5 Jul **Fri**

▶ 11^{00}–11^{50} • **Zsolt Tóth,**
Application of lasers for surface treatment of titanium implants

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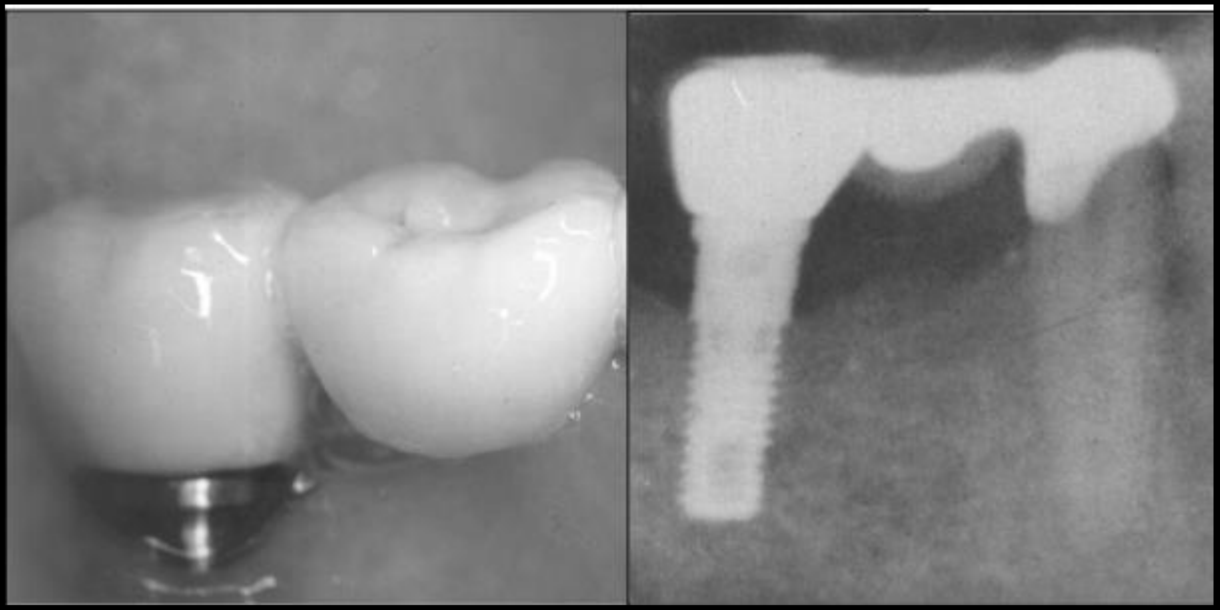
Titanium implants for replacement of missing teeth.

- Dental implantation is a straightforward technique for tooth replacement
- The biological function requires significant load-bearing capability.
- They are generally made from titanium.
- Their biological integration depends on - among others - the surface structure of the metal.



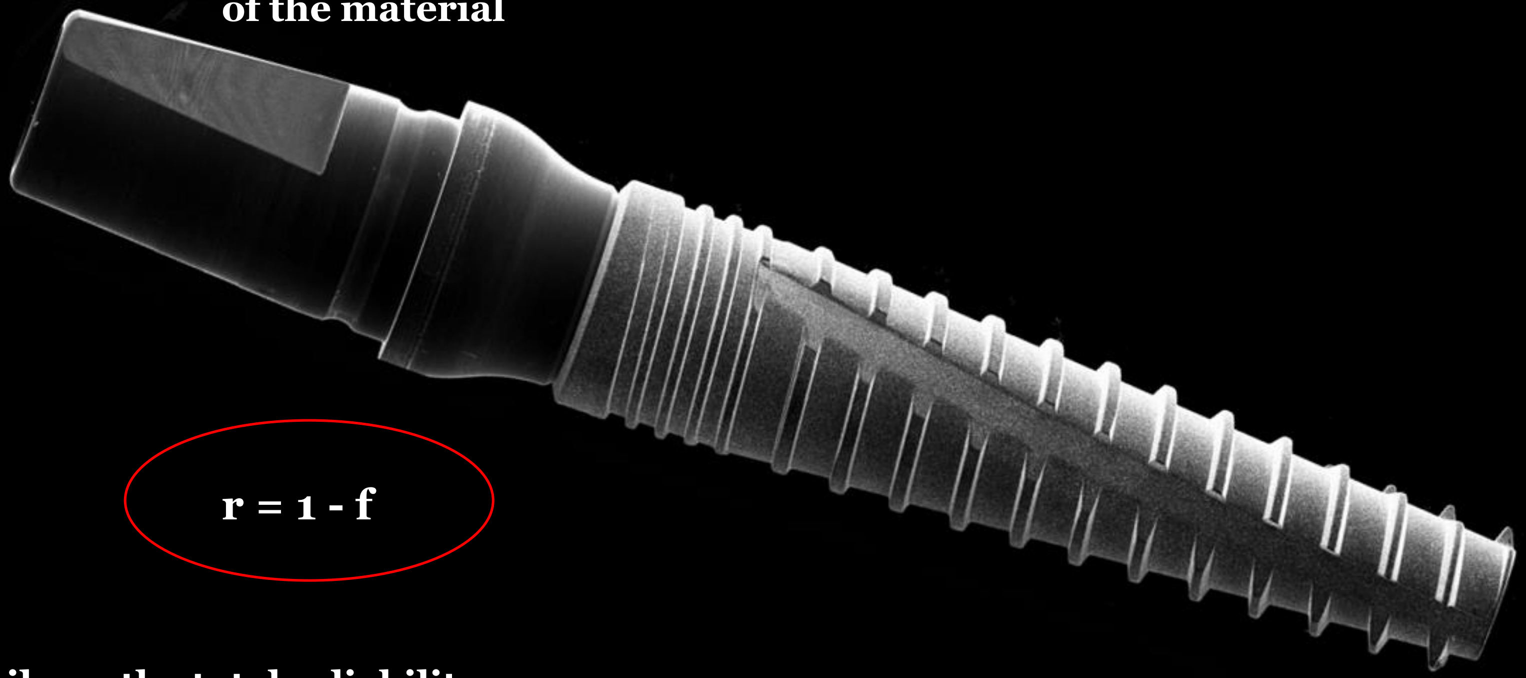
❖basic research highly applicable for industrial and biomedical use.

The successful biointegration of implants depends on:

- Bulk and surface characteristics
- Construction (design)
- Biocompatibility

of the material

- Applied surgical technique
- General health condition and life-quality of the patient



Reliability of a biomaterial:

$$r = 1 - f$$

f – probability of failure

Usually, there are multiple modes of failure, the total reliability:

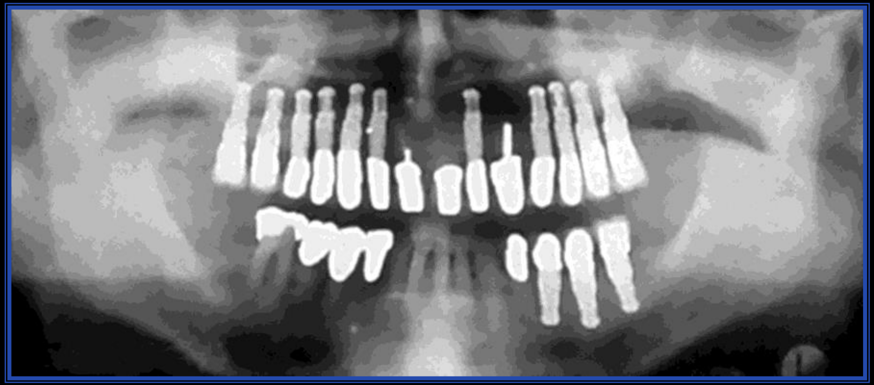
$$r_t = r_1 \cdot r_2 \cdot \ldots \cdot r_n \qquad \text{where} \qquad r_i = 1 - f_i$$

Biocompatibility in implantology

The main challenges in dentistry for centuries have been the development and selection of biocompatible prosthetic materials that can withstand the adverse conditions of the oral environment.

600 A.D.
Mayans used sea-shell segments for implant s

- Oral cavity represents environment with a wide range of circumstances:
  - Foods, abrasion, pH (3-9), temperatures from 5 to 55^{o}C, high magnitude masticatory forces, bacteria, etc.

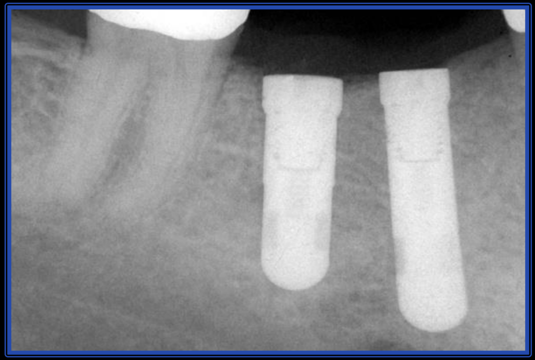


Osseointegrated implants replacing teeth

longer age, more people with missing teeth

up-to-date demand:
optimization of osseointegration

- reducing the 3-6 month healing period

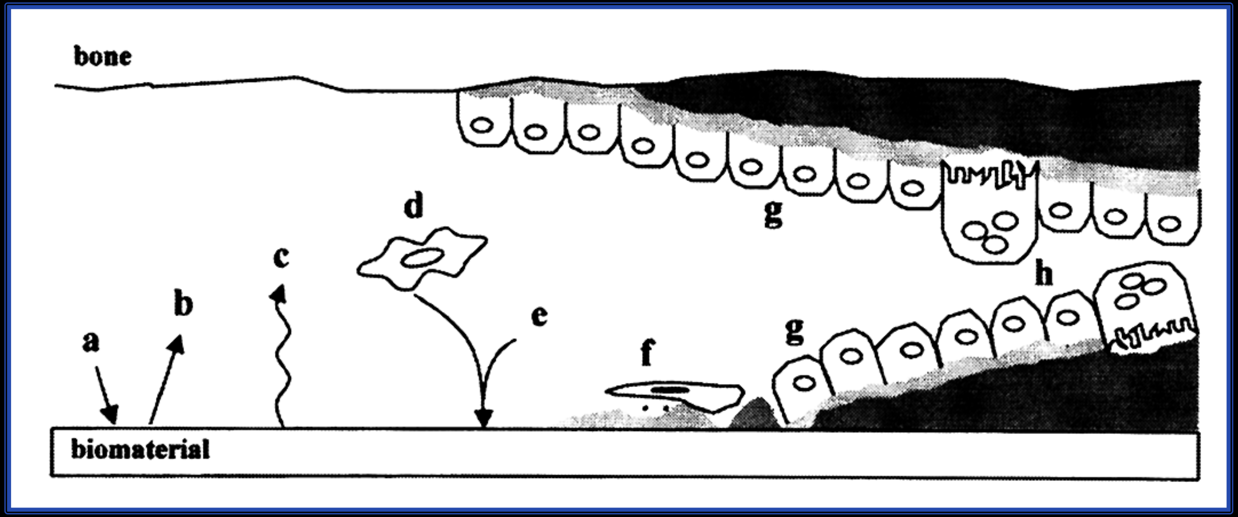


Favorable properties of titanium

- Light material (atomic weight: 47.88)
- Low density (4.43 g/cm^3 ; almost as strong as steel, but 45% lighter)
- Low heat conductivity (21.9 J/(m·s·K))
- Easy to fabricate
- Good radiographic image
- Exceptional corrosion resistance
- High degree of biocompatibility

Widely used as a medical implant material (biomaterial) for fixating or replacing hard tissue in dentistry, implantology, oral and maxillofacial surgery.

Osseointegration



~2 μm/day

Puleo & Nanci, Biomaterials,1999

a. Protein adsorption from blood and tissue-fluid

b. Conformational change and desorption of proteins, formation of a conditioning film.

c. Electrochemical modification of the implant surface and release of particles, ions (Ca, P).

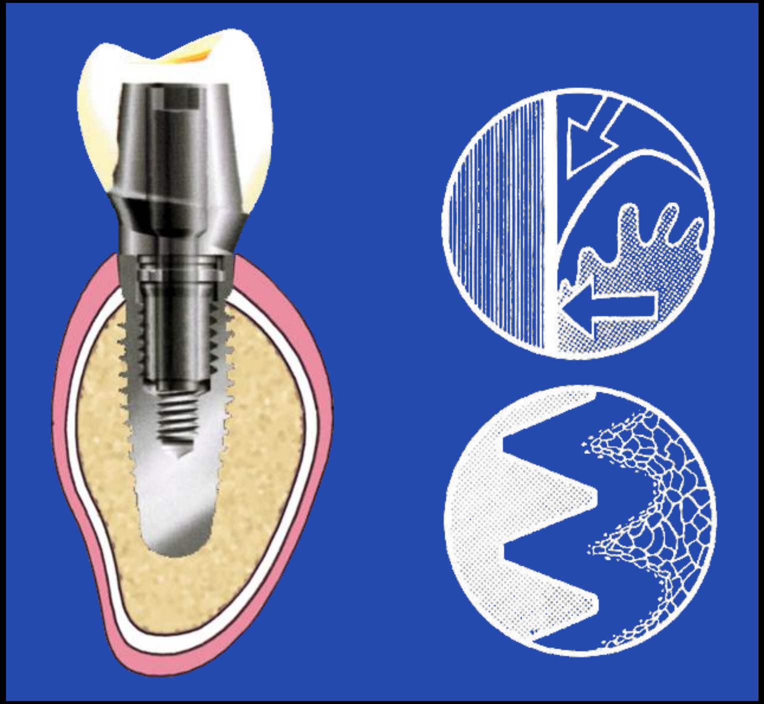
d. Inflammatory and connective tissue cells arrive to the surface.

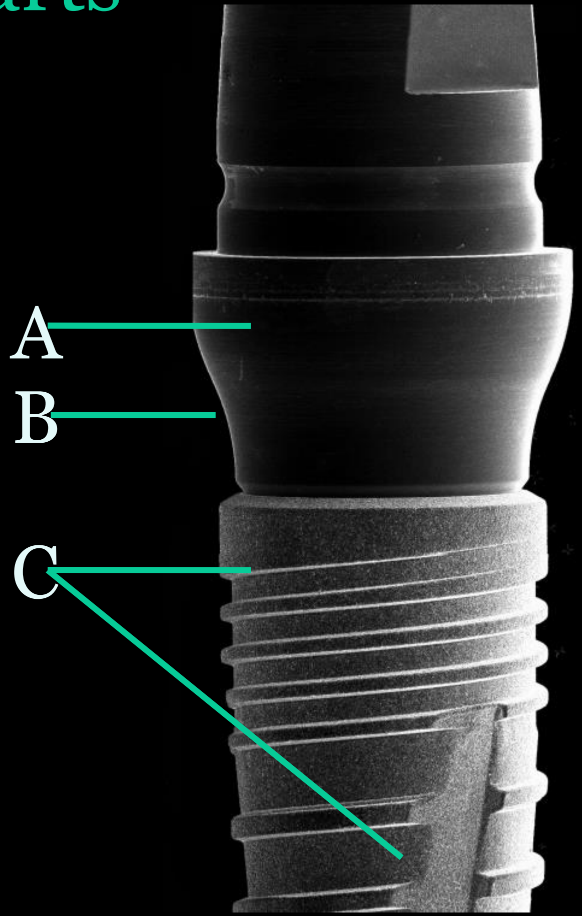
e. Release of matrix proteins, and selective adsorption of proteins.

f. Adhesion of osteogenic cells and formation of lamina limitans (afibrilar interfacial zone).

g, h. Formation of new bone.

