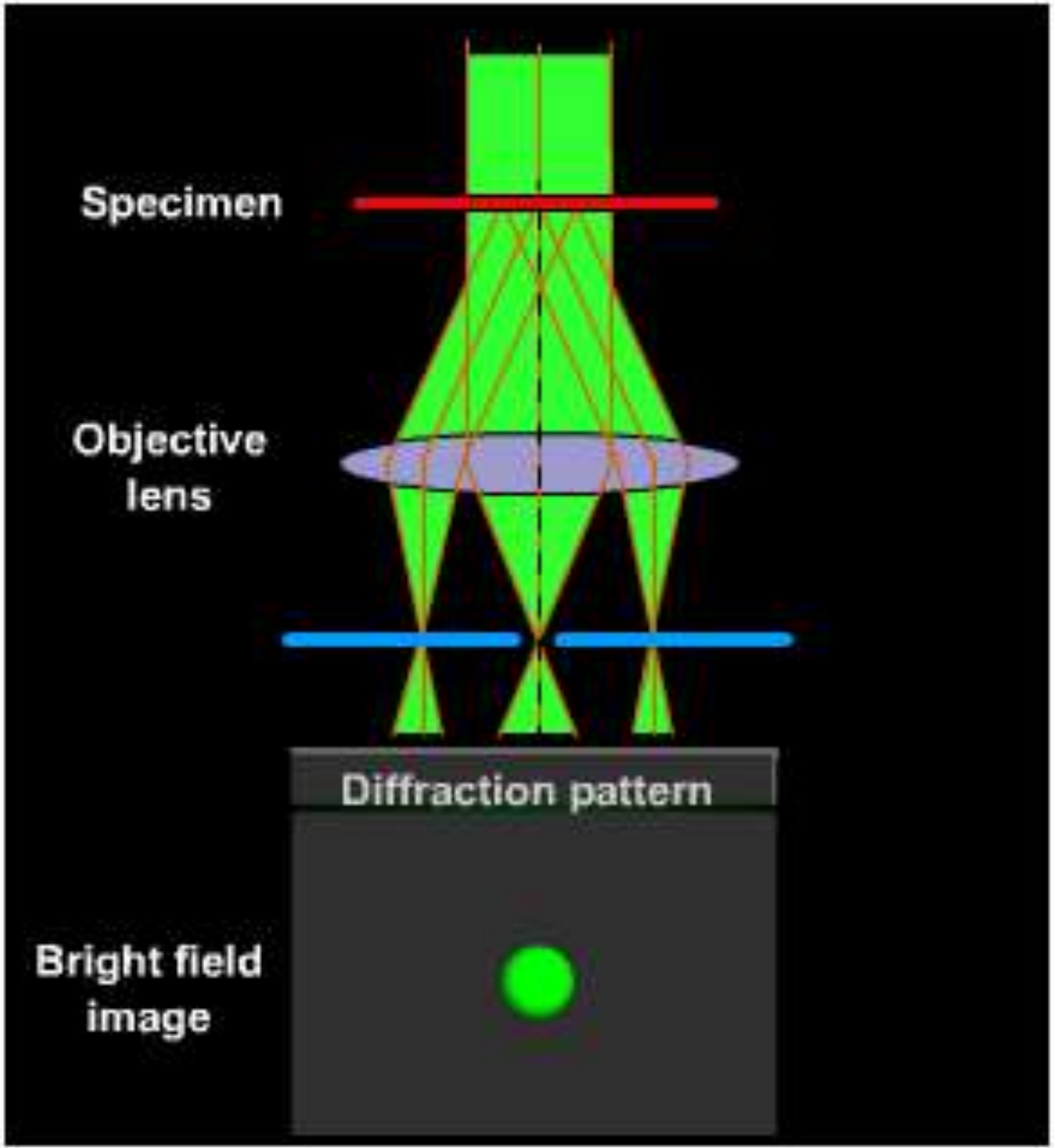
condensor aperture

objective lens

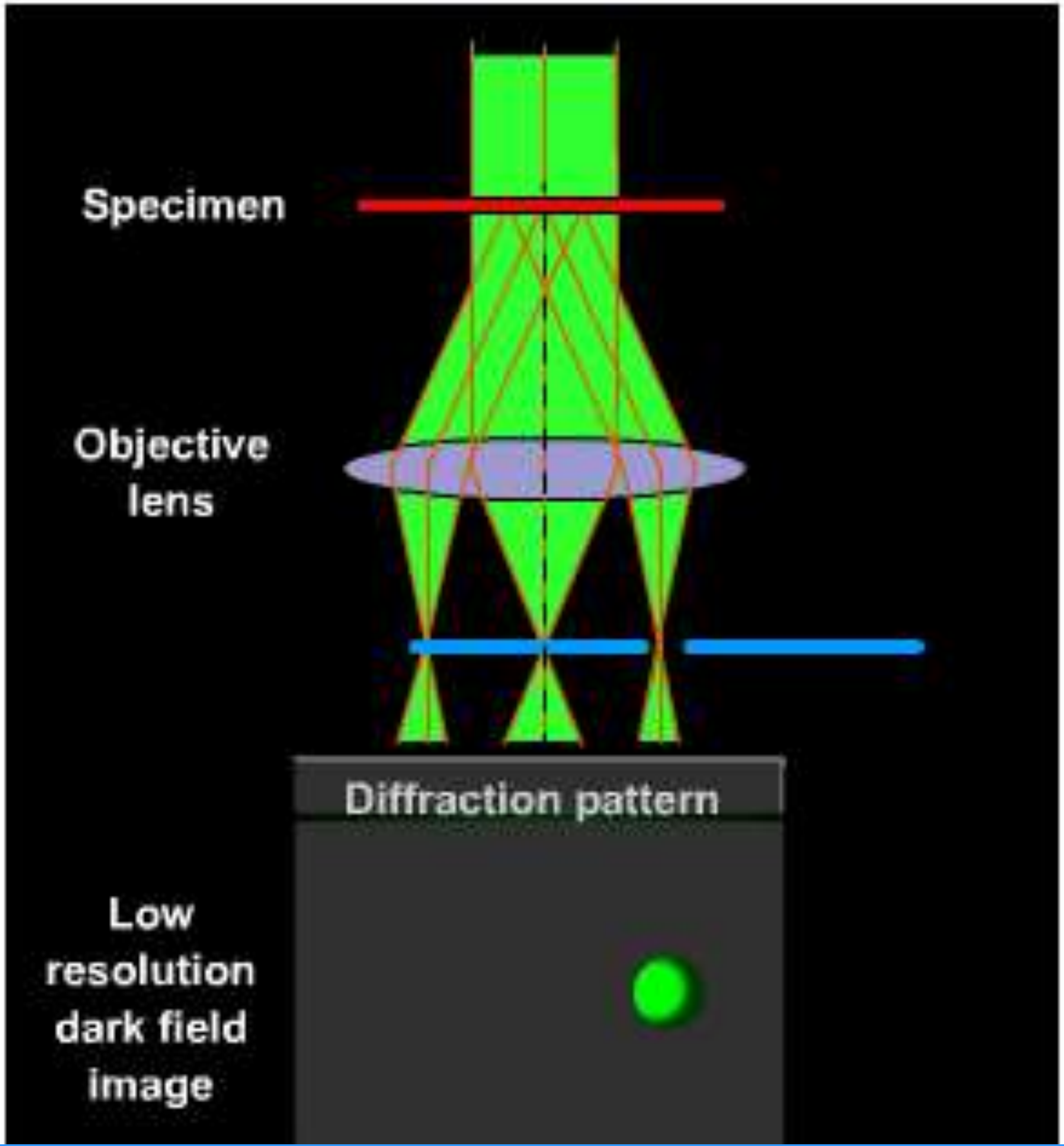


TEM
LAB

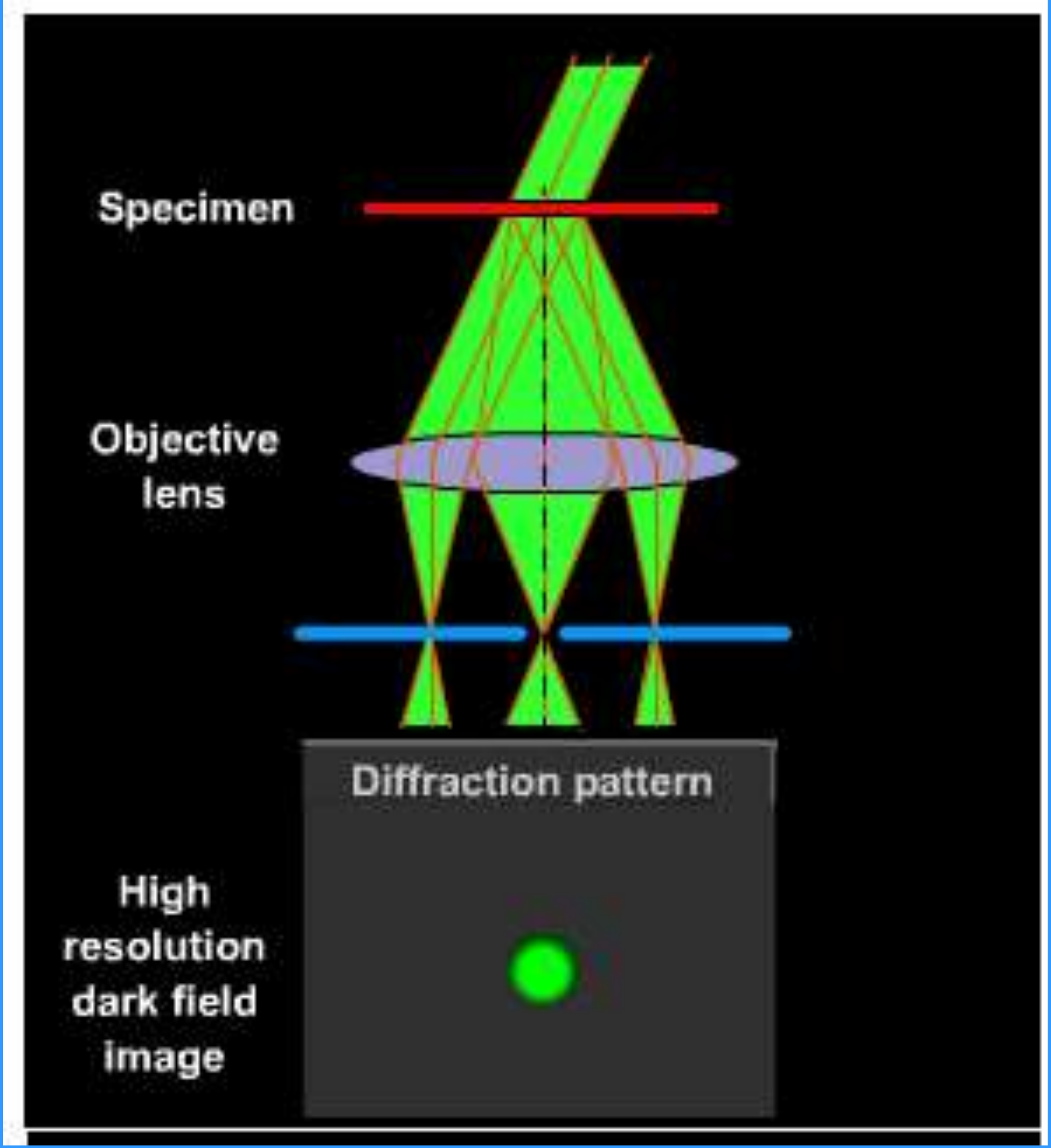

Specimen
Objective lens
Image
Intermediate lens
Focal length: 105
Choose
Back focal plane
Second image

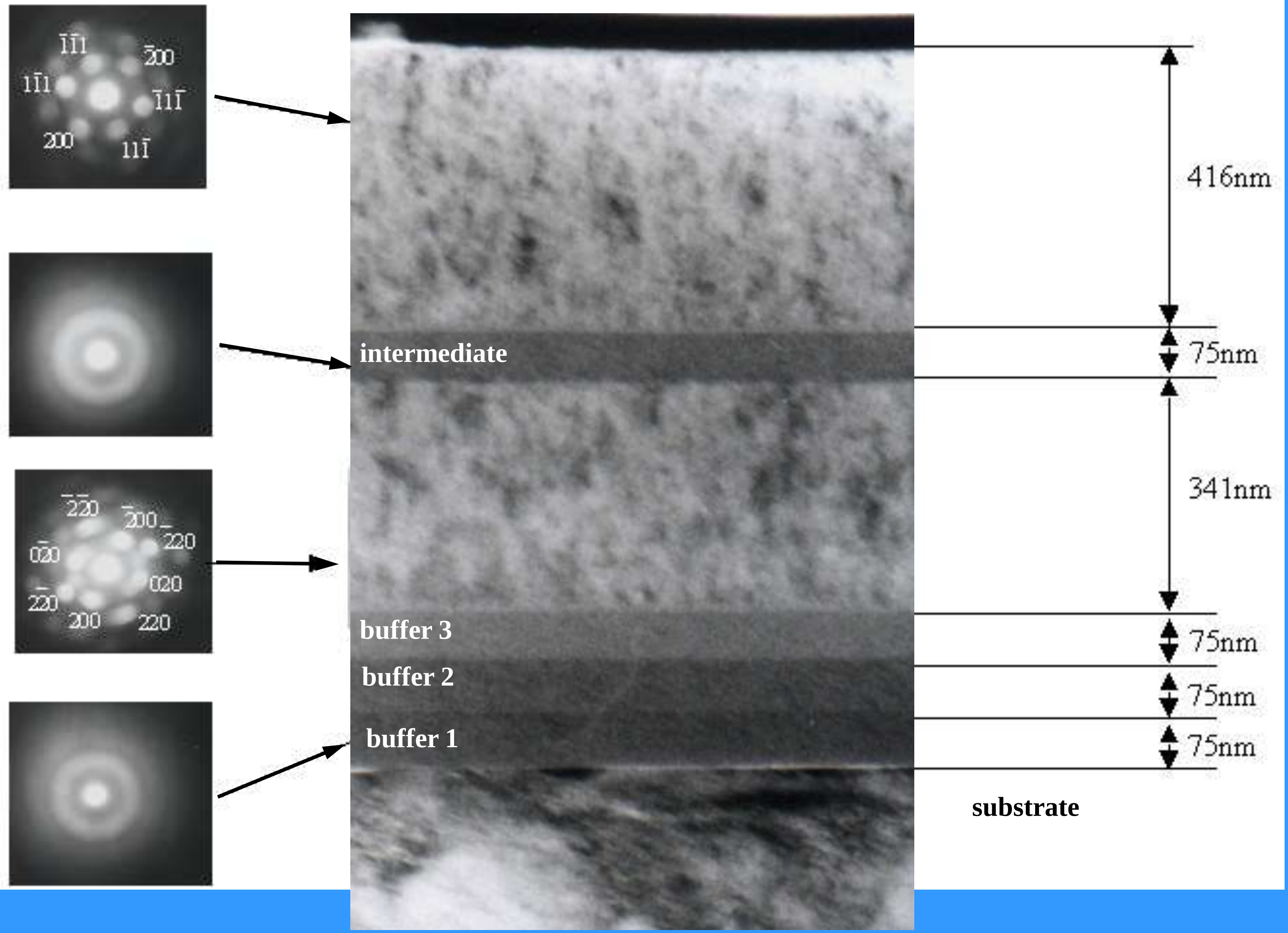

Specimen
Objective lens
Diffraction pattern
Bright field image

TEM
LAB

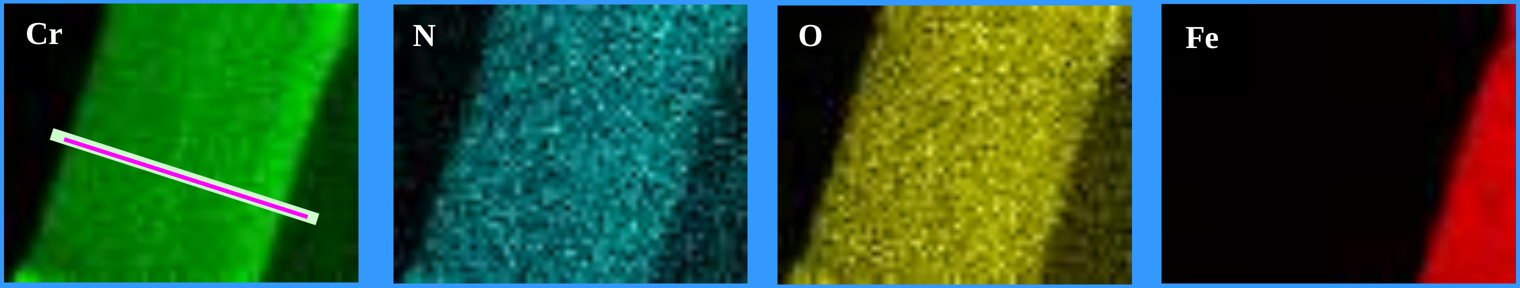

Specimen
Objective lens
Diffraction pattern
Low resolution dark field image

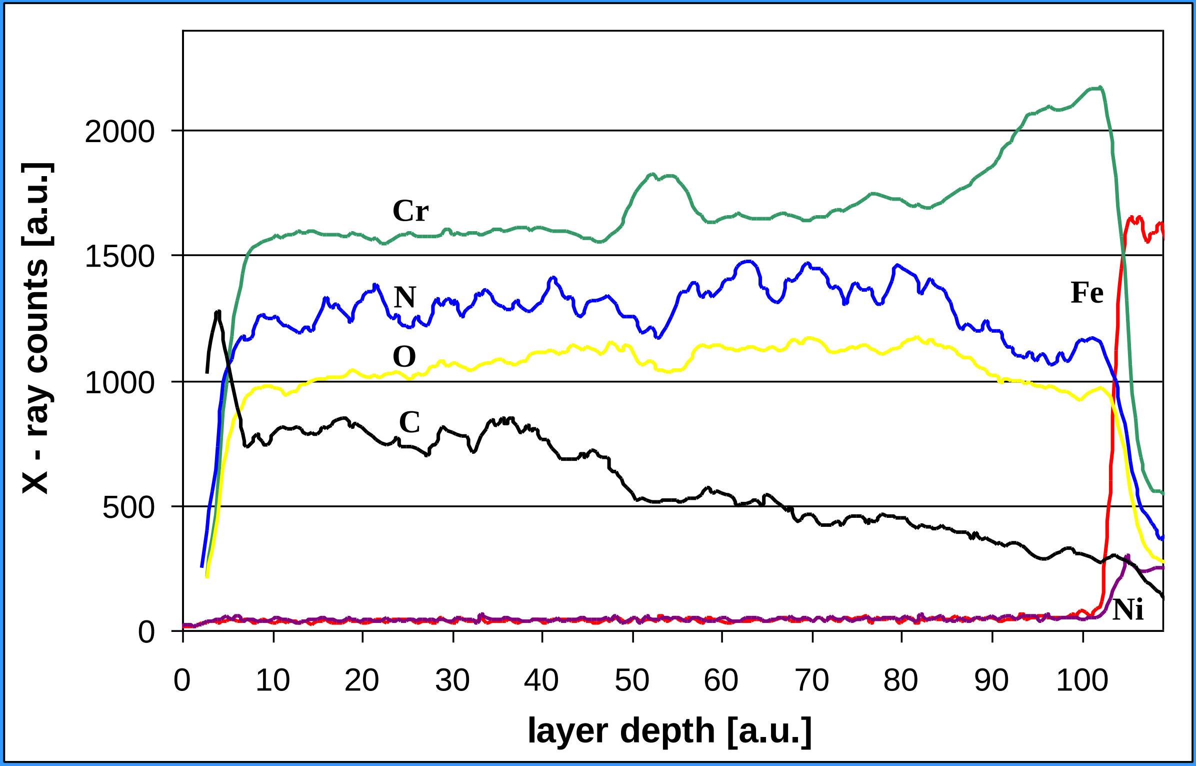
TEM
LAB


Specimen
Objective lens
Diffraction pattern
High resolution dark field image


1̄1̄1
2̄00
11̄1
1̄11̄
200
111̄
2̄2̄0
2̄00
220
02̄0
020
22̄0
200
220
intermediate
buffer 3
buffer 2
buffer 1
substrate
416nm
75nm
341nm
75nm
75nm
75nm

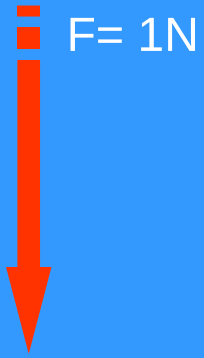
Cr/CrN/Cr/Cr(N,C) – FIB cut samples / „super thin” analitycal transmission electron microscopy (AEM) using enegy dispersive spectroscopy (EDS) attachment

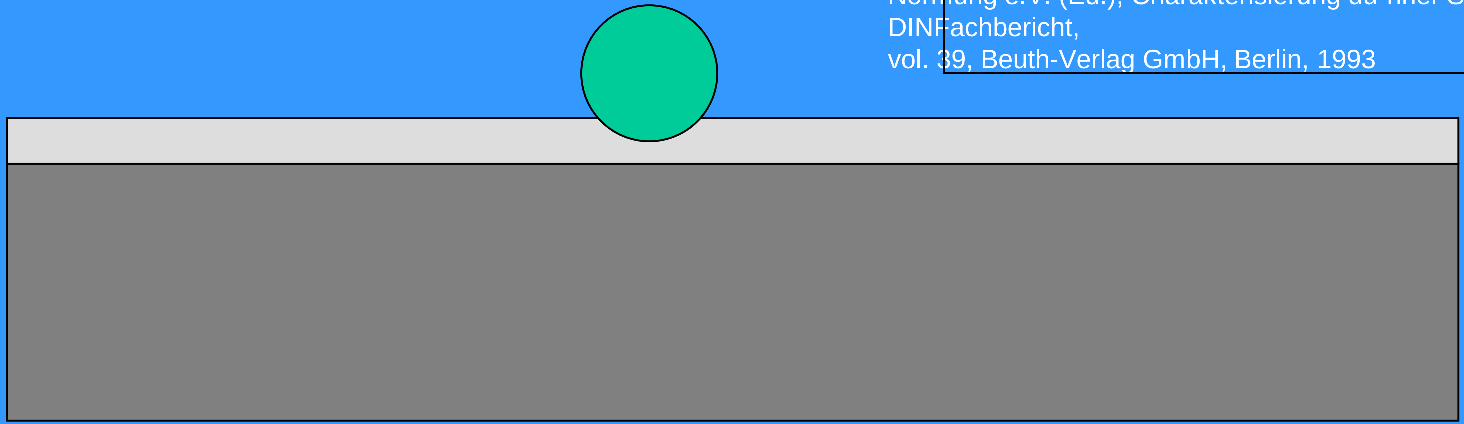


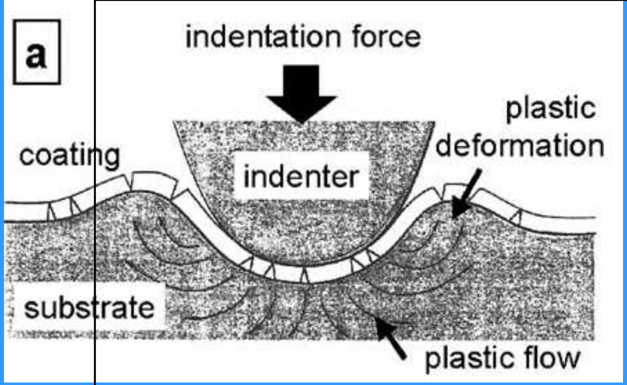


Wear test

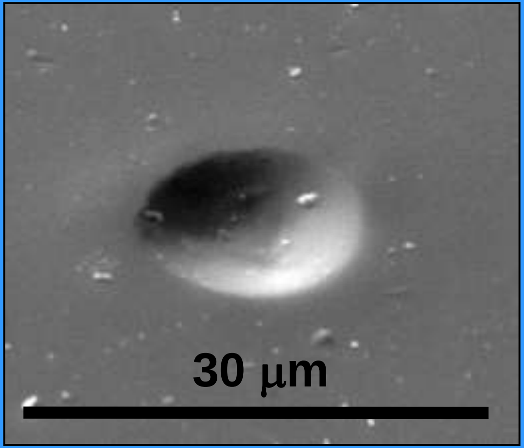
(ball pushed into the coating)







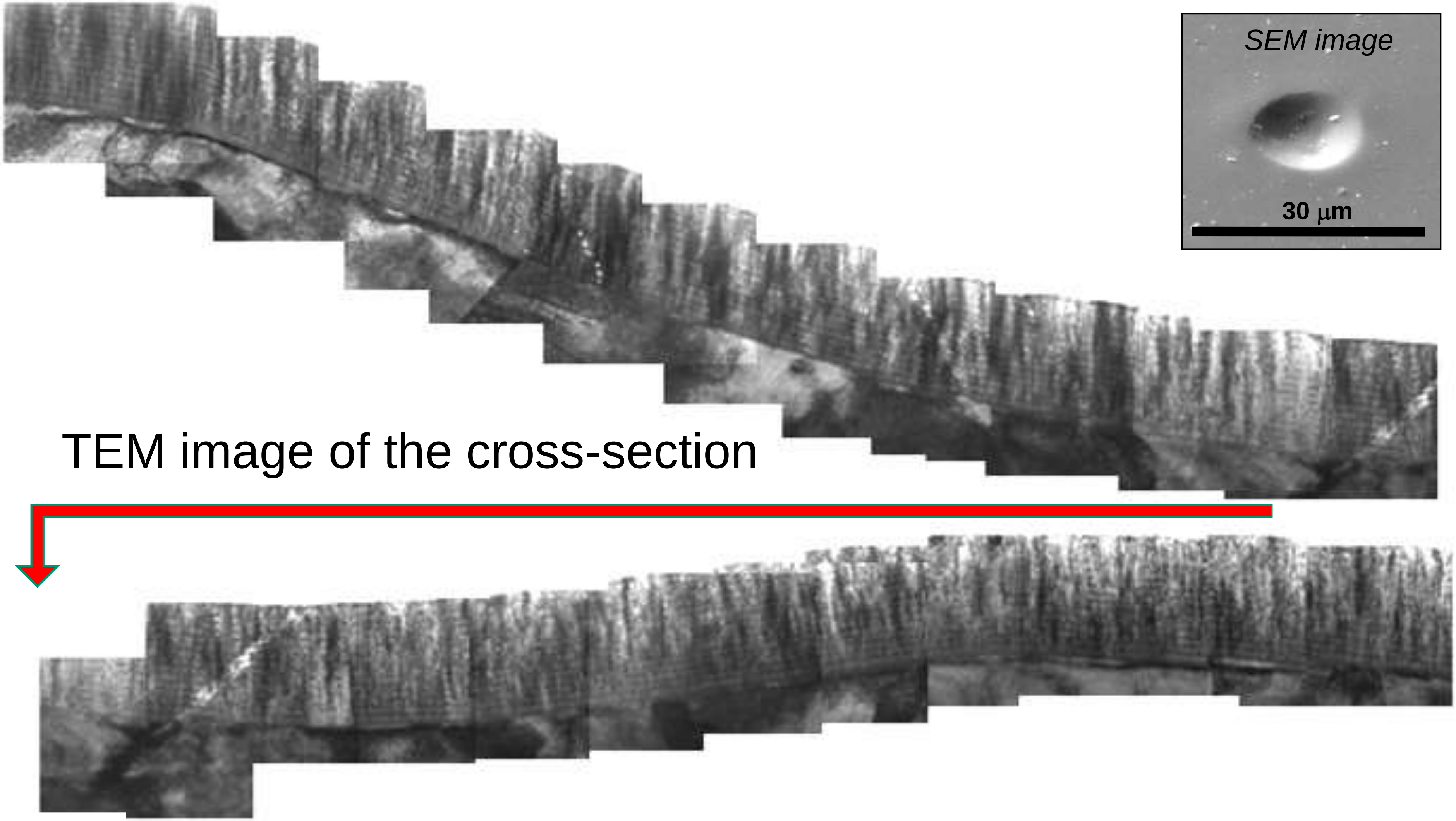
H. Jehn, G. Reiners, N. Siegel, in: DIN Deutsches Institut fu¨r Normung e.V. (Ed.), Charakterisierung du¨nner Schichten, DINFachbericht, vol. 39, Beuth-Verlag GmbH, Berlin, 1993



SEM image of the coating surface after mechanical test

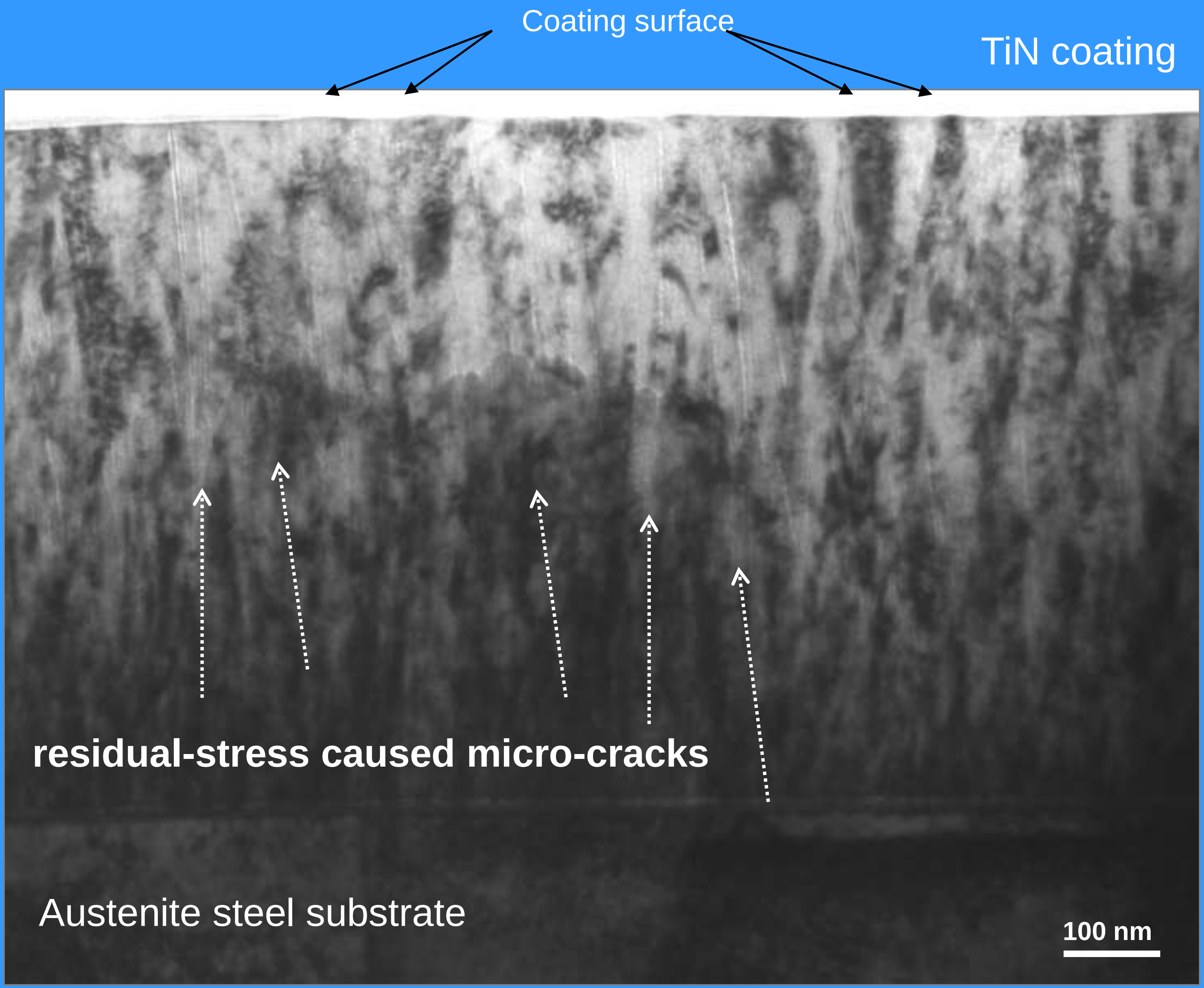
32 layered Ti/TiN coating

Cross- section of the place where penetrator was pushed into the coating



TEM image of the cross-section

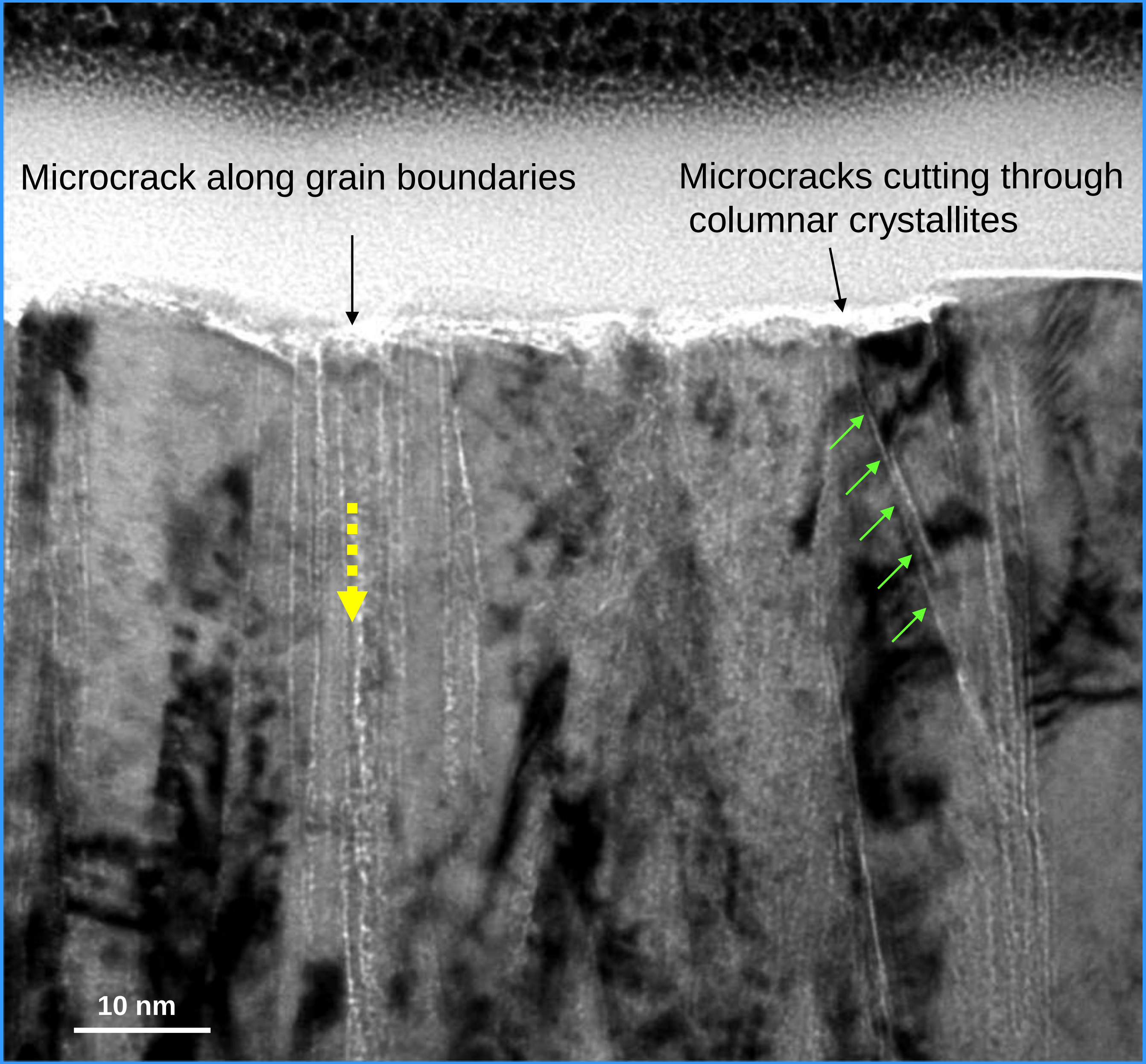
I. as-deposited mono-layer coating



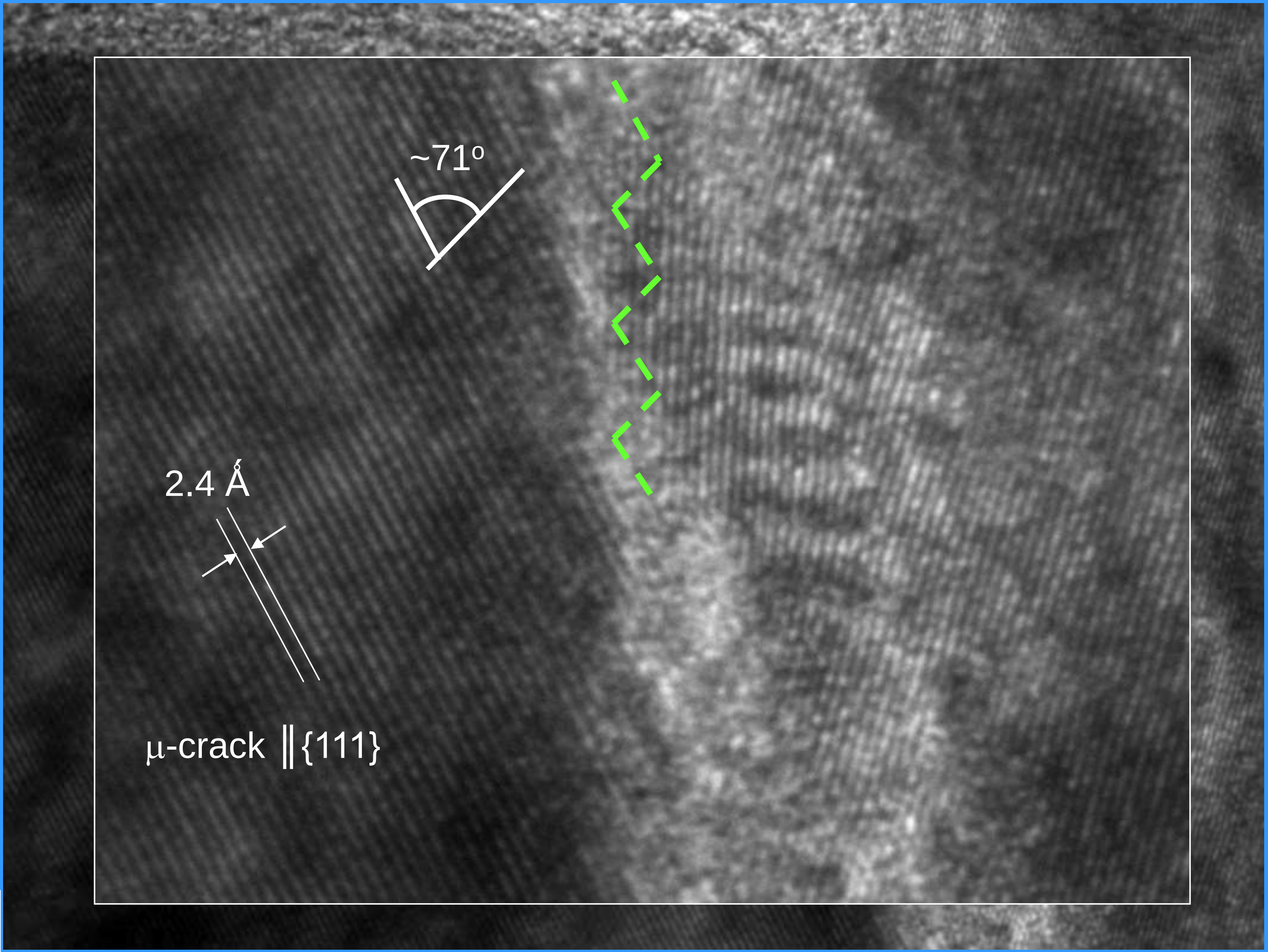
TEM image of the cross-section

Single layered coating- low loading (0.25N)