Functionally three different parts



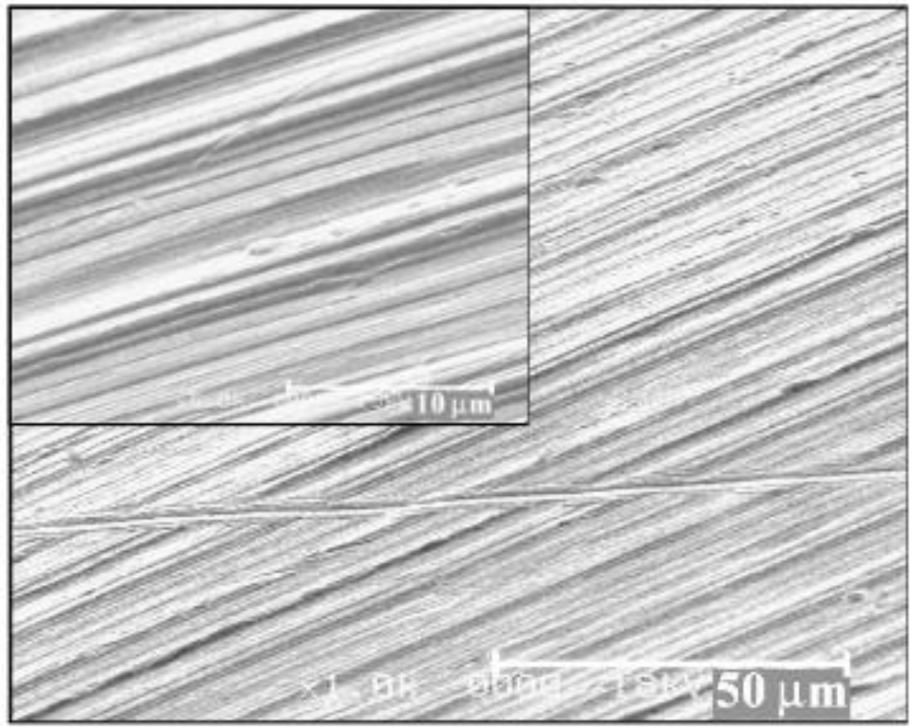


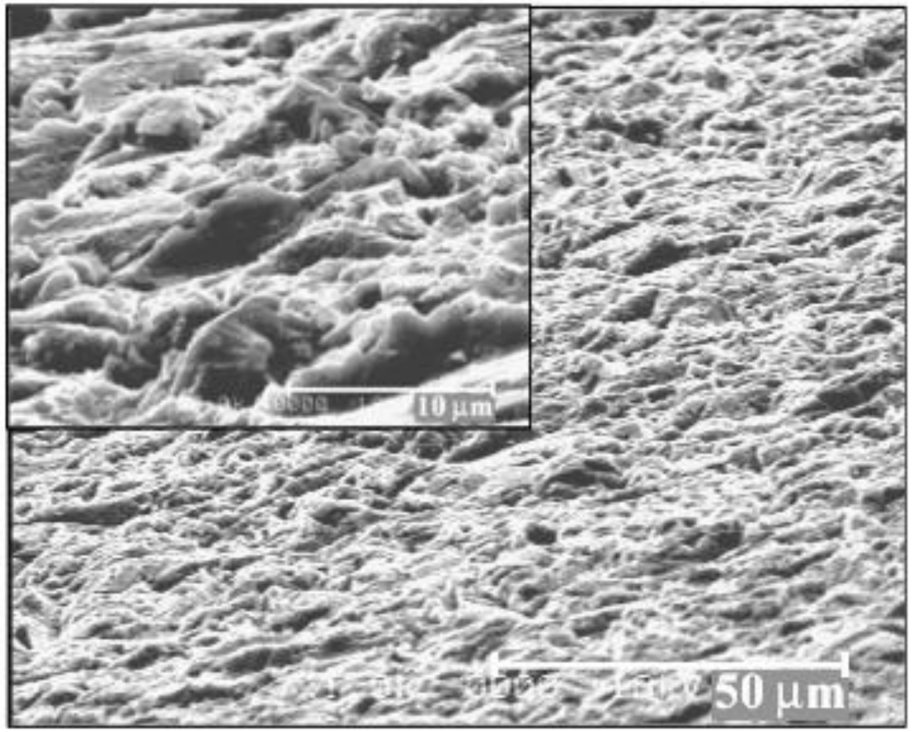
A - smooth surface for epithelial attachment and to prevent plaque formation

B - machined, oblique part for proper connective tissue attachment

C - rough surface, developed for anchorage in the bone

Machined and sand blasted titanium surfaces



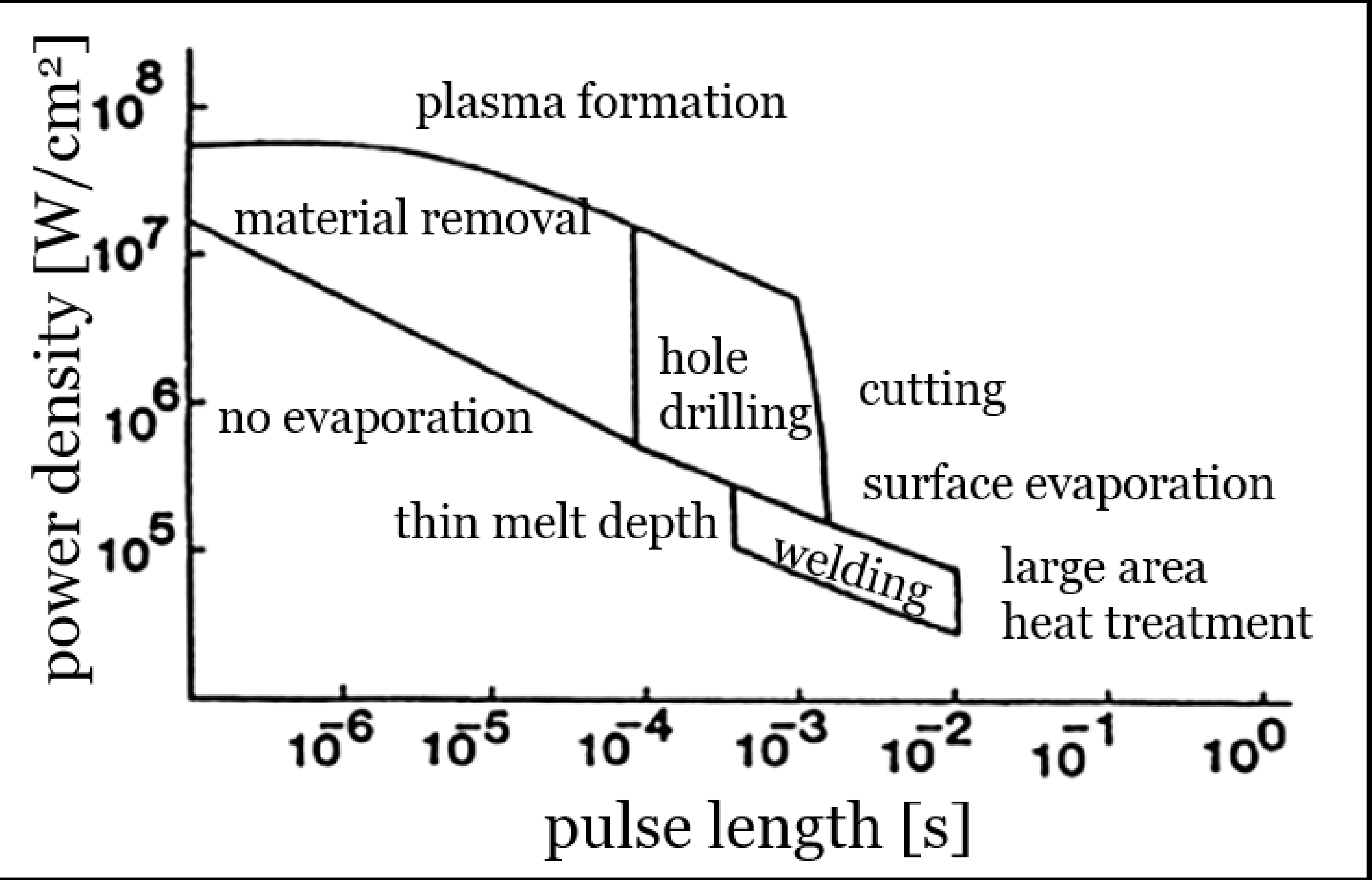


Physical-chemical methods

- **Chemical surface reactions** (e.g.: oxidation, acid-etching)
- **Sand blasting**
- **Ion implantation**
- **Pulsed laser deposition**
- **Coating the surface** (e.g. CaP)
- **Laser ablation**

Surfaces with modified roughness

Laser processing



1. Heat treatment: Condition near to melting point temperature. This is achieved with low power density (kW /cm ^{2}) and high pulse length (> 10^{-2} s).
2. Welding: Condition = molten material Melting without evaporation (power density> 10^5 W/cm^2 , pulse length ~ 10^{-3} s).
3. Cutting: Fast evaporation of material requires high power density (MW / cm ^{2}) with medium pulse length (μs).
4. Drilling: The rapid evaporation of the material requires high power density (10 MW/cm^2), due to the short pulse length (10^{-4} s) and shorter thermal diffusion length, the material does not melt around the hole.
5. Material removal (ablation): Process characteristic of 10-100 MW/cm^2 power density and <10^{-4} s pulse duration.
6. Plasma formation: above 10^8 W/cm^2, the material enters the plasma phase.

Advantages of laser modifications

- Lasers are used more and more for surface modifications (Bauerle, 2000;).
- These techniques must be further improved, since medical applications require high accuracy in both mechanical and chemical characteristics.

- Advantages:
  - Precision in the wavelength of the light
  - Wide range of wavelength
  - High energy density ranges
  - Focusing or widening the light beam
  - Possibility of pulse mode and adjustment of FWHM
  - Advantage of excimer laser treatment compared to the others: the ultraviolet (UV) wavelength range has a sterilizing effect (*Bereznai et al.*, 2003).

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Surface modifications induced by ns and sub-ps excimer laser pulses on titanium implant material

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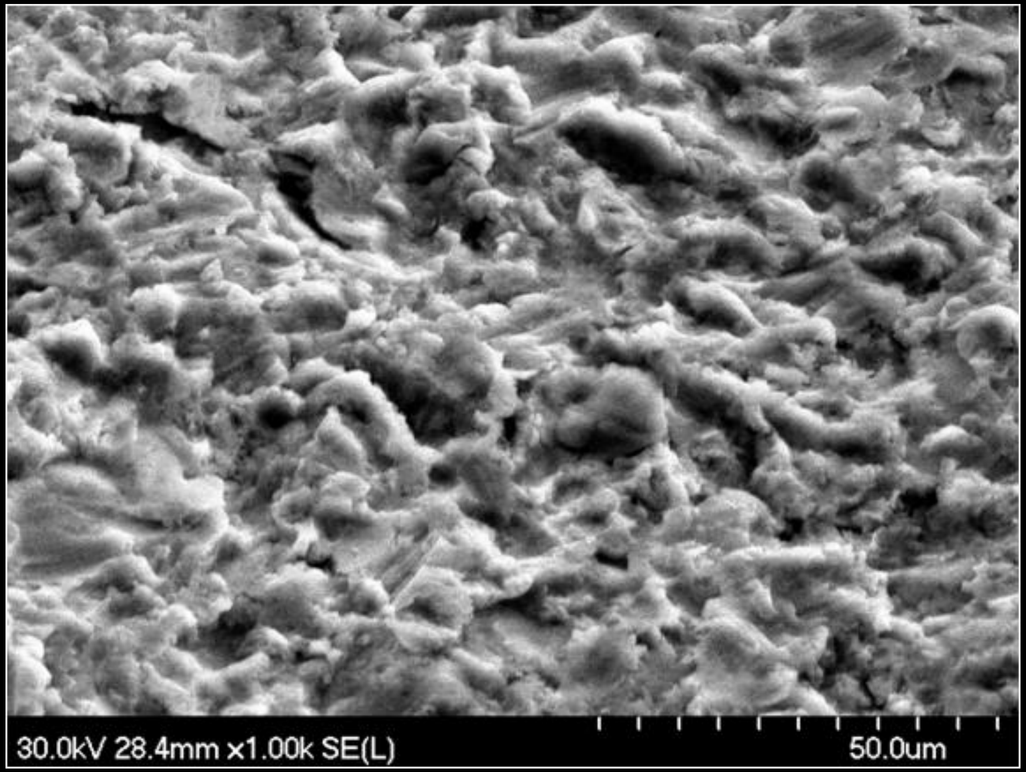
Abstract

Medical implants used in oral and orthopaedic surgery are mainly produced from titanium. Their biological behaviour, e.g. osseointegration, essentially depends on both the chemical composition and the morphology of the surface. Modifications achieved by excimer laser irradiation of titanium samples were investigated in order to improve their surface characteristics so as to facilitate biointegration. To enlarge the effective interfacial area of bone–implant contact, holes were ablated by laser pulses of ns or sub-ps length. During ns ablation, crown-like projecting rims formed around the borders of the holes. Ultra-short (0.5 ps) KrF excimer

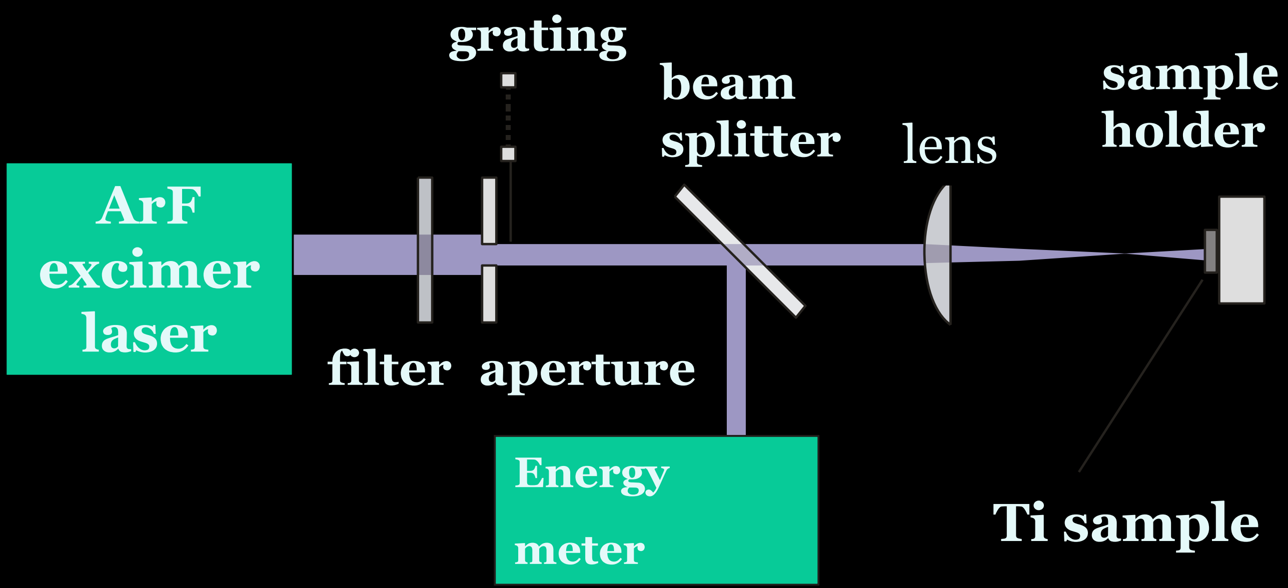
Importance of surface roughness

- Osseointegration is enhanced on rough, micro structured surfaces, as the contact area will be larger.
- Mechanical (morphological) fixation will help the bone ingrowth.



Excimer laser surface modification: polishing and ablation

Laser (Lambda Physics EMG 201):

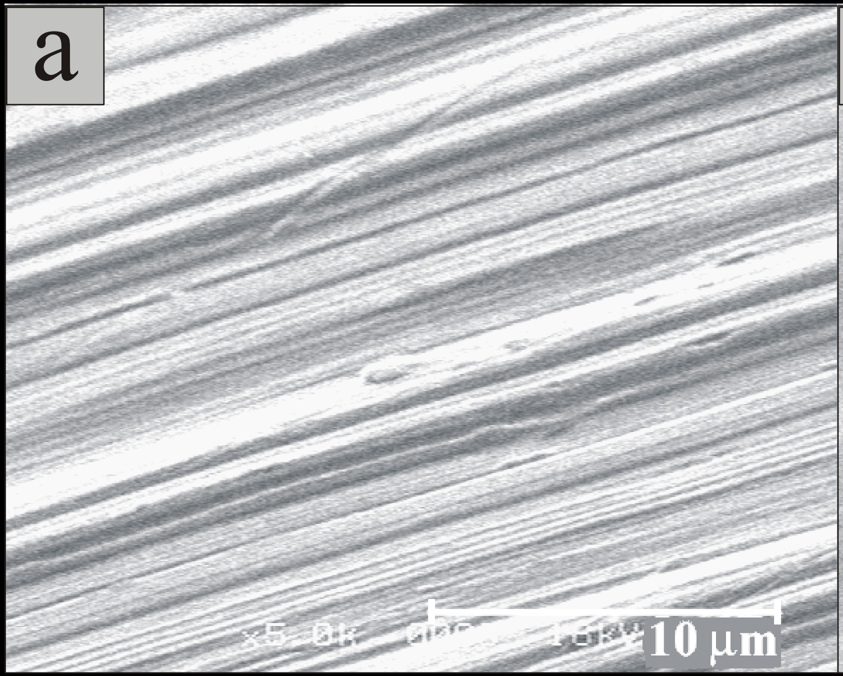


Laser:

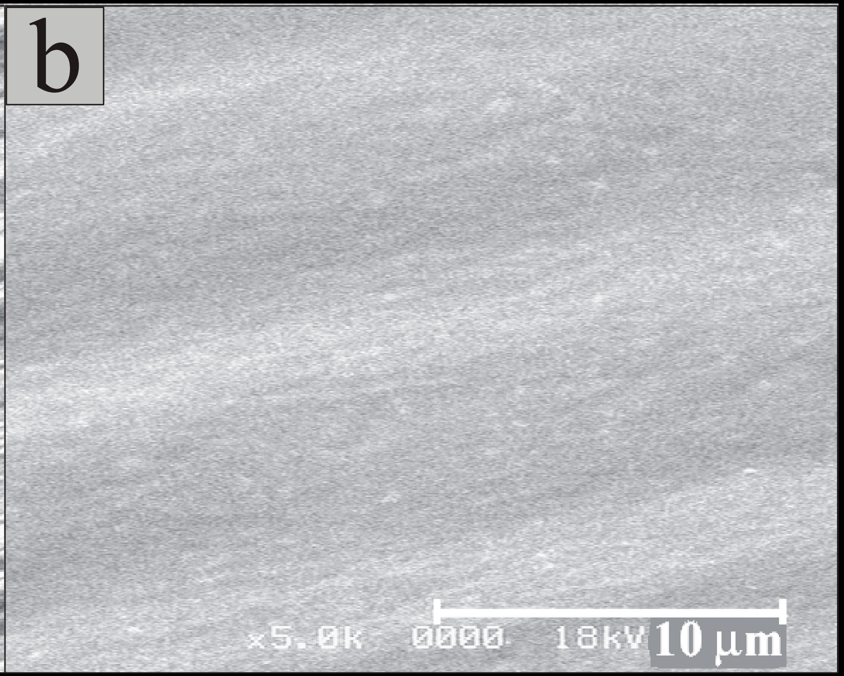
wavelength 193 nm (UV)
pulse duration: 18 ns
pulse energy: 100 mJ

Sample: CP grade 1 Ti-disc
8 mm Ø, 1.25 mm thick

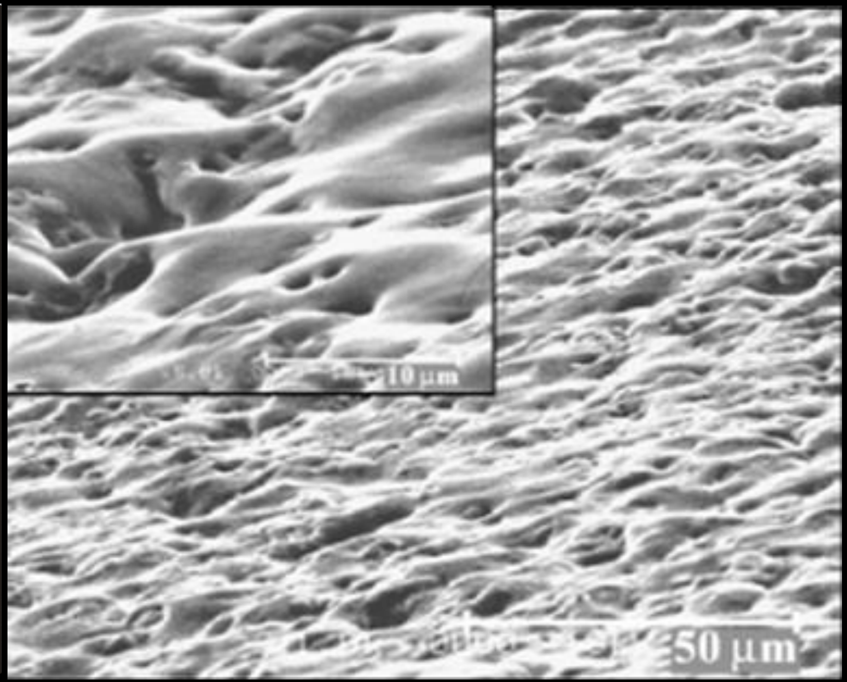
SEM image of laser polished Ti disc



Machined



Laser-polished

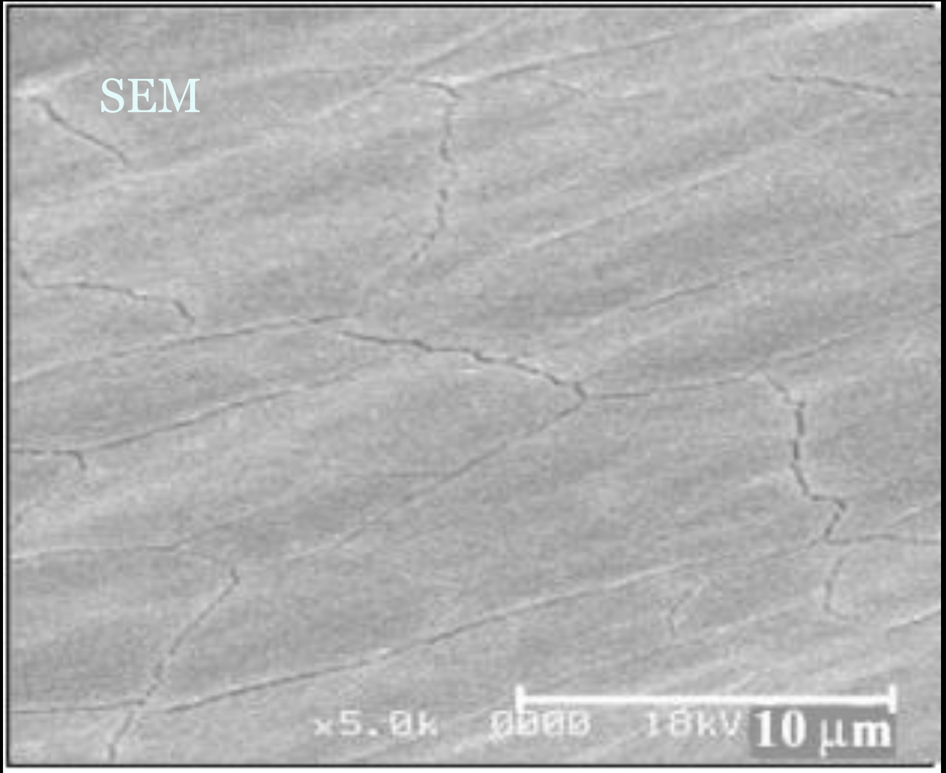


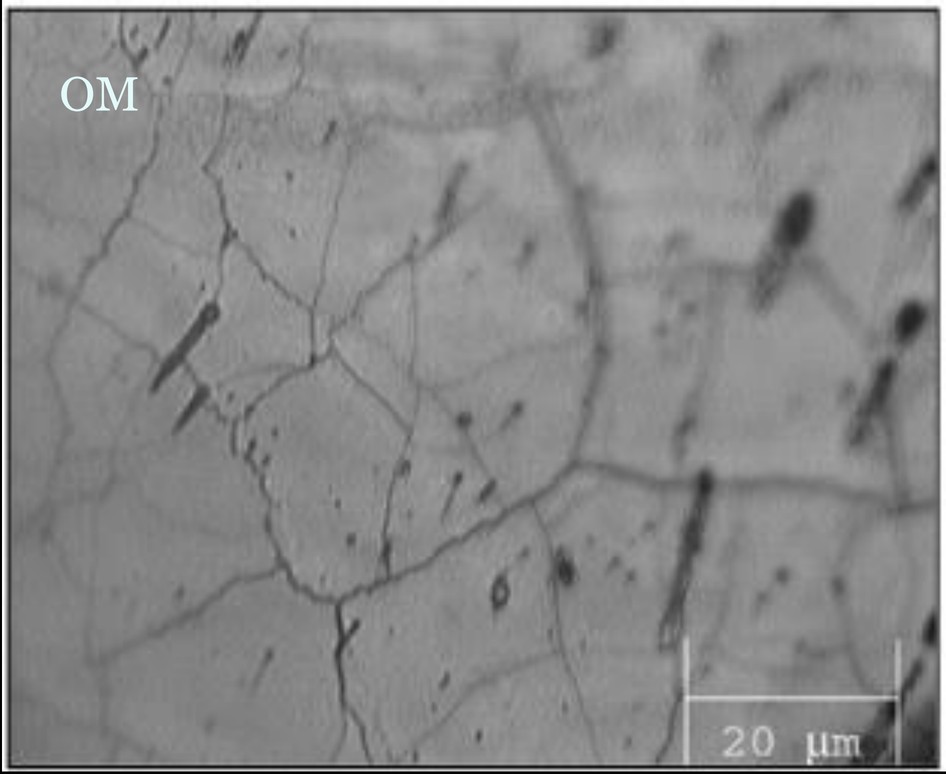
Sand blasted and laser-polished

5 laser pulses, 3.5 J/cm² incident fluence

Result: Ti sample with R_a < 1 mm can be effectively polished by homogenous 3-5 J/cm^2 fluence laser.

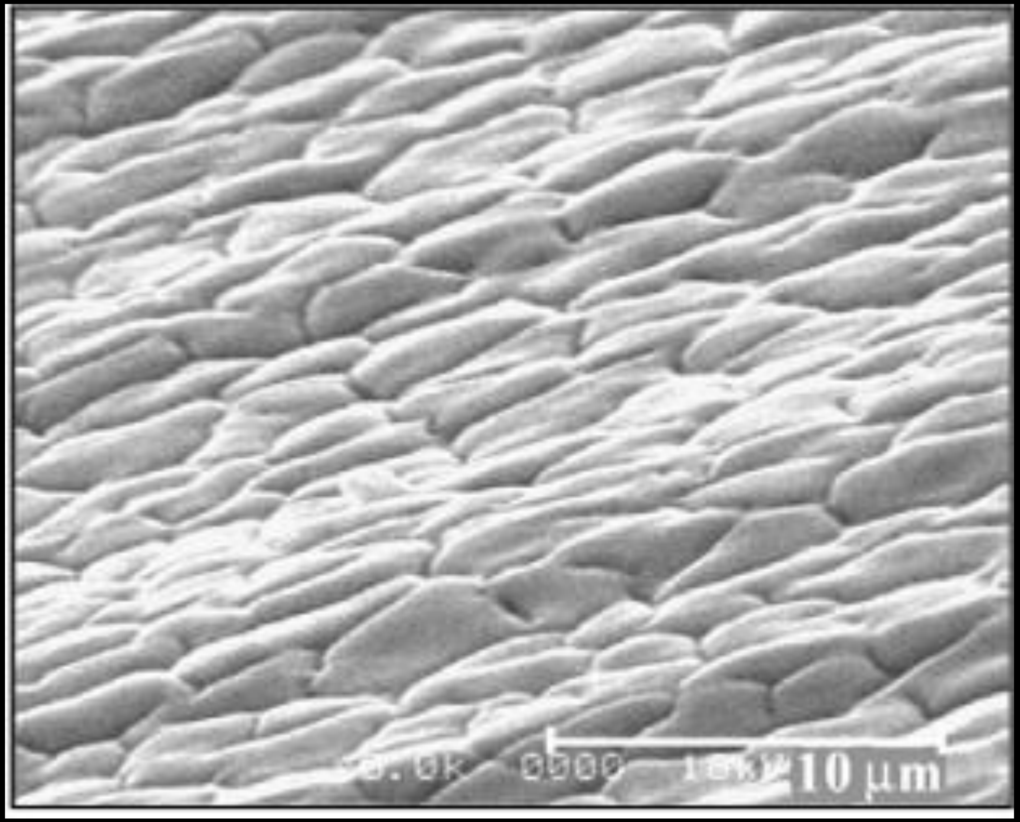
More pulses: crack formations



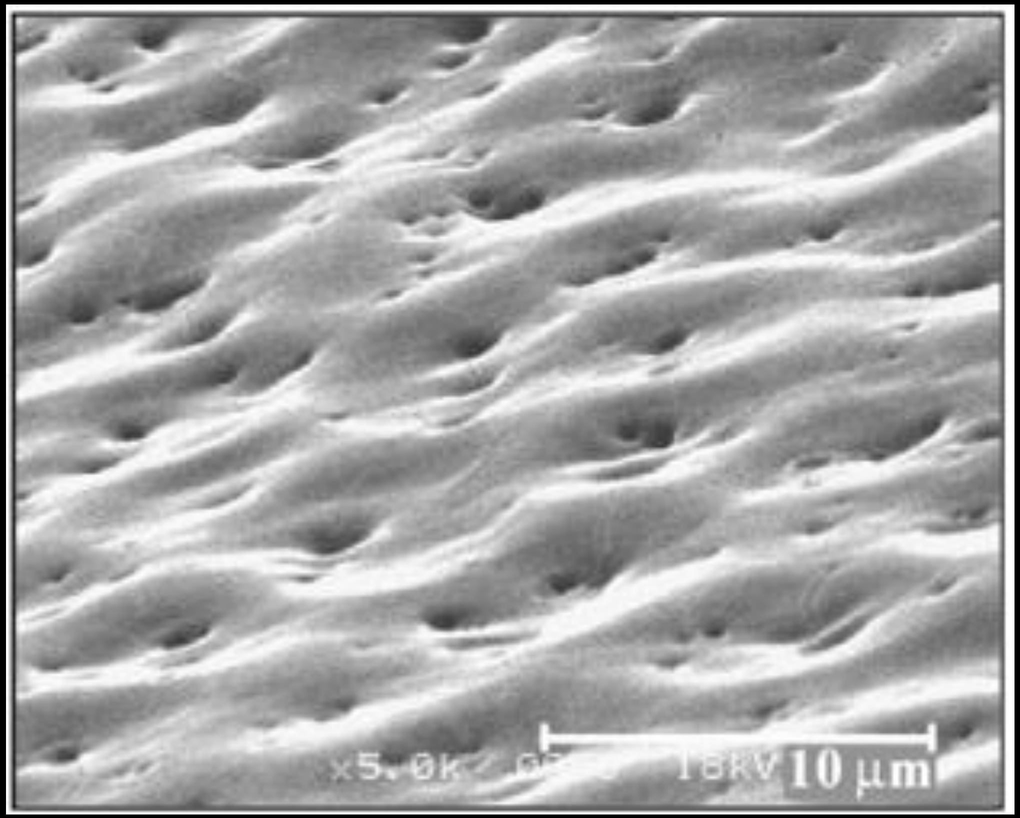


10 laser pulses, 3.5 J/cm² incident fluence

even more laser pulses...