TiN coating

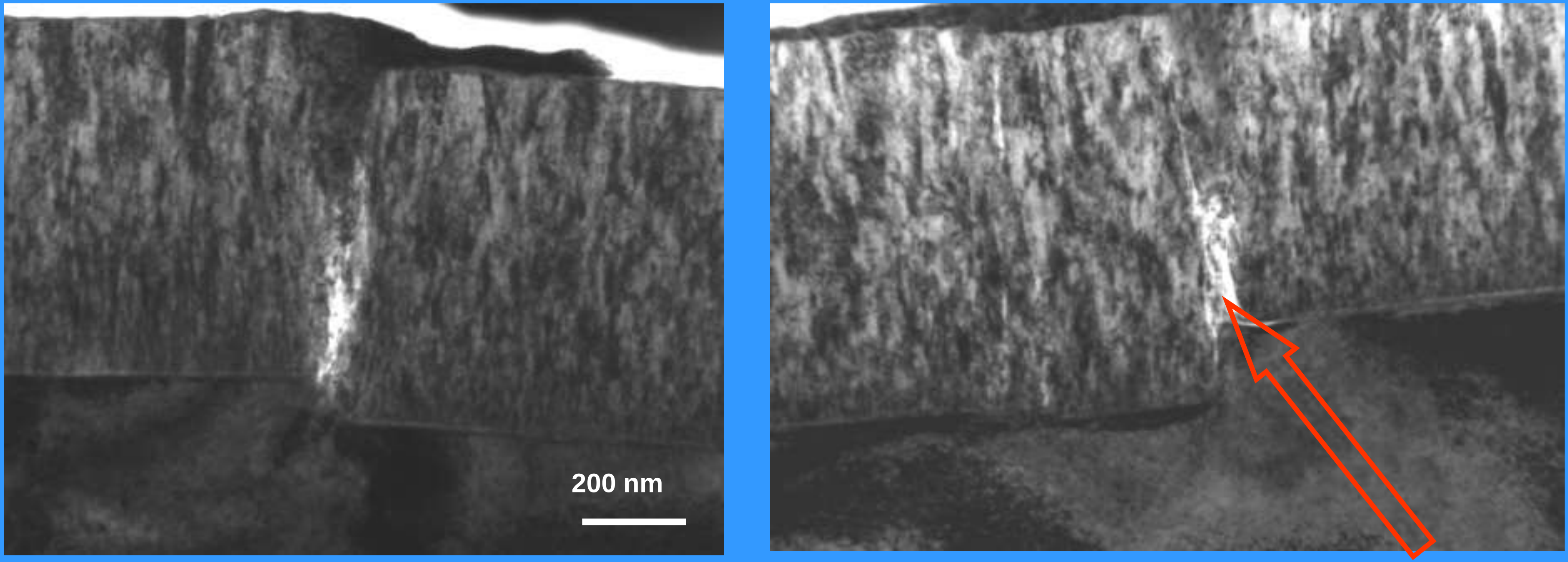


TEM image of the cross-section



HREM image of the crack at the cross-section

Single layered coating- high loading (1N)

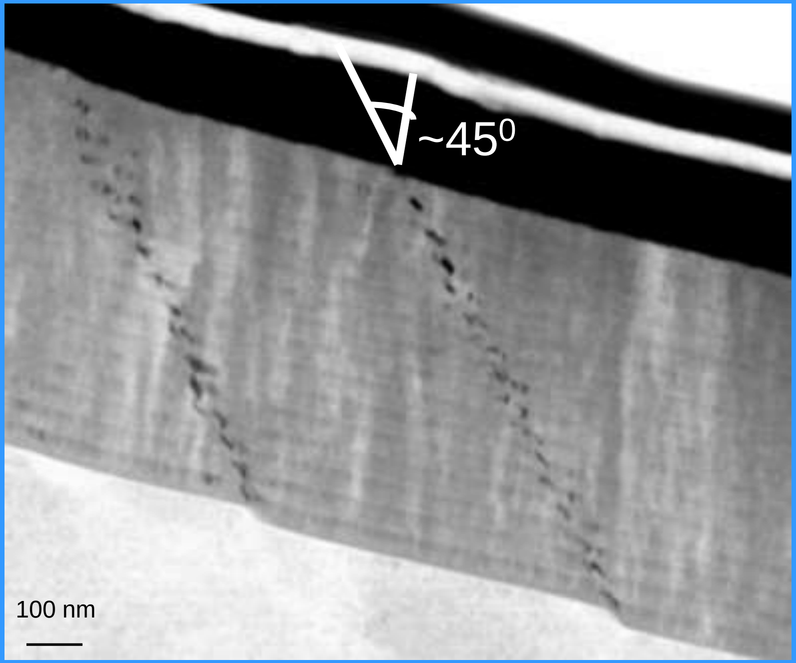


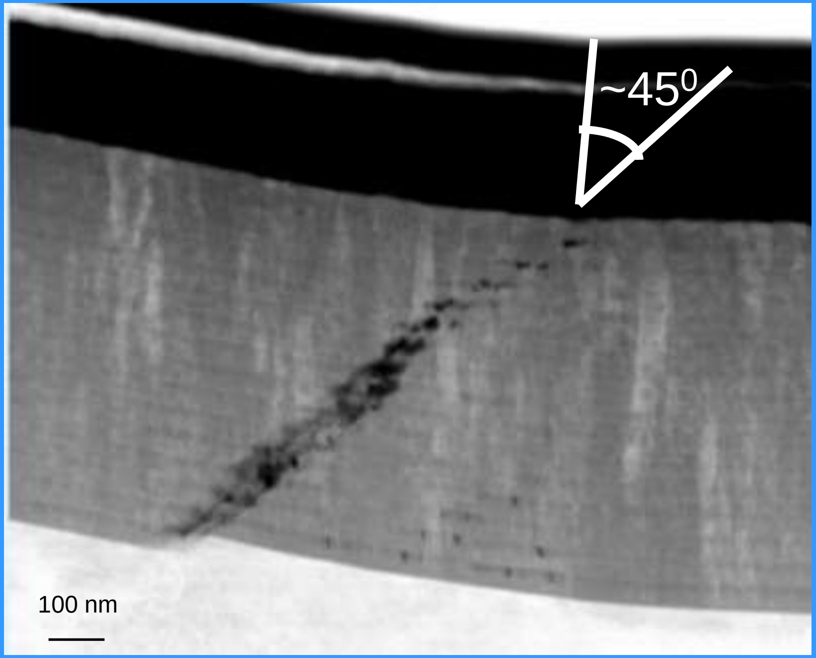
Area endangered by corrosion

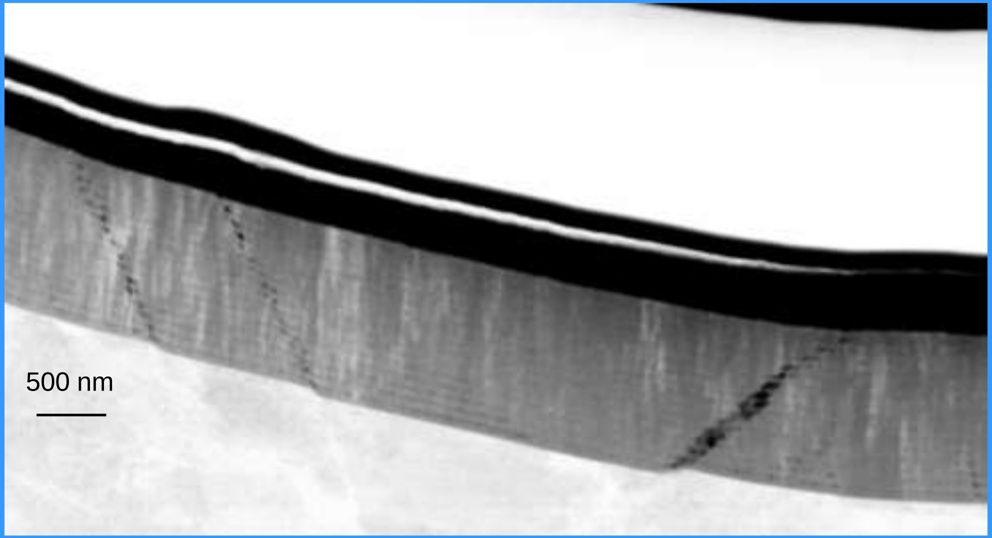
Substrate has a contact with outside environment

TEM image of the cross-section

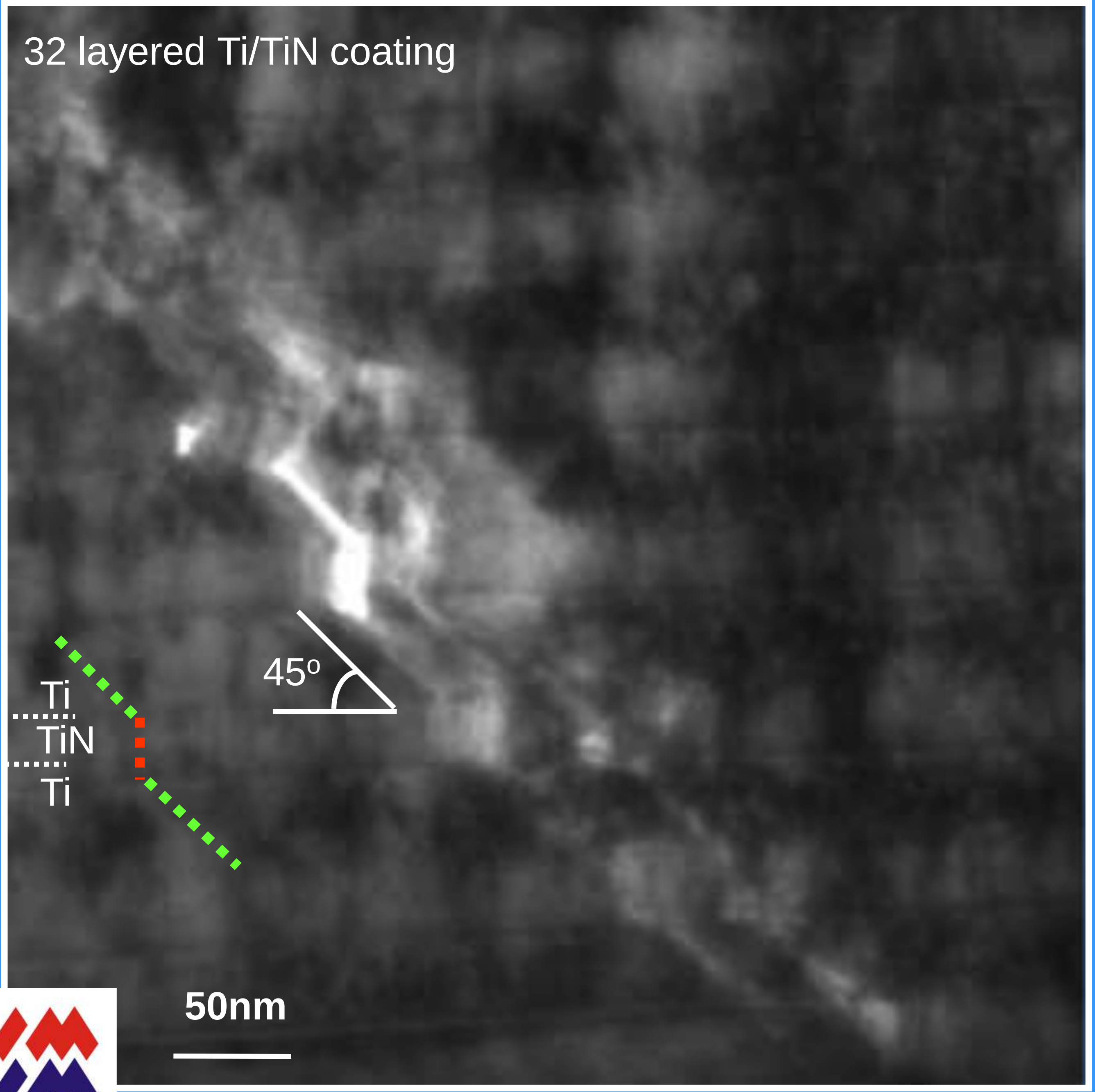
32 layered Ti/TiN coating ratio 1:1

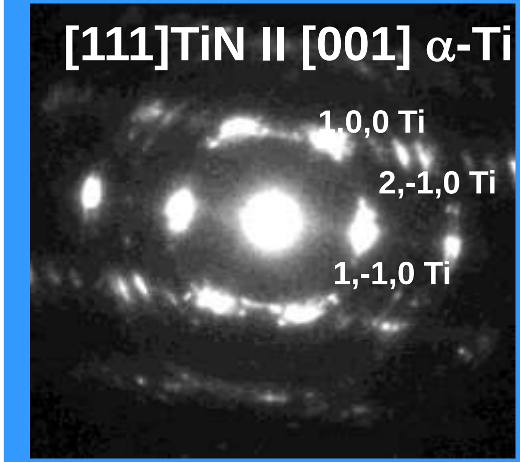






STEM images of cracks propagating across the coating under applied load



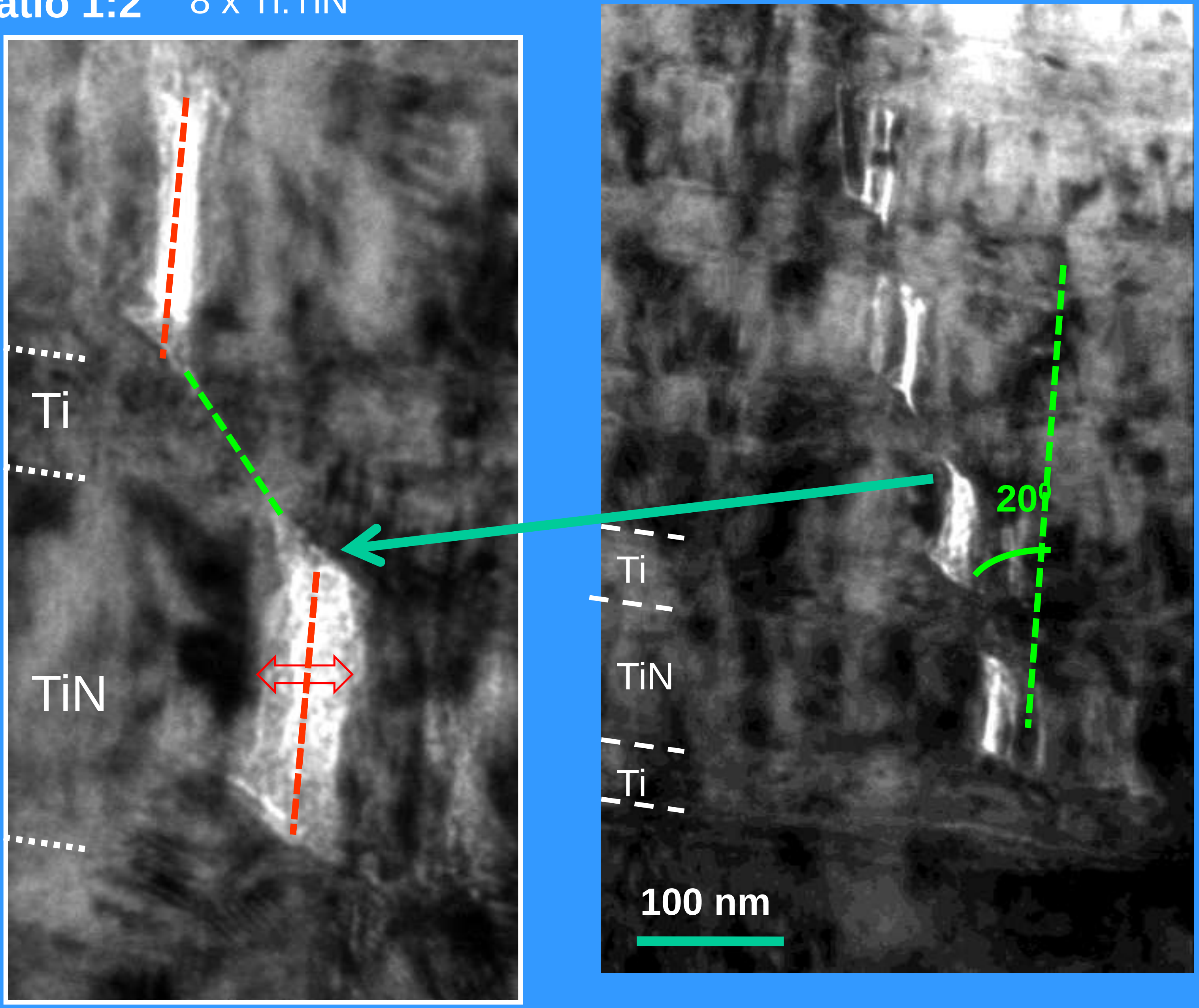


Zone [001]

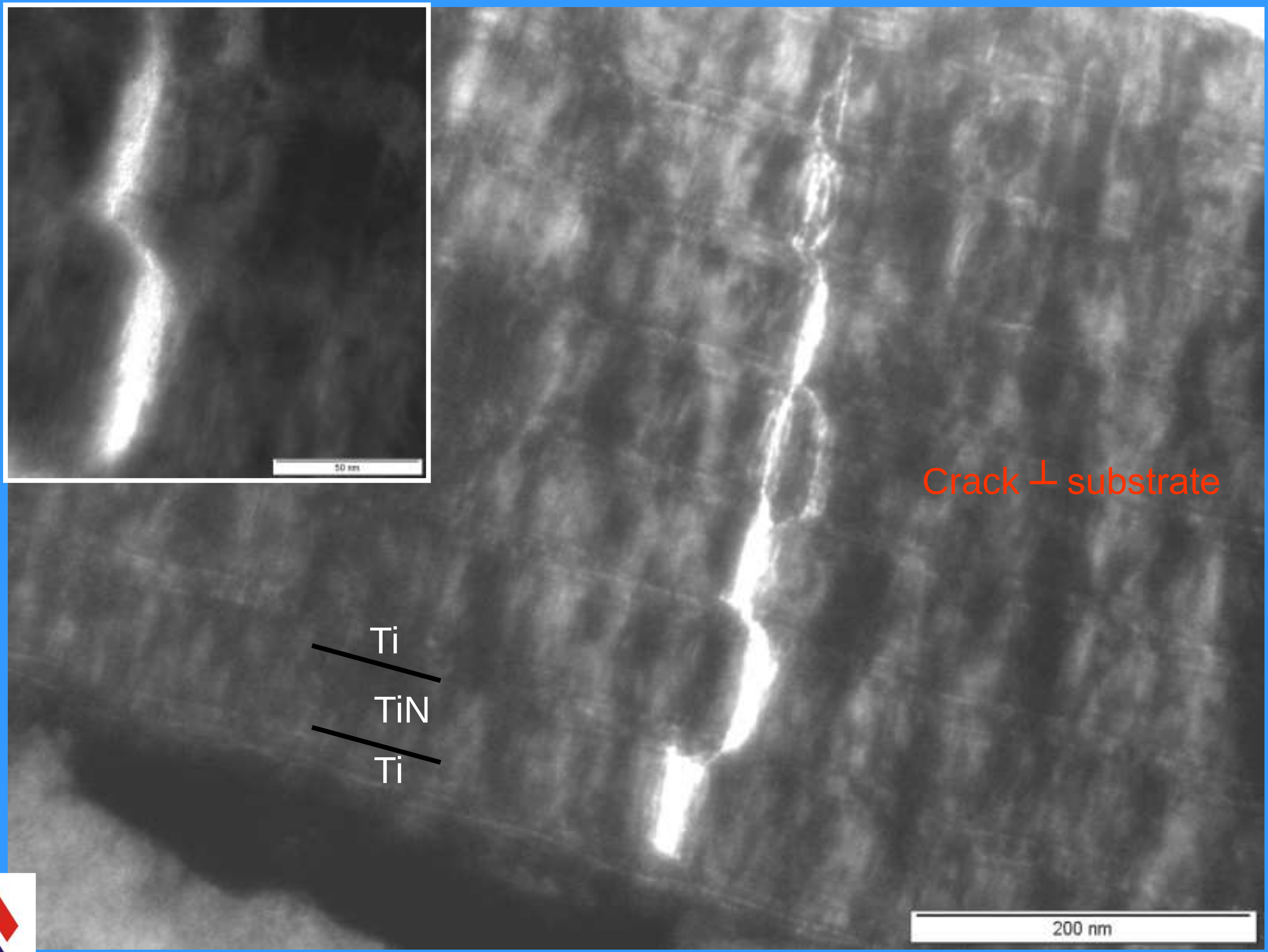
Local plastic deformation
(slip systems)
/cracking

TEM image of the cross-section

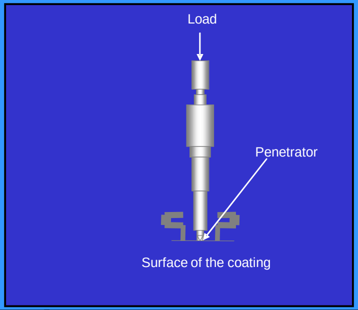
Ratio 1:2 8 x Ti:TiN



Ratio 1:4 8 x Ti:TiN

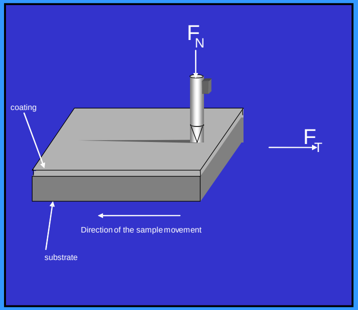


Analysis of mechanical properties



hardness

Type of penetrator: Vickers 136^0
load : 0.02- 30N

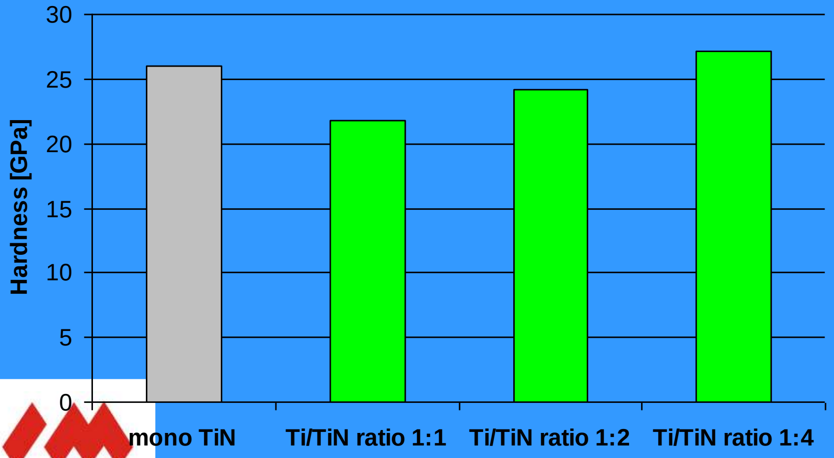


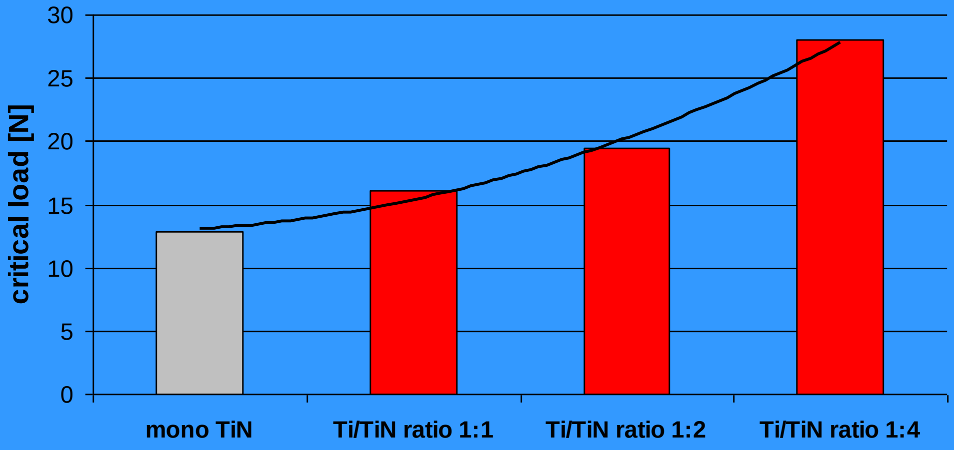
scratch

Type of penetrator: Rockwell 120^0
load : 0.05- 30N
speed : 0.4- 20mm/min
length of scratch : up to 20 mm

H [GPa]	Number of layers		Hardness	
8x(Ti+TiN)		E	10mN	deviation
TiN- mono			**26**	1.40
ratio 1-1	16	247	21.74	1.40
ratio 1-2	16	255	24.14	1.90
ratio 1-4	16	263	27.12	2.10

	Lc1 [N]	Lc2 [N]
TiN- mono	5,1	12,8
8x ratio 1-1	7,2	16,1
8x ratio 1-2	7	19,5
8x ratio 1-4	7	28

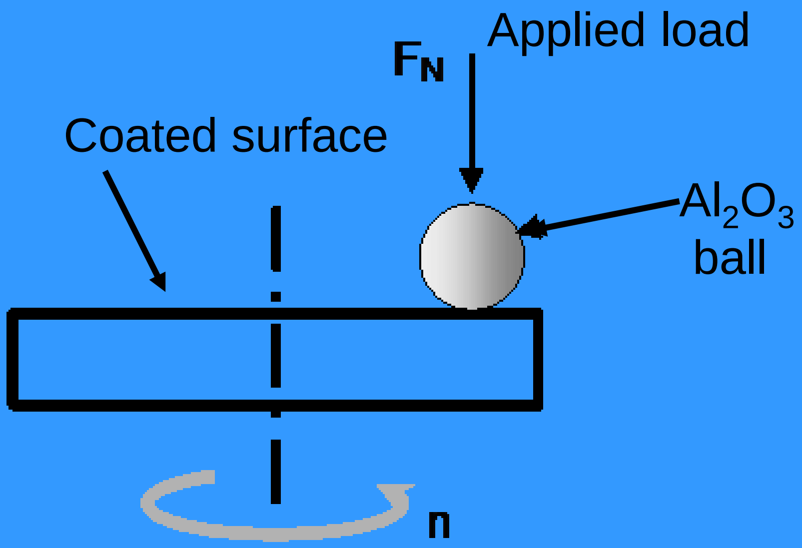




J.F.Archard,
J. Appl. Phys.24(1953)981

Wear - $V_w = K(S*N/H)$

V_w– amount of the removed material, S– distance, N– load, H– hardness, K– wear coefficient

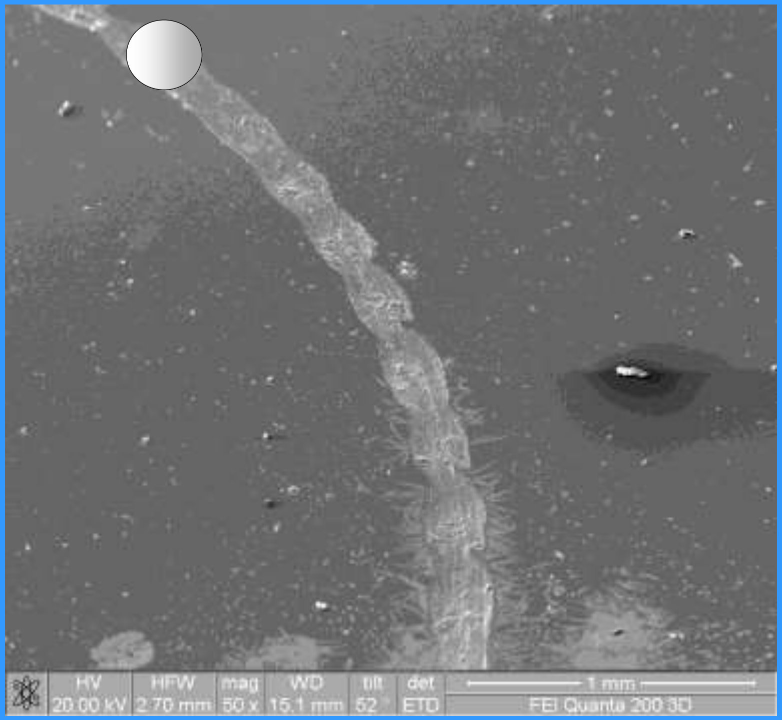

Applied load

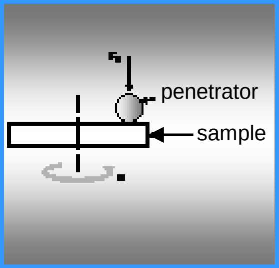
F_N

Coated surface

Al_2O_3 ball

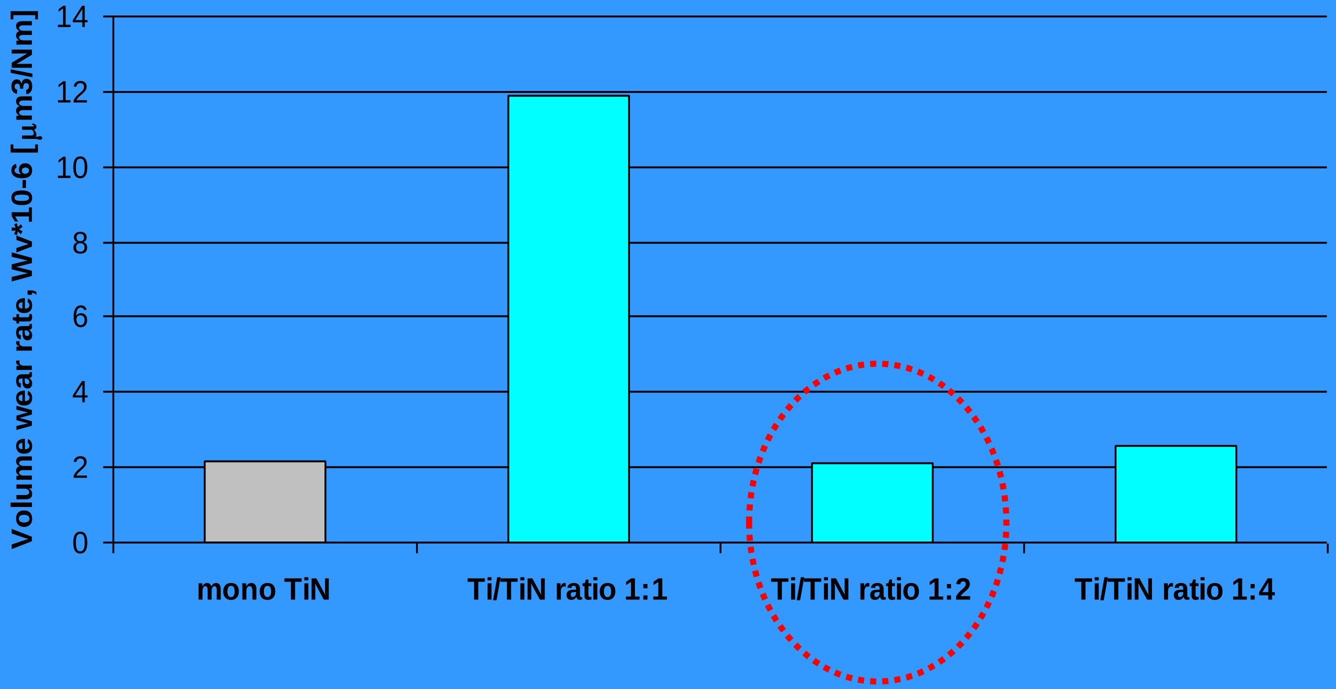
n

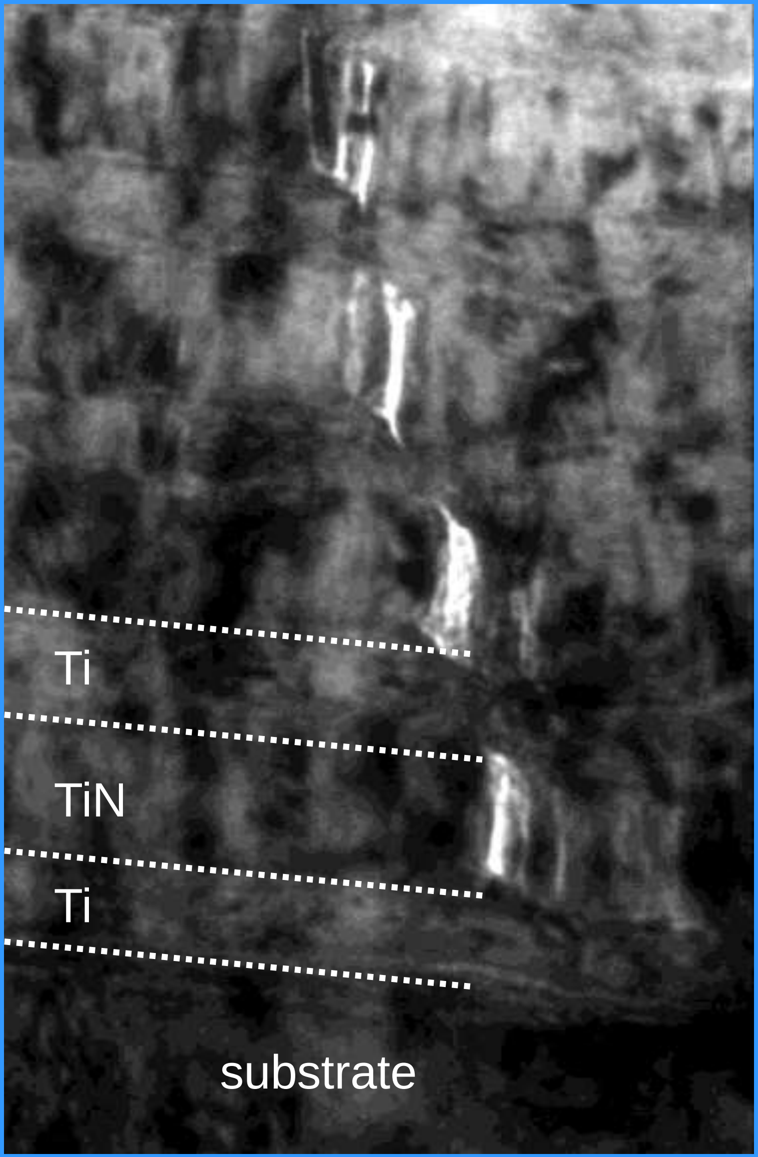




wear

	Wv*10^-6[µm^3/(N*m)]	Deviation.
TiN- mono	2,17	0,6
Ti/TiN-1:1	11,9	2,5
Ti/TiN-1:2	2,115	0,4
Ti/TiN-1:4	2,55	1,02





Conclusions

-As deposited single layered (TiN) coatings were characterised by vertical cracking caused by residual stress. Under the applied load, cracks at grain boundaries open fast leading to coating fragmentation exposing substrate.

- The multilayer TiN/Ti coatings deform both by brittle cracking of ceramic and plastic deformation of metalic layers. The TiN/Ti multilayer hardness and wear was at the level of TiN till the ceramic phase dominated.

- The deformation and wear of multilayer TiN/Ti multilayer coatings proceeds keeping contnuity of metalic layers and therefore protecting substrate (keeping corrosion at bay).