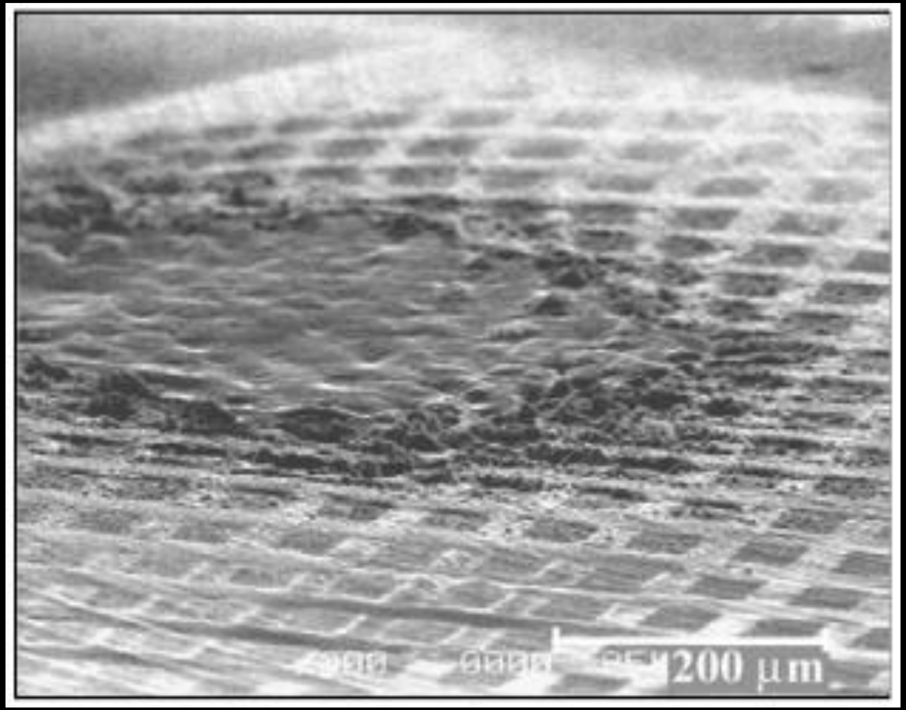


100 laser pulses, 1.6 J/cm² incident fluence

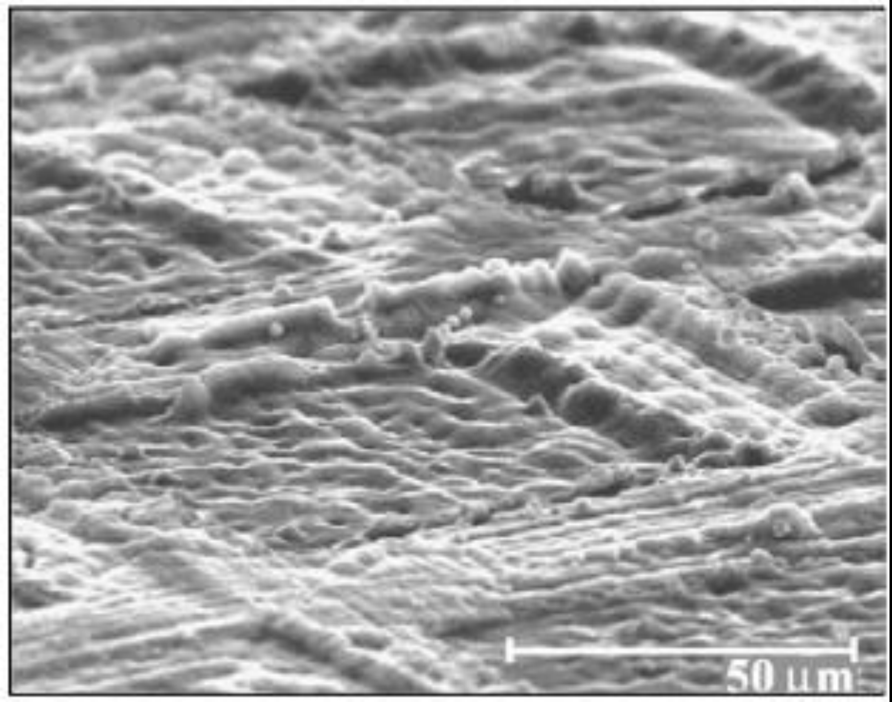


1000 laser pulses, 1.33 J/cm² incident fluence

Contact mask patterning

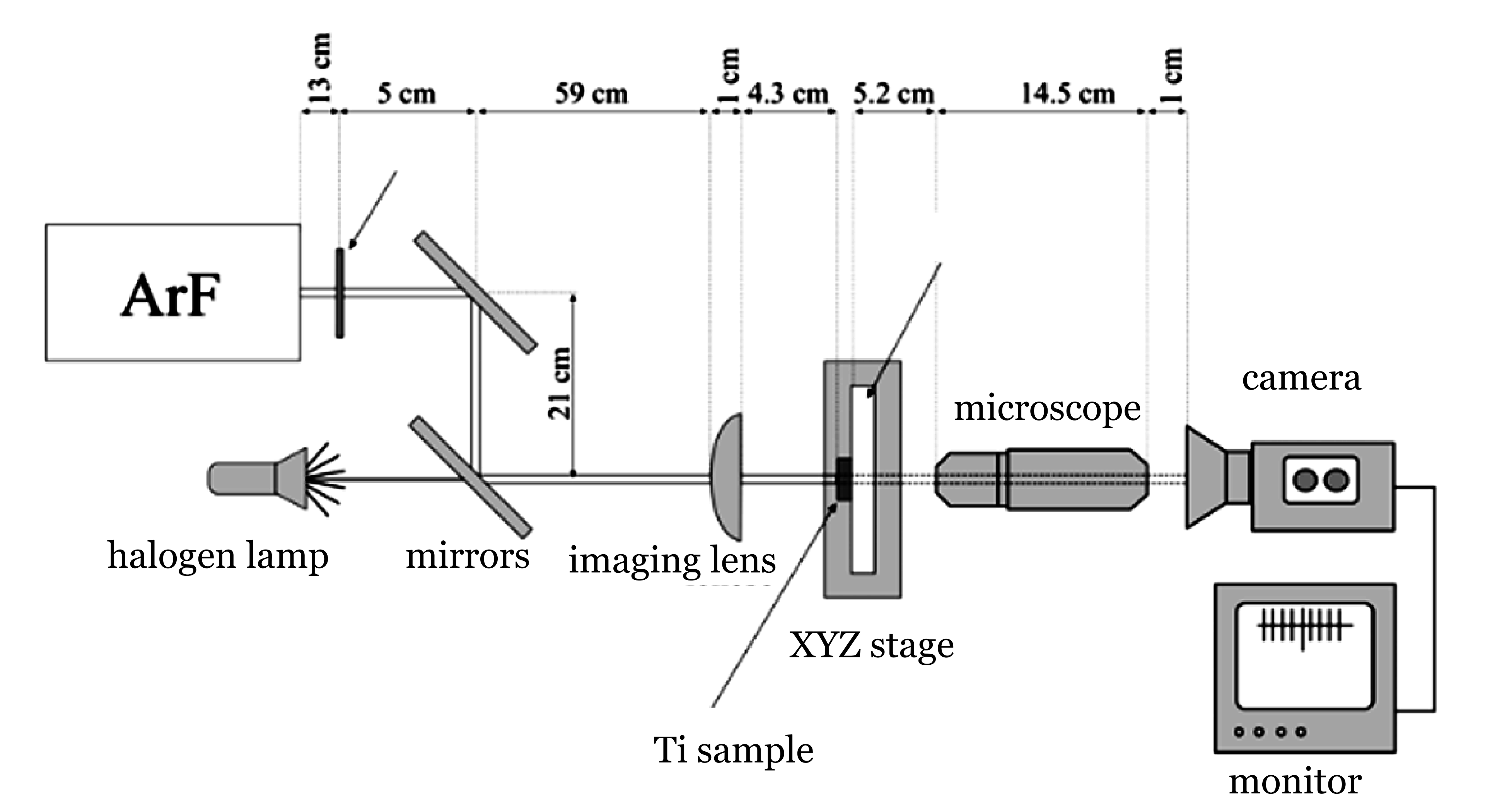


1000 laser pulses, 0.8 J/cm² incident fluence

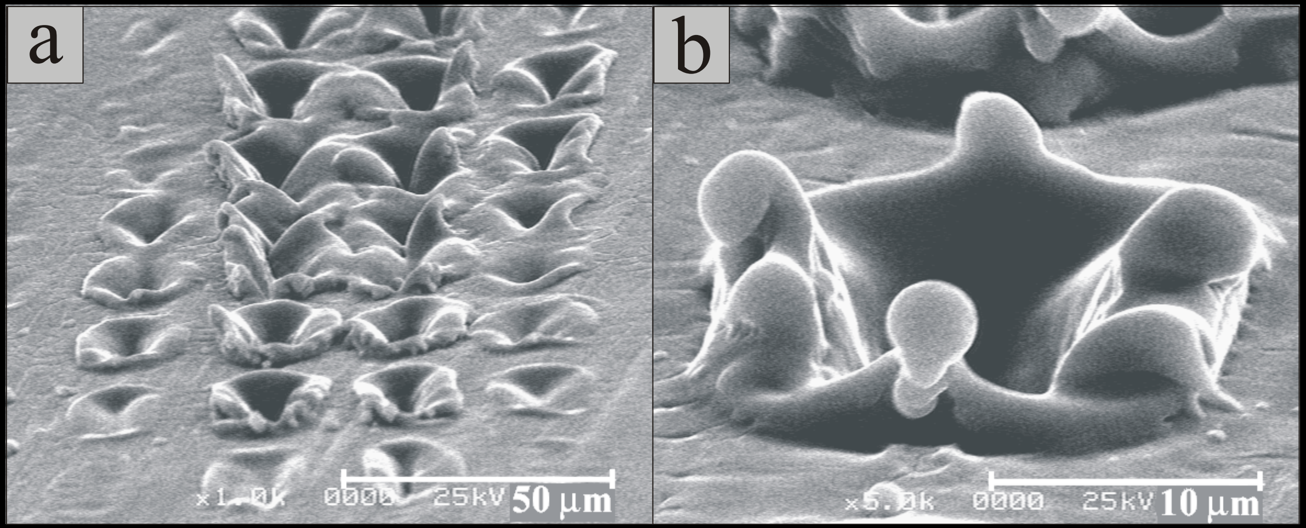


1000 laser pulses, 0.5 J/cm² incident fluence

18 ns ArF- laser ablated Ti surface



SEM images of 18 ns ArF- laser ablated Ti surface



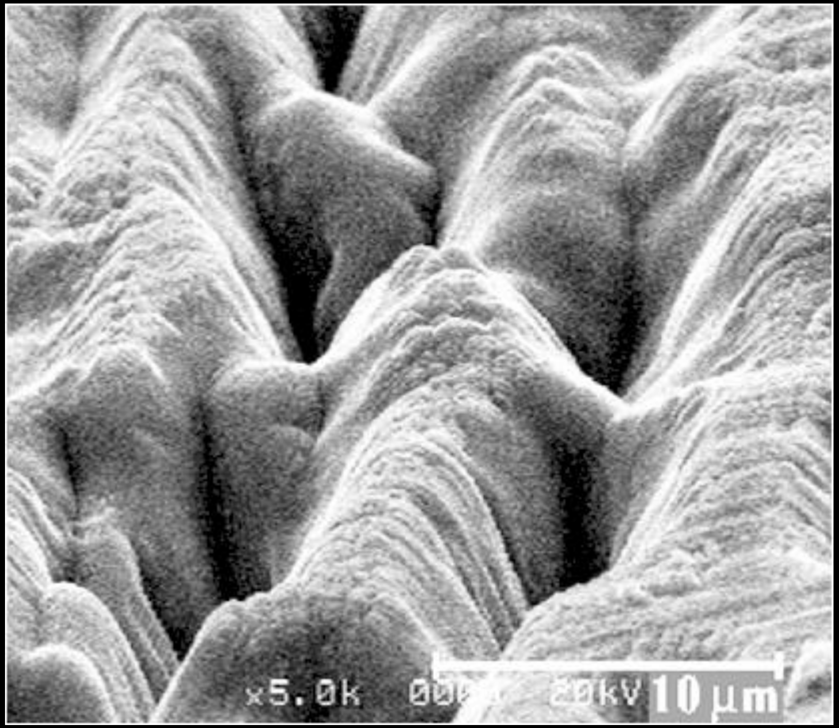
1000 x magnification

5000 x magnification

250 laser pulses, 8.5 J/cm^2 incident fluence

Result: Enlarged contact area, holes of about 20x10 µm, but fragile rims were formed around the holes (due to extensive evaporation and melting, plasma is formed). Inconvenient effect, as the rims may break away from the surface.

SEM image of the surface modifications induced by 0.5 ps KrF excimer laser pulses

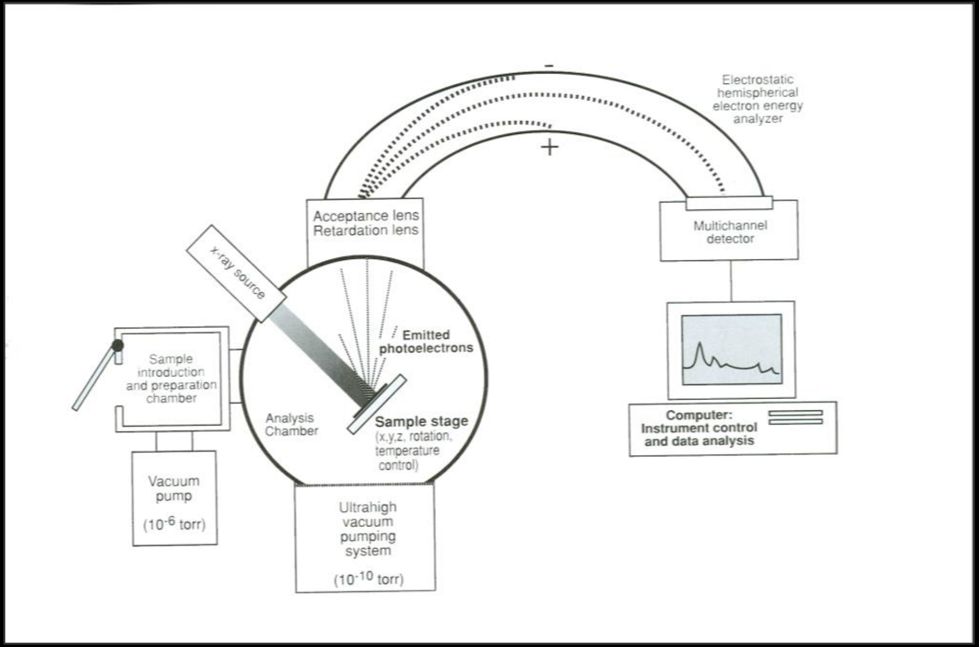


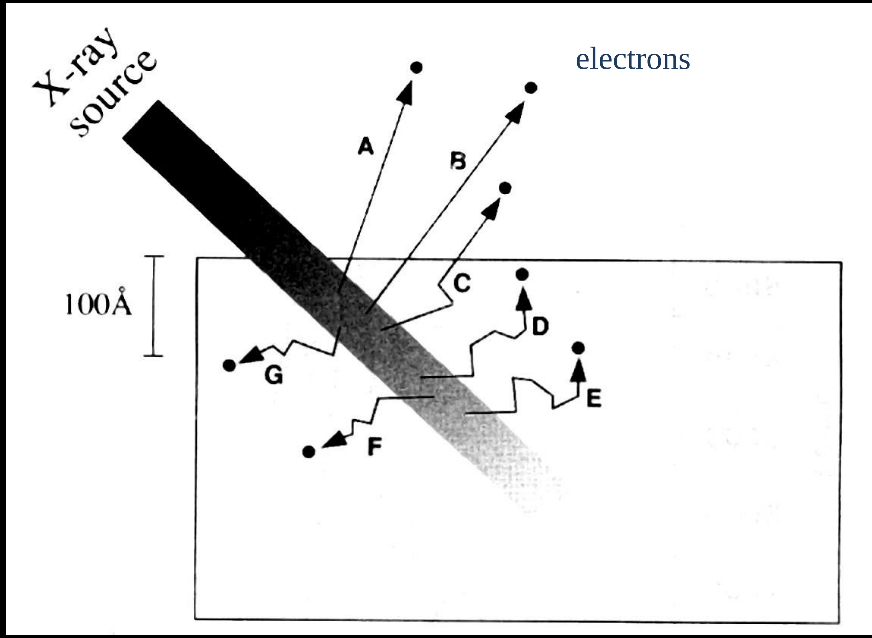
Results:

- Enlarged contact area
- Cleaner surface (XPS, XRD)
- Increased thickness of TiO_2

Laser ablation with KrF excimer laser (λ = 193 nm), pulse duration: 0.5 ps, 5000 x magnification, 1000 laser pulses, 2.4 J/cm² incident fluence.

X-ray photoelectron spectroscopy (XPS or ESCA)

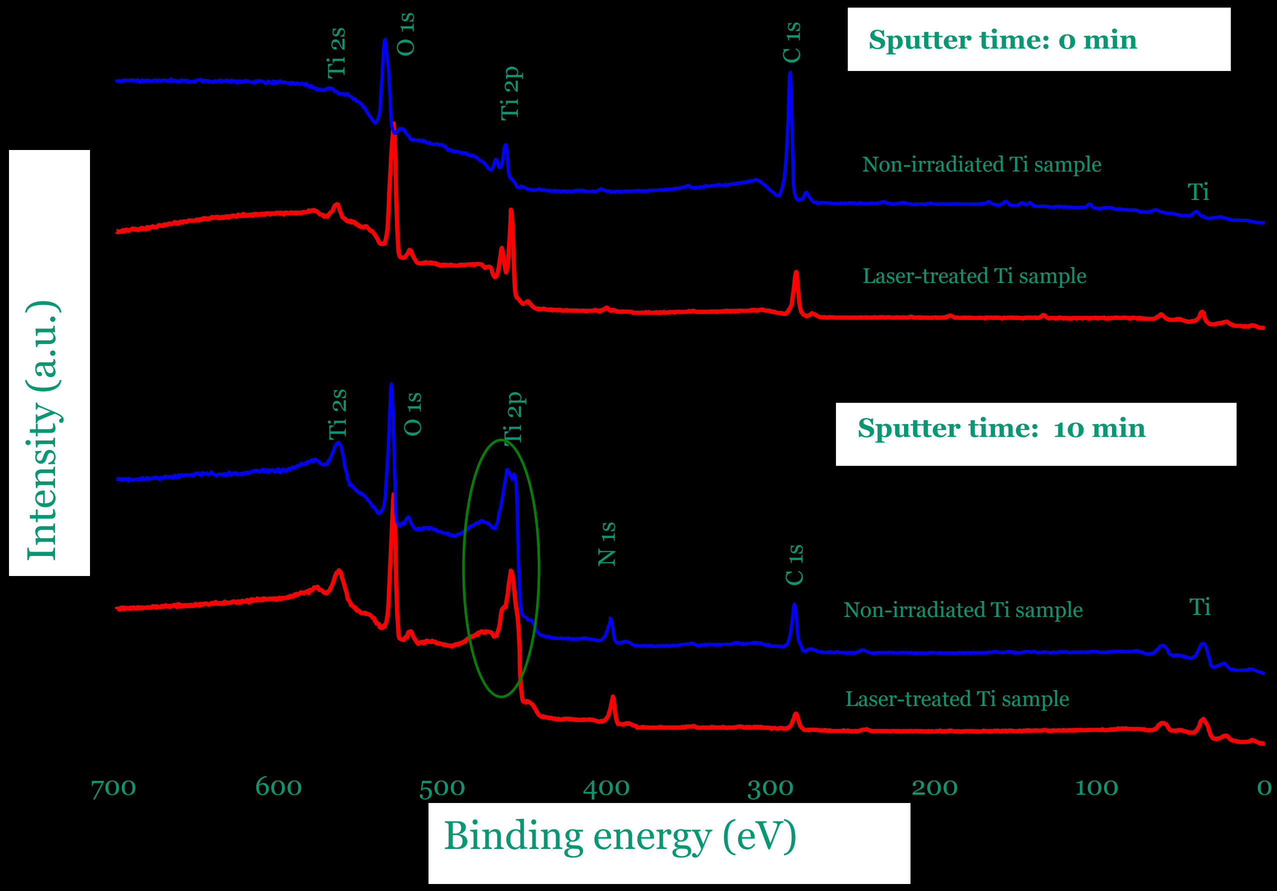




Ar$^+$ bombardment:

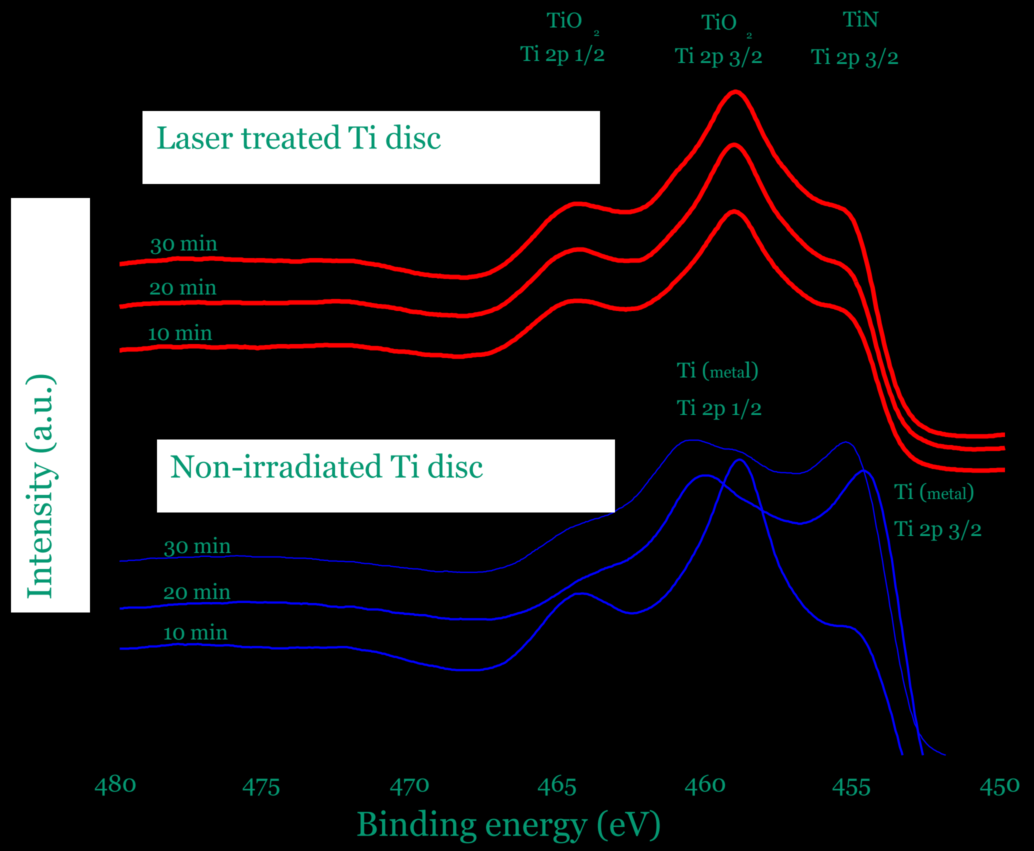
~ 10 nm of material was removed in 10 min.

X-ray photoelectron spectroscopy (ESCA) survey spectra of non-irradiated and ArF laser polished Ti discs



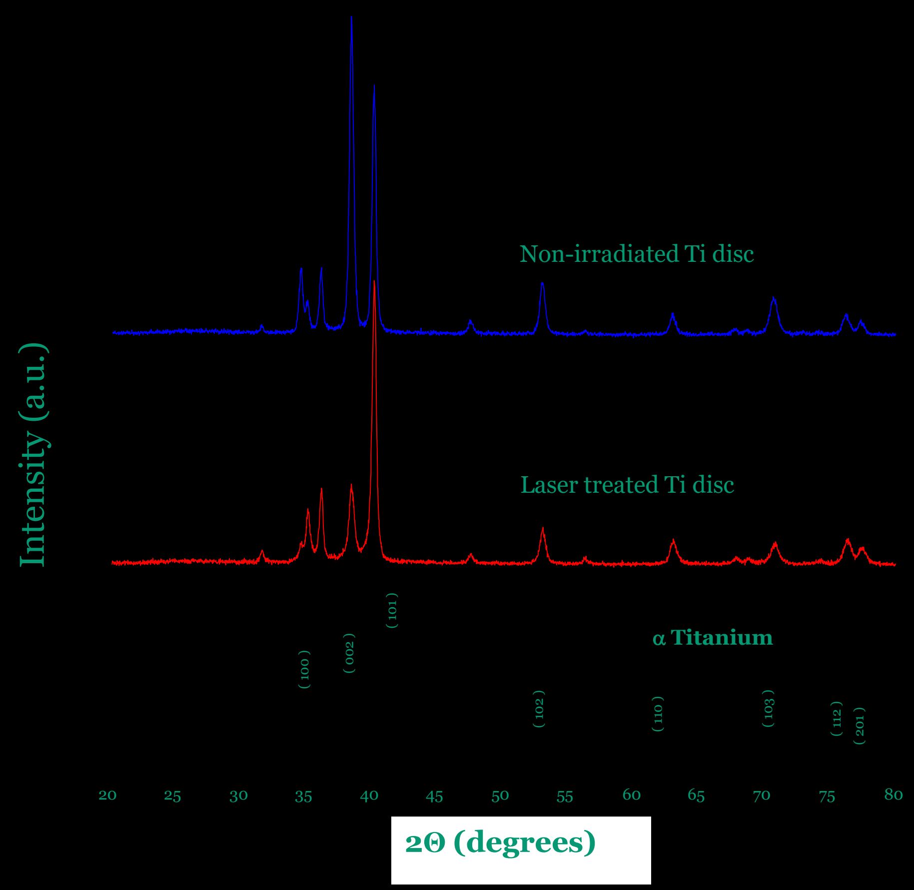
The laser cleans the surface and …

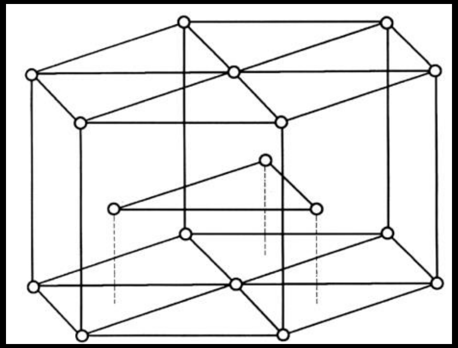
High-resolution XPS spectra of non-irradiated and ArF laser-treated titanium samples



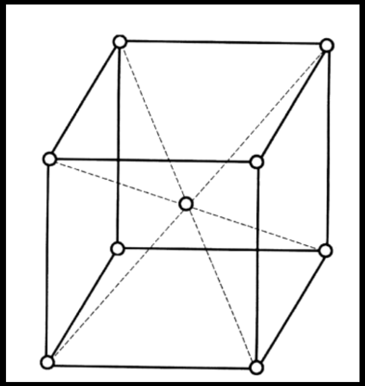
increased the thickness of the TiO_2 layer.

X-ray diffraction spectra of non-irradiated and irradiated Ti samples





α - Hexagonally Closed Packed



β (Body Centered Cubic), above 1158 K

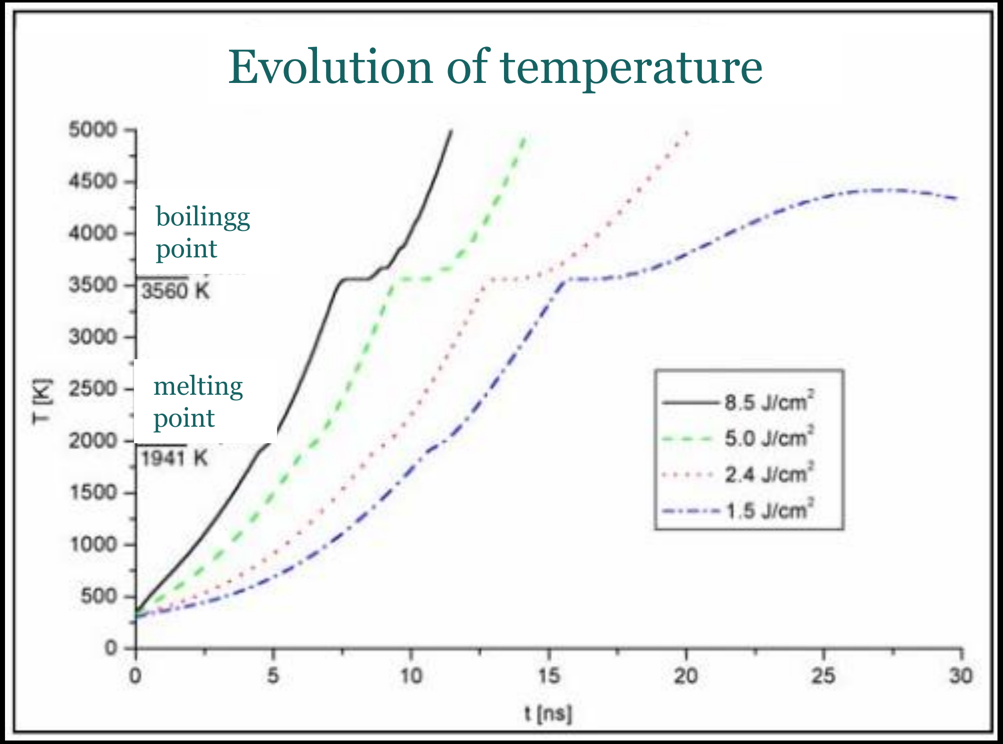
The original crystalline structure is preserved.

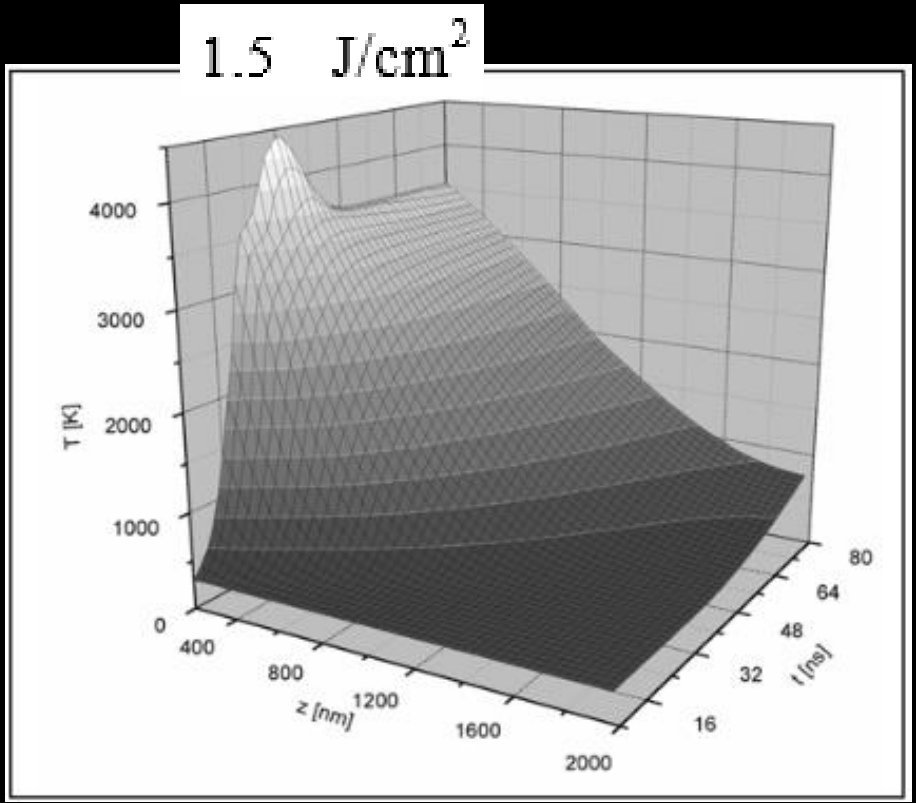
Understanding the processes requires solution of thermal diffusion

$$\frac{\kappa(T)}{D(T)} \cdot \frac{\partial T}{\partial t} = \nabla[\kappa(T) \cdot \nabla T] + Q,$$

$$\frac{\partial T}{\partial t} = \frac{1}{\rho(T) \cdot c(T)} \cdot \frac{\partial}{\partial z}\left[\kappa(T) \cdot \frac{\partial T}{\partial z}\right] + \frac{Q}{\rho(T) \cdot c(T)}$$

$$\frac{\kappa(T)}{D(T)} = \rho(T) \cdot c(T)$$





Implant surface development 2019

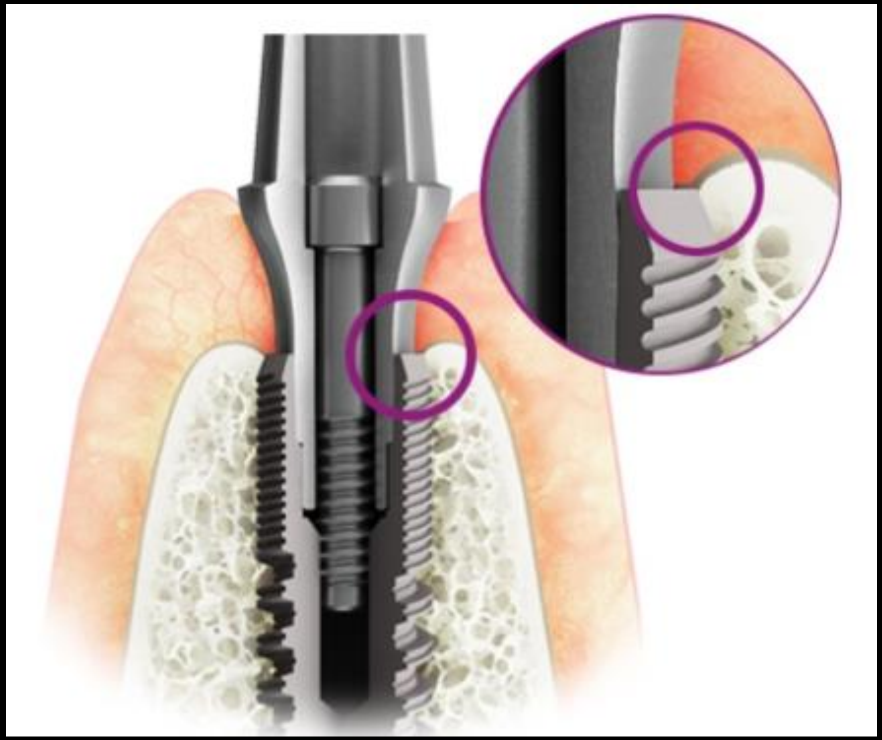
Antibacterial surface development

- Periimplantitis

PROTECTION AGAINST BACTERIAL COLONIZATION

- **macrostructure**
- **microstructure**
- **surface chemical composition**

→ **biological environment**



Hypothesis

The antibacterial effect of silver as an alloy is also present, if formed on the surface of titanium discs, thereby inhibiting the pathological effect of bacteria in the oral cavity.

The surface modification reduces the adhesion and proliferation of bacteria.