Friction elements

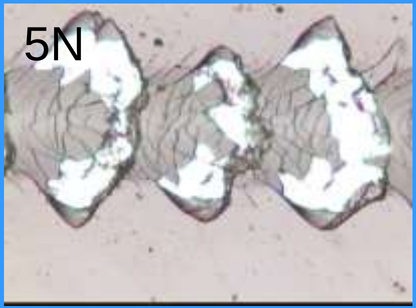
Tribology

DLC		10mN		
	hmax [nm]	HV	HiT [GPa]	E [GPa]
Mean	**150**	**1190**	**12539,1**	**177**
Deviat	**8**	**44,0**	**463,9**	**10**

TiN		10mN		
	hmax [nm]	HV	HiT [GPa]	E [GPa]
Mean	**126**	**1410**	**14865,6**	**273**
Deviat	**8**	**62,6**	**659,3**	**22**

10mN

DLC



Rockwell
200 μm
0.01-30N

TiN

Powłoka	Wskaźnik zużycia	Współczynnik tarcia
DLC	18,11	0,09
TIN	8,86	0,2

Ball-on-disc

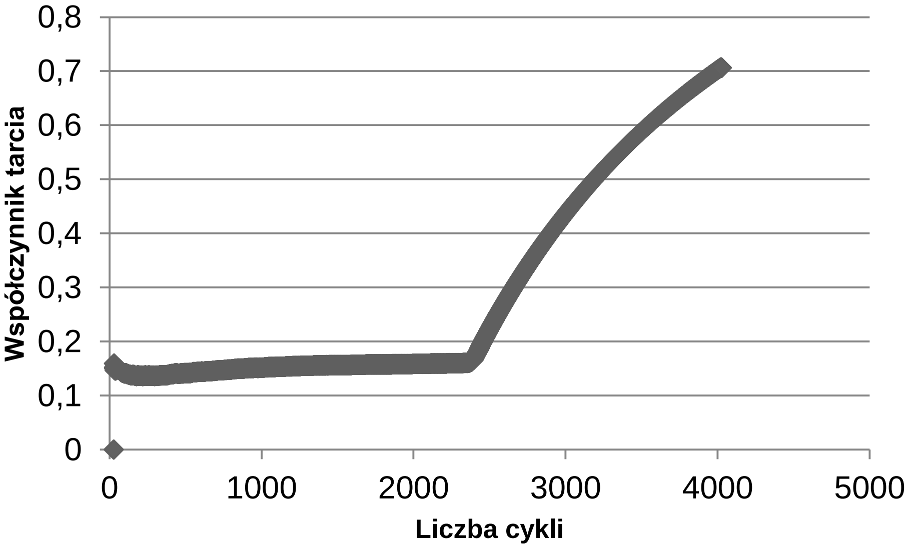
ISO 20808:2004

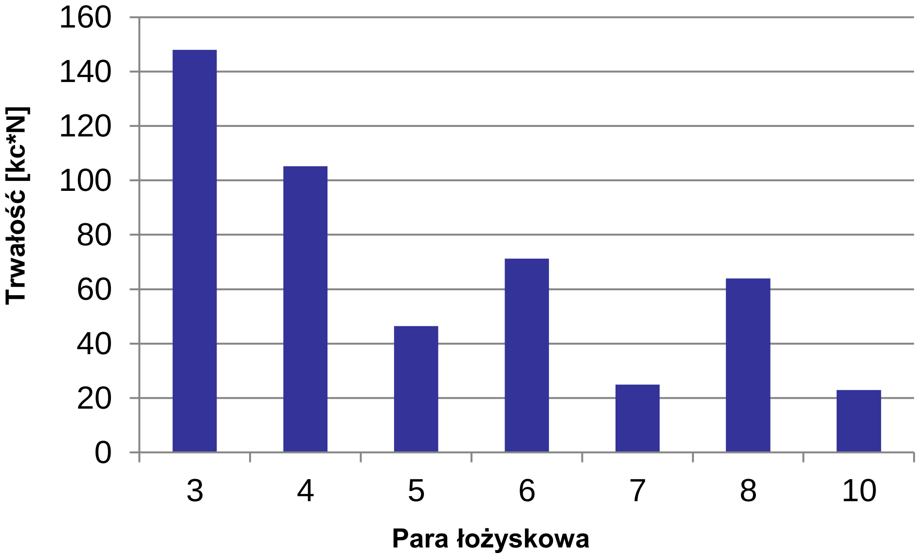
Tribology

Para Force >	Fric. Coeff. 1N	3N	5N	8N	12N
Para 3	0,11	0,11	0,11	0,12	0,15
Para 4	0,08	0,11	0,12	0,13	0,14
Para 5	0,07	0,07	0,14		
Para 6	0,13	0,12	0,14	0,2	
Para 7	0,12	0,14	0,17		
Para 8	0,1	0,12	0,15	0,17	
Para 10	0,12	0,1			

-Friction coefficient uder load 1N, rotation 150rot/min; test 20000 cycle

- Load sequence: 3N-5000cclei, 5N-5000cycle, 8N-5000cycle and 12N-5000cycle

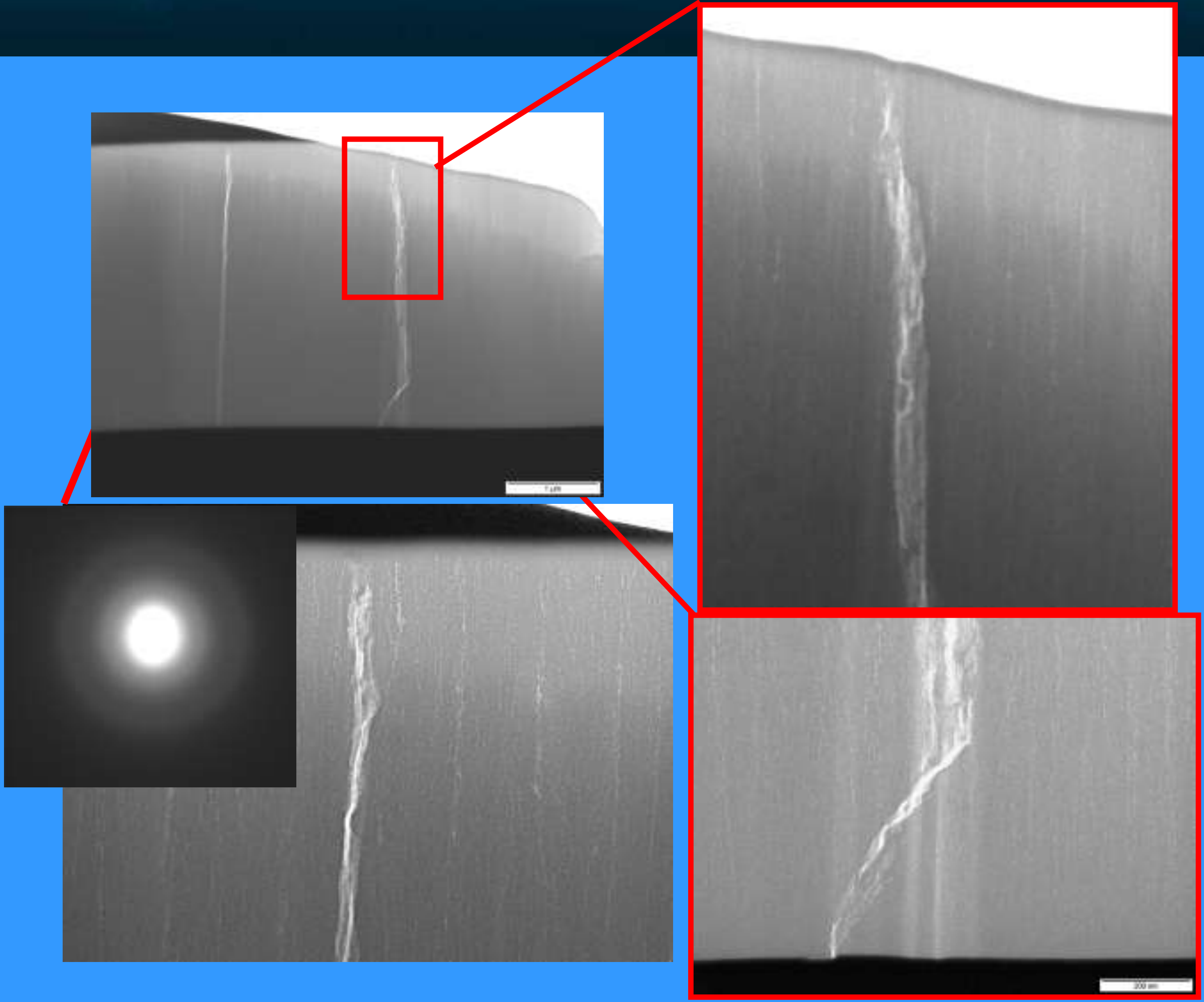




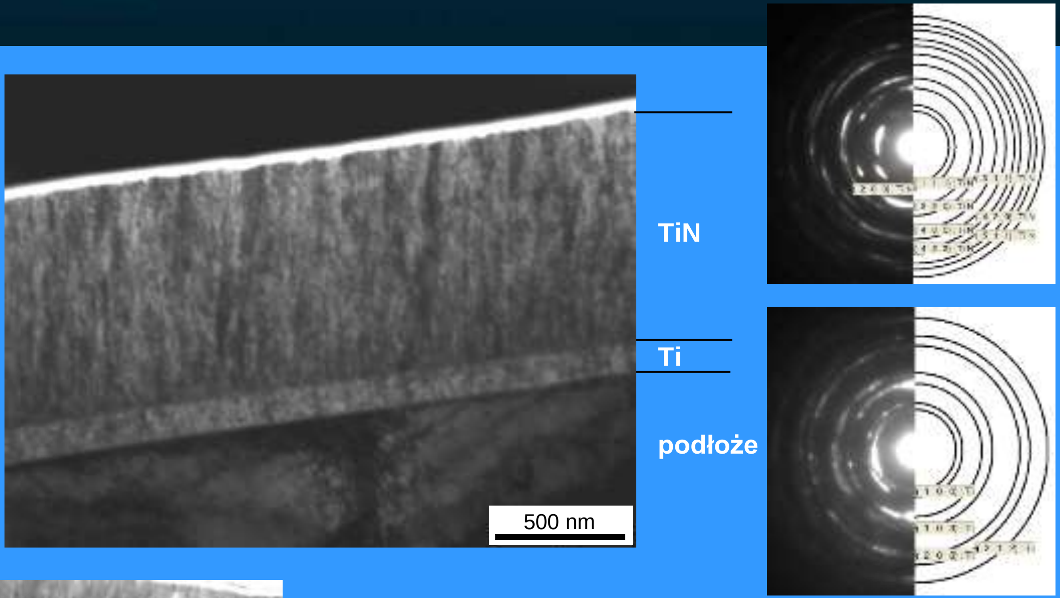
TEM

Friction elements

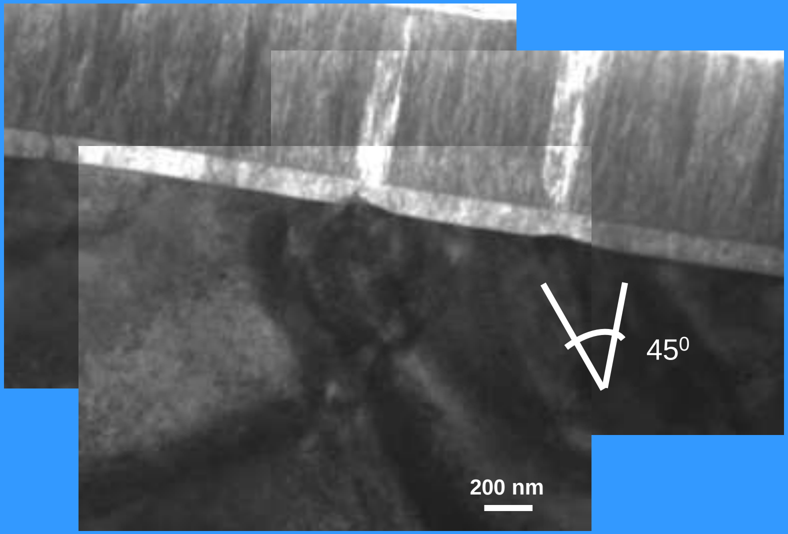
Amorphous carbon coating
Test- 1N/ 2000 cykli

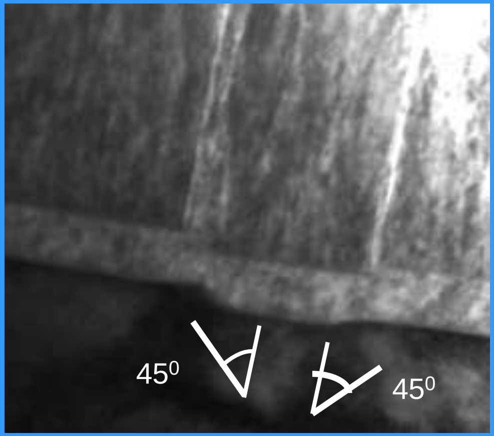


Friction elements



TiN coating
Test- 0,25N/ 20000 cykli





Confocal microscopy

- Confocal modulus LSM 5 Exciter, 2 channels, RGB
- Laser HeNe 633nm 5mW
- Laser HeNe 543nm 1mW
- Laser argon 458/488/514nm, 25mW
- Laser- diode V 405nm
- Main Beam Splitter turret PASCAL
- Software ZEN 2008 LSM 5 EXCITER
- Light division system (405, 458, 488, 514, 543 nm)
- Filter BP 505-530
- Filter BP 505-600
- Filter BP 530-600
- Filter BP 560-615
- Fiter LP 420
- Filter BP 420-480
- System ECU LSM 5 EXCITER
- Modulus DIC I/0,9 with polarysator
- Transmited light detector T-PMT LSM 710
- Heating stage

Mikroskop konfokalny

- Confocal modulus LSM 5 Exciter, 2 channels, RGB
- **Laser HeNe 633nm 5mW**
- **Laser HeNe 543nm 1mW**
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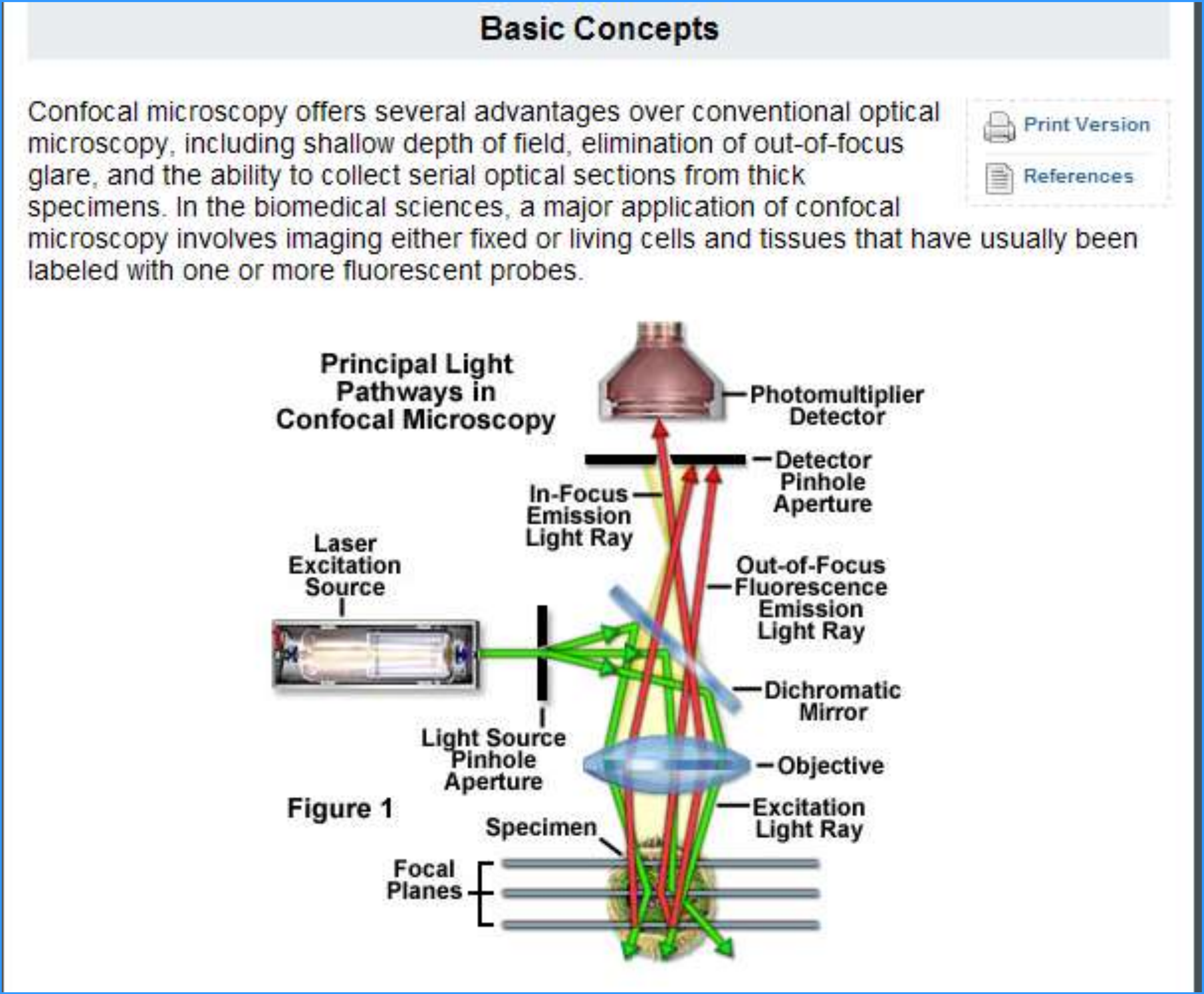
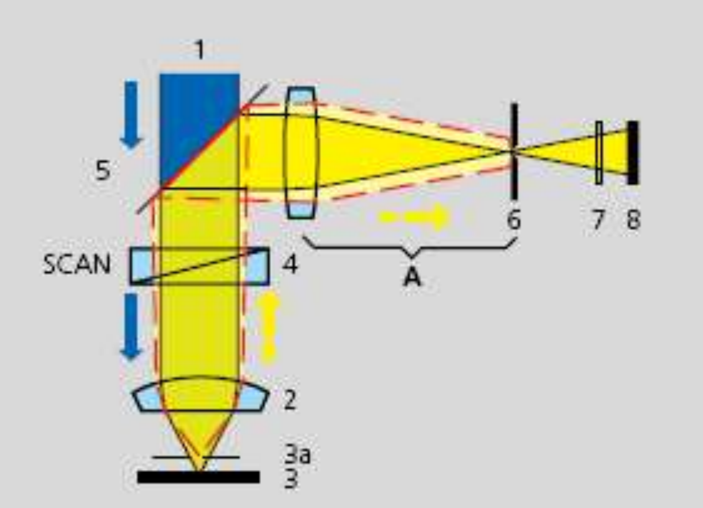


Basic Concepts

Confocal microscopy offers several advantages over conventional optical microscopy, including shallow depth of field, elimination of out-of-focus glare, and the ability to collect serial optical sections from thick specimens. In the biomedical sciences, a major application of confocal microscopy involves imaging either fixed or living cells and tissues that have usually been labeled with one or more fluorescent probes.

Figure 1

Confocal microscopy



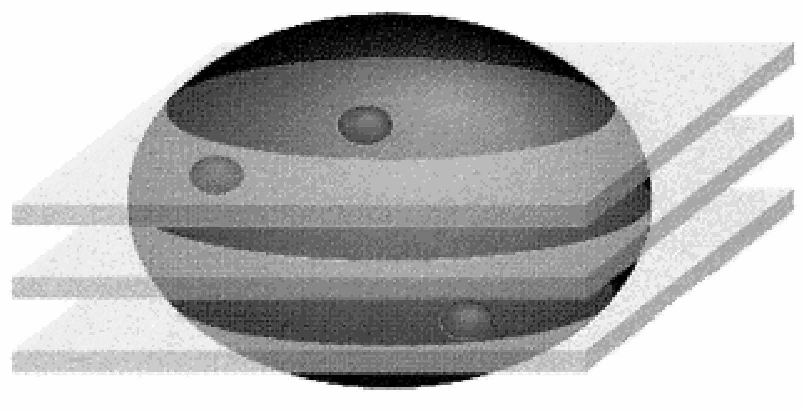
CONCEPT confocal microscopy
Marvin Minsky year 1950, postdoc-Harvard University
patented in 1961

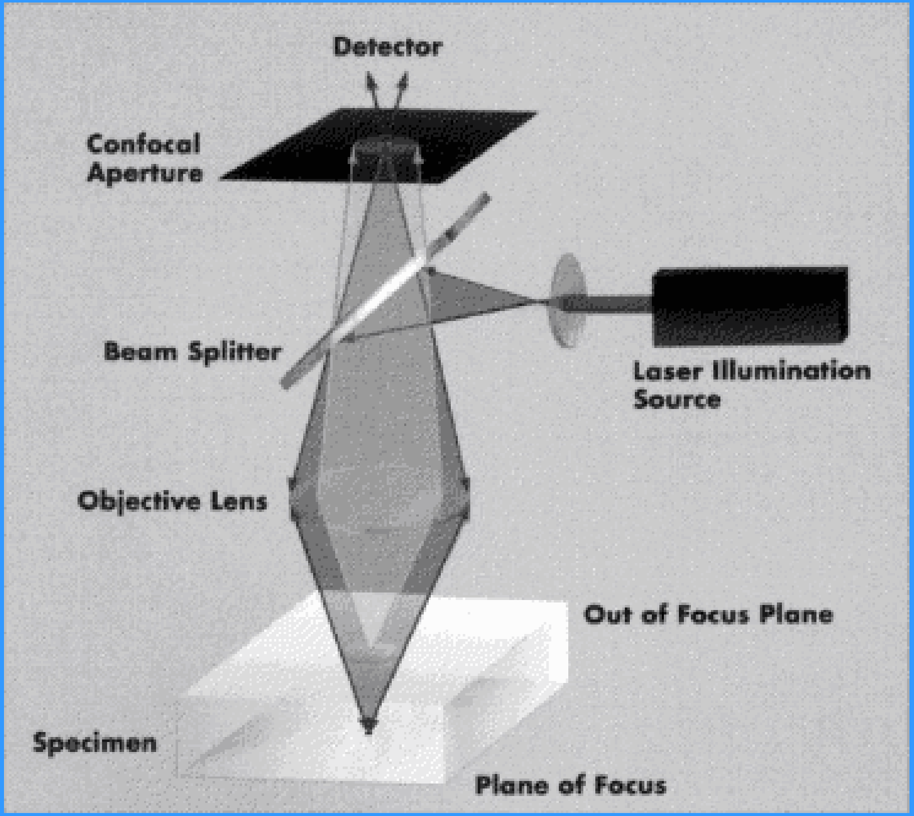
Multi-beam confocal microscopy
David Egger and Mojmir Petran-late 1960s

FIRST INSTRUMENT working
Fred Brakenhoff-1979

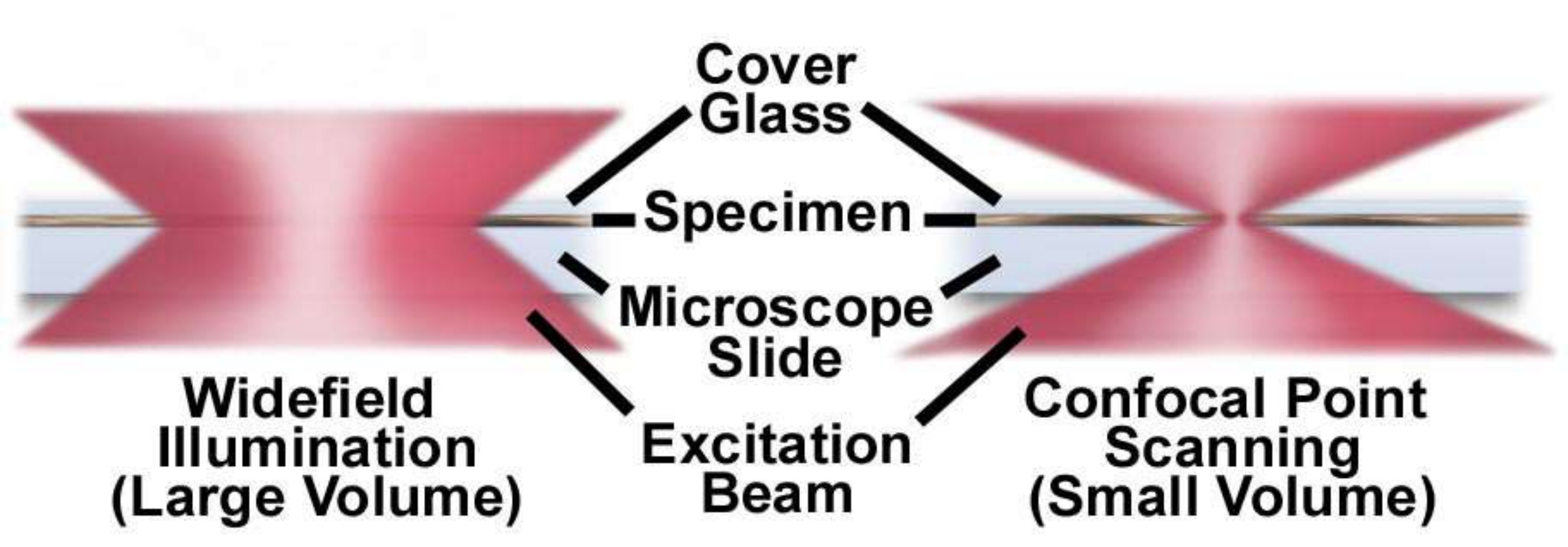
FIRST COMMERCIAL MICROSCOPES 1987

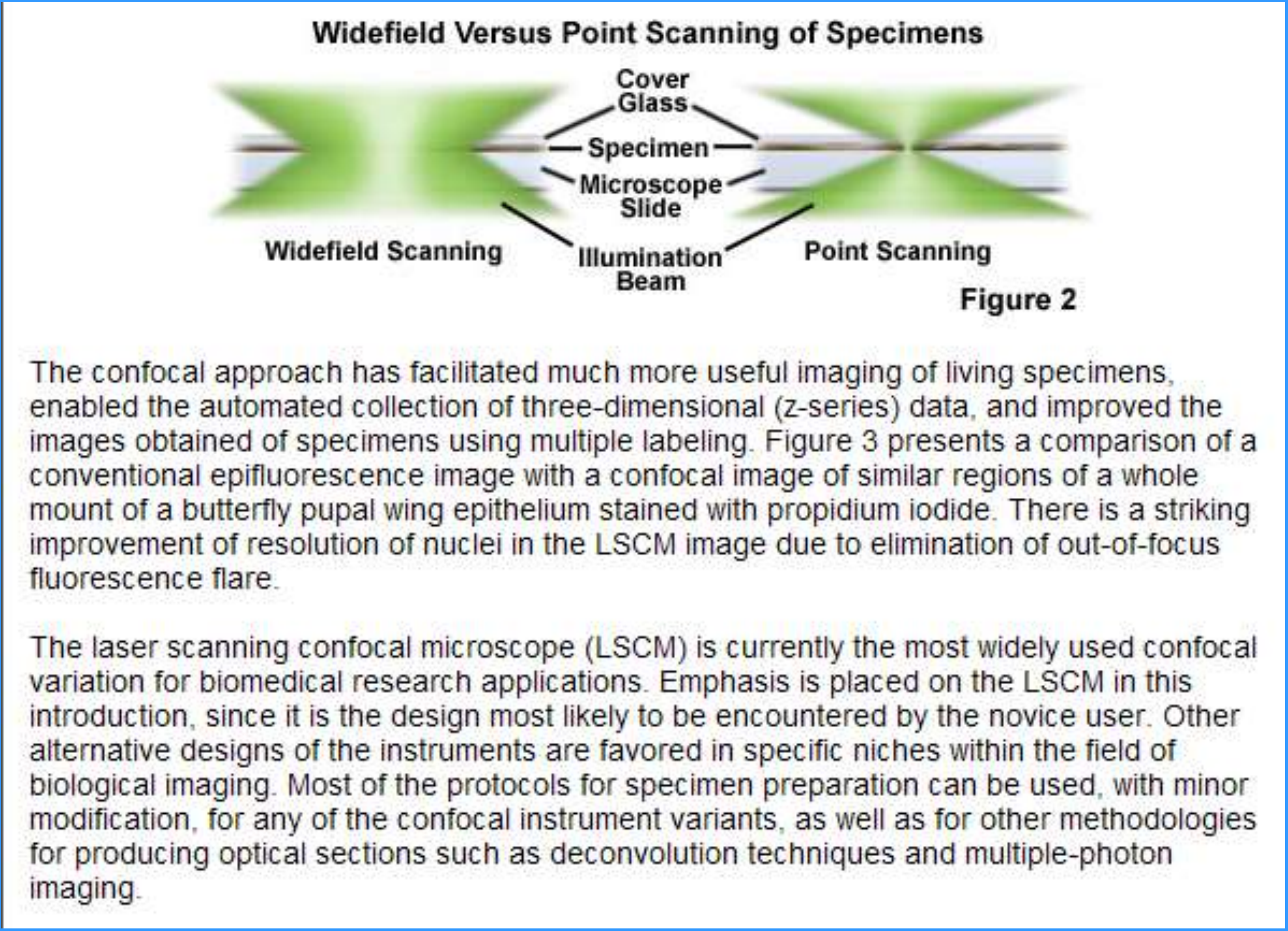
Microbiospektromulti fluorometer
Mikrobiospektromultifluorymetr





Comparison of confocal microscopy and widefield





Widefield Versus Point Scanning of Specimens

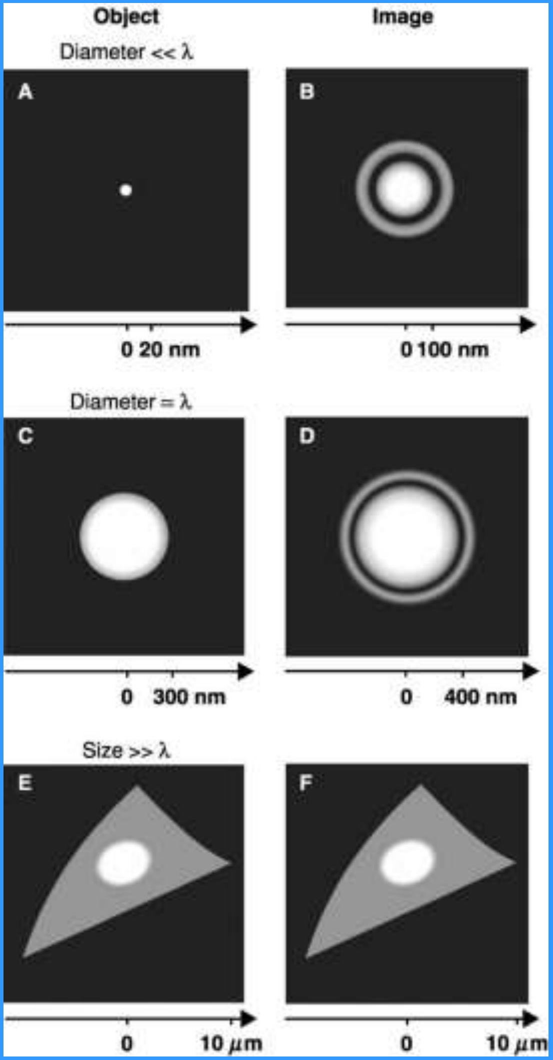
Figure 2

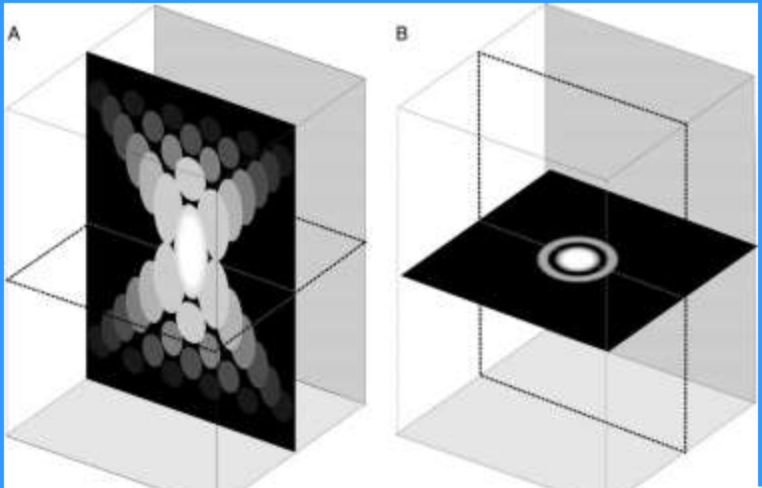
The confocal approach has facilitated much more useful imaging of living specimens, enabled the automated collection of three-dimensional (z-series) data, and improved the images obtained of specimens using multiple labeling. Figure 3 presents a comparison of a conventional epifluorescence image with a confocal image of similar regions of a whole mount of a butterfly pupal wing epithelium stained with propidium iodide. There is a striking improvement of resolution of nuclei in the LSCM image due to elimination of out-of-focus fluorescence flare.

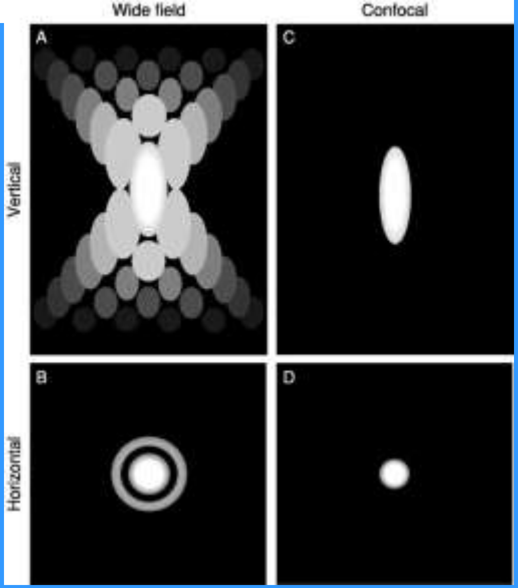
The laser scanning confocal microscope (LSCM) is currently the most widely used confocal variation for biomedical research applications. Emphasis is placed on the LSCM in this introduction, since it is the design most likely to be encountered by the novice user. Other alternative designs of the instruments are favored in specific niches within the field of biological imaging. Most of the protocols for specimen preparation can be used, with minor modification, for any of the confocal instrument variants, as well as for other methodologies for producing optical sections such as deconvolution techniques and multiple-photon imaging.