Scientific background

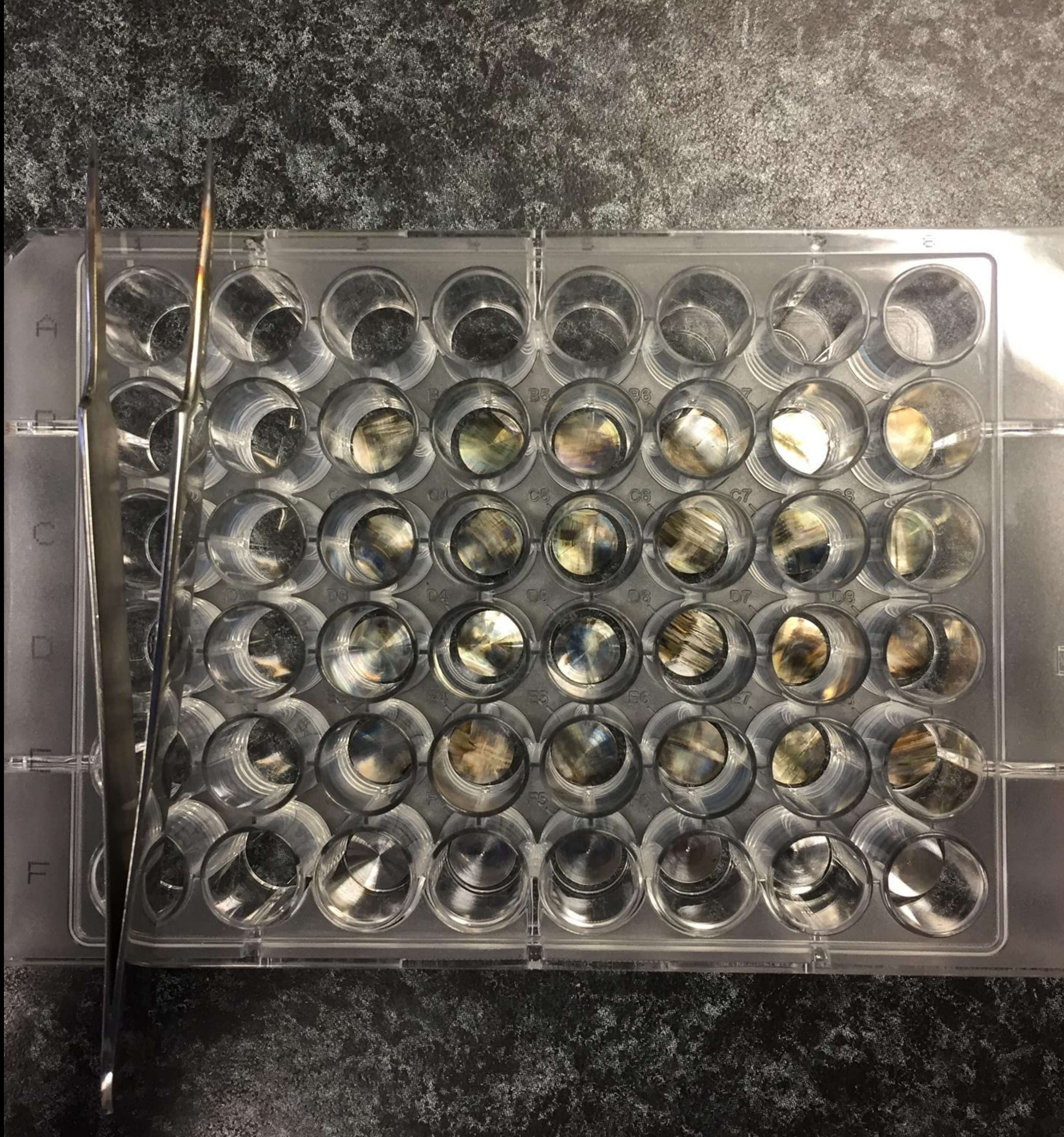
- Surface Treatment Procedures: Plasma Spraying, Sandblasting, Acidification, Anodizing, or Combination
- Antibacterial surface changes: surfaces treated with antibiotics, organic and inorganic antimicrobials (2)
- Silver surface modifications (3): ion implantation, plasma electrolyte oxidation, in situ synthesis of silver nanoparticles, ion exchange, sol-gel coatings, magnetic cathode sputtering

2. Zhao L, Chu PK, Zhang Y, Wu Z. Antibacterial coatings on titanium implants. J Biomed Mater Res B Appl Biomater. 2009 Oct;91(1):470–80.
3. Duraccio D, Mussano F, Faga MG. Biomaterials for dental implants: current and future trends. J Mater Sci. 2015 Jul 1;50(14):4779–812.

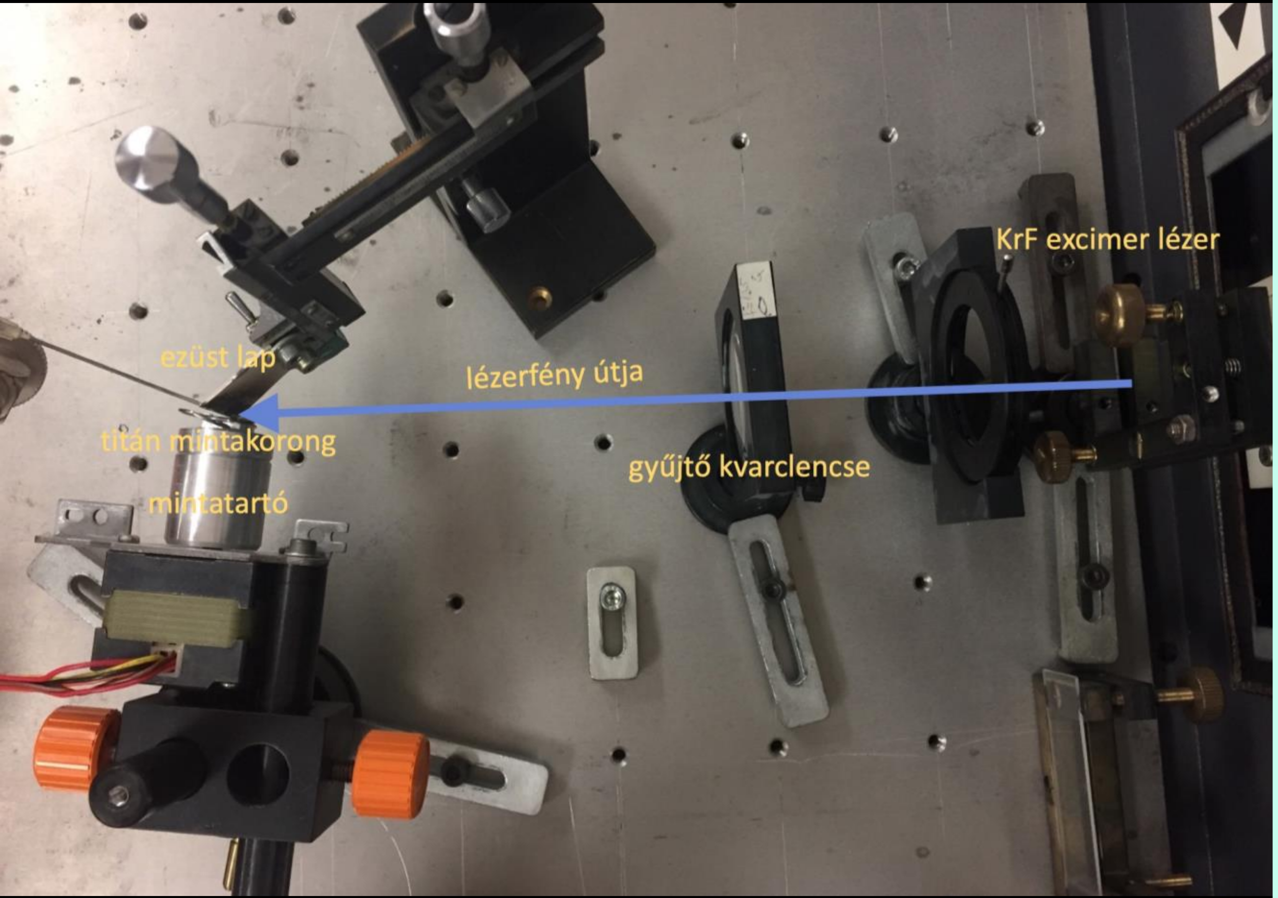
Materials and methods

Sample preparation

- 84 CP5/ Grade 5 ELI titanium discs
  - 1. setup: 24 pieces 9 mm diameter discs
  - 2. setup: 20 pieces 9 mm diameter and 40 pieces 8 mm diameter discs
- high purity (99.999%) silver sheet
- KrF pulse lase
- quartz lenses
  - 1. setup focusin lens
  - 2. setup cylindric lens

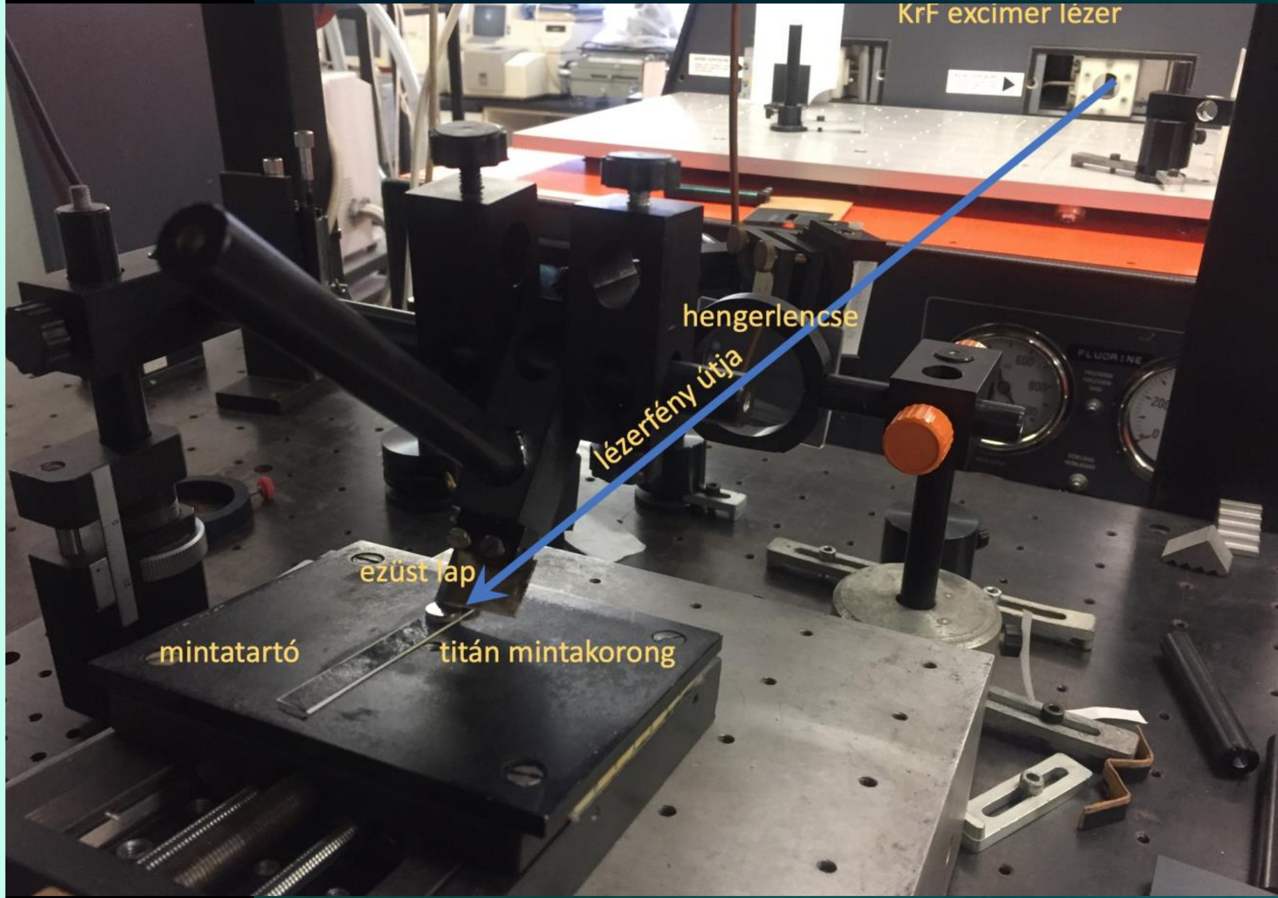


1. setup



samples made with point plasma source

2. setup



samples made with a line-like plasma source

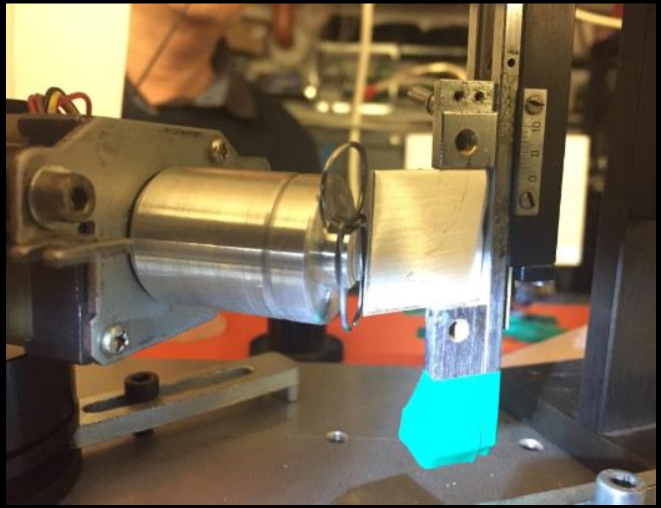
Examination of the physical and biological properties of the created surface

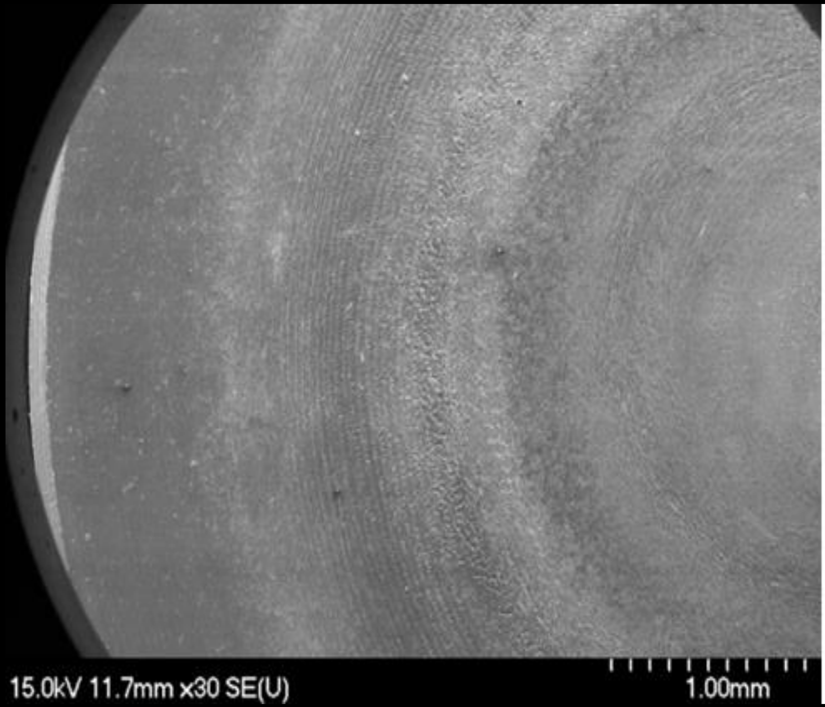
Biological properties

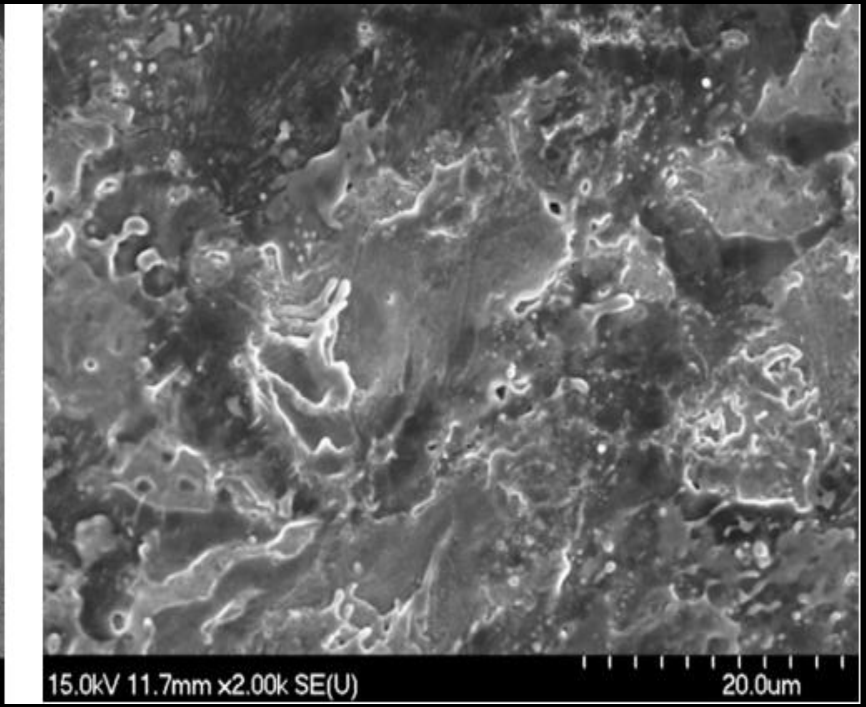
- Bacteriological tests
- Procedure 1: Str. Salivarius, 16 treated and 8 control 9 mm diameter disc discs
- Method 2: Str. Salivarius and S. aureus, 24 treated and 12 untreated (control) 8 mm diameter disc discsSejtkultúrás vizsgálatok (2. eljárás)
  - 20 pieces of silver treated and 20 pieces of 9 mm diameter disc disc
  - primary human osteoblast cells
  - MTT and LDH tests