Assumptions of confocal microscopy

The advantages of confocal microscopy

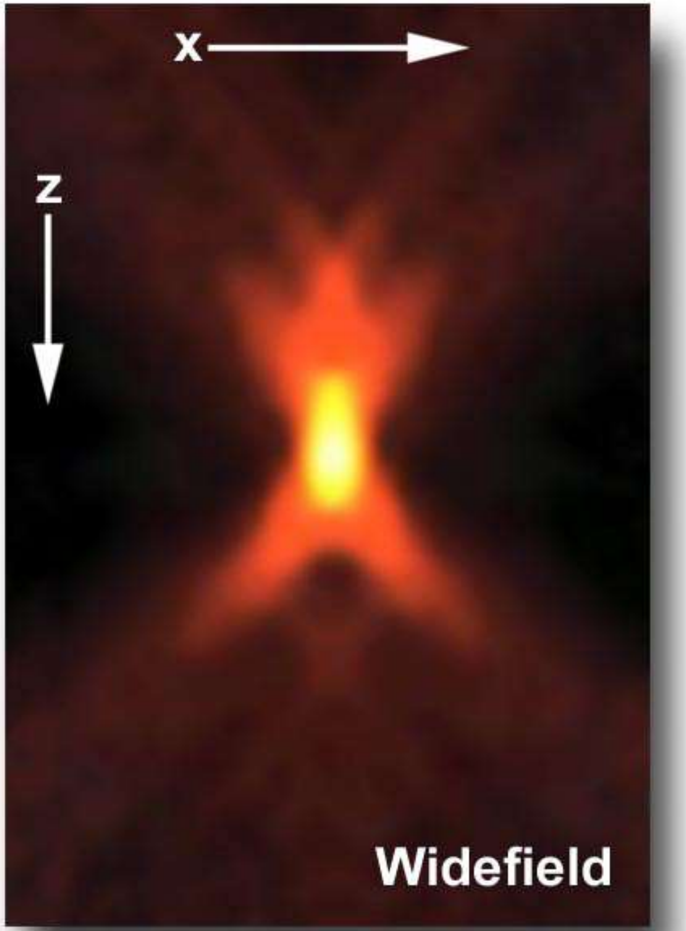


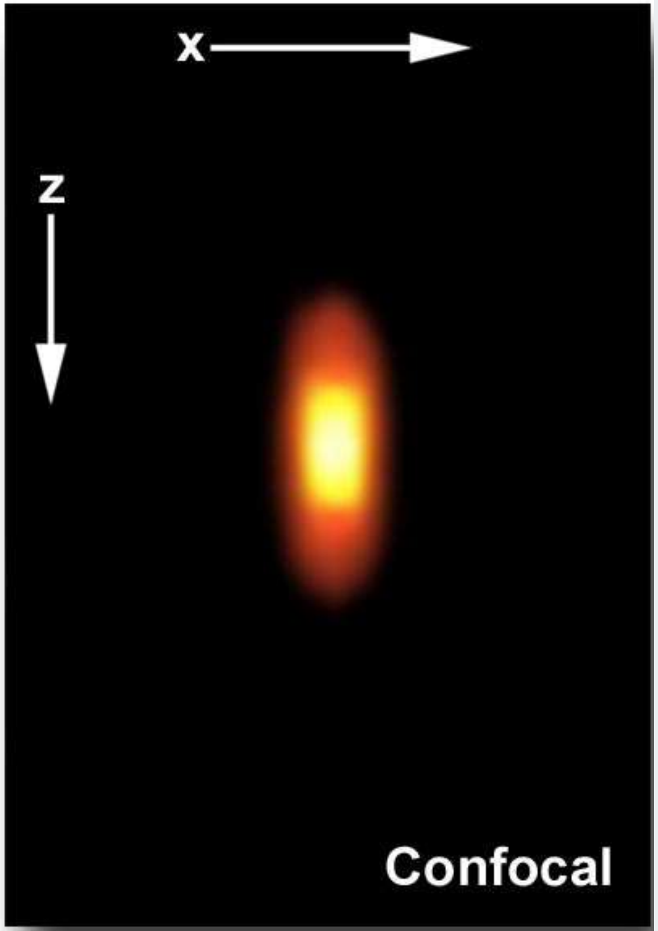


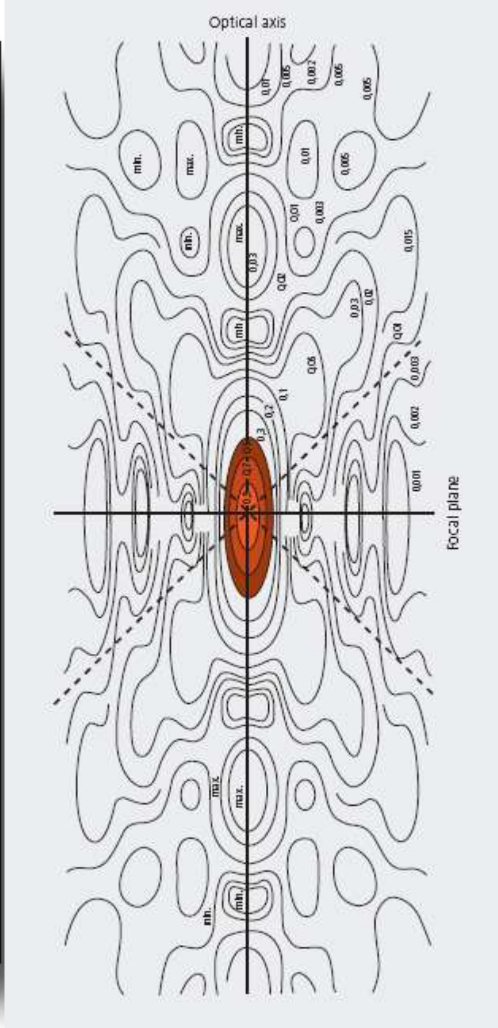


Assumptions of confocal microscopy

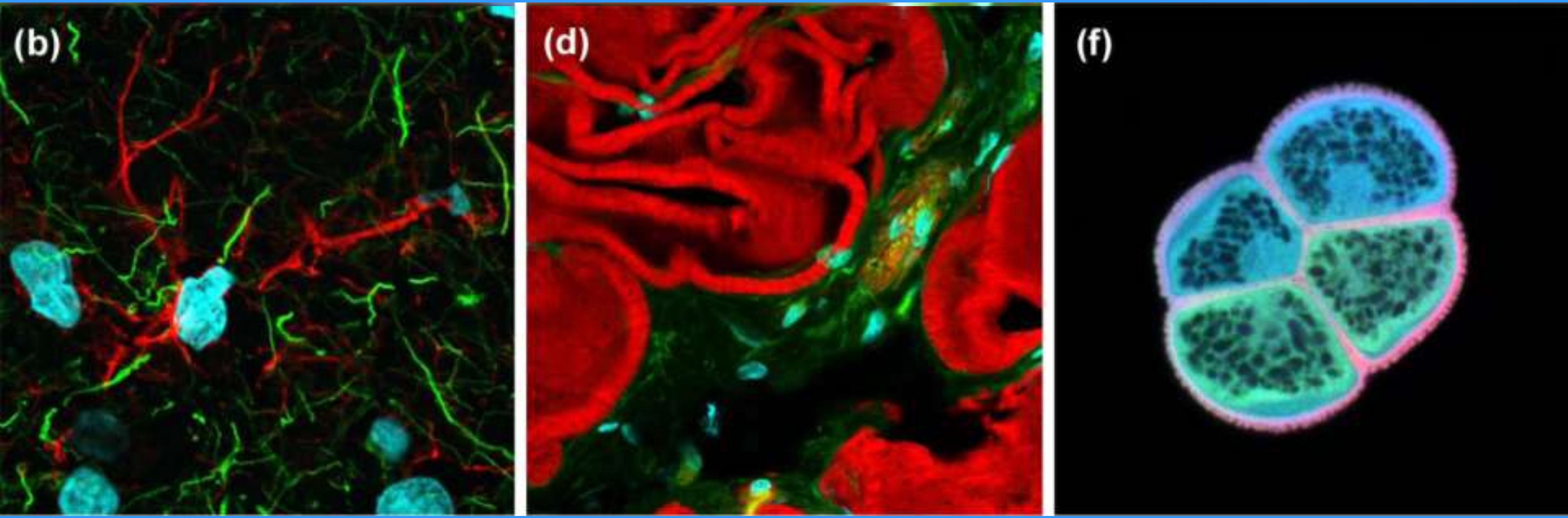
Airy Discs



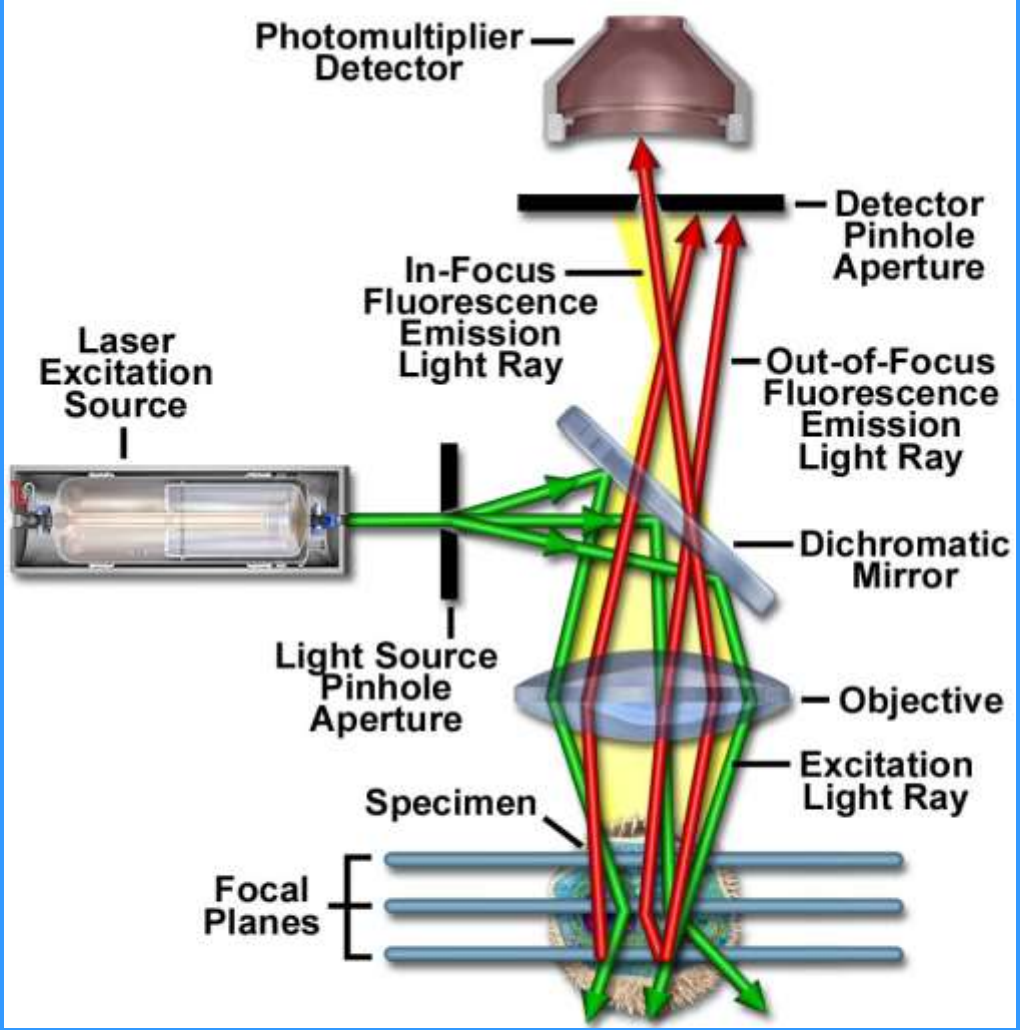




Comparison of confocal microscopy and widefield



Layout of CLSM



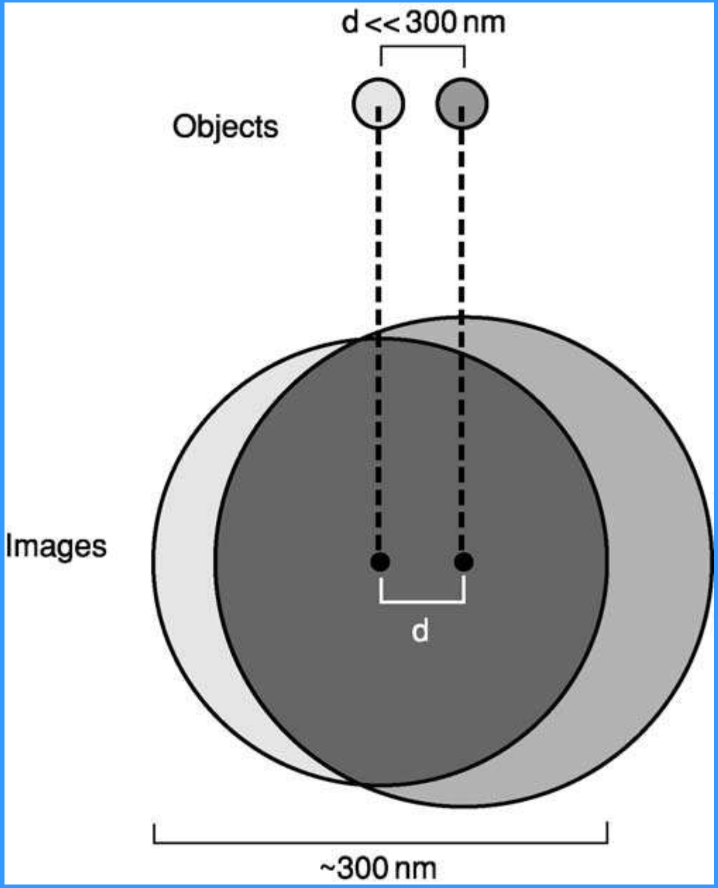
Assumptions of confocal microscopy

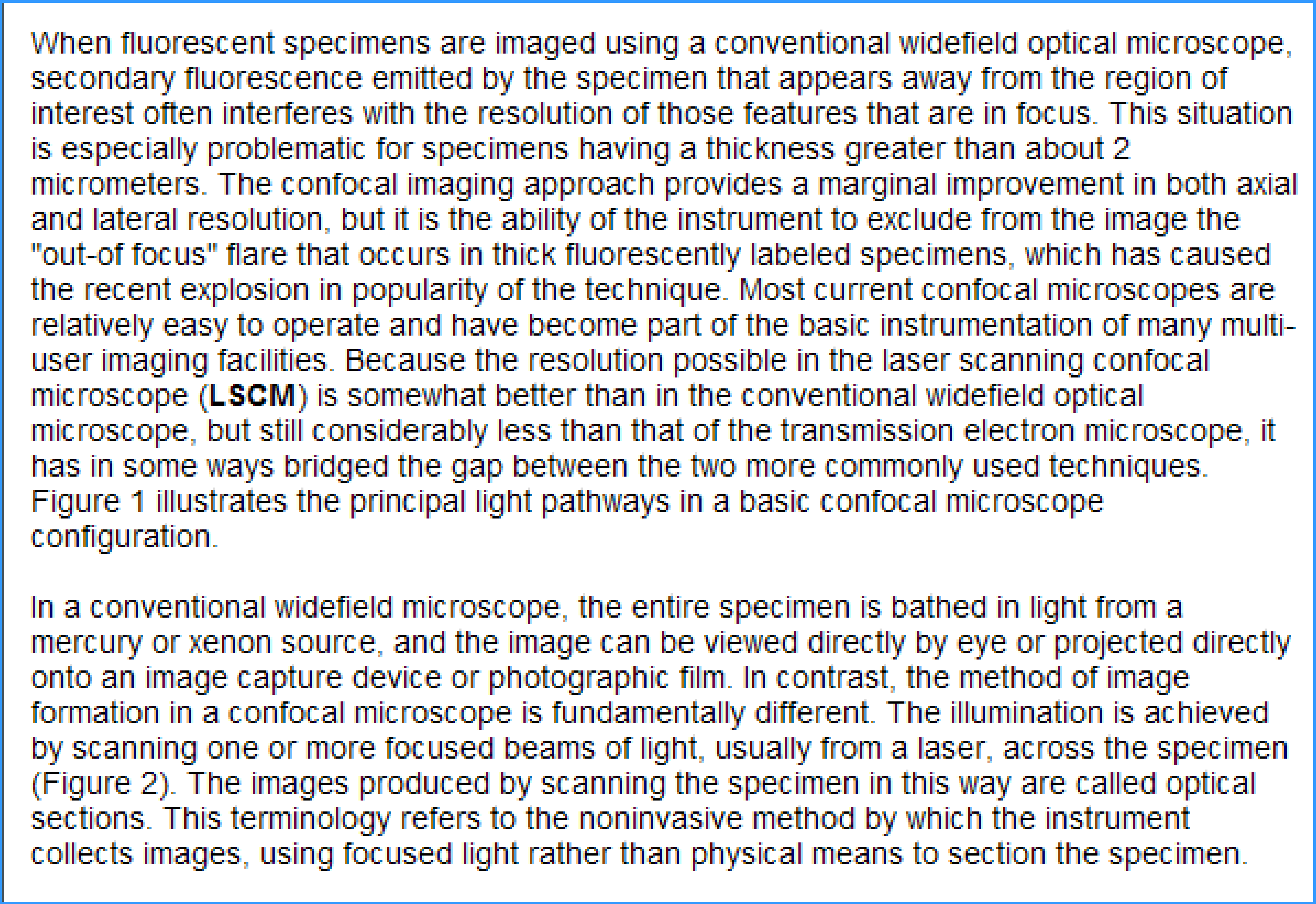
Scanner

Assumptions of confocal microscopy

Resolving

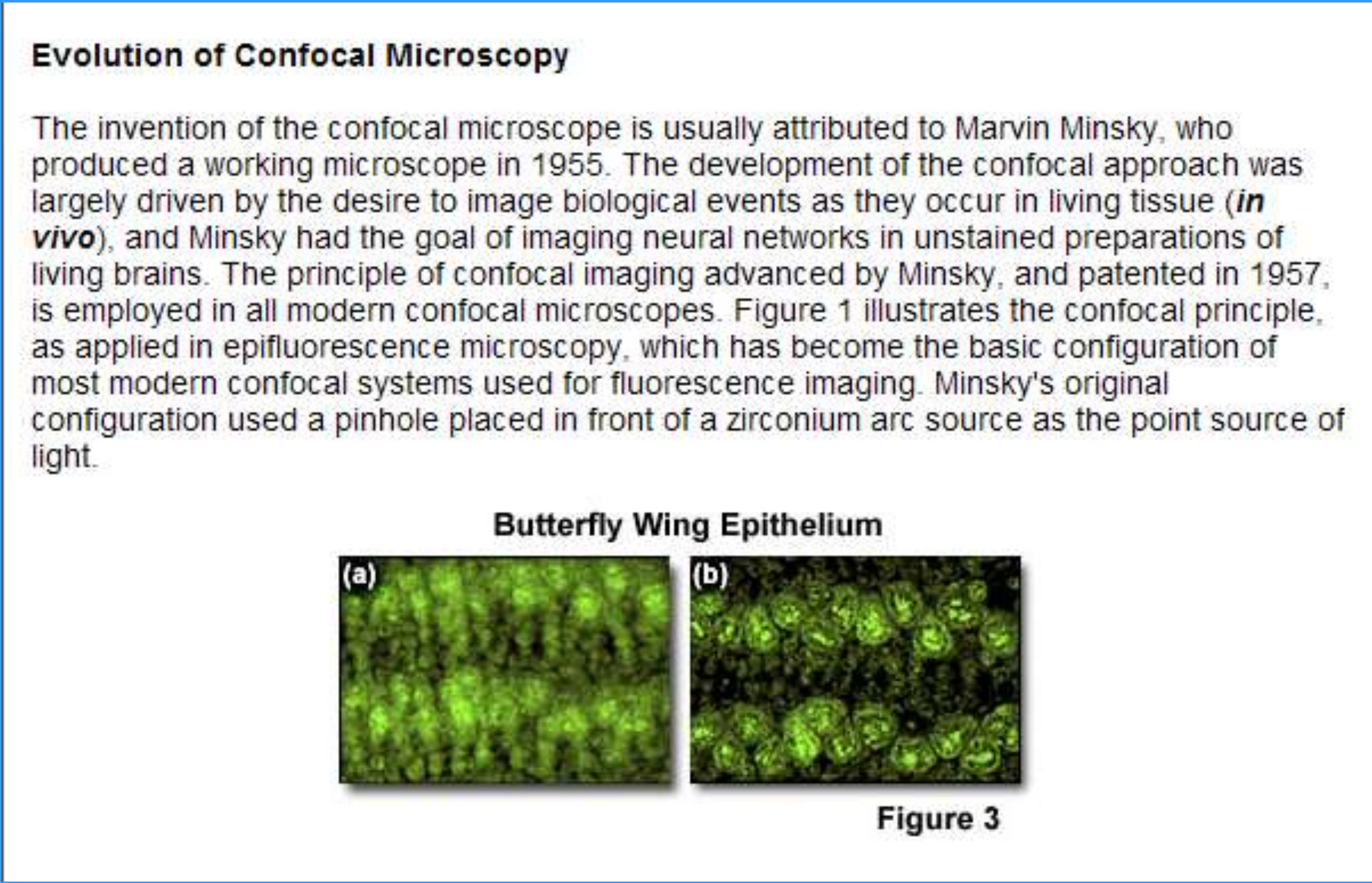
$$d = a \cdot \lambda \left[n \cdot \sin\alpha\right]^{-1}$$





When fluorescent specimens are imaged using a conventional widefield optical microscope, secondary fluorescence emitted by the specimen that appears away from the region of interest often interferes with the resolution of those features that are in focus. This situation is especially problematic for specimens having a thickness greater than about 2 micrometers. The confocal imaging approach provides a marginal improvement in both axial and lateral resolution, but it is the ability of the instrument to exclude from the image the "out-of focus" flare that occurs in thick fluorescently labeled specimens, which has caused the recent explosion in popularity of the technique. Most current confocal microscopes are relatively easy to operate and have become part of the basic instrumentation of many multi-user imaging facilities. Because the resolution possible in the laser scanning confocal microscope (**LSCM**) is somewhat better than in the conventional widefield optical microscope, but still considerably less than that of the transmission electron microscope, it has in some ways bridged the gap between the two more commonly used techniques. Figure 1 illustrates the principal light pathways in a basic confocal microscope configuration.

In a conventional widefield microscope, the entire specimen is bathed in light from a mercury or xenon source, and the image can be viewed directly by eye or projected directly onto an image capture device or photographic film. In contrast, the method of image formation in a confocal microscope is fundamentally different. The illumination is achieved by scanning one or more focused beams of light, usually from a laser, across the specimen (Figure 2). The images produced by scanning the specimen in this way are called optical sections. This terminology refers to the noninvasive method by which the instrument collects images, using focused light rather than physical means to section the specimen.

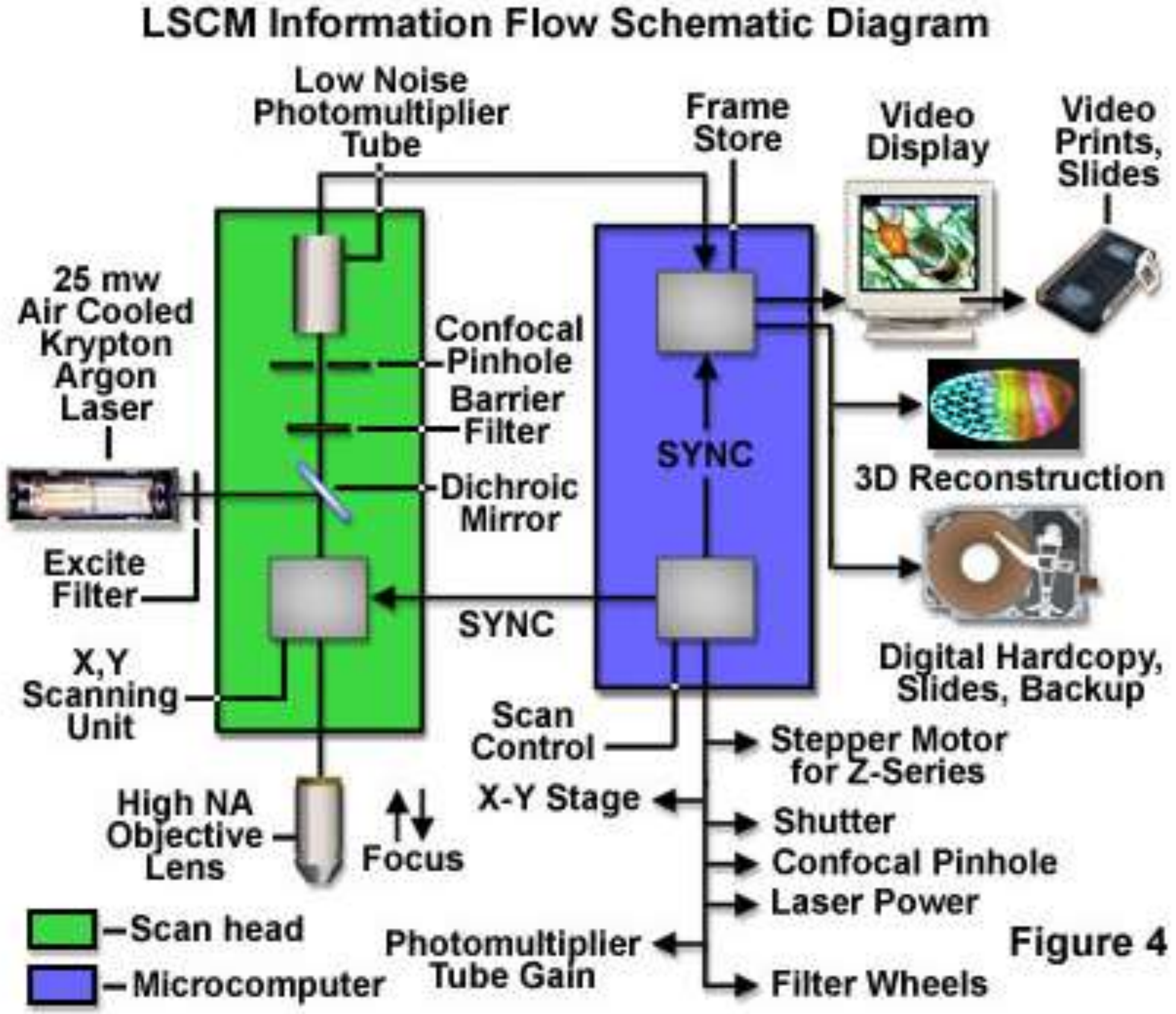


Evolution of Confocal Microscopy

The invention of the confocal microscope is usually attributed to Marvin Minsky, who produced a working microscope in 1955. The development of the confocal approach was largely driven by the desire to image biological events as they occur in living tissue (***in vivo***), and Minsky had the goal of imaging neural networks in unstained preparations of living brains. The principle of confocal imaging advanced by Minsky, and patented in 1957, is employed in all modern confocal microscopes. Figure 1 illustrates the confocal principle, as applied in epifluorescence microscopy, which has become the basic configuration of most modern confocal systems used for fluorescence imaging. Minsky's original configuration used a pinhole placed in front of a zirconium arc source as the point source of light.

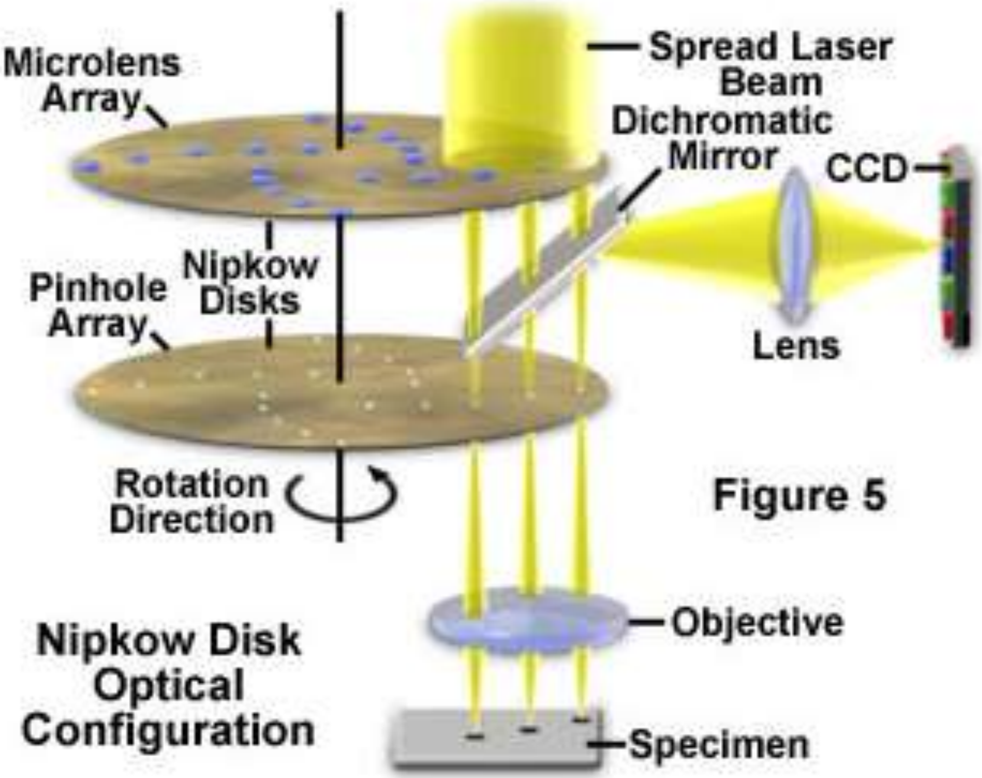
Butterfly Wing Epithelium

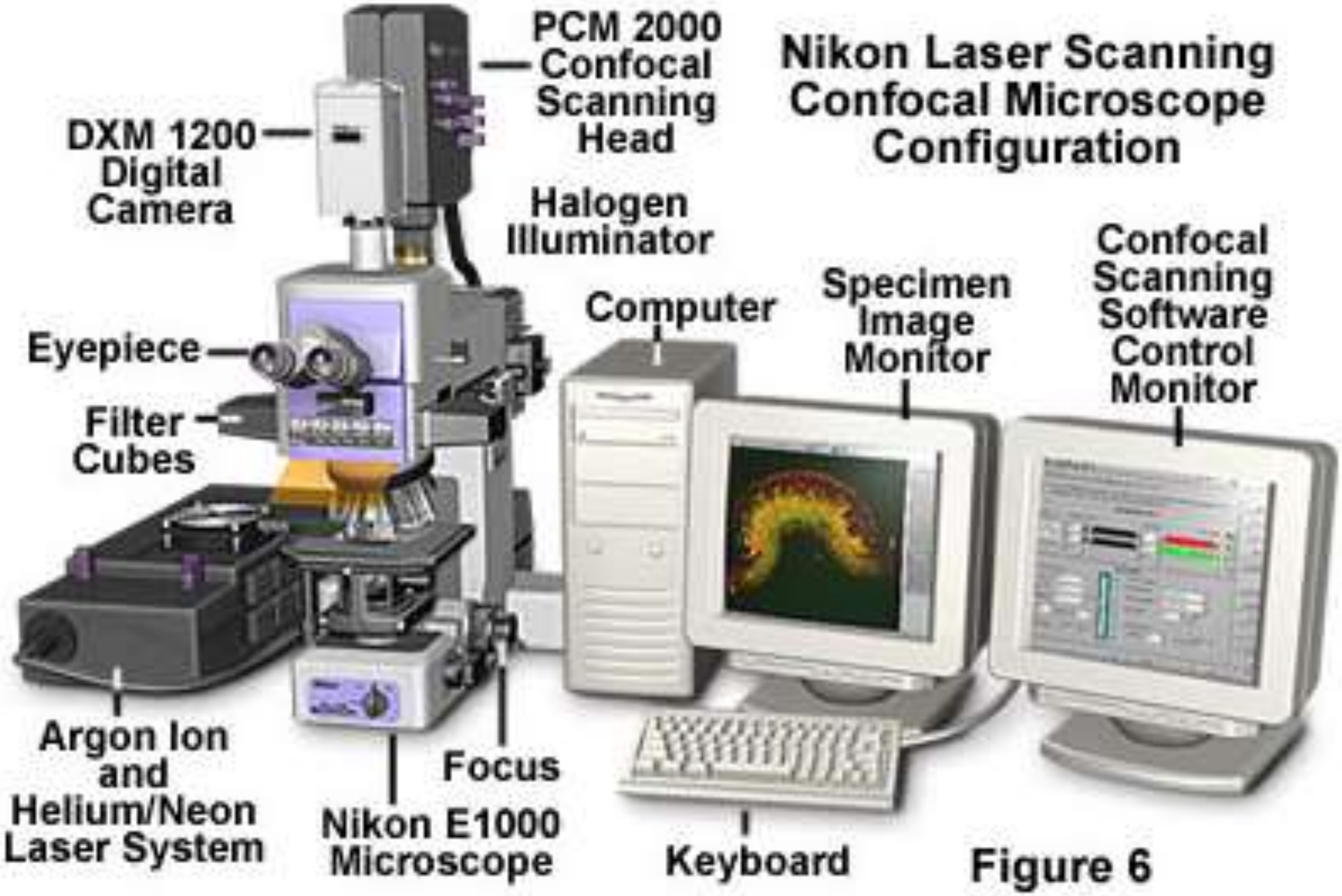
Figure 3



LSCM Information Flow Schematic Diagram

Figure 4


Microlens Array
Spread Laser Beam
Dichromatic Mirror
CCD
Pinhole Array
Nipkow Disks
Lens
Rotation Direction
Figure 5
Objective
Nipkow Disk Optical Configuration
Specimen



Nikon Laser Scanning Confocal Microscope Configuration

Figure 6

Deconvolution ZEN 2008
Physiology ZEN 2008
Topography
Main control program

AxioVision 4 Module AutoMeasure Plus

Segmentacja, binarna obróbka obrazu i pomiary automatyczne. Segmentacja: - Programowanie przy pomocy histogramu (manualne, automatyczne, dynamiczne) - Identyfikacja regionów zbieżnych - Detekcja krawędzi - Identyfikacja ciemnych linii na jasnym tle ("Valleys") Obróbka binarna: - Zmiany morfologiczne obiektów (erozja, dylatacja, "Open", "Close") - Uzupełnianie „dziur”, usuwanie obiektów binarnych; operacje logiczne (AND, OR, XOR, NOT) - Skeletonizacja obiektów wyseparowanych Pomiary automatyczne: - Pomiary geometryczne i densytometryczne

AxioVision Rel. 4.8

AxioVision 4 Module AutoMeasure

Generator makr wykonawczych dla pomiarów automatycznych. Generator wykonawczy:
Funkcje podstawowe obróbki obrazu
- Całkowita lub lokalna segmentacja granic obiektów, programowanie przy pomocy histogramu

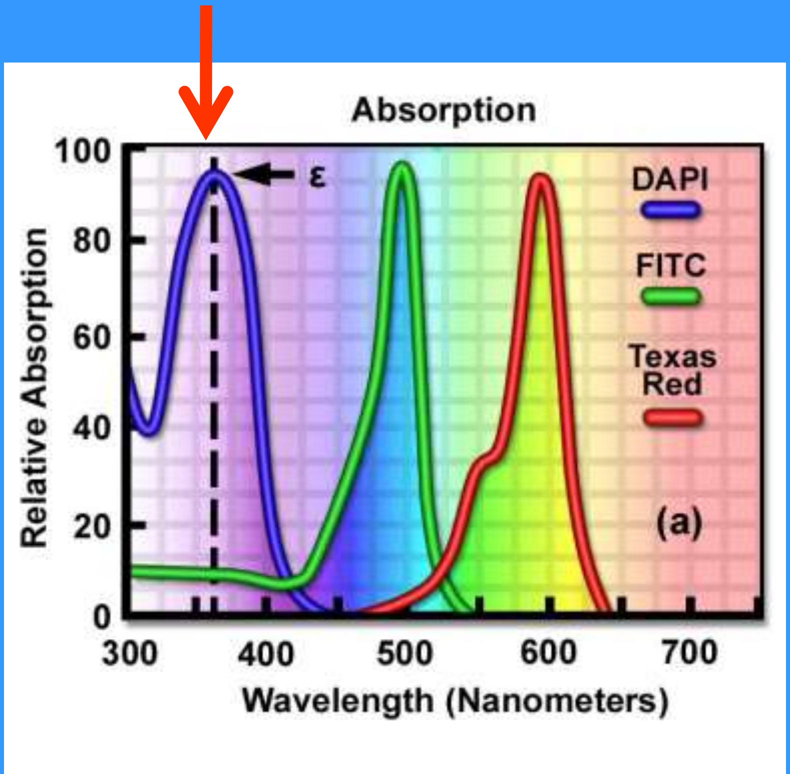
Automatyczna segmentacja obiektów oraz interaktywna obróbka masek pomiarowych
-Pomiary geometryczne i densytometryczne pojedyńczych obiektów.
-Zaznaczanie obiektów mierzonych, przedstawianie wyników w płaszczyźnie obrazu - Zapisywanie obrazów w formacie *.CSV kompatybilnym dla plików Excell Wykonywanie programów pomiarowych: - Grupowanie procesów dla dowolnej liczby zdjęć.
- Aktywowanie i dezaktywowanie jak również zmiany parametrów mierzonych podczas wykonywania pomiarów.

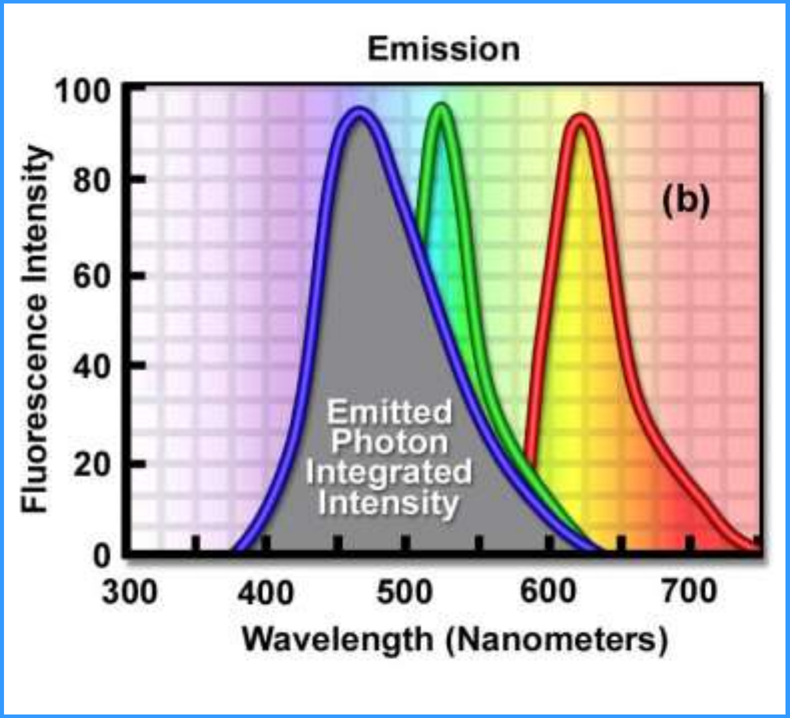
Upgrade of LSM

Incubation chamber

Assumptions of confocal microscopy

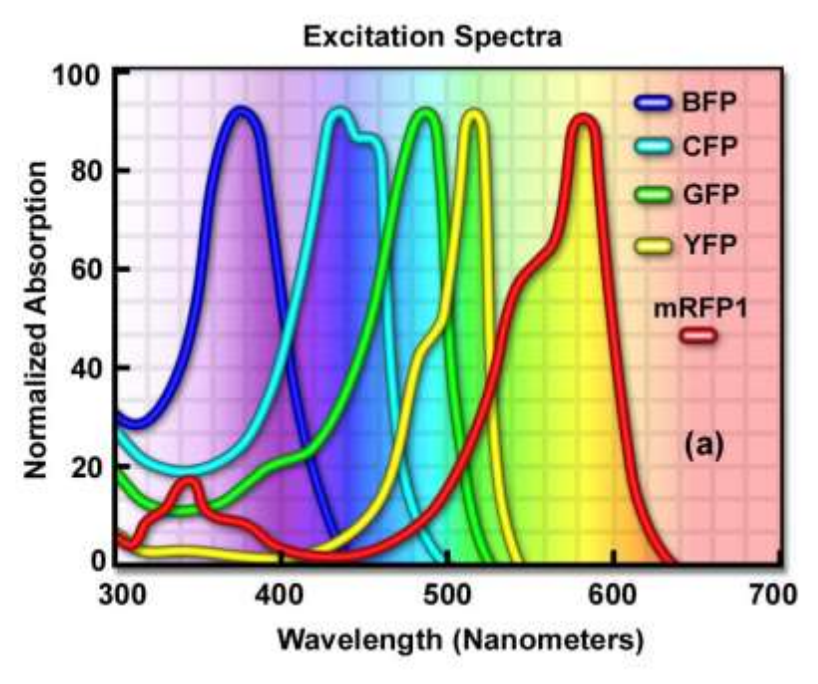
Cataloging of fluorochromes

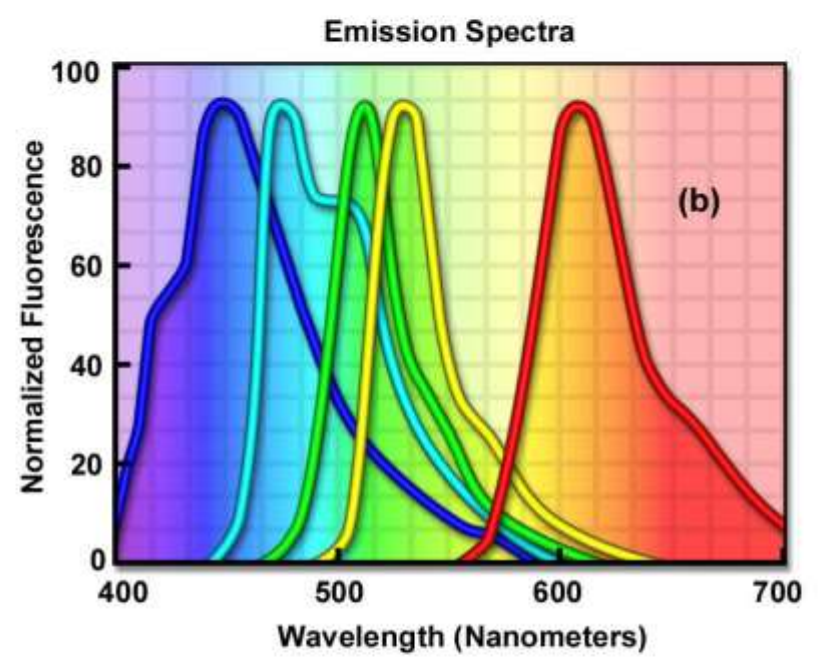




Absorption and fluorescence
Wavelength of absorption and emission
Fluorescence instensity of emitted light

Basic characteristics of the fluorochromes





- 488 nm blue-green argon laser
- 543 nm helium-neon green laser
- 633 nm helium-neon red laser.