Results

Results - SEM images and EDS results from point-source plasma samples

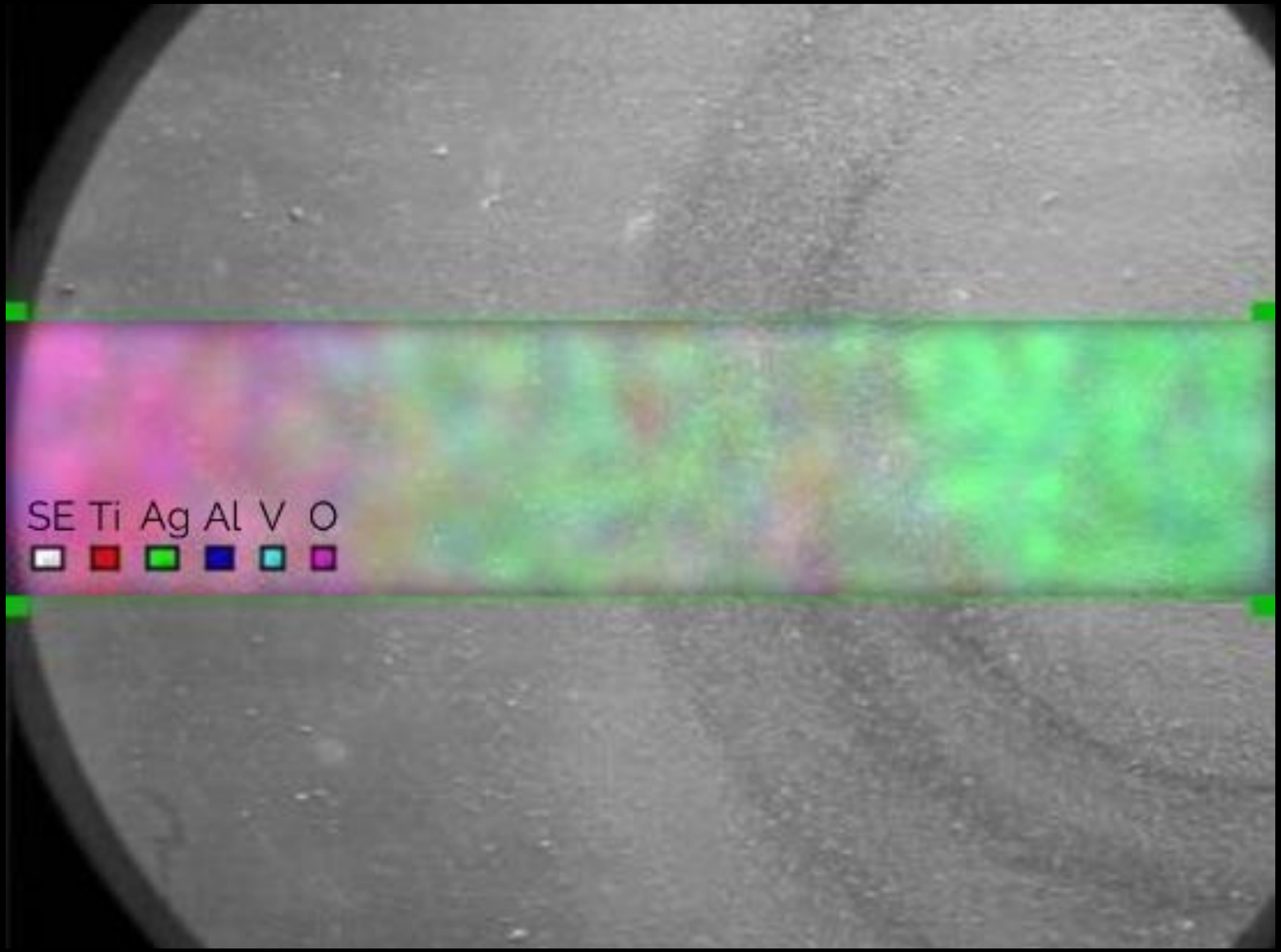




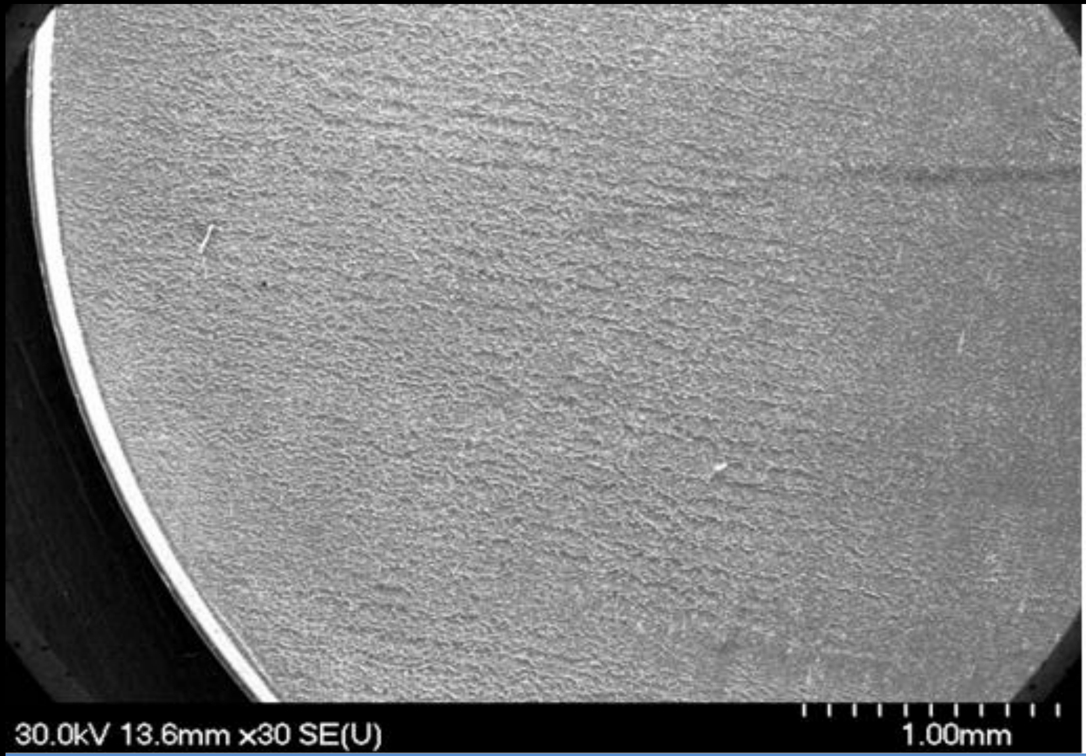


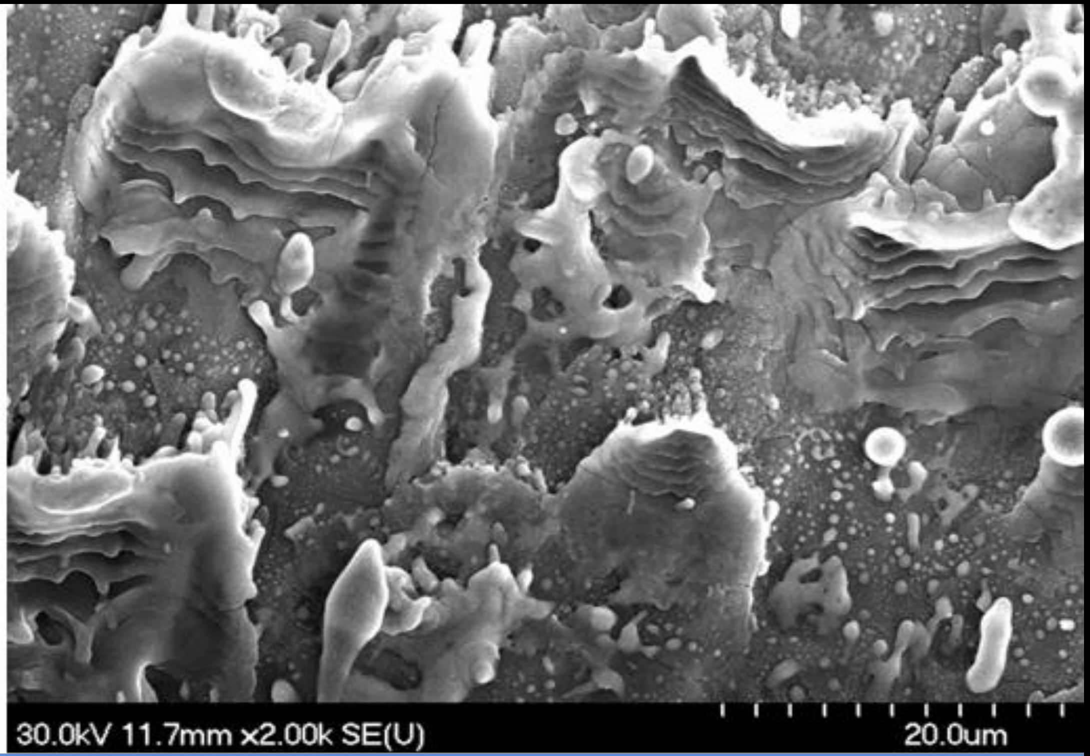
Element	line	norm. wt. %	at. %	Error [%]
Aluminum	K	1,767775	4,802247	0,426597
Titanium	K	32,096	49,13388	2,737788
Vanadium	K	1,480361	2,130003	0,867217
Silver	L	64,65586	**43,93387**	5,269454

- Elemental analysis, X-ray map



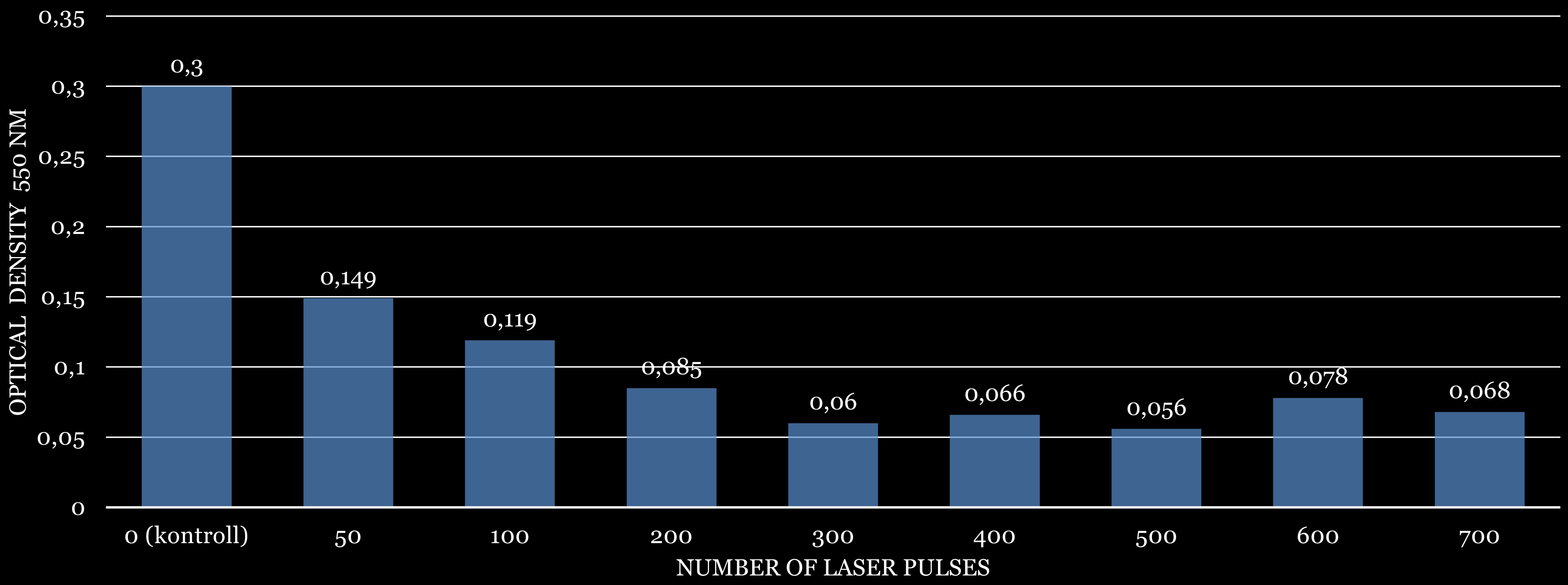
Results - SEM images and EDS results were made by line-like plasma source





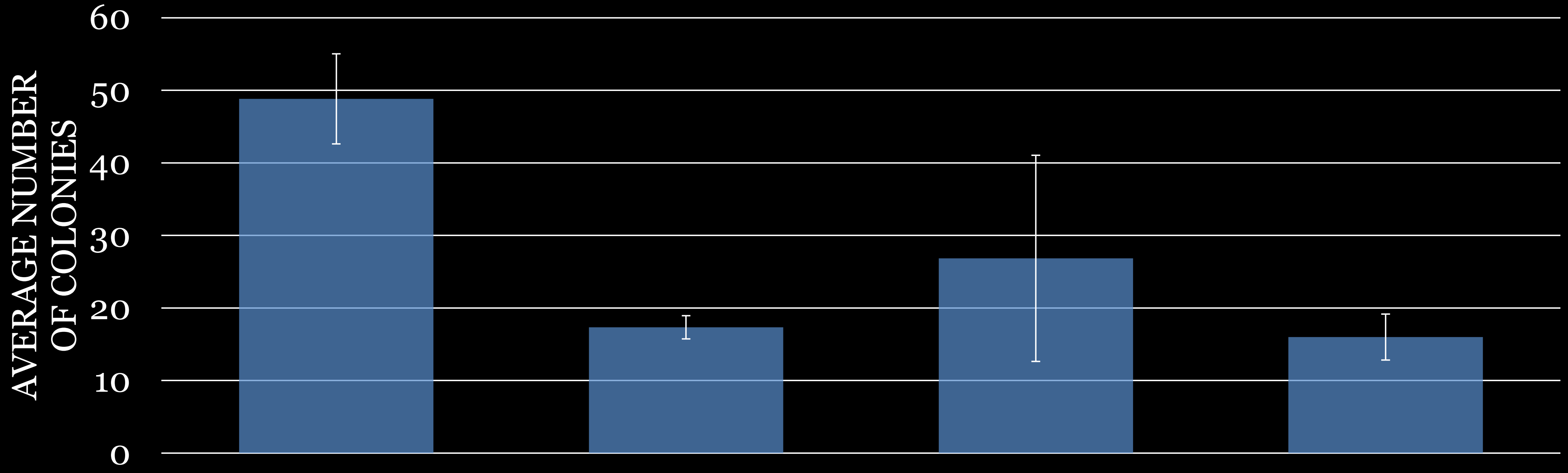
Element	line	norm. wt. %	at. %	Error [%]
Aluminum	K	2,888053786	5,772061	0,173580538
Titanium	K	70,07548717	78,92314	2,023407641
Vanadium	K	3,201897897	3,389441	0,211917606
Silver	L	23,83456115	**11,91535**	0,81977926

Results – bacteriological examinations point source deposition



The concentration of bacteria measured by the number of laser pulses.