405nm

UV

Fluorescent dyes

I
- small molecule
- fluorescent proteins

II
- specific
- nonspecific

III
- Penetrating the integral cell membrane
- Do not penetrate the integral cell membrane

Examples of specific fluorescent dyes

1. Dyes binding to nucleic acids

TOTO, YOYO, DRAQ5, bromek etydyny, DAPI, Hoechst

2. Lipophilic dyes, coloring lipid membranes

DiO, DiI

3. Dyes accumulated in the mitochondria, thanks the potential to mitochondrialnemuRodamina 123, TMRE, JC-1

4. PH indicator dyes

BCECF

5. Dyes indicating the concentration ratios of Ca + +

Fura-2, Indo1, Fluo-4

The advantages of confocal microscopy

The possibility of receiving the optical sections (0.5-1.5 mm) through the sample fluorescence of up to 50 mm

The information received in the form of the image comes from a well defined plane

Reducing background fluorescence

Non-invasive tomographic imaging technique that allows the analysis of living cells and established

Limitations of fluorescence microscopy

1. Cytotoxicity

2. Photobleaching

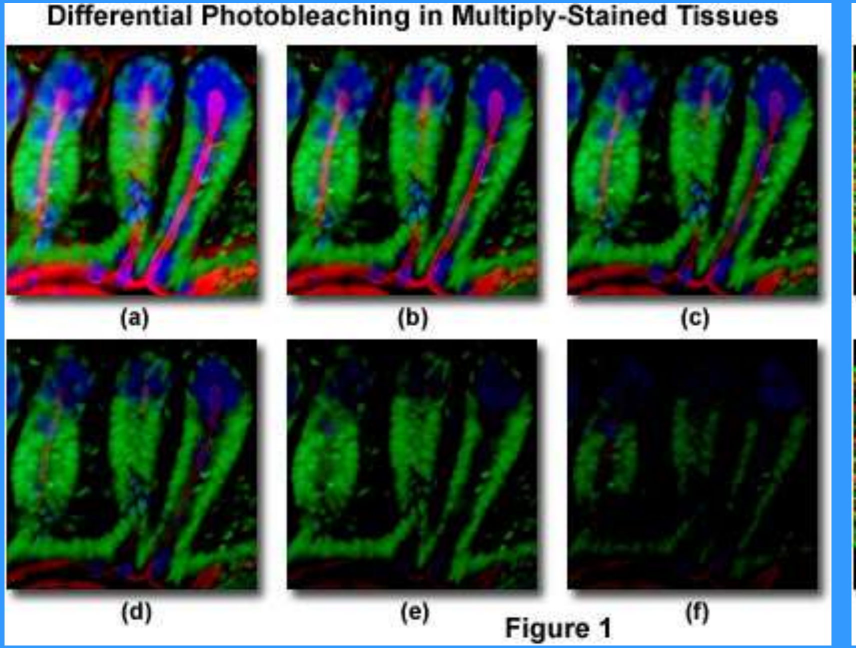

Differential Photobleaching in Multiply-Stained Tissues

Figure 1

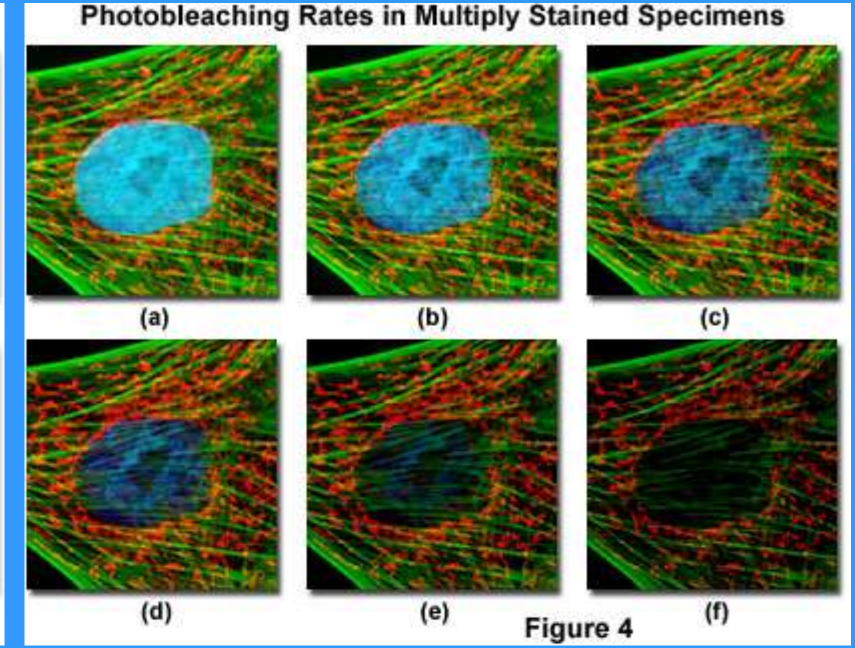
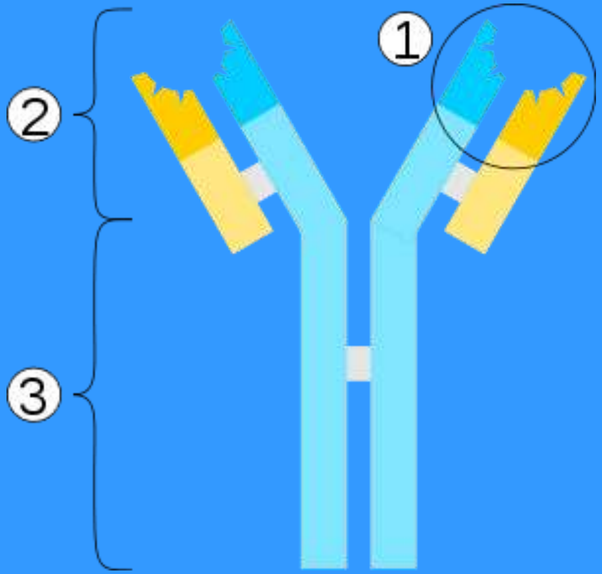

Photobleaching Rates in Multiply Stained Specimens

Figure 4

3. Phototoxicity

Fluorescence



antigen-binding fragment

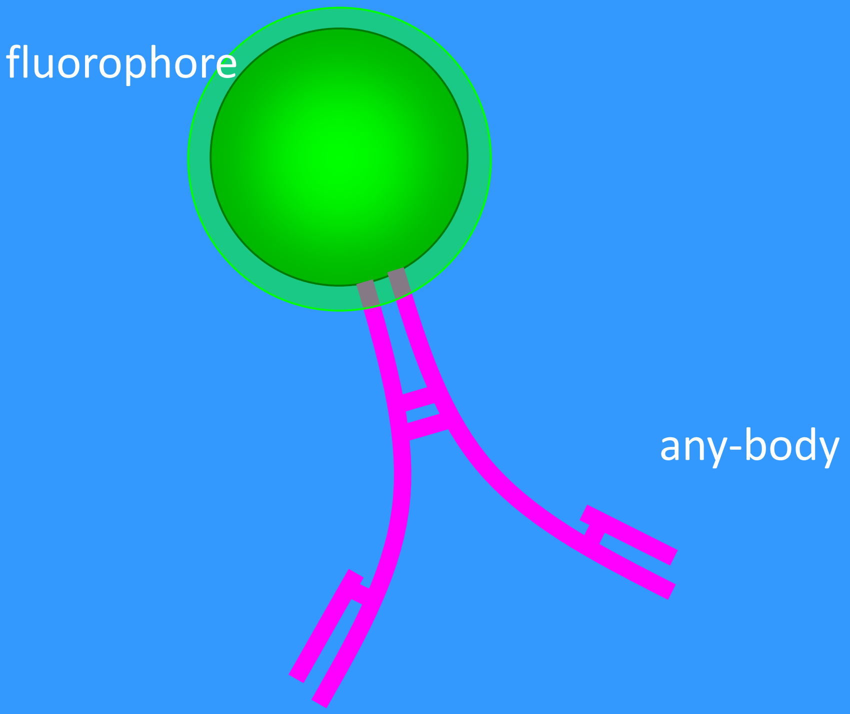
CD62P

CD45

CLSM- aktywacja komórkowa

CONFOCAL LASER SCANNING MICROSCOPY

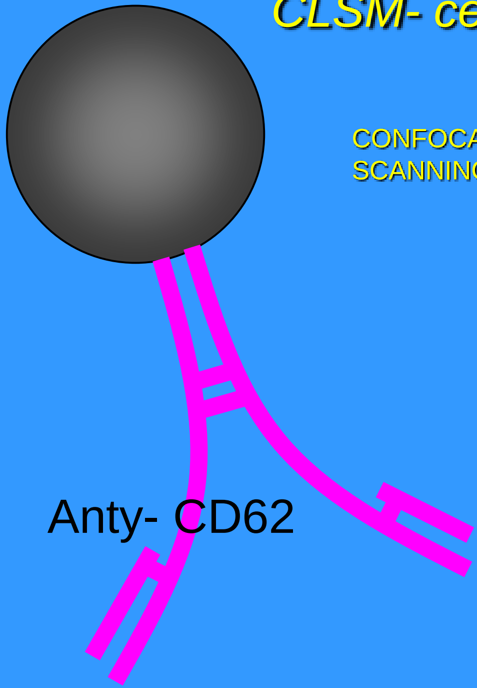
Fluorescence



CLSM- cell activation

Fluorescence colouring antybody

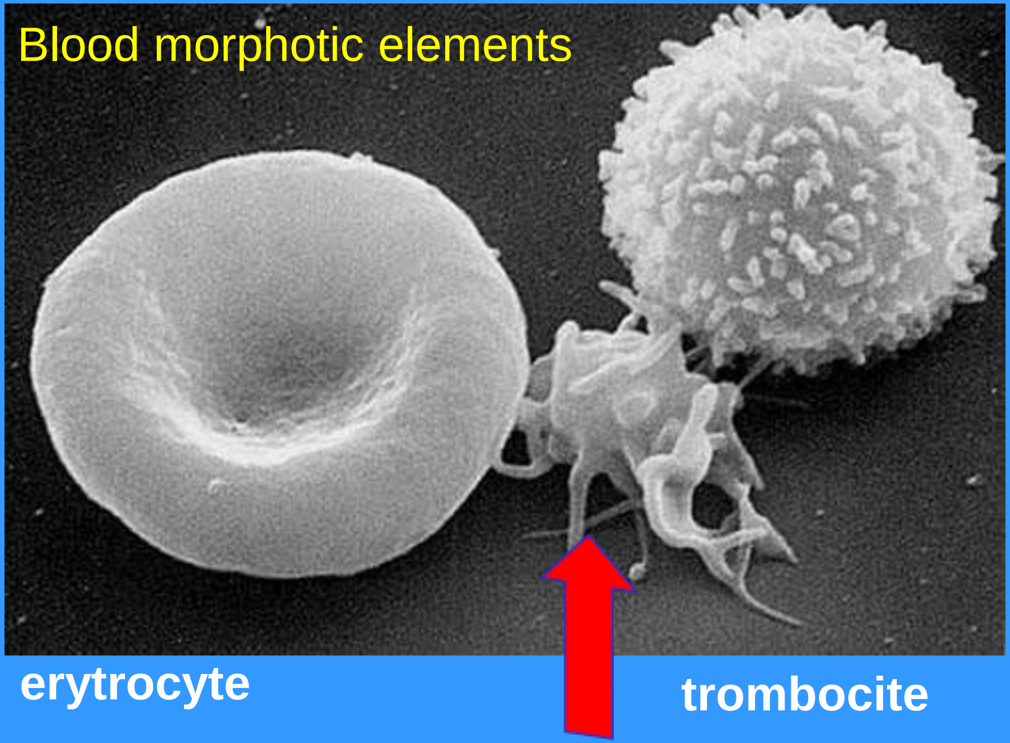
CONFOCAL LASER
SCANNING MICROSCOPY



Fluorescence

Anty- CD62

Blood morphotic elements



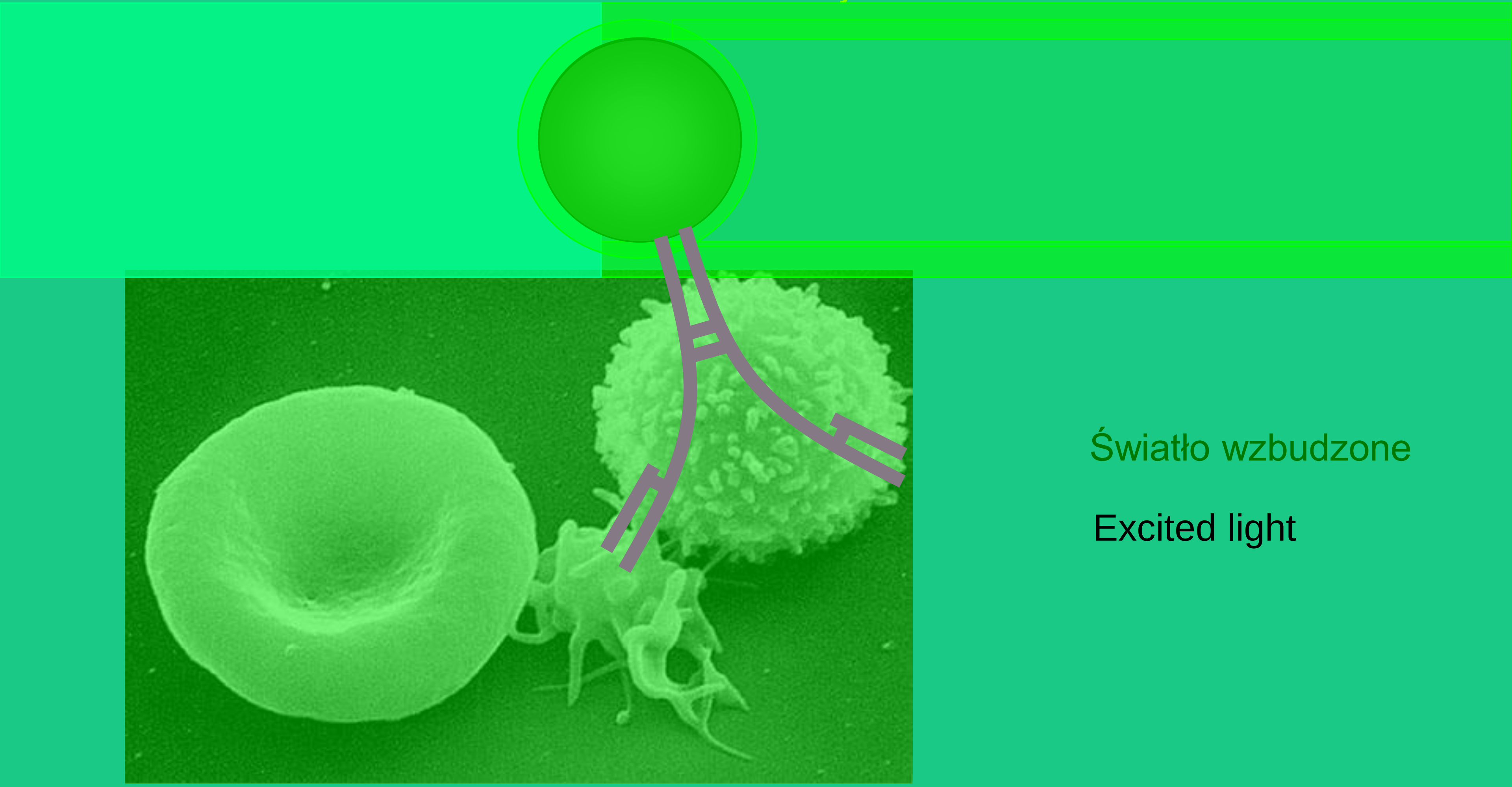
leucocyte

erytrocyte

trombocite

CLSM- aktywacja komórkowa

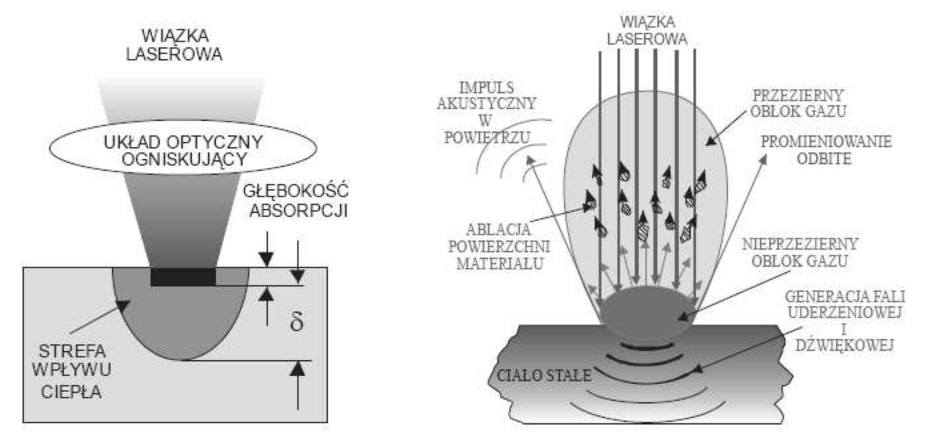
CONFOCAL LASER SCANNING MICROS



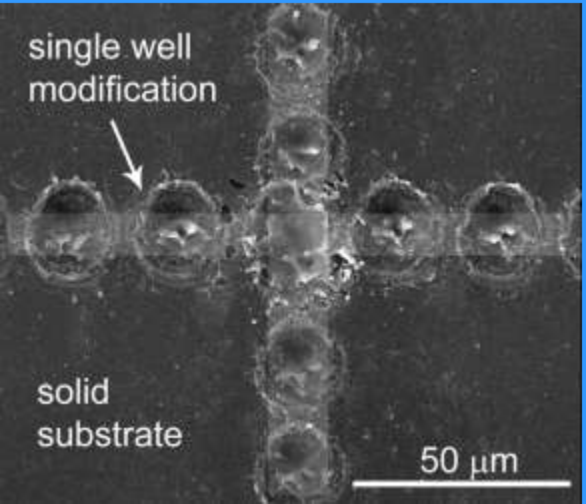
Światło wzbudzone

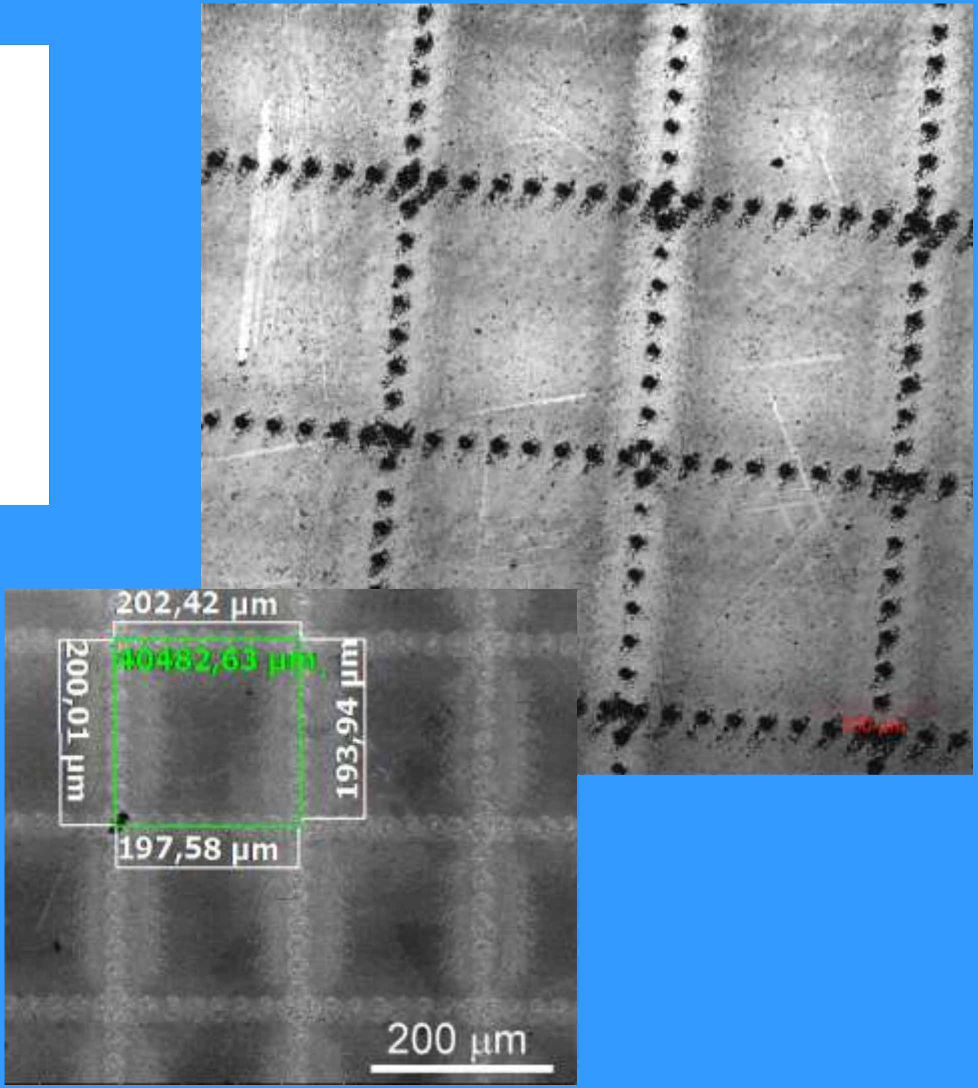
Excited light

Migration channels

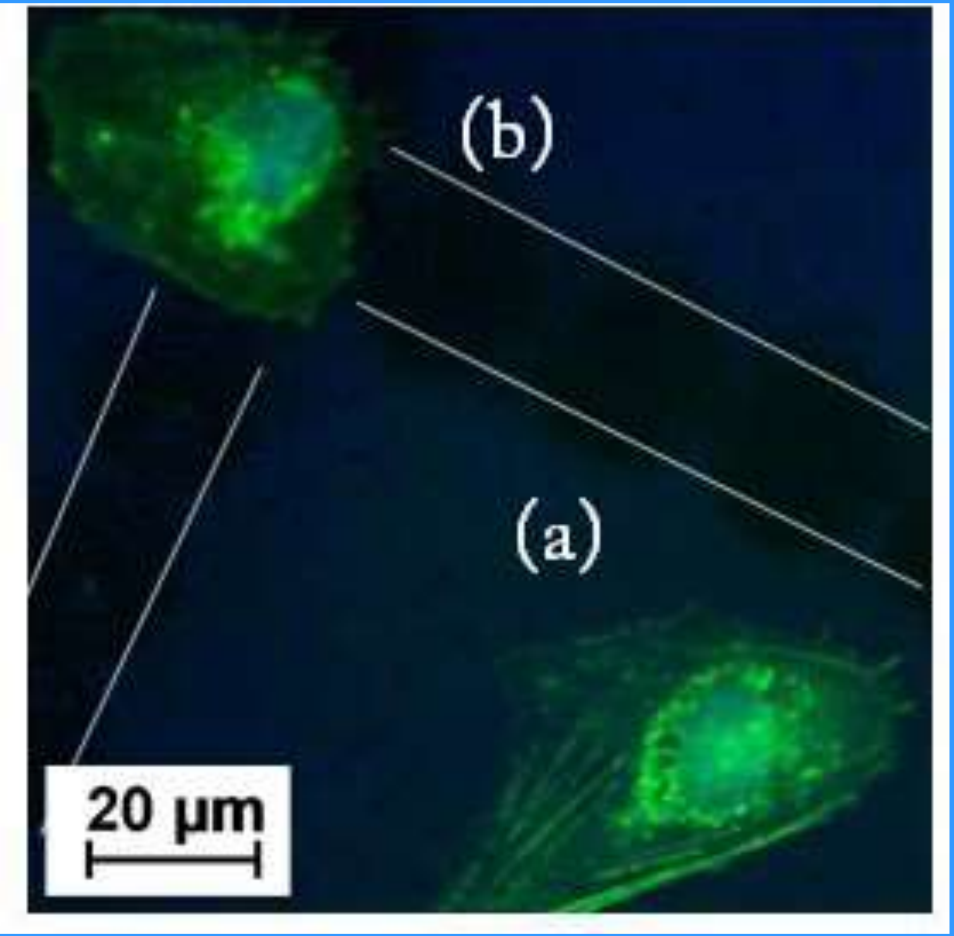


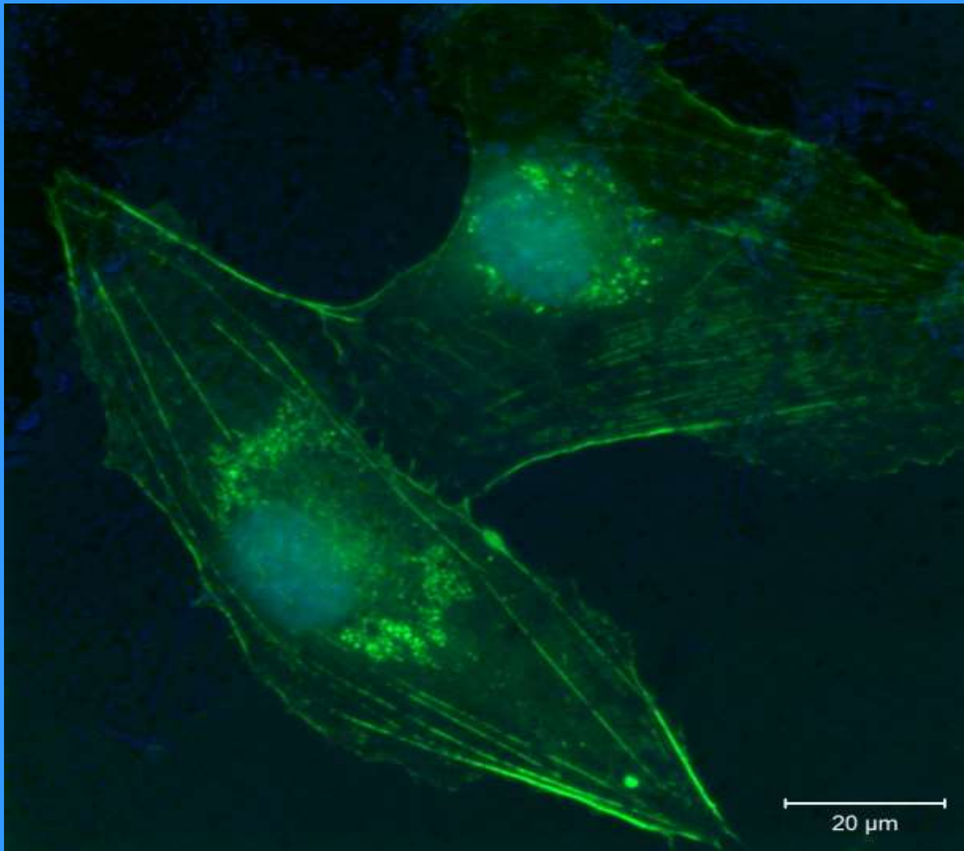
Lase ablation



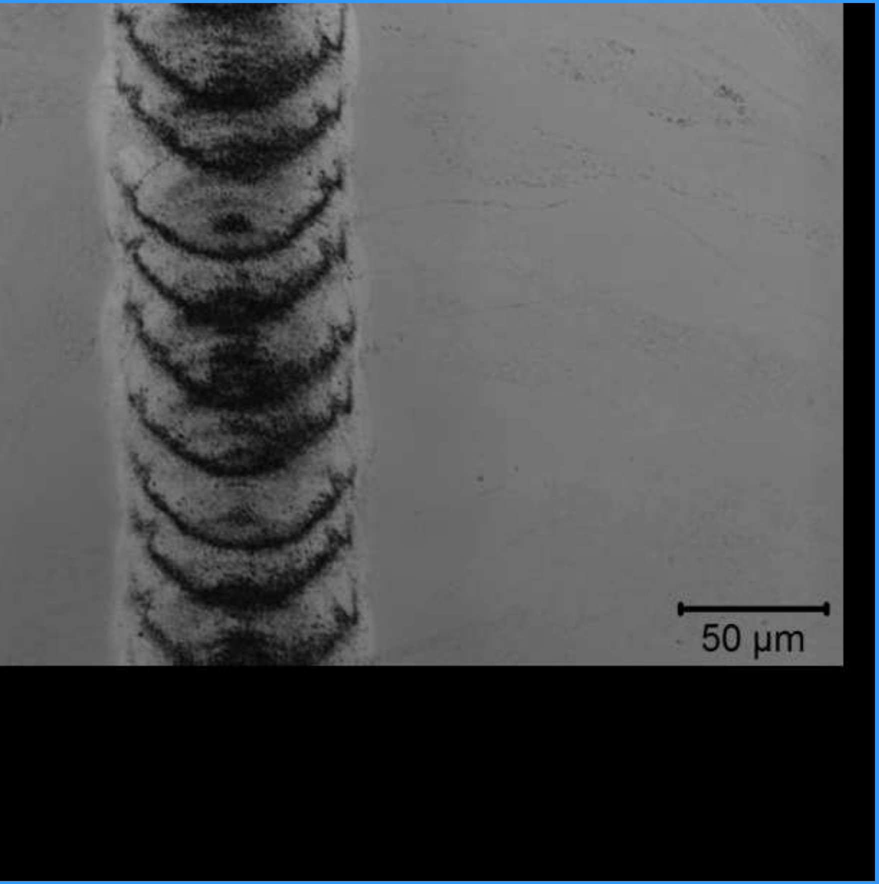


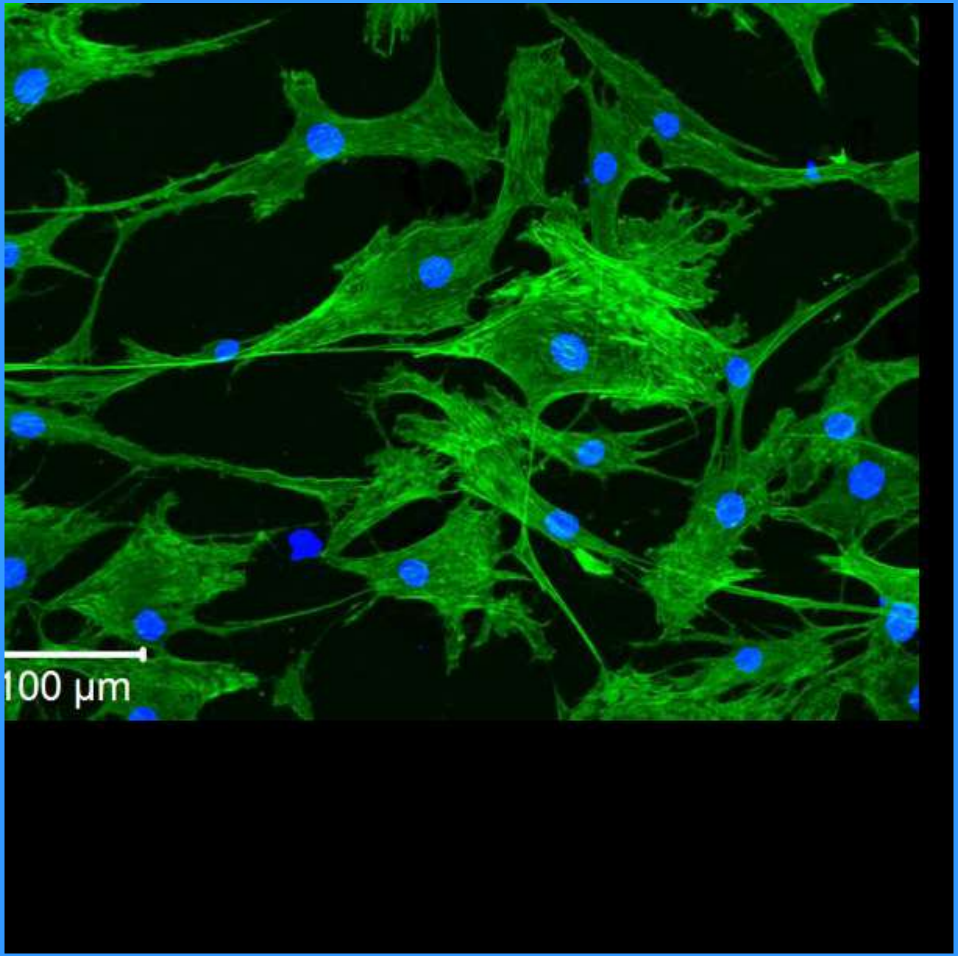
Migration channels (HUVEC)



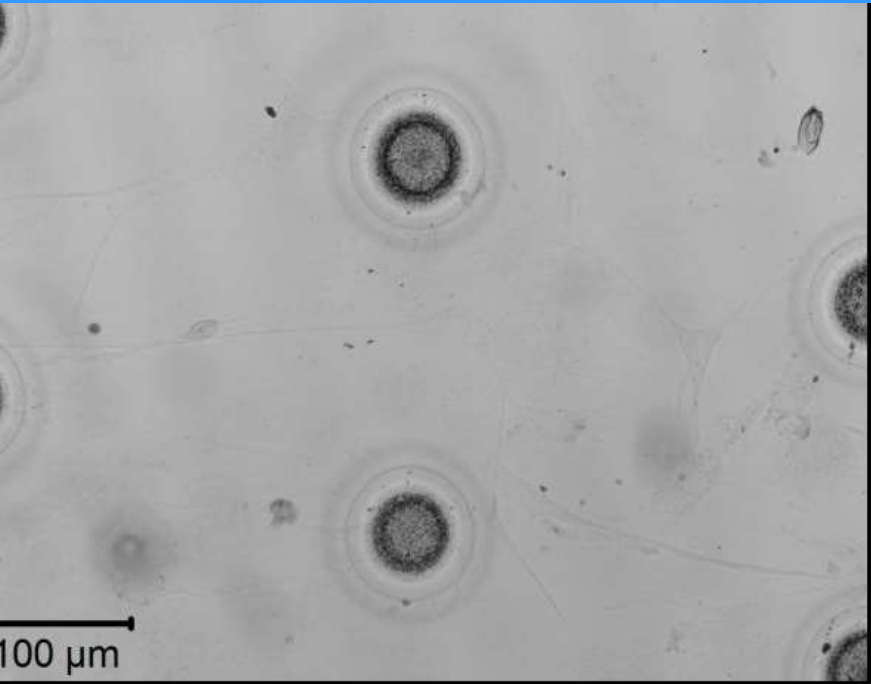


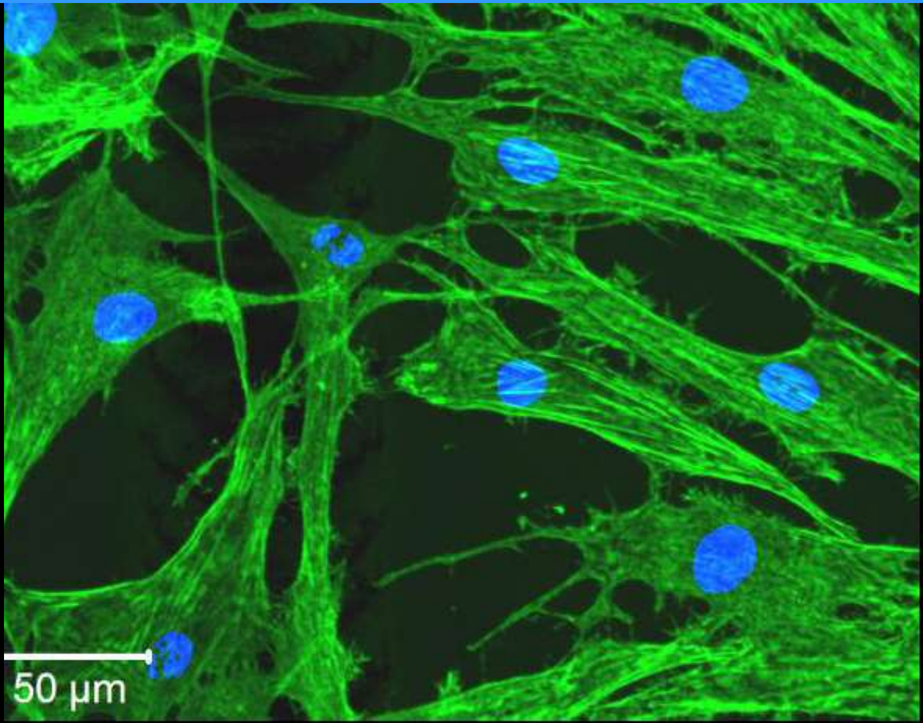
Migration channels (muscule cells)

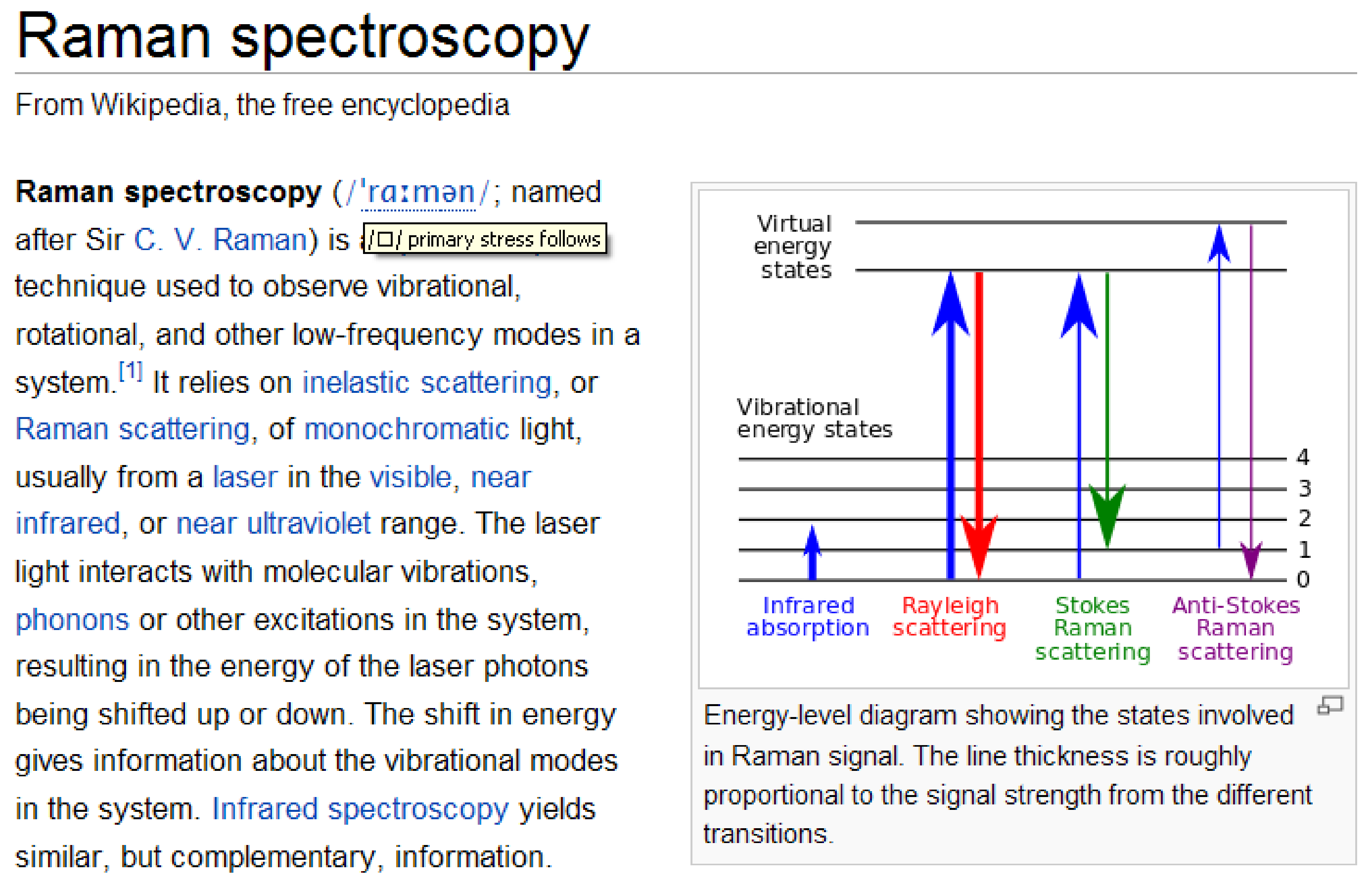




Migration channels (muscule cells)





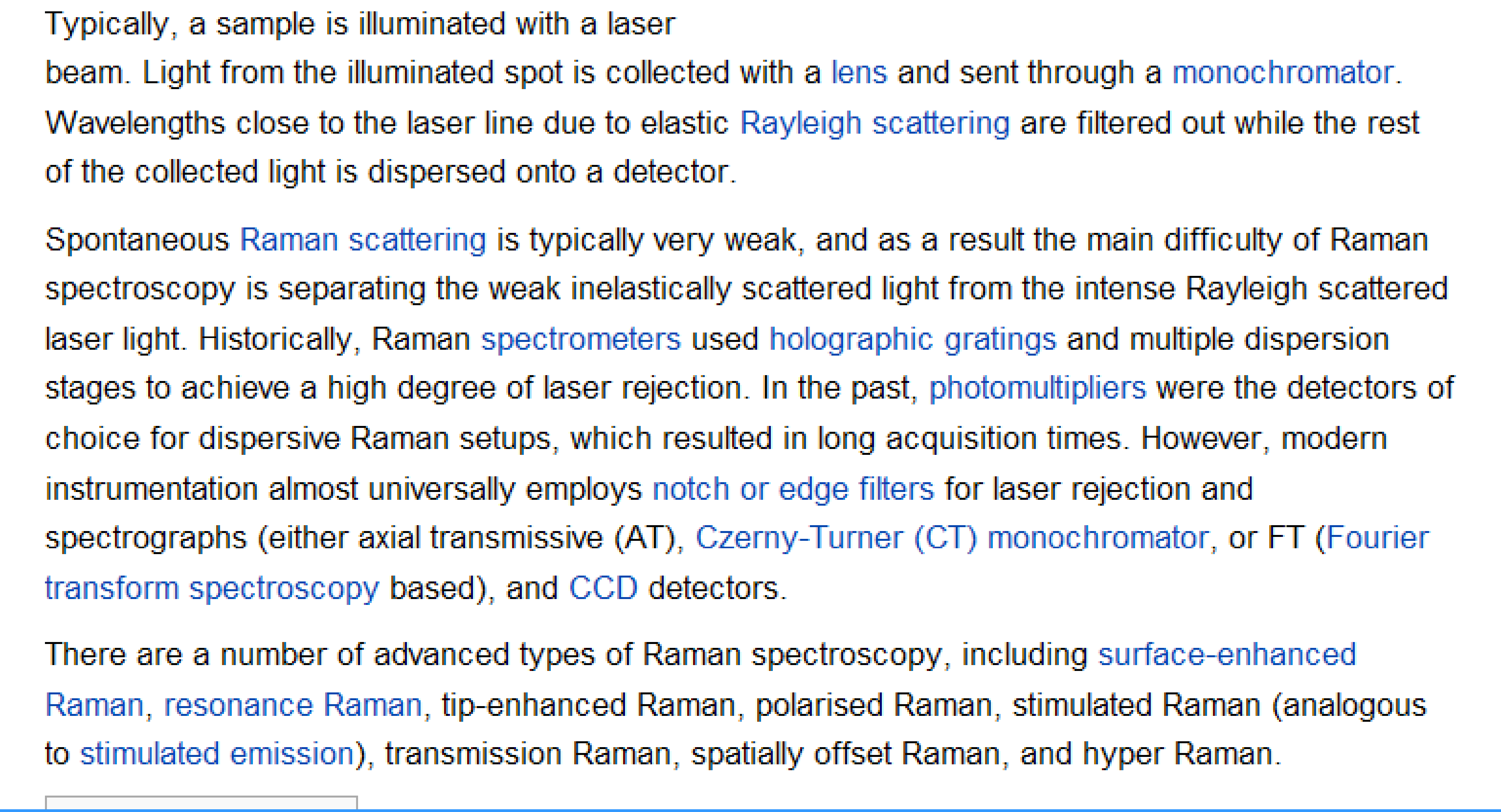


Raman spectroscopy

From Wikipedia, the free encyclopedia

Raman spectroscopy (/ˈrɑːmən/; named after Sir C. V. Raman) is /□/ primary stress follows technique used to observe vibrational, rotational, and other low-frequency modes in a system.[1] It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.

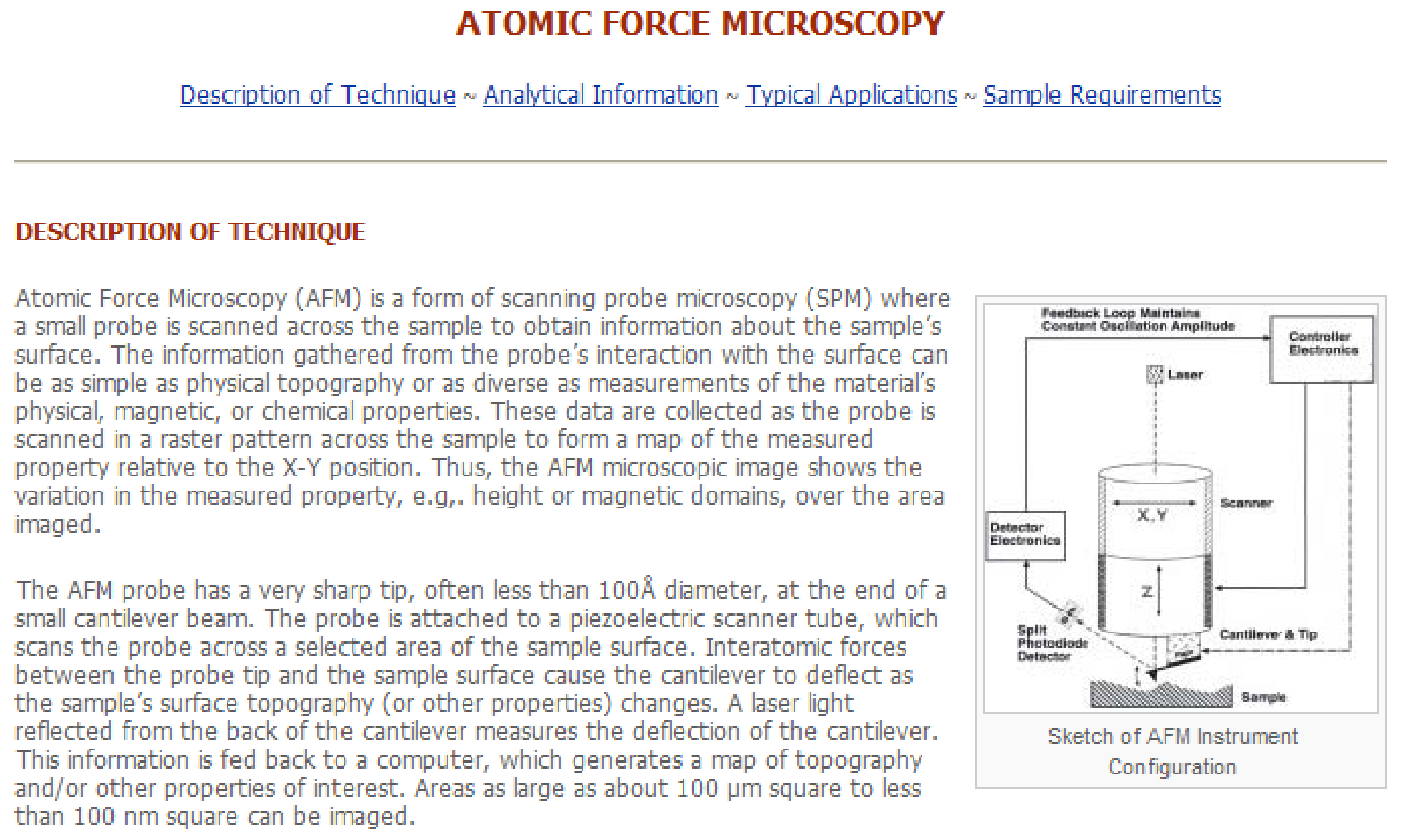
Energy-level diagram showing the states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.



Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line due to elastic Rayleigh scattering are filtered out while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Historically, Raman spectrometers used holographic gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, photomultipliers were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either axial transmissive (AT), Czerny-Turner (CT) monochromator, or FT (Fourier transform spectroscopy based), and CCD detectors.

There are a number of advanced types of Raman spectroscopy, including surface-enhanced Raman, resonance Raman, tip-enhanced Raman, polarised Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially offset Raman, and hyper Raman.



ATOMIC FORCE MICROSCOPY

Description of Technique ~ Analytical Information ~ Typical Applications ~ Sample Requirements

---

DESCRIPTION OF TECHNIQUE

Atomic Force Microscopy (AFM) is a form of scanning probe microscopy (SPM) where a small probe is scanned across the sample to obtain information about the sample's surface. The information gathered from the probe's interaction with the surface can be as simple as physical topography or as diverse as measurements of the material's physical, magnetic, or chemical properties. These data are collected as the probe is scanned in a raster pattern across the sample to form a map of the measured property relative to the X-Y position. Thus, the AFM microscopic image shows the variation in the measured property, e.g,. height or magnetic domains, over the area imaged.

The AFM probe has a very sharp tip, often less than 100Å diameter, at the end of a small cantilever beam. The probe is attached to a piezoelectric scanner tube, which scans the probe across a selected area of the sample surface. Interatomic forces between the probe tip and the sample surface cause the cantilever to deflect as the sample's surface topography (or other properties) changes. A laser light reflected from the back of the cantilever measures the deflection of the cantilever. This information is fed back to a computer, which generates a map of topography and/or other properties of interest. Areas as large as about 100 µm square to less than 100 nm square can be imaged.

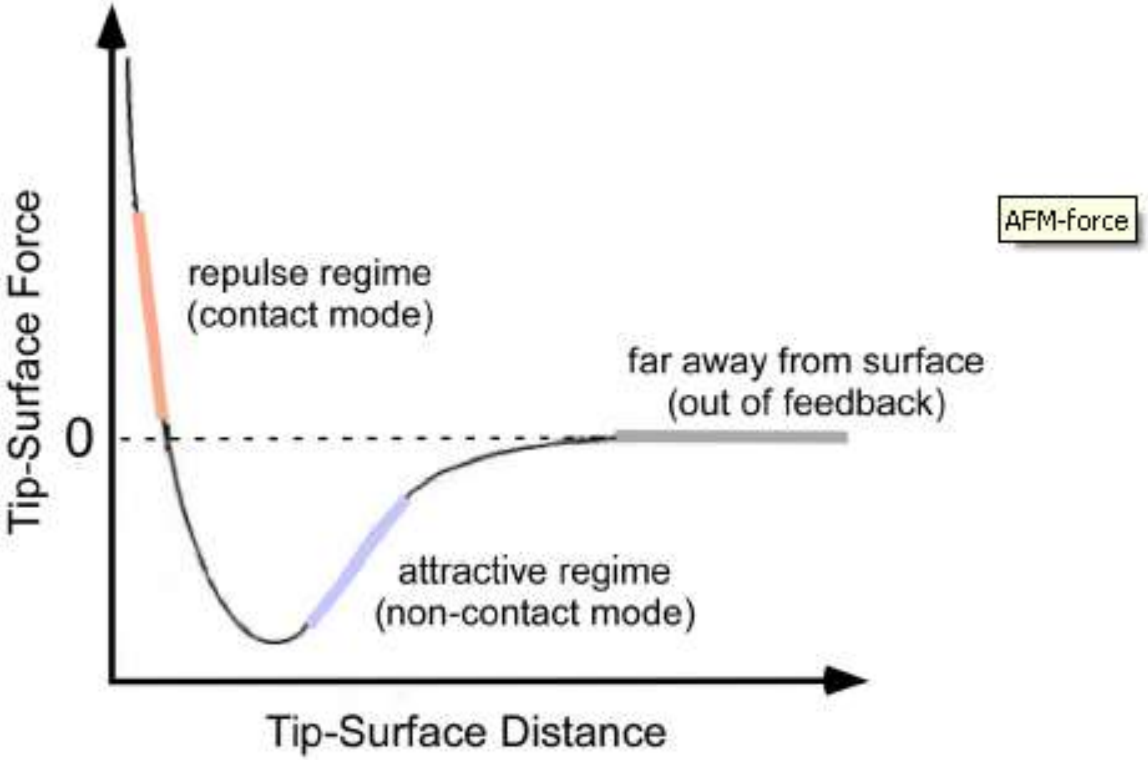
Sketch of AFM Instrument Configuration

Atomic force microscopy (AFM) is a technique for analyzing the surface of a rigid material all the way down to the level of the atom . AFM uses a mechanical probe to magnify surface features up to 100,000,000 times, and it produces 3-D images of the surface.

The technique is derived from a related technology, called scanning tunneling microscopy (STM). The difference is that AFM does not require the sample to conduct electricity, whereas STM does. AFM also works in regular room temperatures, while STM requires special temperature and other conditions.

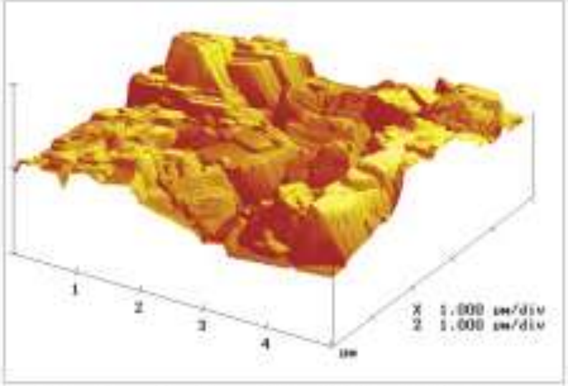
AFM is being used to understand materials problems in many areas, including data storage, telecommunications, biomedicine, chemistry, and aerospace. In data storage, it is helping researchers to "force" a disk to have a higher capacity. Today's magnetic storage devices typically have a capacity limit of between 20 and 50 gigabits (billions of bits) per square inch of storage medium. Researchers are looking into AFM to help raise read and write densities to between 40 gigabits and 300 gigabits per square inch. No one has yet commercialized AFM technology for this purpose, but IBM and others are actively pursuing it.

Atomic interaction



ANALYTICAL INFORMATION

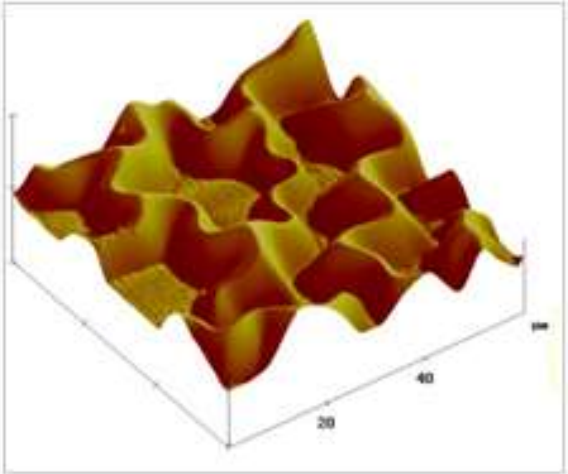
Contact Mode AFM - The AFM probe is scanned at a constant force between the probe and the sample surface to obtain a 3D topographical map. When the probe cantilever is deflected by topographical changes, the scanner adjusts the probe position to restore the original cantilever deflection. The scanner position information is used to create a topographical image. Lateral resolution of <1 nm and height resolution of <1 Å can be obtained.



Surface Profile of Crystalline Material

Intermittent Contact (Tapping Mode) AFM - In this mode, the probe cantilever is oscillated at or near its resonant frequency. The oscillating probe tip is then scanned at a height where it barely touches or "taps" the sample surface. The system monitors the probe position and vibrational amplitude to obtain topographical and other property information. Accurate topographical information can be obtained even for very fragile surfaces. Optimum resolution is about 50 Å lateral and <1 Å height. Images for phase detection mode, magnetic domains, and local electric fields are also obtained in this mode.

Lateral Force Microscopy - This mode measures the lateral deflection of the probe cantilever as the tip is scanned across the sample in contact mode. Changes in lateral deflection represent relative frictional forces between the probe tip and the sample surface.



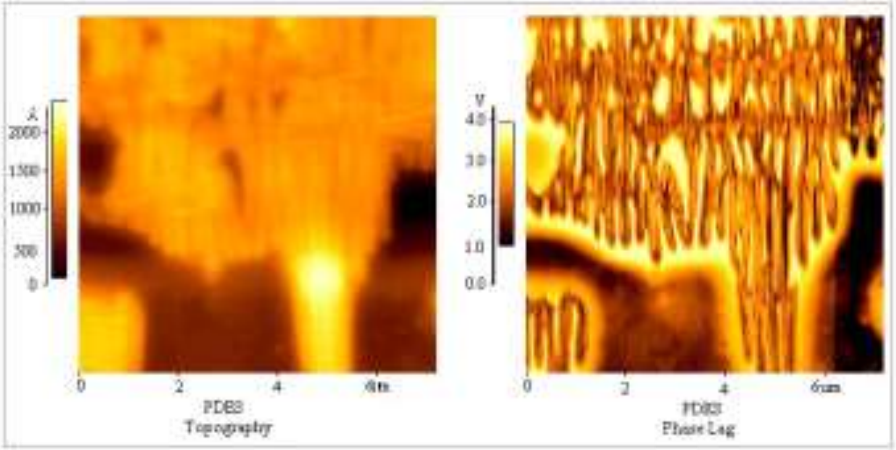
AFM Image of Defect on Coated Glass

Phase Detection Microscopy - With the system operating in Tapping mode, the cantilever oscillation is damped by interaction with the sample surface. The phase lag between the drive signal and actual cantilever oscillation is monitored. Changes in the phase lag indicate variations in the surface properties, such as viscoelasticity or mechanical properties. A phase image, typically collected simultaneously with a topographical image, maps the local changes in material's physical or mechanical properties.

Magnetic Force Microscopy - This mode images local variations in the magnetic forces at the sample's surface. The probe tip is coated with a thin film of ferromagnetic material that will react to the magnetic domains on the sample surface. The magnetic forces between the tip and the sample are measured by monitoring cantilever deflection while the probe is scanned at a constant height above the surface. A map of the forces shows the sample's natural or applied magnetic domain structure.

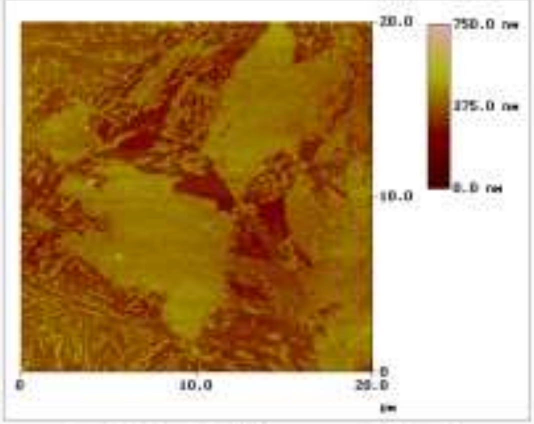
Image Analysis - Since the images are collected in digital format, a wide variety of image manipulations are available for AFM data. Quantitative topographical information, such as lateral spacing, step height, and surface roughness are readily obtained. Images can be presented as two-dimensional or three-dimensional representations in hard copy or as digital image files for electronic transfer and publication.

Nanoindentation - A specialized probe tip is forced into the sample surface to obtain a measure of the material's mechanical properties in regions as small as a few nanometers. (See the Handbook section on Nanoindentation Hardness Testing.)



Height and Phase Mode Image of a Polymer Sample

TYPICAL APPLICATIONS

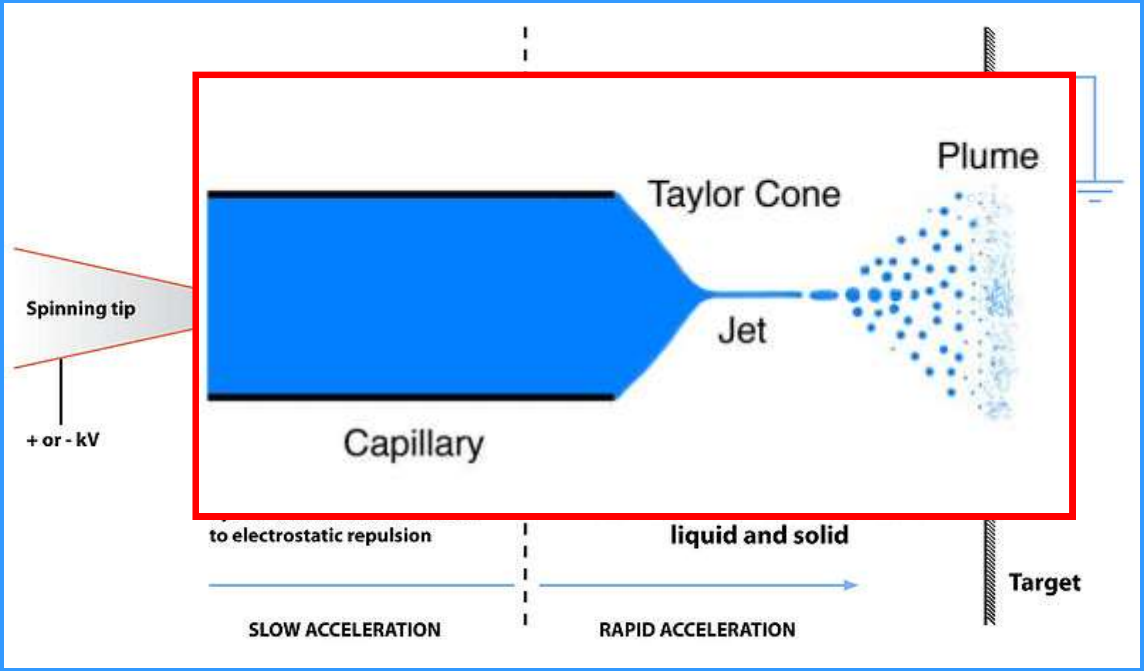


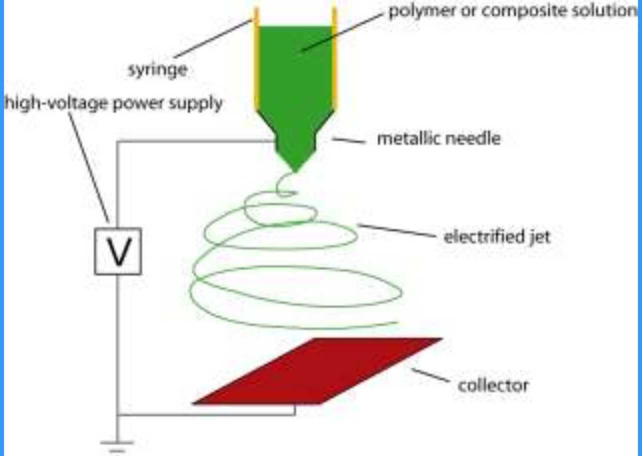
Top View AFM Image of Steel Microstructure

- 3-dimensional topography of IC device
- Roughness measurements for chemical mechanical polishing
- Analysis of microscopic phase distribution in polymers
- Mechanical and physical property measurements for thin films
- Imaging magnetic domains on digital storage media
- Imaging of submicron phases in metals
- Defect imaging in IC failure analysis
- Microscopic imaging of fragile biological samples
- Metrology for compact disk stampers

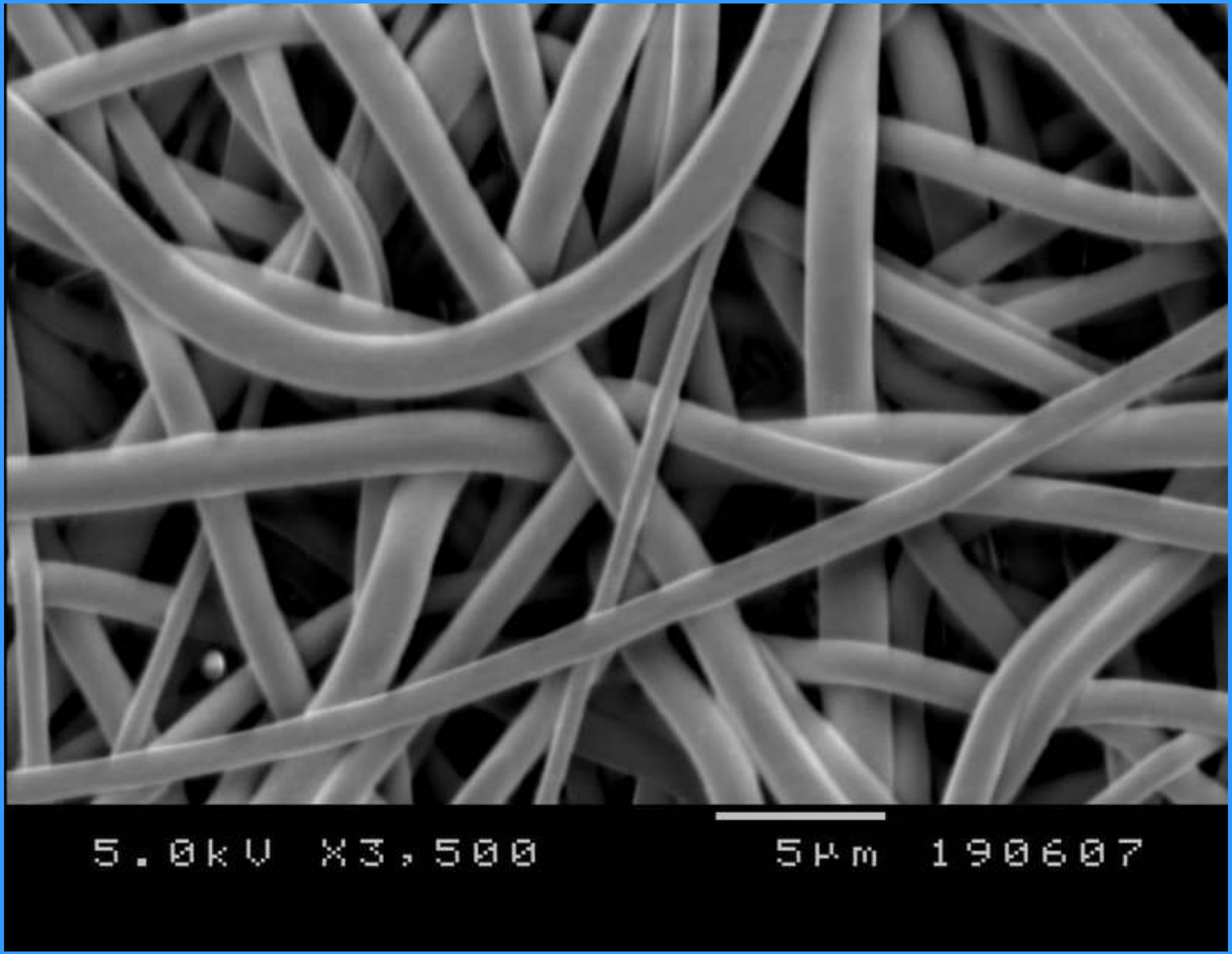
Electrospinning

Tissue precursors – Electrospinning technology





Tissue precursors - electrospinning

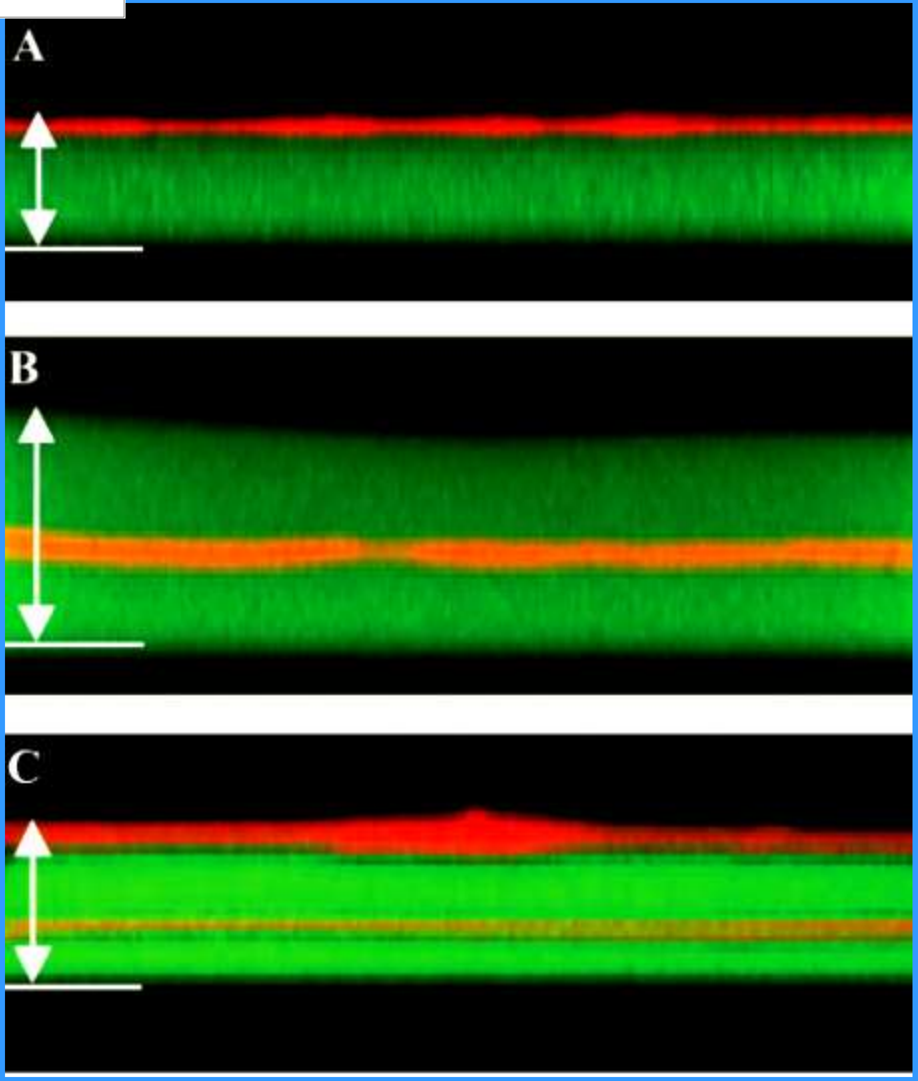


Center for Biomedical Engineering and Physics;
Medical University Viena AKH Austria,
Centrum Materiałów Węglowych i Polimerowych PAN Zabrze

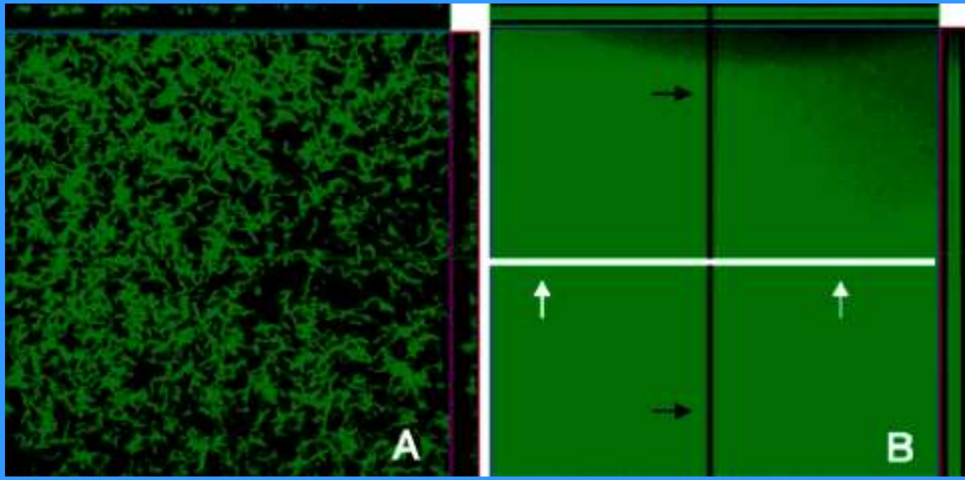
Polyelectrolites

PLL/HA

poly-L-lysine/hyaluronic acid



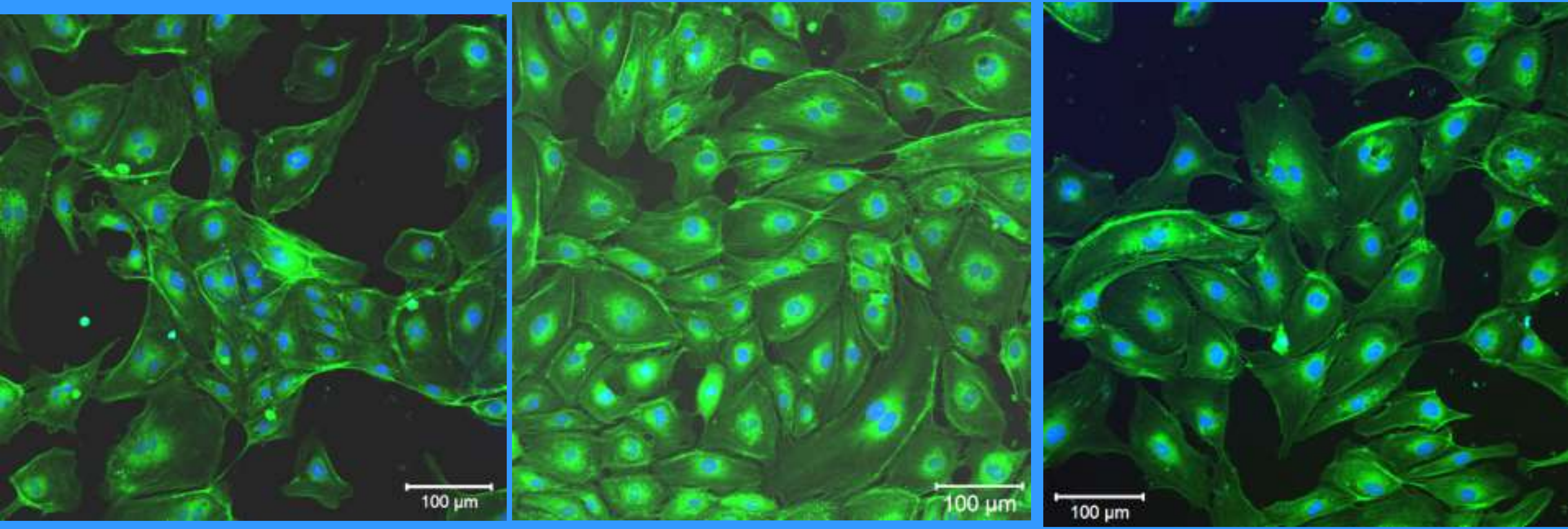
C. Picart, J. Mutterer, L. Richert, Y. Luo, G. D. Prestwich, P. Schaaf, J.C. Voegel, and P. Lavalle Molecular basis for the explanation of the exponential growth of polyelectrolyte multilayers; PNAS October 1, (2002) vol. 99 no. 20 p 12531–12535



- *Ludovic Richert, Fouzia Boulmedais, Philippe Lavalle, Jerome Mutterer, Emmanuelle Ferreux, Gero Decher, Pierre Schaaf, Jean-Claude Voegel and Catherine Picart; Improvement of Stability and Cell Adhesion Properties of Polyelectrolyte Multilayer Films by Chemical Cross-Linking; Biomacromolecules (2004), 5,284-294*

Cell answer

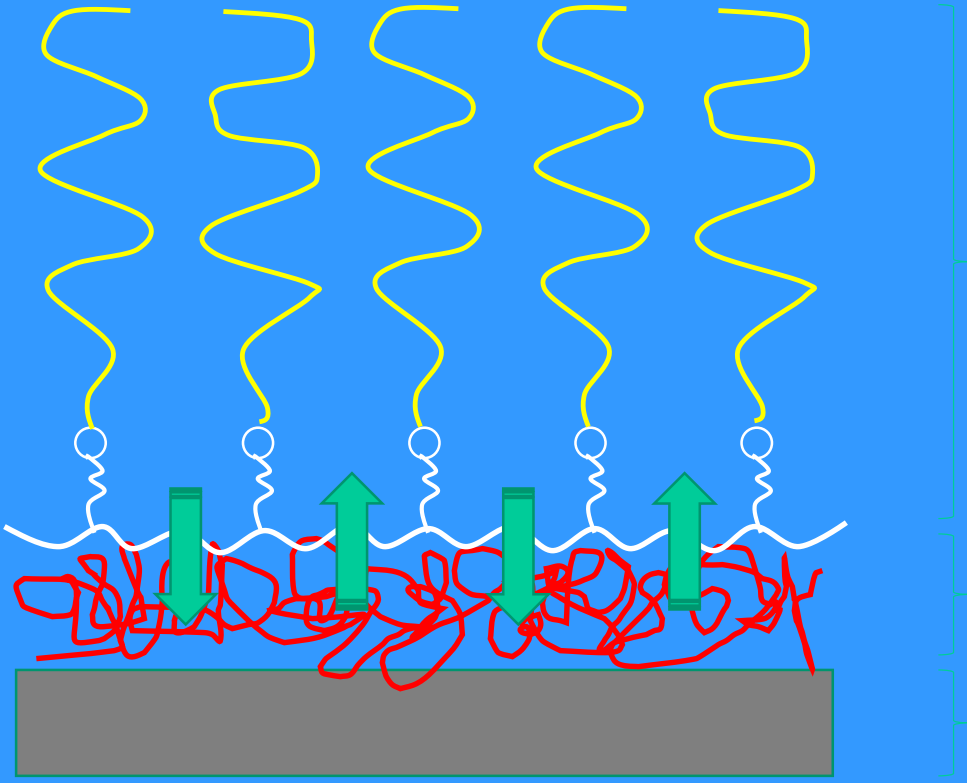
12 (PLL-HA) cross +PLL+ fibronectin + HUVEC