Results – bacteriological examinations line deposition

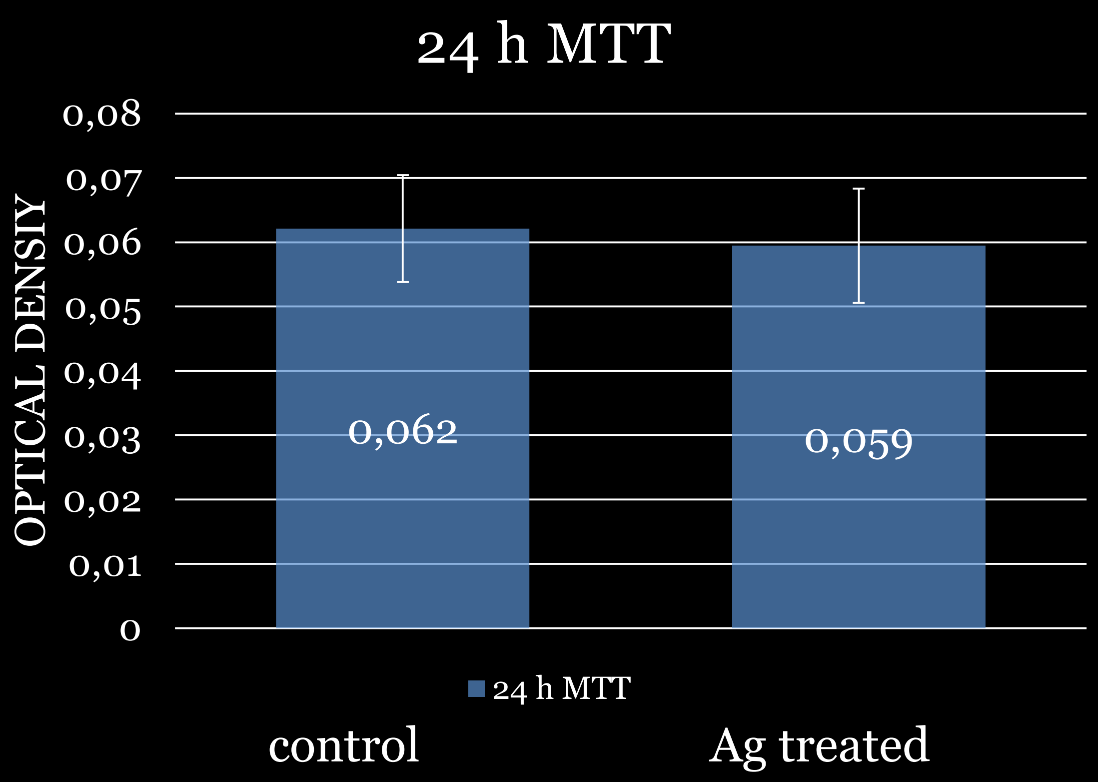


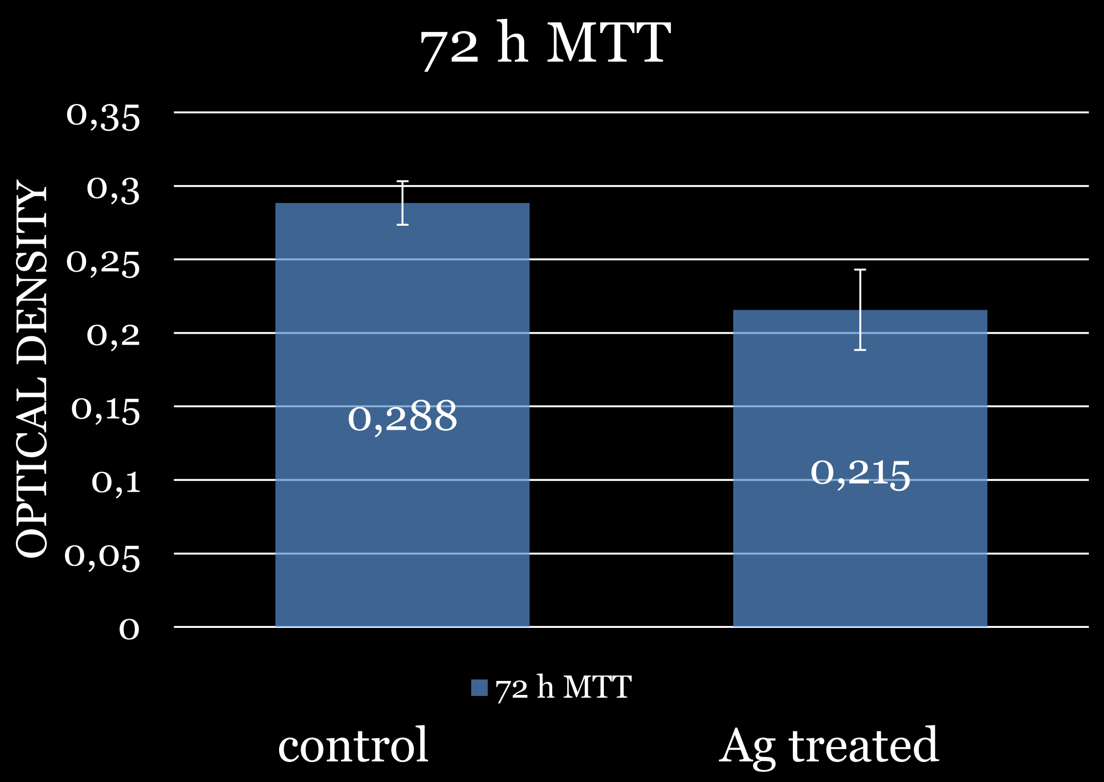
	S. aureus control	S. aureus treated	Str. Salivarius control	Str. Salivarius treated
Average	48,83	17,33	26,83	16,00
SD	15,23	4,77	34,80	10,50
deviation from average	6,22	1,59	14,21	3,17

Results - bacteriological tests

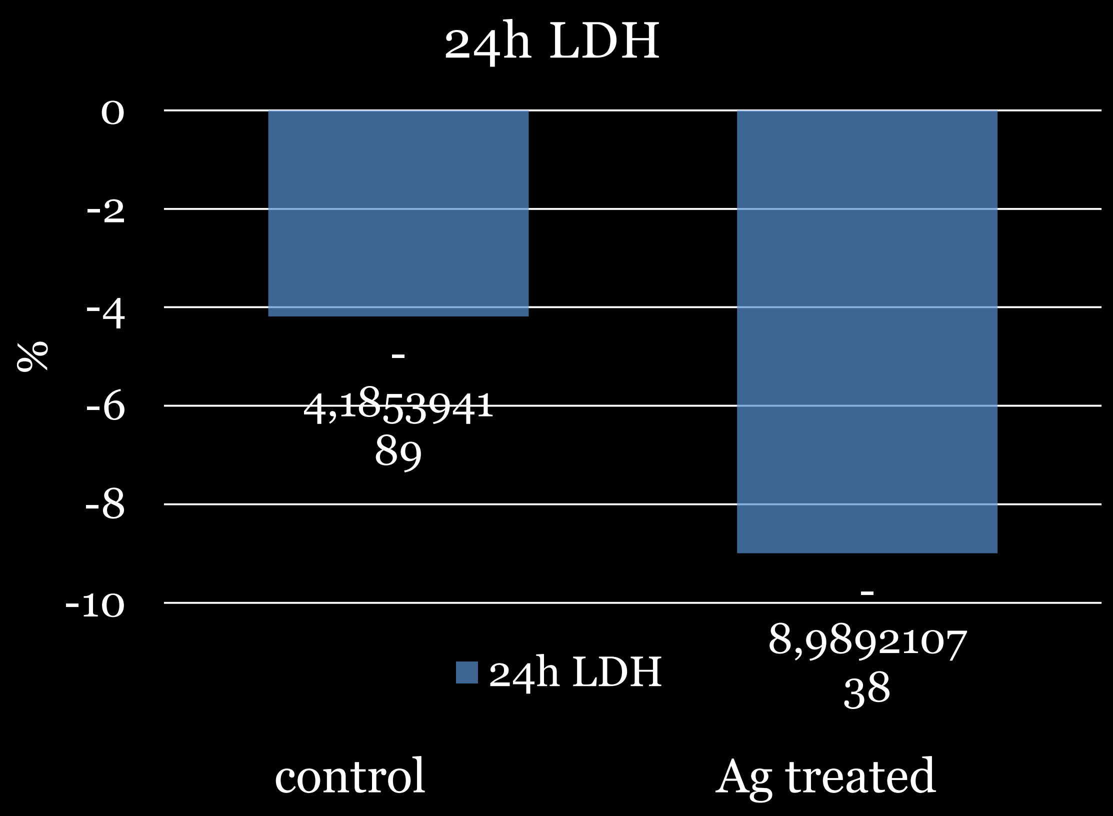
- statistical tests: non-parametric procedures (Mann-Whitney U-test, Kolmogorov-Smirnov test)
- for S. aureus, there is a significant difference between silver and control samples
- Mann-Whitney U-test: $p=0,002$, less than 0.05
- Kolmogorov-Smirnov Test: $p=0,005$, which is also less than 0.05
- There was no significant difference between silver and control in S. salivarius bacterial sites
- Mann-Whitney U-test: $p = 0.880$, greater than 0.05

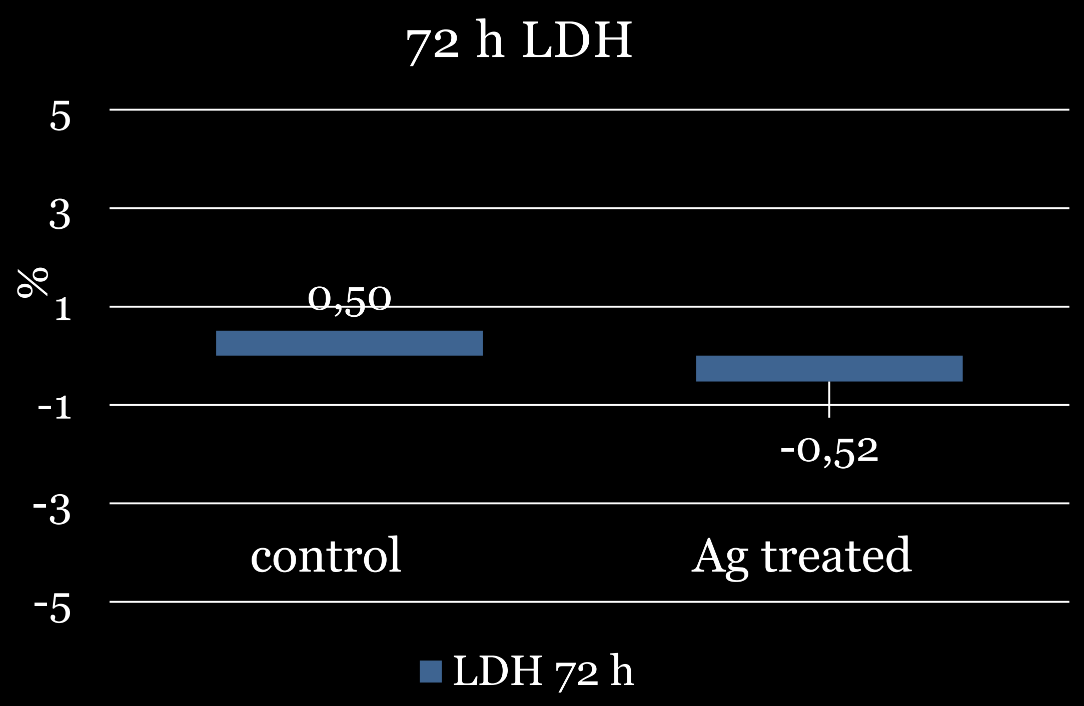
Results - Cell Culture Tests Samples from Linear Plasma Source





Results - Cell Culture Tests Samples from Linear Plasma Source





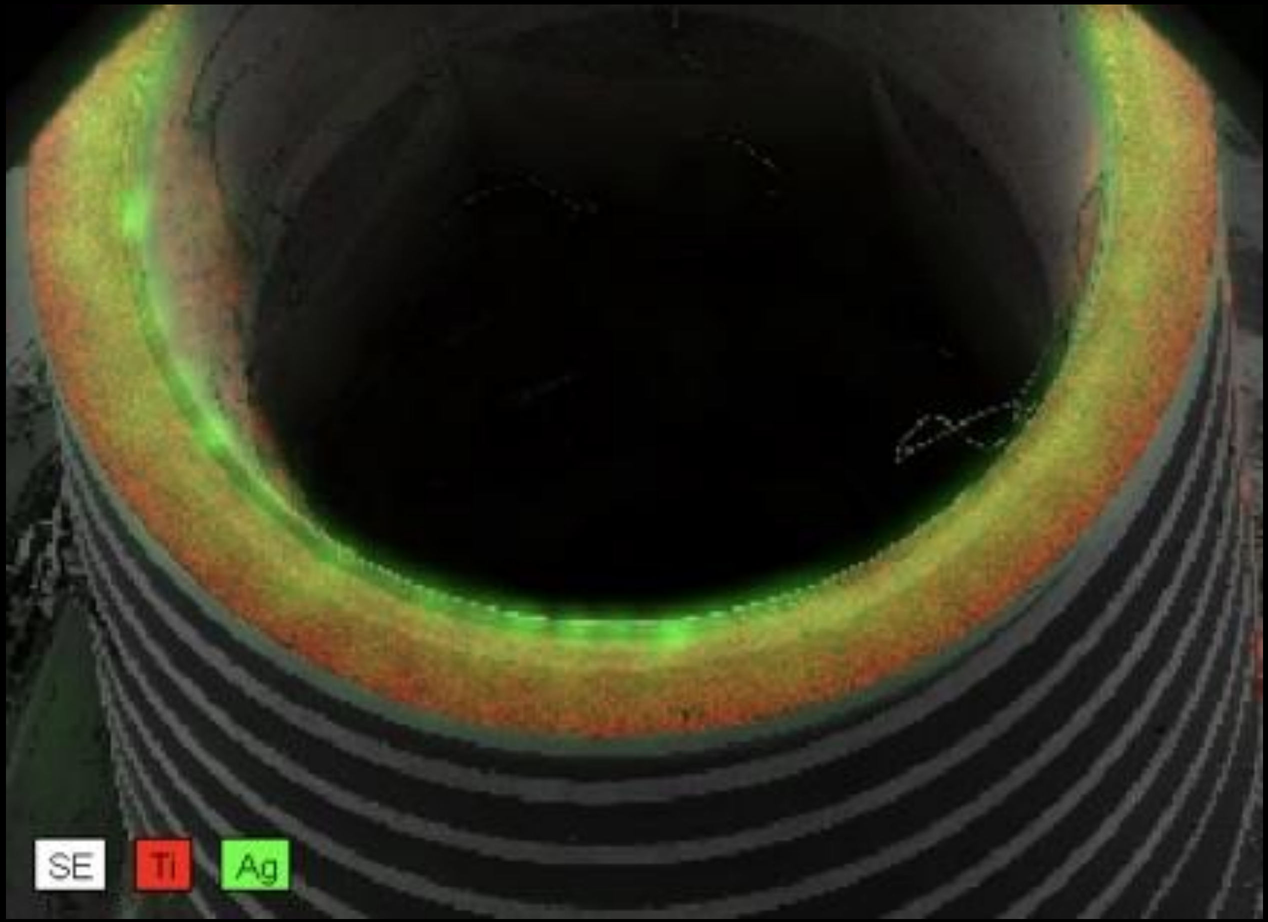
Clinical relevance

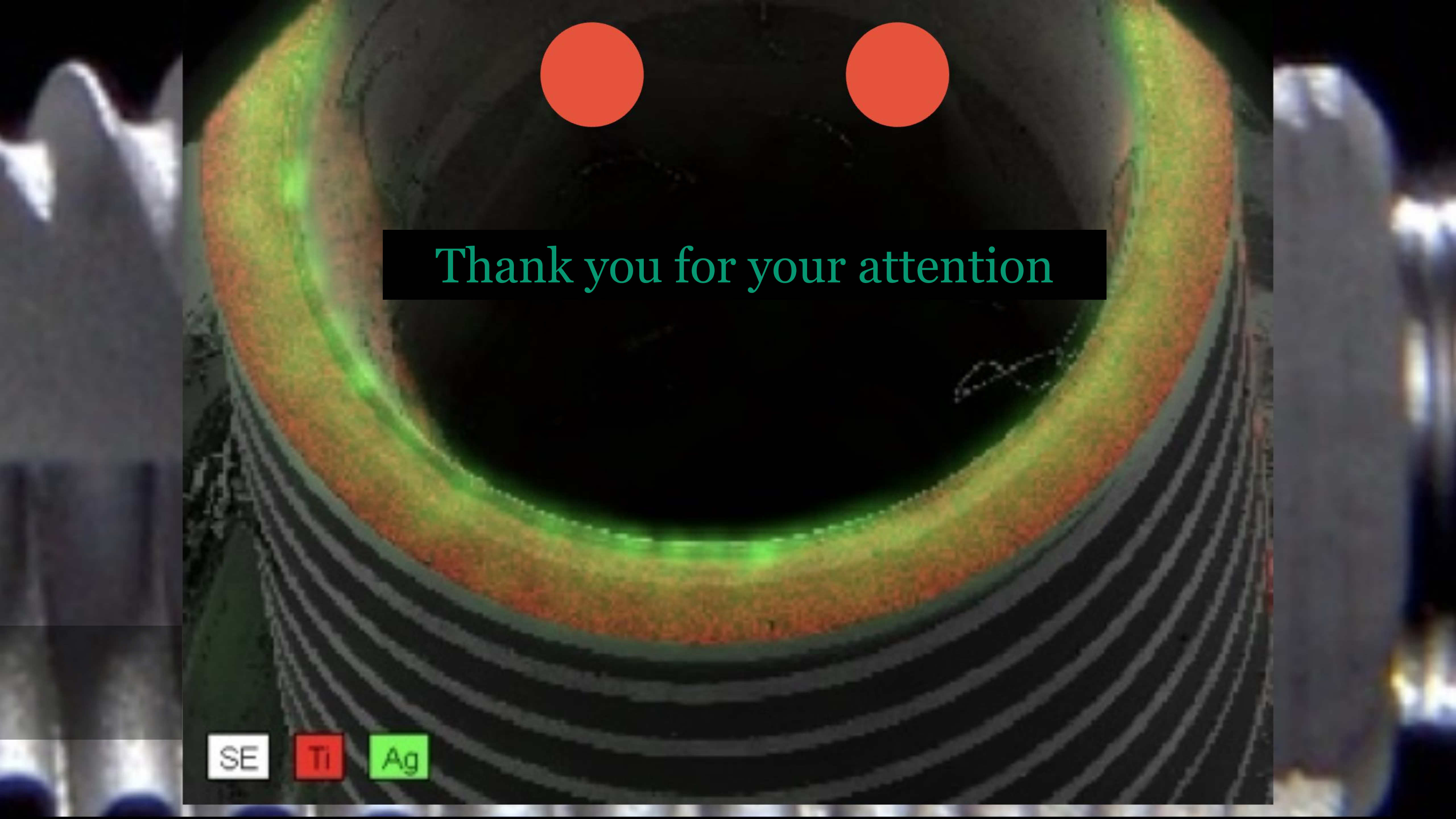
- Surface alloying of Grade 5 ELI Implant

point-like plasma source

- Local surface modification on the ring-shaped surface of the platform.

- Antibacterial gate





Thank you for your attention