200 mM **400 mM** **800 mM**

Functional semi-porous materials

Proposition



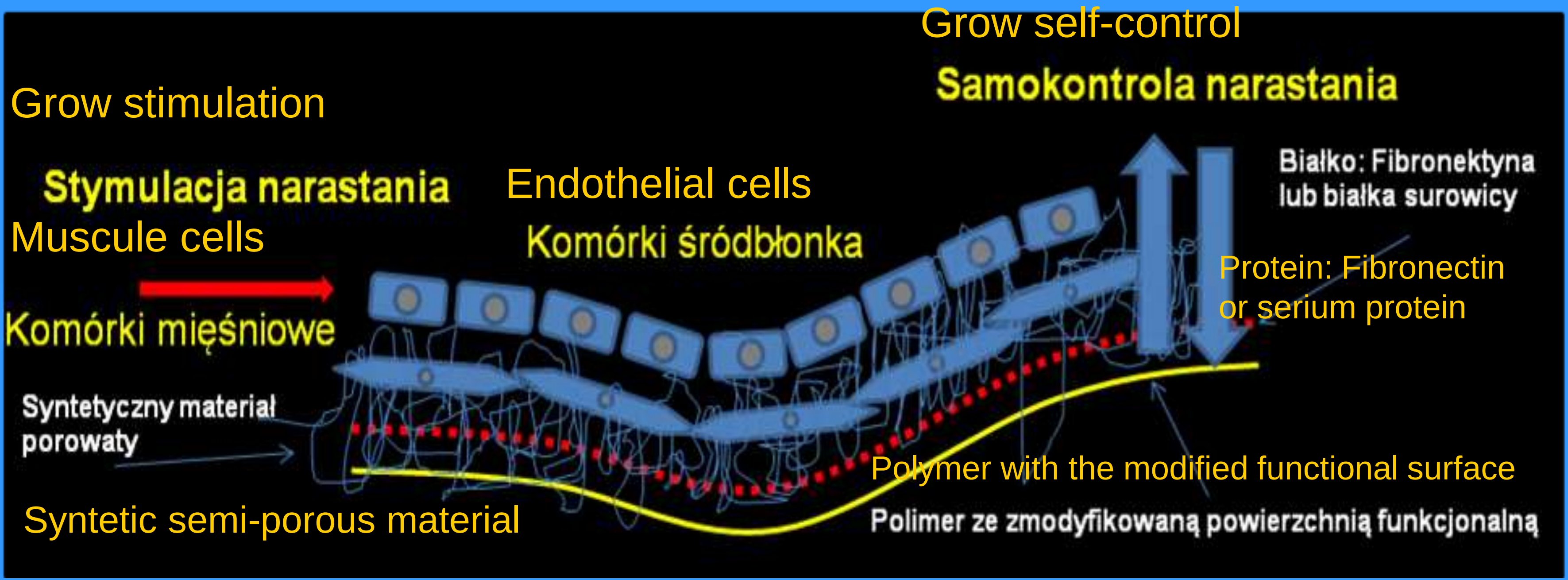
Antythrombogenic function

Porous coatings

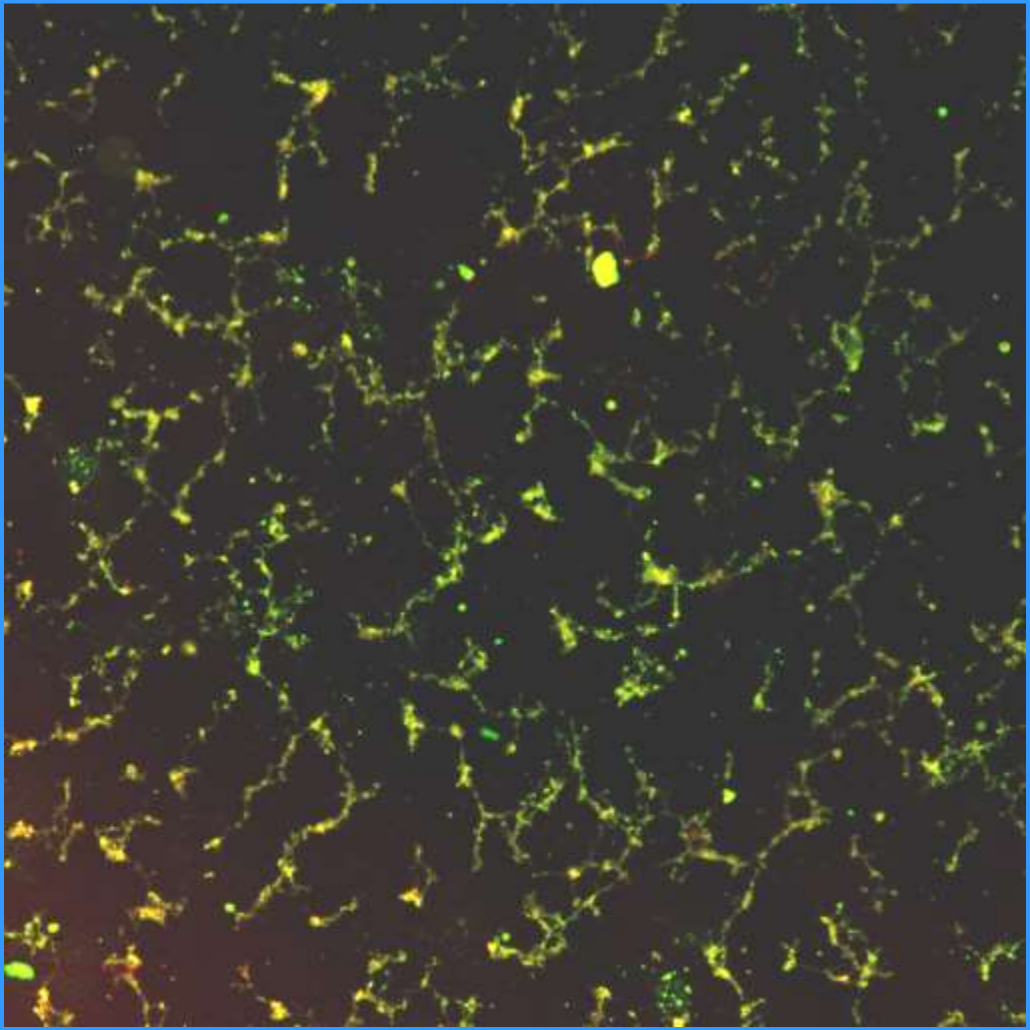
Substrate with ceramic/metallic coatings

Sara Morgenthaler, Christian Zink, Brigitte Städler, Janos Vörös, Seunghwan Lee, Nicholas D. Spencer,a and Samuele G. P. Tosatti; Poly L-lysine-grafted-poly„ethylene glycol-based surface-chemical gradients. Preparation, characterization, and first applications; Biointerphases 1„4, American Vacuum Society December 2006

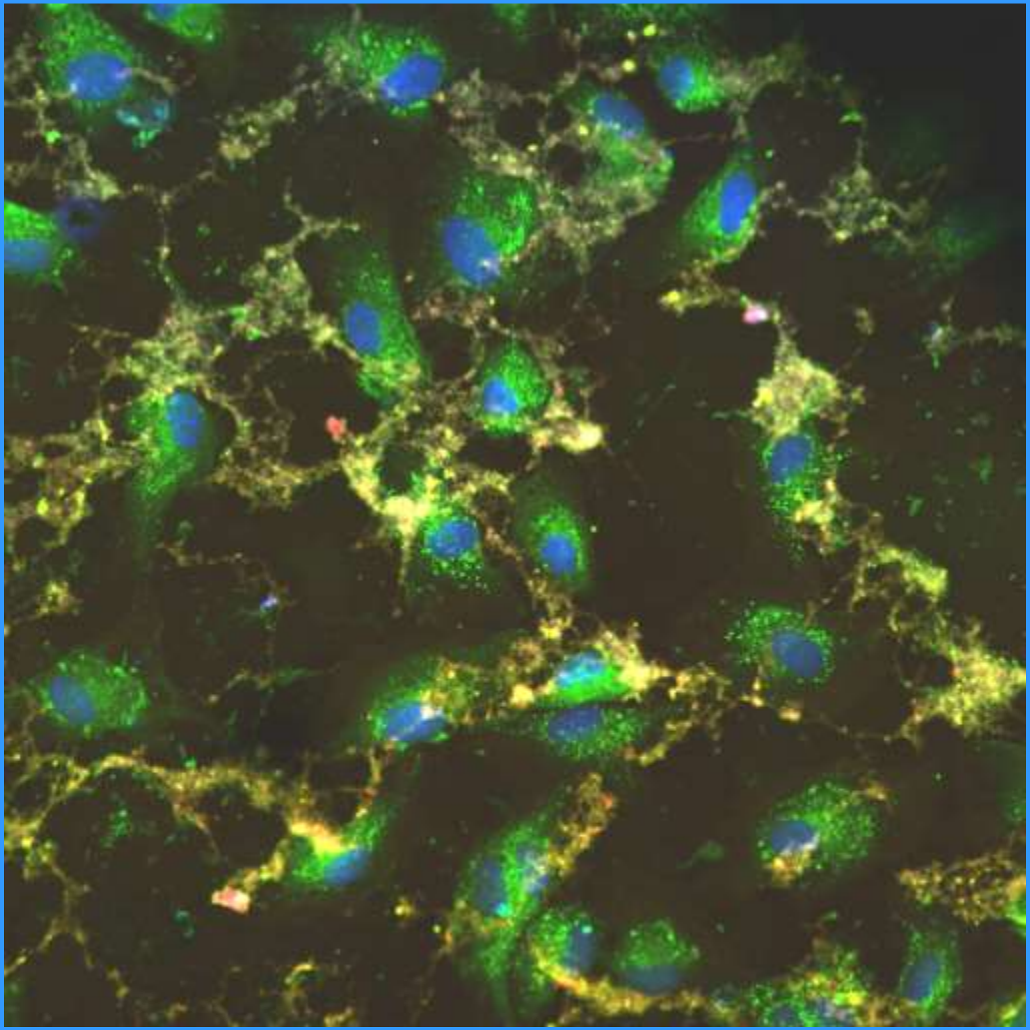
Architecture of semi-porous coating



*Surface CLSM **PEG** (poly-ethylene-glycol)*



CLSM PEG+RGD (protein domains)+HUVEC



c. Residual stress and method of measurement

- Essence of stress
- Classification of residual stress
- Influence of residual stress on the physical properties of the material

Measurement methods

-optical

-X-rays

-neutron

-removing layers

-Raman spectroscopy

-ultrasound

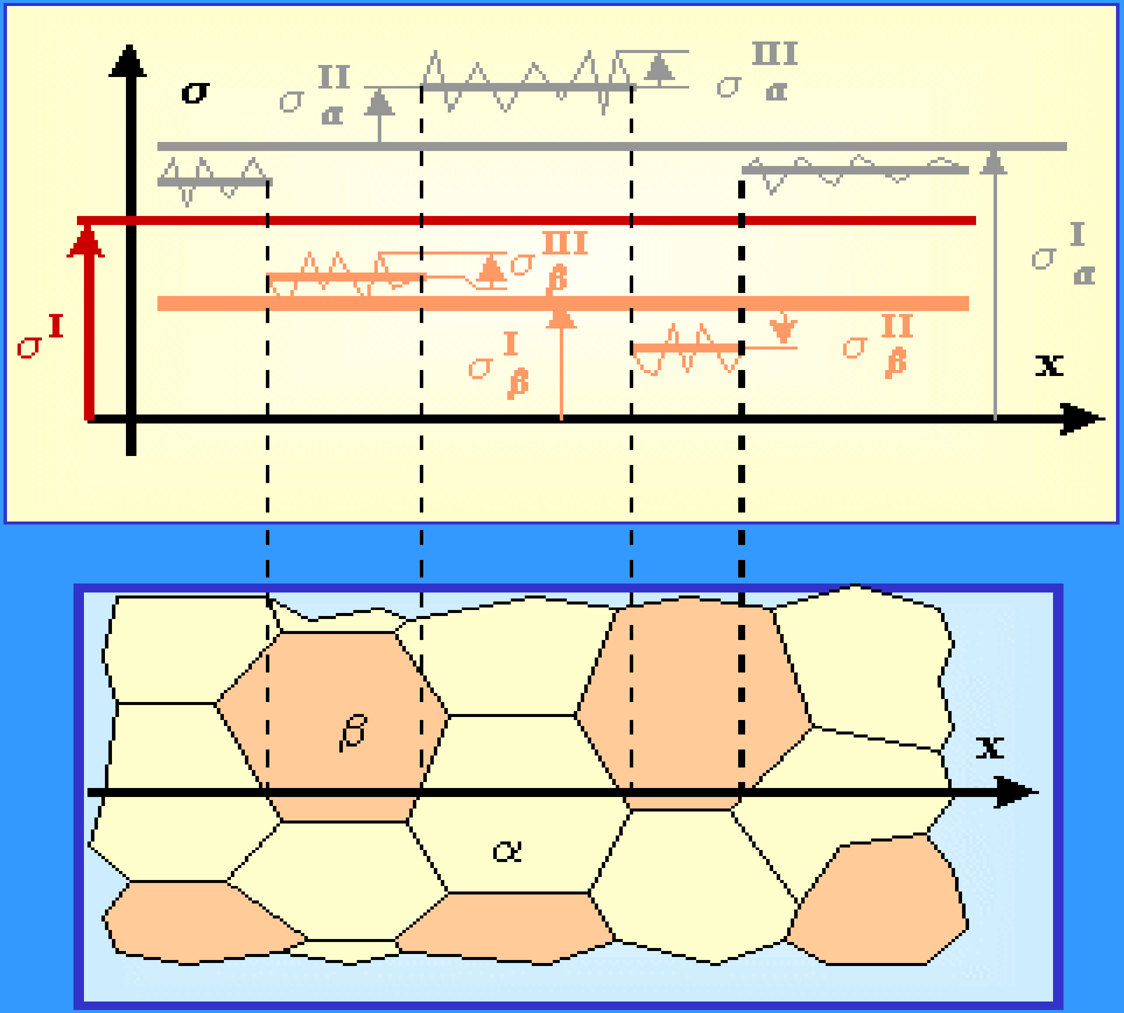
-magnetic

Essence of residual stress

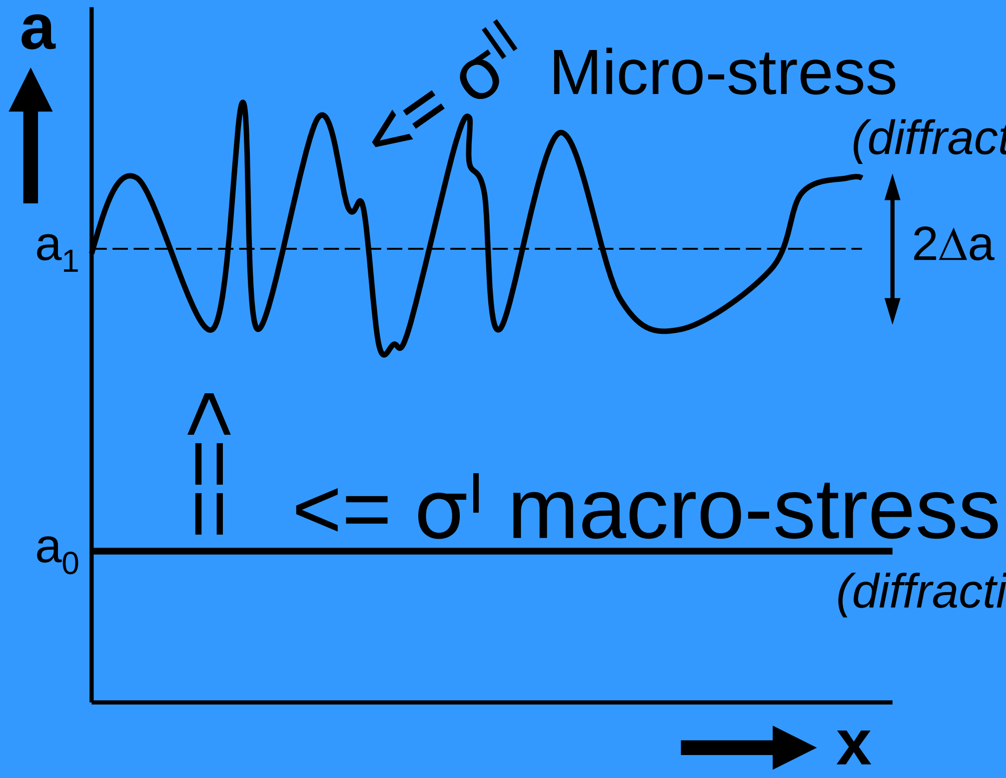
Residual stress is the stress in the material remaining in the absence of external loads (forces applied, temperature gradients, etc.).

They are the natural result of technological processes.

Classification of residual stress



Residual stress



<= σ^{II} Micro-stress

(diffraction lines broadening)

<= σ^{I} macro-stress

(diffraction lines shifting)

Residual stress

Measuring methods

Destroying

mechanical

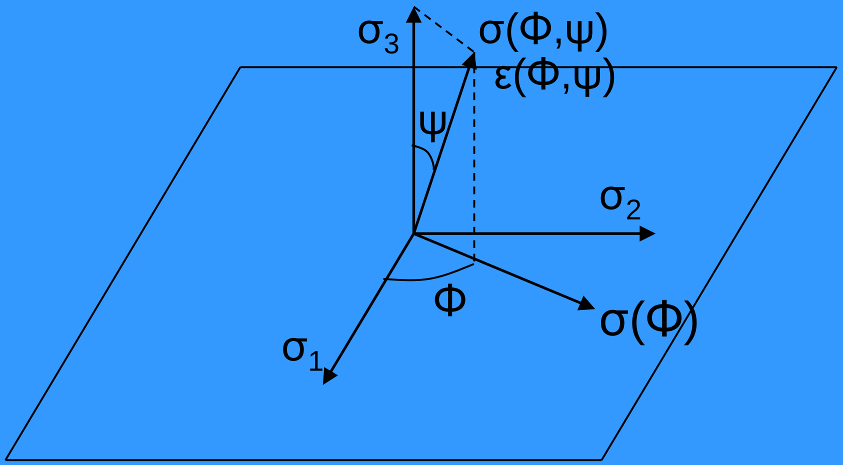
- ☐ Waisman-Phillips / flat plate /
- ☐ Dawidenkow-Sachs-Birger /cut open ring/
- ☐ drilling whole

Not-destroying

- ☐ ultrasound
- ☐ electrical / resistance, inductive /
- ☐ magnetic /Barkhausen noise/
- ☐ X-ray, neutronographic /sin2φ/

Method $\sin^2\psi$

$\varepsilon(\Phi,\psi) = \Delta d(\Phi,\psi)/d$



Hook‚s low:

$\varepsilon(\Phi,\psi) = (1+v/E)\,\sigma(\Phi,\psi) - (v/E)\,(\sigma_1 + \sigma_2 + \sigma_3)$

Stress $\sigma(\Phi,\psi)$ may be the result of $\sigma(\Phi)$ and σ_3

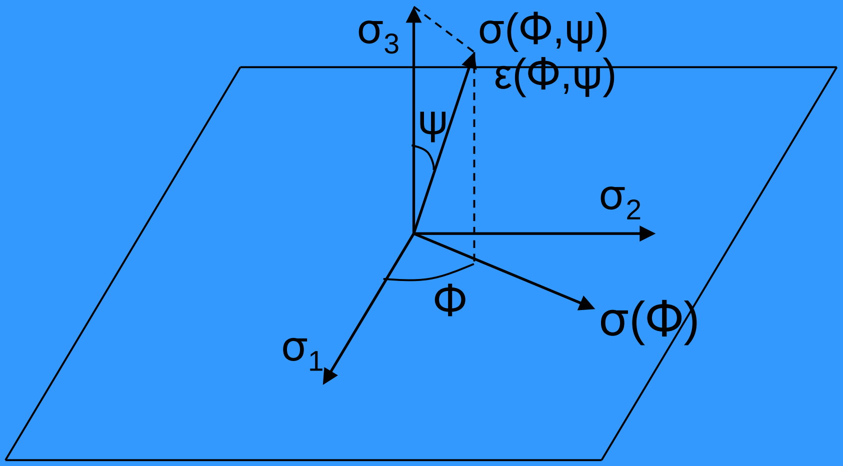
$\sigma(\Phi,\psi) = \sigma(\Phi)\sin^2\psi + \sigma_3\cos^2\psi$

σ_3 is relaxed

Deformation:

$\varepsilon(\Phi,\psi) = (1+v/E)\,\sigma(\Phi)\sin 2\psi - (v/E)(\sigma_1 + \sigma_2)$

Metoda $\sin^2\psi$



$\varepsilon(\Phi,\psi) = \Delta d(\Phi,\psi)/d$

Prawo Hooka:

$\varepsilon(\Phi,\psi) = (1+v/E)\ \sigma(\Phi,\psi) - (v/E)\ (\sigma_1 + \sigma_2 + \sigma_3)$

Naprężenie $\sigma(\Phi,\psi)$ może być wypadkową $\sigma(\Phi)$ oraz σ_3

$\sigma(\Phi,\psi) = \sigma(\Phi) \sin^2\psi + \sigma_3 \cos^2\psi$

σ_3 ulega relaksacji

Odkształcenie:

$$\varepsilon(\Phi,\psi) = (1+v/E)\ \sigma(\Phi) \sin 2\psi - (v/E)(\sigma_1 + \sigma_2)$$

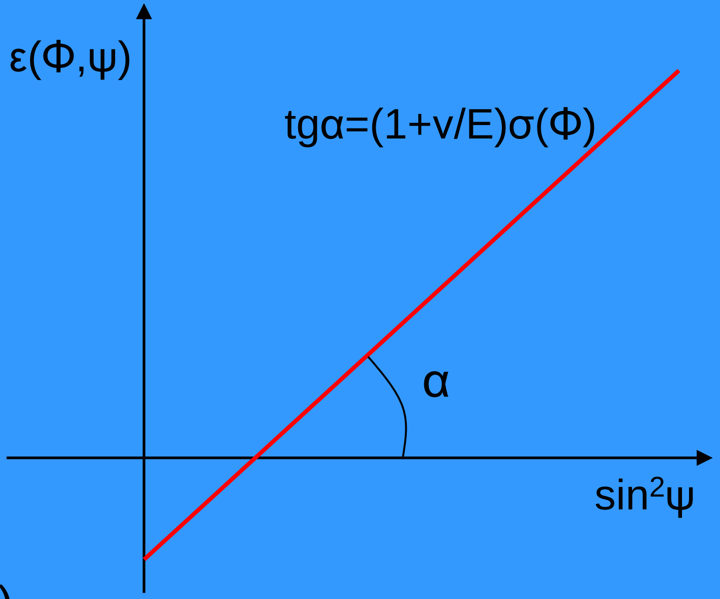
Method $\sin^2\psi$

Principle $\sin^2\psi$: stress component $\sigma(\Phi)$

can be determined from the slope of the linear dependence:

$\varepsilon(\Phi,\psi)$ versus $\sin^2\psi$:

$$\frac{d\,\varepsilon(\Phi,\psi)}{d\sin^2\psi} = \frac{1+v}{E}$$



$$\varepsilon(\Phi,\psi) = 1/2S_{2hkl}\sigma_{\Phi}\sin^2\psi + S_1(\sigma_{11}+\sigma_{22})$$

$1/2S_2 = 1+v/E$ $\quad$ $S_1 = -v/E$

Influence of residual stress on the physical properties of the material

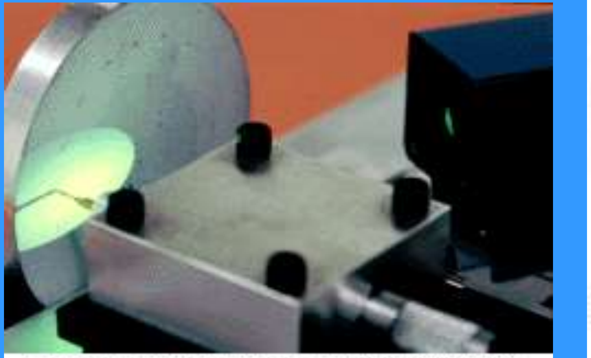
- mechanical properties
- corrosion properties
- magnetic properties

Wpływ naprężeń własnych na właściwości fizyczne materiału

- Właściwości wytrzymałościowe
- Właściwości korozyjne
- Właściwości magnetyczne

Optical measurements

- holography
- polarized light

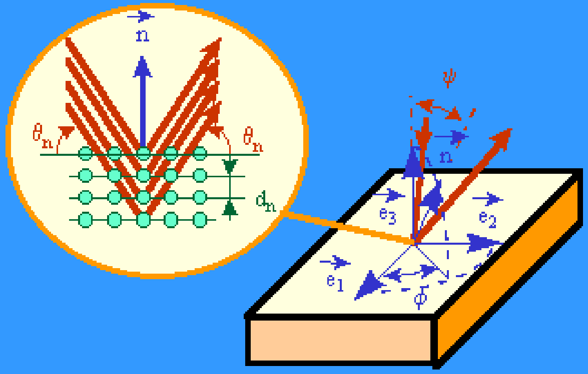


Closeup of the PRISM Residual Stress Measurement drill setup

Hologram Obtained from Residual Stress Measurement on a component

- Real-time holographic hole drilling eliminates strain gages
- Windows based software
- Results in under 5 minutes
- Fully integrated systems

X-ray measurements

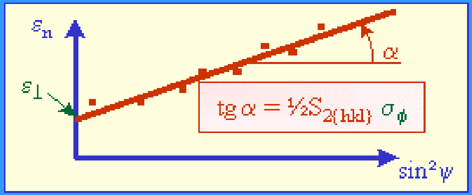


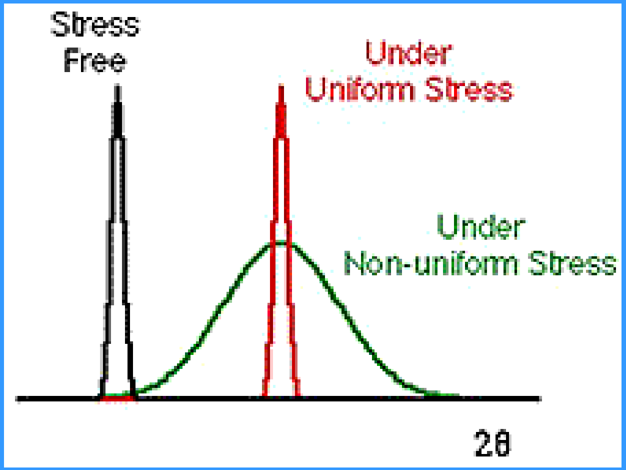
$$\varepsilon_n = \frac{d - d_0}{d_0}$$

$$\lambda = 2\, d_n \sin\theta_n$$
$$\lambda = 2\, d_0 \sin\theta_0$$

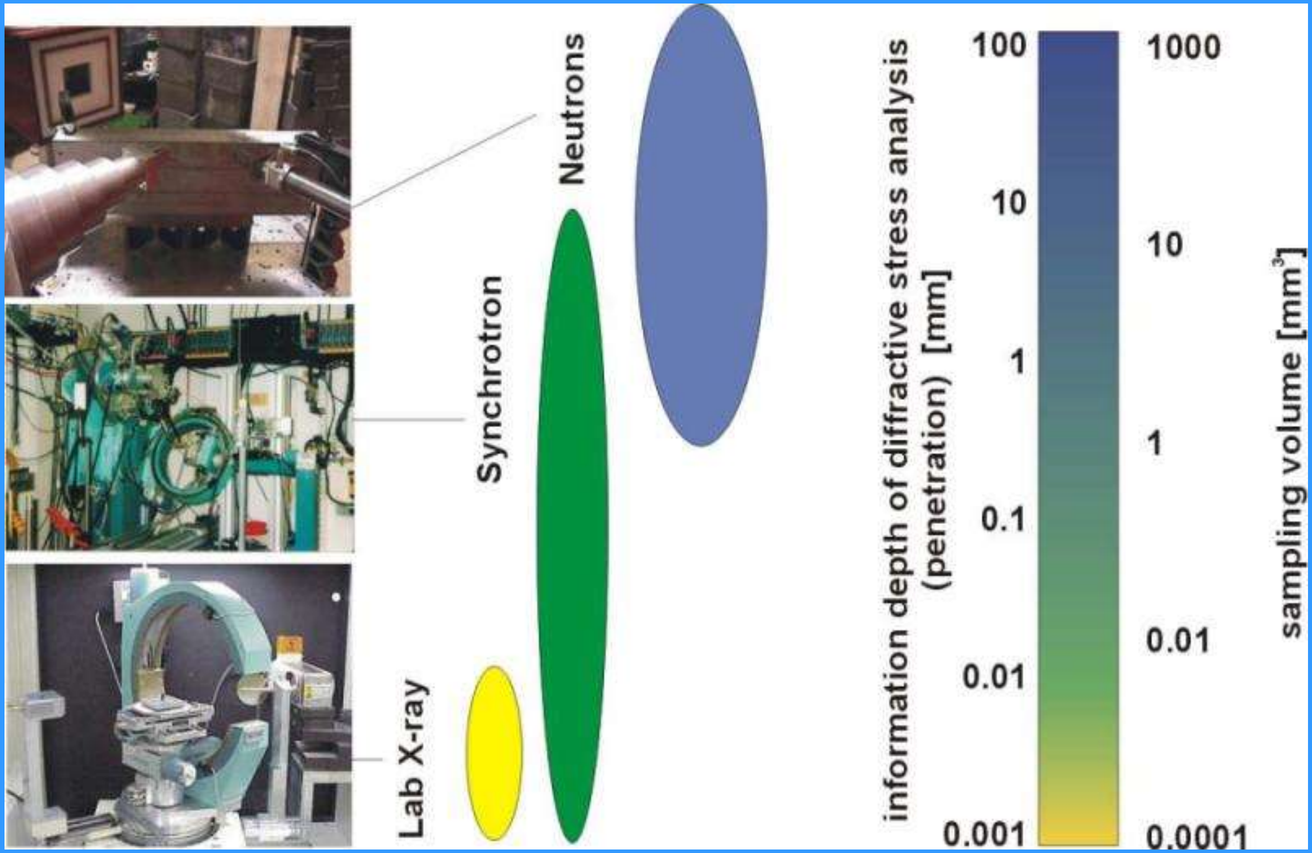
$$\varepsilon_n = \frac{\sin\theta_0 - \sin\theta_n}{\sin\theta_n}$$

$$\varepsilon_n = \tfrac{1}{2}S_{2\{hkl\}}\sigma_\phi \sin^2\psi + \varepsilon_\perp$$

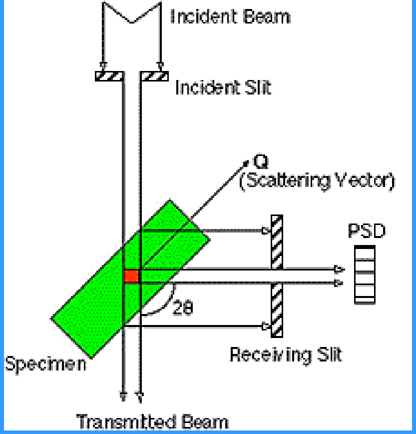


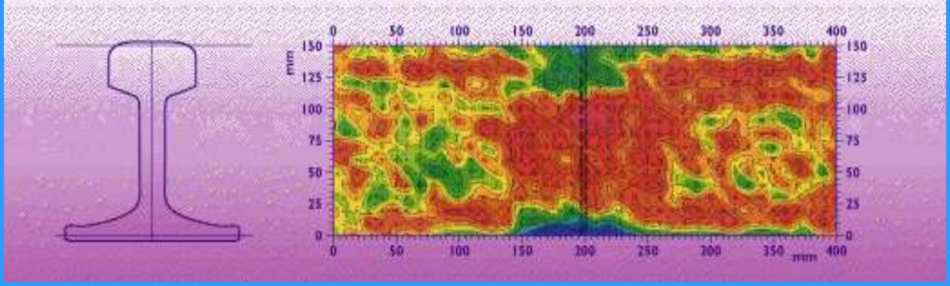


Synchrotrone radiation

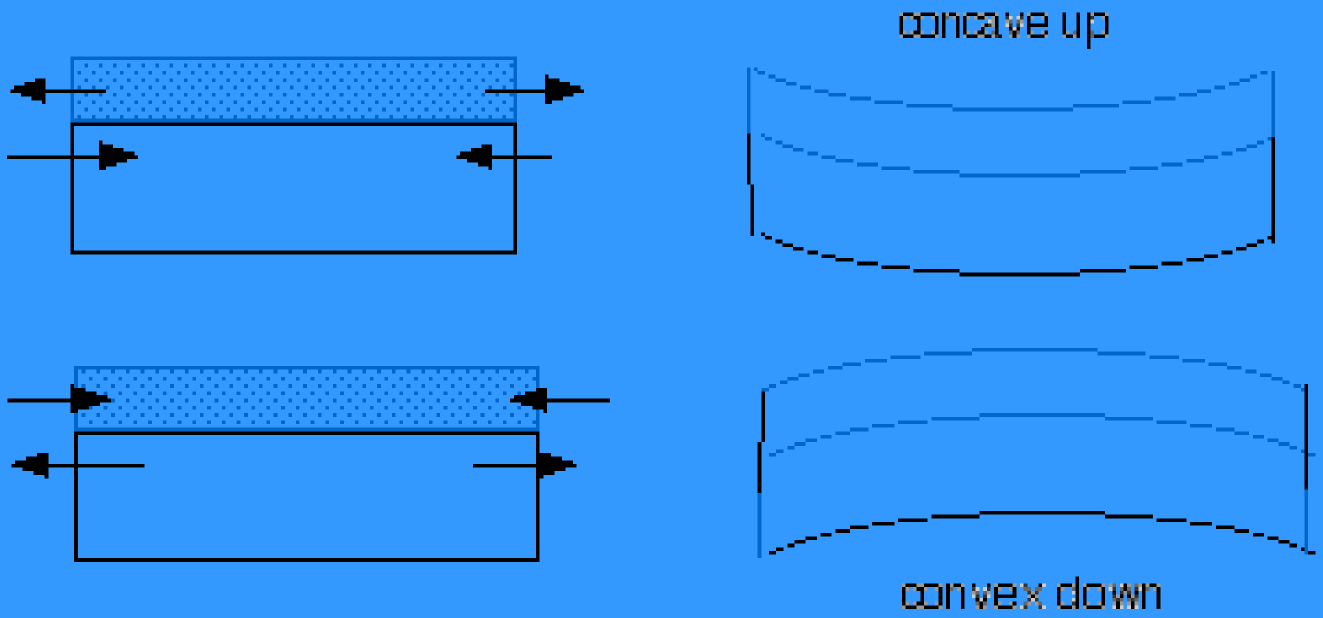


Neutrons


Incident Beam
Incident Slit
Q
(Scattering Vector)
PSD
2θ
Specimen
Receiving Slit
Transmitted Beam


mm
0
50
100
150
200
250
300
350
400
150
125
100
75
50
25
0
mm

Removing layers



Raman spectroscopy

- Analysis of the spectrum of the scattered laser radiation
- Raman line shift is directly proportional to the variation of hydrostatic stress
- Surface analysis
- Analysis of the volume only for transparent materials

Ultrasounds

- Measuring the speed of propagation of ultrasonic waves in the material
- Poor resolution of methods

Magnetism

- Influence of residual stresses on the clustering of magnetic domains
- The test response of magnetic material (only ferromagnetics)

Barkhausen noises

d. diagnosis of micro-mechanical properties

Micro-Combi-Tester

Measurement of hardness and elastic modulus
dynamic indenters

Device parameters:
Types of indenters: Vickers-angle pyramid 136deg
Berkovich pyramid-angle 65deg
Setting range of indenter loading force: 0.02-30 [N]
Penetration depth measurement accuracy: 0.3nm

Parametry urządzenia:

- Rodzaje wgłębników: Vickers- kąt piramidy 136^0
  Berkovich- kąt piramidy 65^0
- Zakres nastawy siły obciążającej wgłębnik: 0.02- 30[N]
- Dokładność pomiaru głębokości penetracji: 0.3nm

Hardness

- Brinell ball - 10, 5, 2.5 mm HB load F

- Rockwell A - 1200 HRA cone load 60kG
- Rockwell C - 1200 HRC cone load 150kG
- Rockwell B - ball 1/16 inch HRB load 100kG

- 1360 HV Vickers pyramid load F
- (Knoop - 1200 fingerprint rhomb, diamond pyramid)

Methods for determining the micromechanical properties, thin films

Micro-Combi-Tester

Features:

Determination of hardness and Young's modulus for soft, hard, brittle and ductile materials

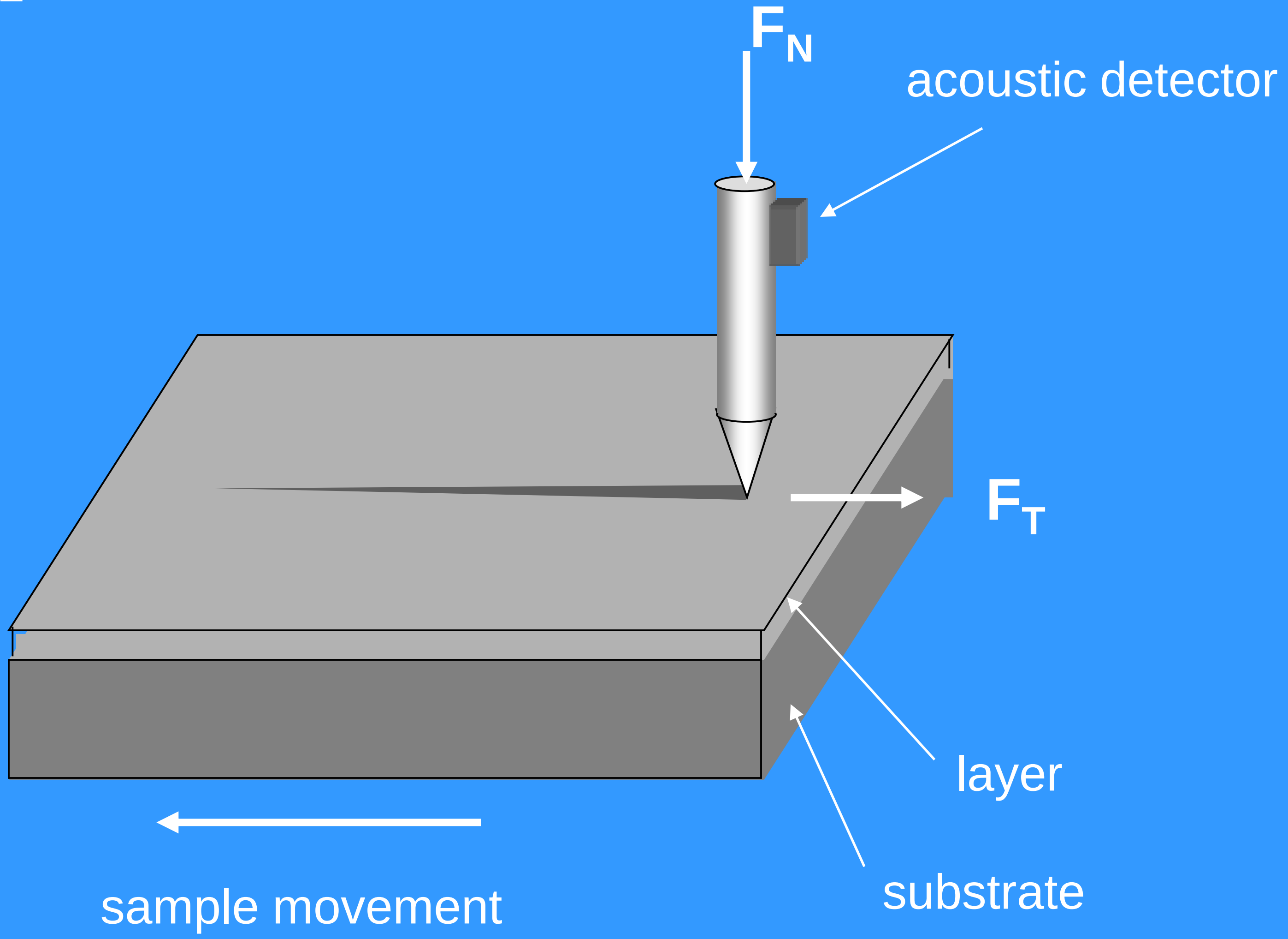
Execution of test-scratch-scratch test

Performance test "ball on disk" - wear test

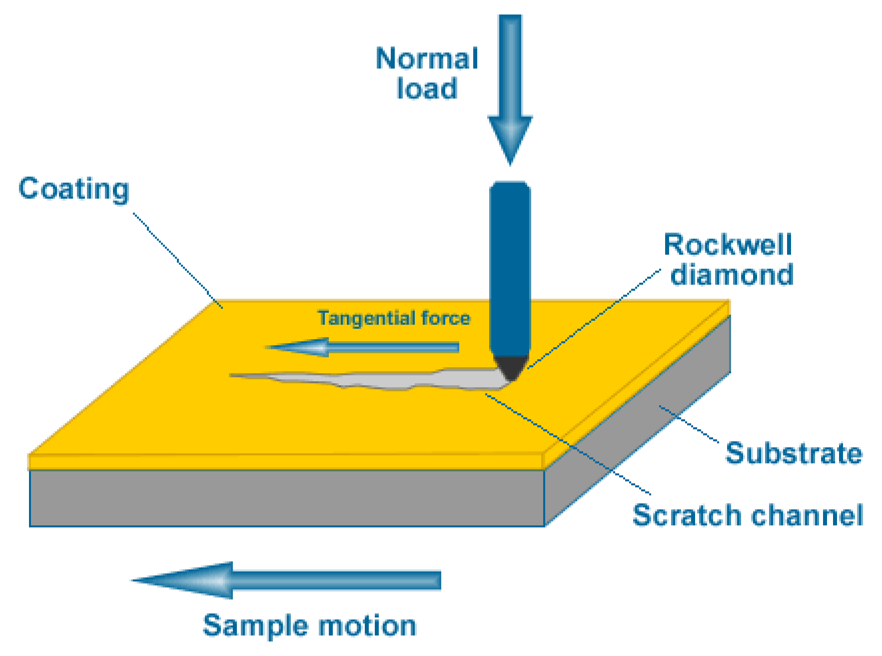
Micro-Combi-Tester

Scratch test

Parameters measured and recorded as a function of the road scratching:
Normal force FN aggravating indenter
FT resistance force during the motion put of indenter
The surface profile of the sample P
Indenter penetration depth while working movement Pd
Depth cracks after unloading (ie the size of the return spring) Rd
Acoustic emission AE

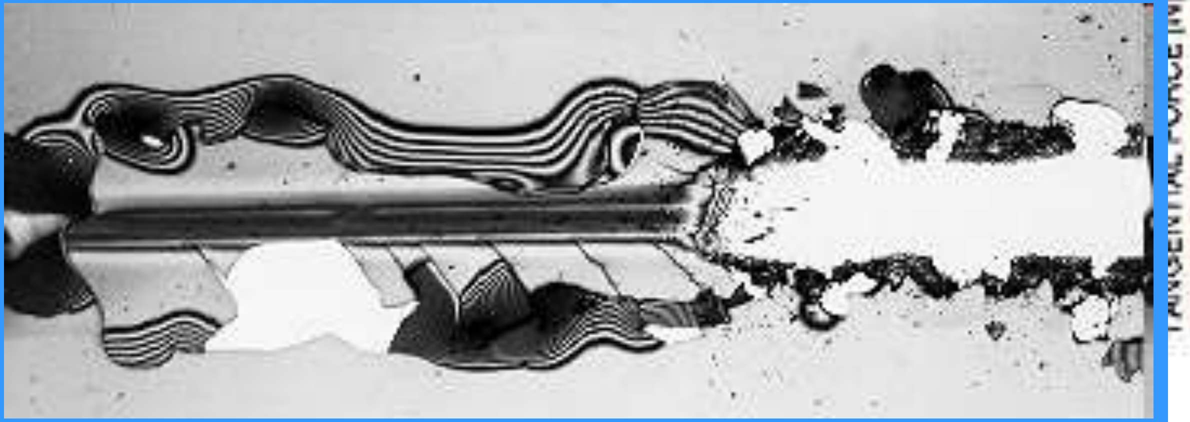


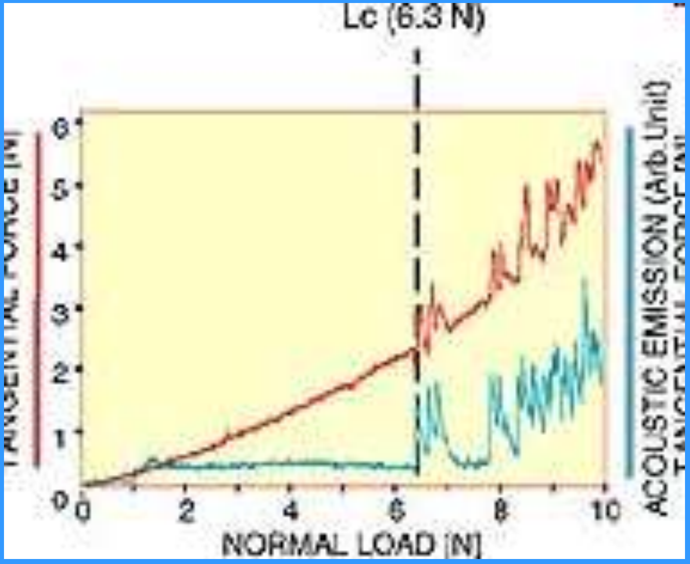
Adhesion of thin films - scratch method (micro-scratch test)



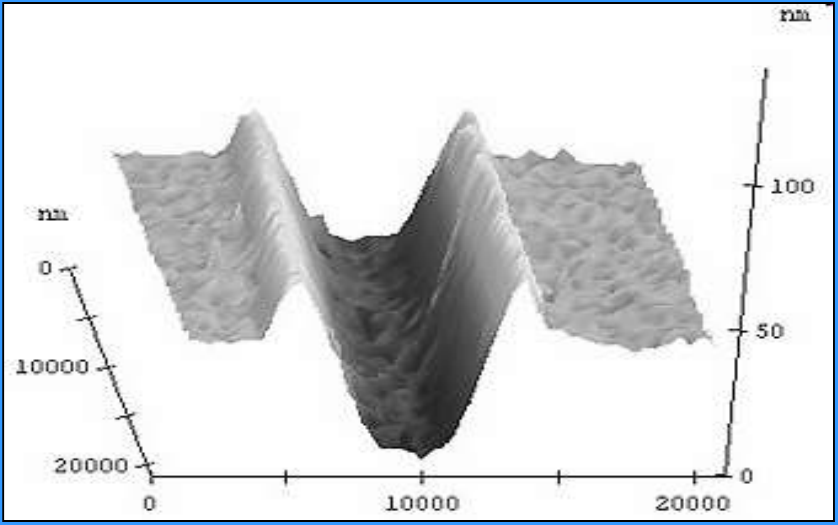
The rounded metal or diamond tipped blade is dragged with increasing load on the coating. After a certain critical load layer is punctured and separated from the substrate.

Critical load is determined with high accuracy by using an acoustic sensor attached to the tip holder, the friction force, the depth of penetration and optical microscopy. Critical load values can be used to estimate the adhesion properties of different coating-substrate combinations



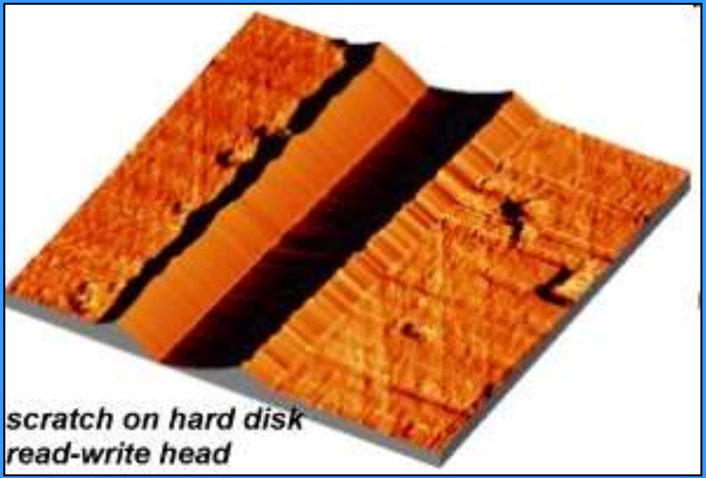


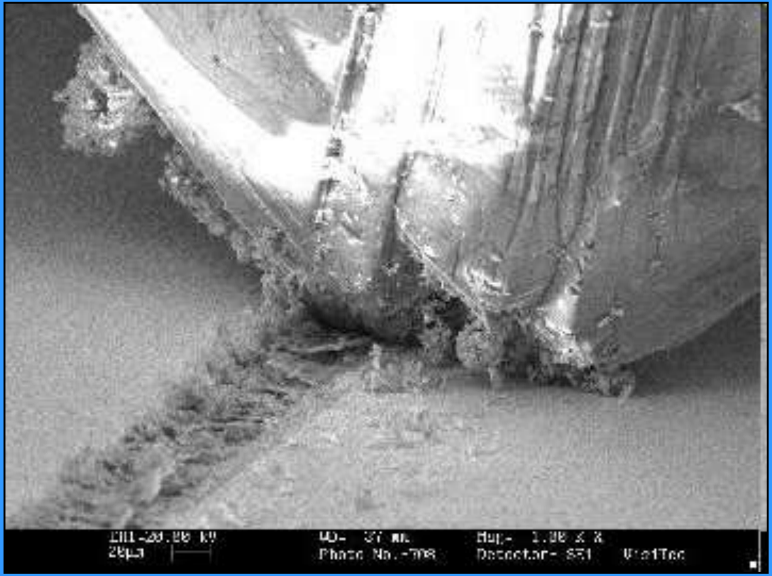
Adhesion of thin films-features method (nano-scratch test) combined with the observation of atomic force microscopy AFM



The lens is placed in the AFM microscope in place of the standard optical lens.

This combination makes it opens up a whole range of possibilities of using the method features:
- Ability to follow a large sample area coupled with the resolving power of the order of nanometers.
- Study of the arrangement of the material around the crack.
- Measurements of the critical dimension.
- Research and structures etched semiconductor surface roughness.
- Coatings profile and thin films

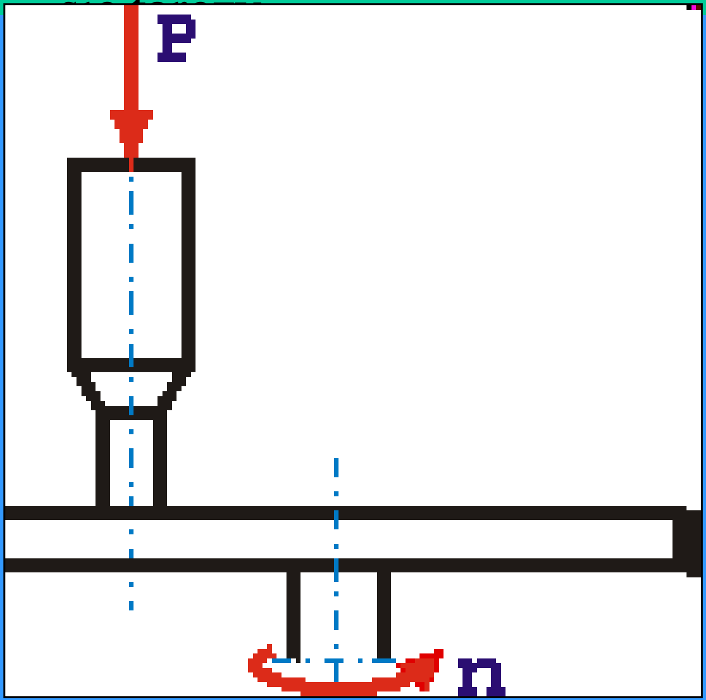


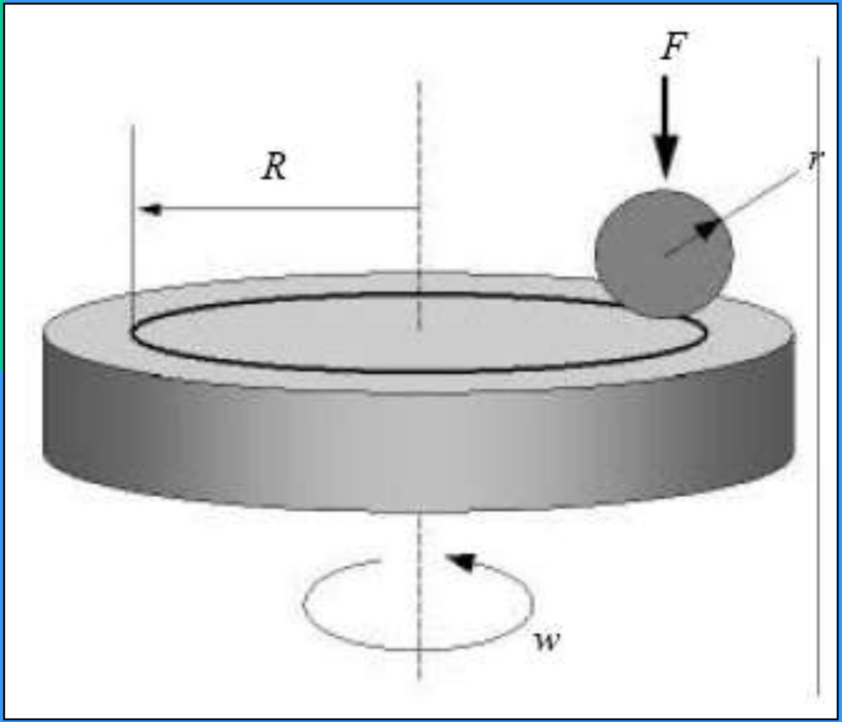


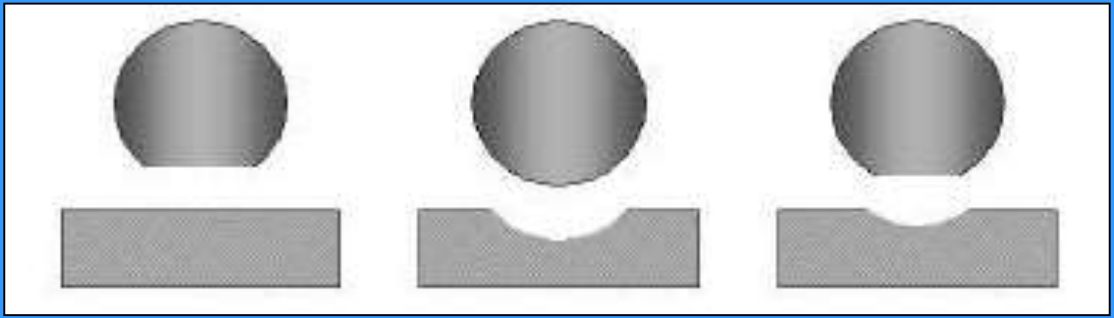
Diamond tip scratch the ceramic surface (SEM)

Tester ze skojarzeniem trzpień-tarcza // kula-tarcza

- <u>odporność na zużycie i współczynnik tarcia</u> materiału przy ślizganiu po innym materiale, w zależności od prędkości poślizgu, nacisków powierzchniowych, obecności i rodzaju środka smarowego, zanieczyszczeń i innych czynników
- Nieruchoma próbka w postaci trzpienia lub kulki dociskana jest siłą P do obracającej

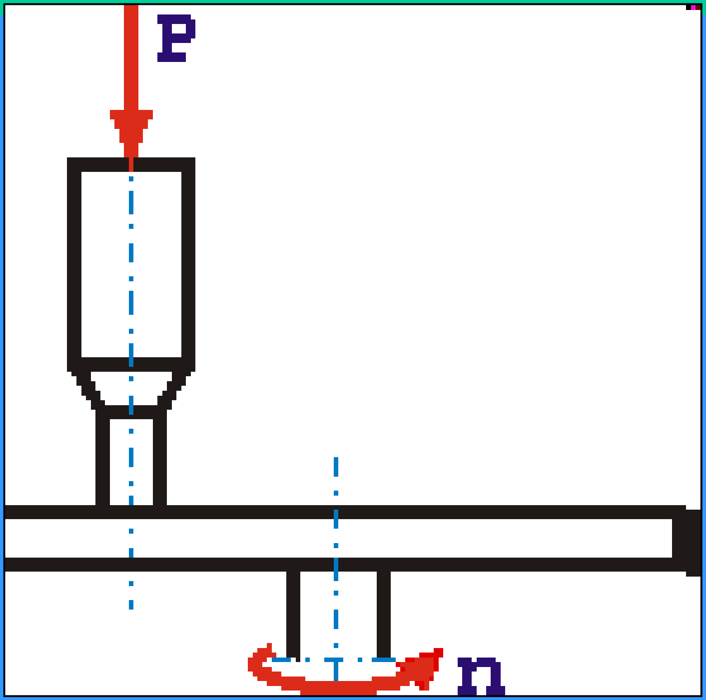


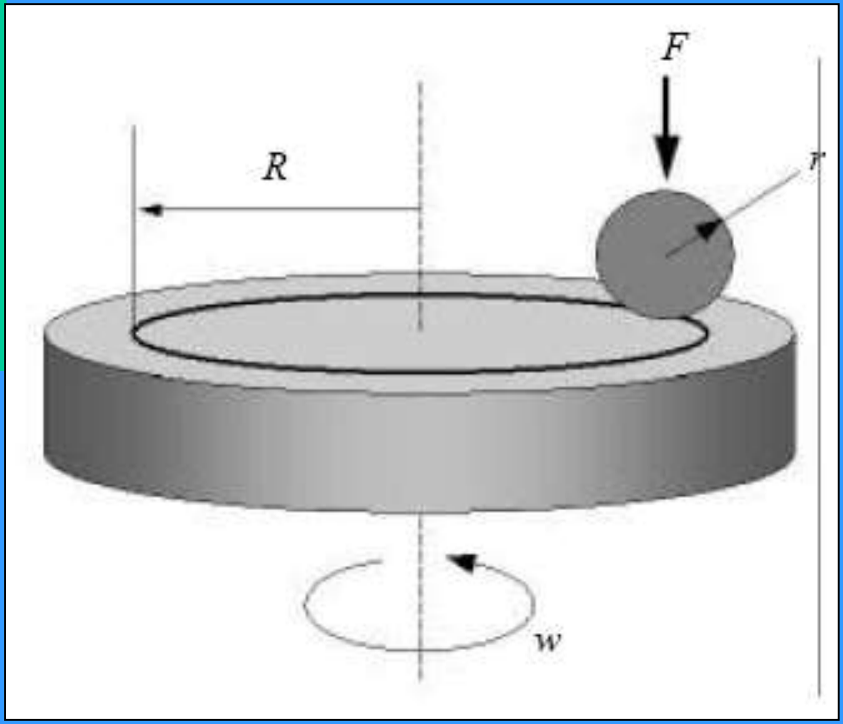


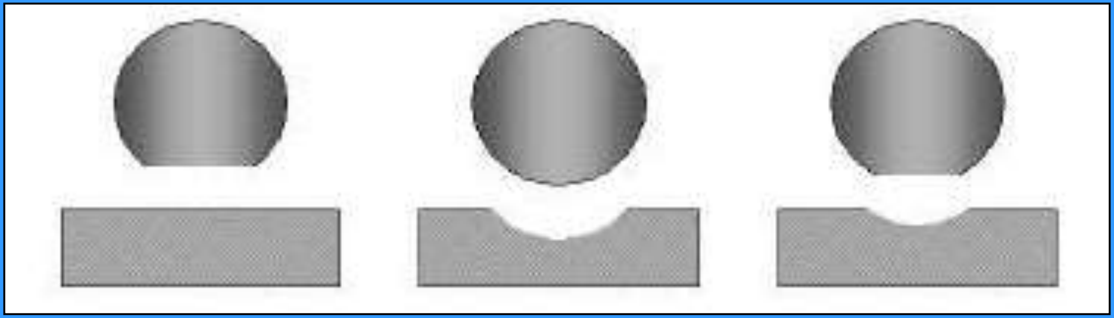


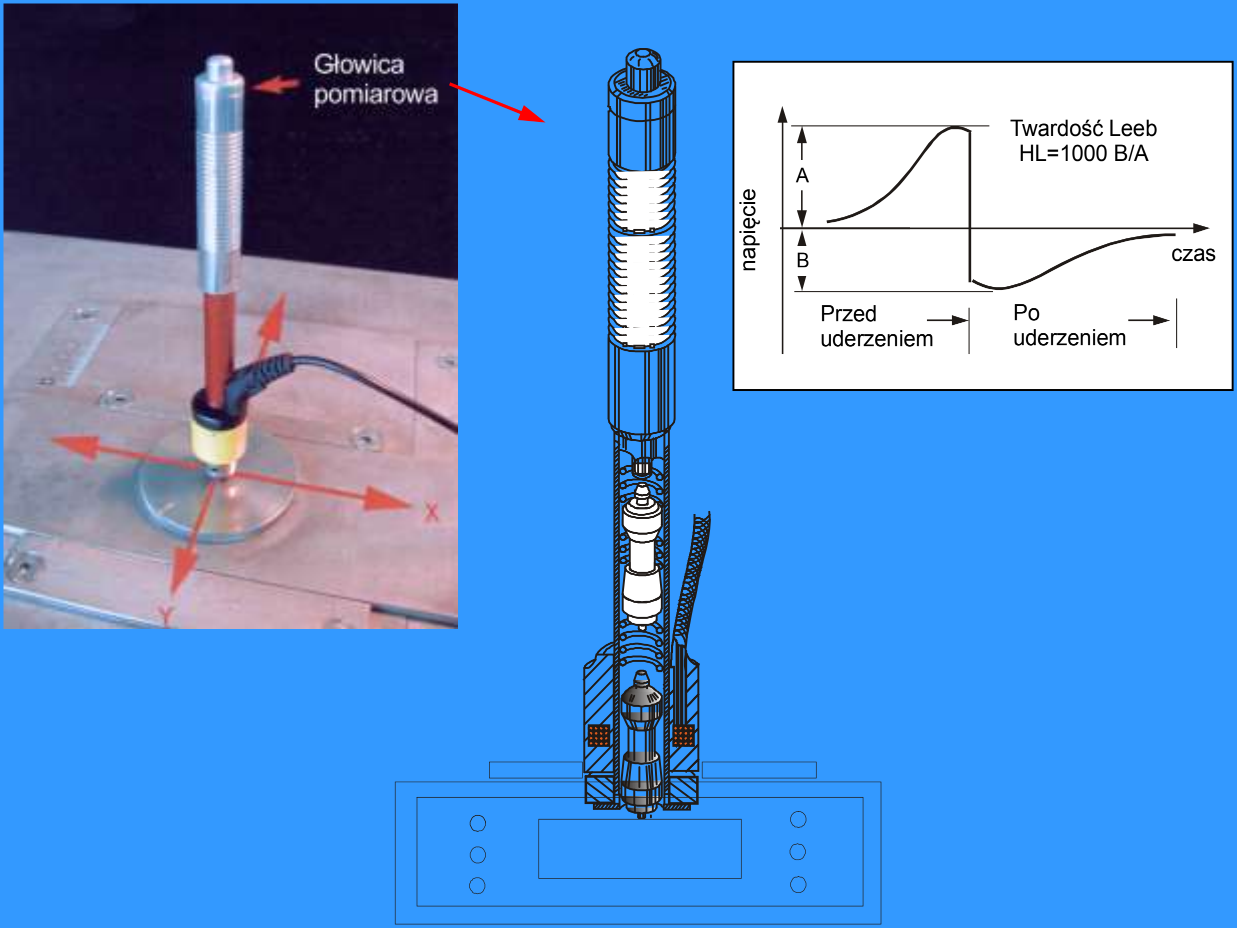
Tester with the combination of pin-on-disc / / ball-on-disc

- wear resistance and friction coefficient for the sliding of the material on other materials, depending on the slip speed, surface pressure, the presence and type of lubricant contamination and other factors
- fixed sample in the form of rod or ball pressed against a force P to the rotating disk.









Leeb hardness test

22. Hard and superhard coatings based on nitrides, carbides, borides and nanocomposites

Properties of thin films such as:

coating hardness, strength, corrosion resistance, heat resistance (creep resistance, heat resistance) depends on:

particle size

morphology

porosity (packing)

residual stresses

Requirements for hard coatings:

Optimum surface quality, tribological properties, the consumption of coolant and lubricant

The high surface hardness, good wear resistance

Maximum resistance to shock loads, the connection hardness of fatigue strength

Excellent resistance to oxidation / corrosion in the conditions of a dry / humid

Requirements of the composition-structure-properties meet the best:

carbides / nitrides based on titanium and tungsten

Characterization and properties of hard coatings:

Def. Hard coating is an area of small size limited the surrounding atmosphere from the top and from the bottom of the substrate

Thickness

optimal t = R x H / E,

where 1 / E, = 1/E1 + 1/E2 , H - hardness of the coating;

E1 and E2 - Young's modulus of the coating and the substrate

For cutting tools for metal surfaces t = approximately 5 mm

For tribological coatings t = about 1-3 microns

Chemical composition

Materials with high Young's modulus, high energy bonds, nitrides and carbides of transition metals / sp orbital hybridization and p /

Resistance to oxidation and corrosion, stability of oxide layers

Structure

Regular structure is more rigid than amorphous materials; tendency to form regular structures (cubic) decreases with increasing ordinal group metal in the periodic table. Metastable structure have a high density of defects, leading to the presence of large residual stresses in the coatings.

Morphology and particle size

Motility adatomów influences the morphology, motility, promotes the formation of a small column structure, morphology is controlled by the deposition rate, temperature, pressure, and tension of the substrate (Thornton model)

The mechanical properties as a function of grain size describes the dependence of the Hall-Petch

Film hardness H = H0 + k/D1/2

where H0-intrinsic hardness / high grain / k-constant materials, grain size D

Applicability of Hall-Petch law is limited to single or multilayer coatings with modulation of more than 10 nm bilayer

Surface roughness and morphology

Roughness affects the tribological properties, high roughness and polishing can significantly reduce the adhesion between the coating and the substrate

Residual stress

Hard coatings applied to the soft substrate can have a high level of compressive stress / up to 10 GPa /.

Residual stress of 3 GPa in some applications is desirable

Adhesion

Def. ASTM adhesion is a condition where the surfaces are joined with interphase forces .

Aadhesion can be measured by the force or energy

Hardness

Hardness is the resistance to plastic deformation of the material caused by indenter

Hardness can be increased by: creating solid solutions, deposition of the second phase, nono-crystallization or multilayer deposition of nanometric dimensions

Depends on the morphology, columnar structure generally reduces the hardness for the compact causing anisotropy

Young's modulus

Less dependent on the characteristics of the coating and strongly on the chemical composition and therefore nitrides and carbides with strong and short bonds and high degree of binding covalency have large modules kowale

Plasticitz coefficient $\boldsymbol{\delta_H = 1-14,3(1-ύ-ύ^2)H/E}$

Double metal nitrides and carbides

- Nitride and titanium carbide
- Nitride and tungsten carbide

Triple nitrides

- Titanium aluminum nitride
- Titanium-tungsten nitride

Nano-composites based multilayer nitride

New materials with high hardness / toughness and stress their beneficial and good adhesion;

hardness and / or ductility is improved by reducing the modulation of the bilayer, whereas the adhesion by increasing

Hardness in the low low modulation Λ recognized Hall-Petch relationship

$H = H_0 + k \Lambda^{-\beta}$

ß-constant with a value of 0.5-1

The increase in hardness is attributed to the creation of super-lattice

23. Coatings for thermal barrier

Thermal barrier coatings are used in gas turbines or diesel engines

Usually consist of two layers; binding (metal), and insulation (ceramic - outside)

Binding:

a) (platinum-) intermetal based on aluminium

b) MCrAlY M = Ni or Co

The choice of the binder depends on the method of preparation of the outer layer.

The most common application of the outer layer is used electron beam PVD (EB PVD) and atmospheric plasma sprying (ASP)

Recent external coating based on zirconium oxide $ZrO2$

/ stabilized MgO, CaO or Y2O3, structure or regular tetragonal YSZ /

24. Polymer film obtained by plasma polymerization

Plasma-induced chemical reactions:

- plasma polymerization
- plasma interaction, surface modification (introduction of functional groups containing nitrogen-oxygen-fluorine polymer chains)
- plasma co-polymerization

Plasma polymerization is the interaction of plasma with monomer molecules that are activated to initiate the polymerization reaction, the substrate surface covered with a thin polymer film

24. Powłoki polimerowe uzyskiwane poprzez polimeryzację plazmową

Reakcje chemiczne wywoływane plazmą:

- Polimeryzacja plazmowa
- Oddziaływanie plazmy; modyfikacja powierzchni (wprowadzanie grup funkcjonalnych zawierających tlen- azot- fluor do łańcuchów polimerowych)
- Ko-polimeryzacja plazmowa

Polimeryzacja plazmowa polega na oddziaływaniu plazmy z molekułami monomerów, które są aktywowane do zainicjowania reakcji polimeryzacji; powierzchnia podłoża pokrywa się cienkim filmem polimerowym

Plasma polymerization is different from the conventional

It includes two processes:

- molecules growth
- polymer fabrication

In the chemical sense

- Radical polymerization / propagation reaction of the monomers to the polymerization step is initiated by the particles in the free-radical polymer chain /
- Ionic polymerization / promote chemical reactions by ionic particles /

Promoting polymerization of the particles in the plasma are not the plasma, the plasma is the source of energy to initiate polymerization

The atomic composition of the polymers after plasma polymerization are presented in Table

Polimeryzacja plazmowa różni się od konwencjonalnej

Zawiera dwa procesy:

- wzrost molekuł
- wytwarzanie polimeru

W znaczeniu chemicznym

- Polimeryzacja rodnikowa /propagacja reakcji monomerów na etap polimeryzacji inicjowana jest przez cząstki rodnikowe w łańcuchach polimerowych/
- Polimeryzacja jonowa /reakcje chemiczne propagują się przez cząstki jonowe/

Propagujące się cząstki w polimeryzacji plazmowej nie są plazmą, plazma jest źródłem energii do zainicjowania polimeryzacji

Skład atomowy polimerów po polimeryzacji plazmowej przedstawia Tablica

Monomer used for plasma polimeryzation	Atomic composition of monomer	Atomic composition of plasma polymer
Etylen	C_2H_2	$C_2H_{2.6}O_{o.4}$
Etylen/N_2	C_2H_2 /N_2	$C_2H_{2.6}O_{o.4}$
Acetylen	C_2H_2	$C_2H_{1.6}O_{o.3}$
Acetylen/N_2	C_2H_2 /N_2	$C_2H_{2.2}$ $N_{o.5}$ $O_{o.3}$
Acetylen/H_2O	C_2H_2 /H_2O	$C_2H_{2.7}O_{o.6}$
Acetylen/N_2/H_2O	C_2H_2 /N_2 /H_2O	$C_2H_{2.9}$ $N_{0.5}$ $O_{o.7}$
Allen (propadien)	C_3H_4	$C_3H_{3.7}O_{o.4}$
Allen/N_2	C_3H_4/N_2	$C_3H_{3.8}$ $N_{0.7}$ $O_{o..5}$
Allen/H_2O	C_3H_4/H_2O	$C_3H_{4.2}O_{o.6}$
Allen/N_2/H_2O	C_3H_4/N_2/H_2O	$C_3H_{24.4}$ $N_{0.45}$ $O_{o.6}$
Akrylonitryl	C_3H_3N	C_3H_3 $NO_{o.4}$
Propionitryl	C_3H_5N	$C_2H_{4.7}$ $NO_{o.8}$
Propylamin	C_3H_9N	C_3H_5 $NO_{o.4}$
Allylamin	C_3H_6N	$C_3H_{4.7}$ $NO_{o.4}$
Tlenek etylenu	C_2H_4O	$C_2H_{2.9}O_{o.4}$

Plasma polymers can not be interpreted based on the concept of repeating monomer units

/ significant difference in the atomic composition between the plasma polymer and monomer used;

molecules present in the plasma used for plasma polymerization, /even nitrogen and water vapor/ are components of a plasma polymer

Plasma polymerization reaction is not a chain reaction of monomer molecules

"Atomic polymerization" is the concept of plasma polymerization

by. Yasuda

When the monomer molecules are injected into the plasma, they are bombarded with the active particles, such as electrons and ions remaining in the plasma, are crushed into small pieces that will gradually build more recombinant molecules.

Creation and recombination of radicals in the plasma is repeated, leading to the plasma polymer on the surface of the substrate

Polimery plazmowe nie mogą być interpretowane w oparciu o koncepcję powtarzania jednostki monomeru zastosowanego do polimeryzacji plazmowej

/znaczna różnica w składzie atomowym pomiędzy polimerem plazmowym i zastosowanym monomerem;

molekuły występujące w strefie plazmy zastosowanej do polimeryzacji plazmowej, nawet azot i para wodna, stają się składnikami polimeru plazmowego

Reakcja polimeryzacji plazmowej nie jest reakcją łańcuchową molekuł monomeru

„polimeryzacja atomowa" jest koncepcją reakcji polimeryzacji plazmowej

wg. Yasuda

Gdy molekuły monomeru zostaną wstrzyknięte do plazmy, zostaną bombardowane przez aktywne cząstki takie jak: elektrony i jony pozostające w plaźmie, zostają rozdrobnione w małe fragmenty, które stopniowo ulegną rekombinacji budują większe molekuły. Tworzenie rodników i rekombinacja jest powtarzana w plaźmie prowadząc do osadzenia polimeru plazmowego na powierzchni podłoża

The mechanism of plasma polymerization(Pau. 20.1)

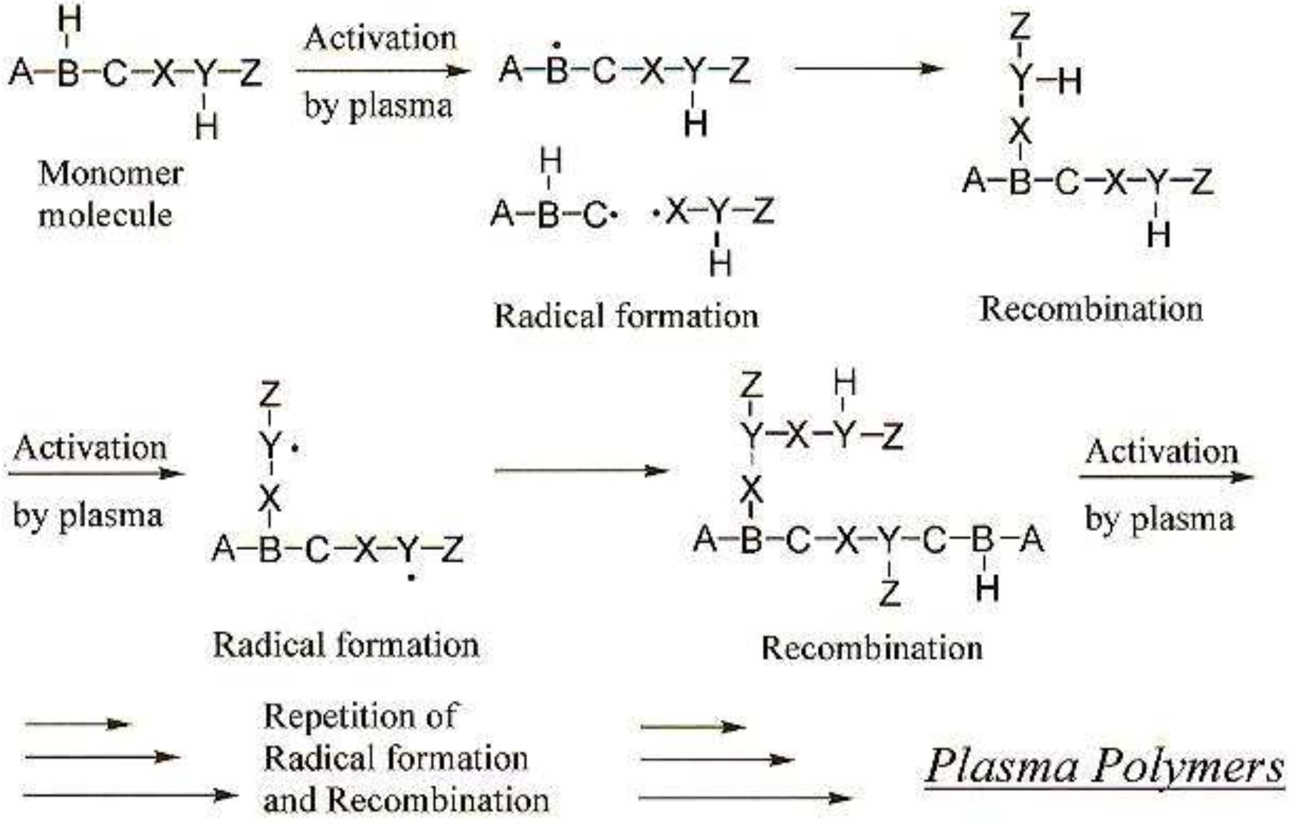


Figure 20.1: Overall plasma polymerization mechanism.

25. Trends in development of surface engineering - Foresight 2020

- Modern technologies of synthesis of ceramic layers, metal-ceramic, polymer
- Nanomaterials for bio-engineering, biomaterials for implantation and regenerative medicine
- Biodegradable and recyclable materials
- Materials and surface engineering processes for the automotive and aerospace

- Materials from renewable energy sources and nano-exchanger
- Technologies and materials for fuel cells
- Materials and technologies for medical instruments
- Improving the life cycle of engineering materials, regeneration technology of vehicles and functional products
- Organic and ceramic materials for electronics, optoelectronics and photonics
- Crystalline materials with oriented structure and monocrystals

- Porous materials
- Materials and layers of low friction
- Composite functional layers and gradient layers
- Materials and technologies for micro-and nano-bio- intelligent robots
- New generation of contact materials, surface drainage and diffuse heat flux
- Implants addressed (personal)
- Materials with a high strength to density ratio and polymers with nano-additions
- New generation of optical fibers and nano-multiferroitic materials

- Materials for digital electronics and data transmission
- Materials for ballistic resistance
- Advanced and intelligent textiles (geofibers, geotextiles) and textronic systems and equipment for the integration with textiles and clothing
- Constructional materials with modified surface layers and layered materials comprizing polymers
- Materials and technologies for the production and storage of hydrogen