

Laser structuring of titanium-based alloy and metallic thin films under controlled atmospheric conditions

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OUTLINE

- ▶ **Motivation**

- ▶ **Samples / lasers / methods**

- ▶ **Bulk material**

- ▶ **Thin films**

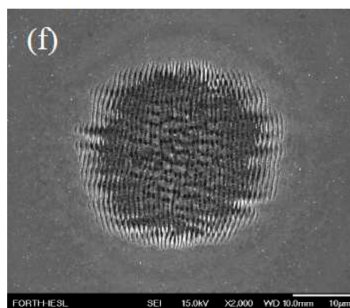
- ▶ **Material characterization**

- ▶ **Longevity studies**

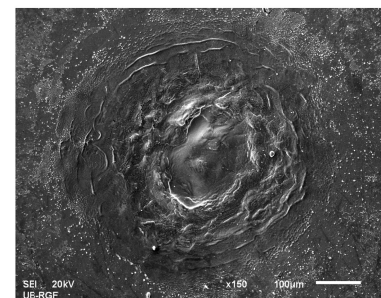
INTRODUCTION

Titanium, its alloys and Ti-based thin films/coatings are extensively used in aerospace, nuclear, marine and biomedical applications due to their superior physico-chemical properties, such as excellent corrosion resistance and biocompatibility, high specific strength and good ductility.

The significance of metallic thin films with nanometer-scale thicknesses is recognized for various applications, including microelectronics, biosensors, solar engineering, optical components, etc.



Si/Ti/Al Yb:KGW)
Laser_fs_50 p



T6Al4V_NdYag_ns N2_400 p

Surface processing by laser modification is highly competitive compared to other techniques because of the non-contact, controlled and precise processing and modification of the surface. Strongly dependent on material properties and laser light parameters.

MOTIVATION

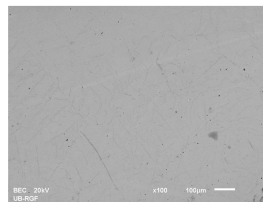
The research interest is continuously focused on application of lasers in enabling **prolonged usage** and **better performance** of Ti-based materials, by:

- improving their wear resistance or increasing the active surface by direct laser action
- improving the mechanical properties / by laser shock peening, with and without protective coating
- mitigating negative effects like reduced ductility under intense neutron flux by laser nitriding
- managing the thin films selective removal or modification that must be performed locally

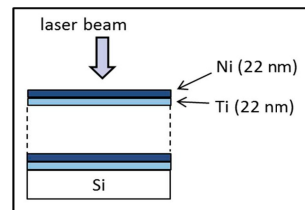
SAMPLES

Ti based alloy Ti6Al4V - The content (%) of elements in commercially available Ti64 alloy are following:
Aluminum (5.5-6.75), Vanadium (3.5-4.5), Carbon (maximum 0.1), Iron (maximum 0.3), Oxygen (maximum 0.02), Nitrogen (0.05), Titanium (balance, ~ 90).

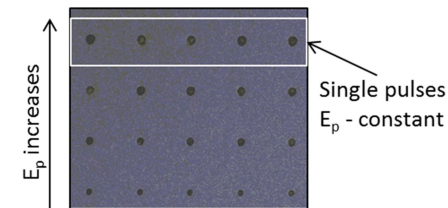
Ni/Ti multi-layer thin film – 440 nm thickness, composed of 20 single layers with thicknesses of 22 nm each. Chosen based on their electronic structures, thermo-mechanical properties and acoustic impedance



Ti6Al4V



10x(Ni/Ti) multi-layer thin film



Photonics 2024, 11, 1054.
<https://doi.org/10.3390/photonics11111054>

Micromachines 2024, 15, 5.
<https://doi.org/10.3390/mi15010005>

Physica Scripta 2014 (T162), 014017

LASERS / METHODS

Yb:KGW laser - wavelength 1026 nm, pulse duration 170 fs, spatial distribution Gaussian

Ti:sapphire system - wavelength 775 nm, pulse duration 200 fs, Gaussian spatial profile of the beam.

Nd:YAG lasers, wavelengths 1064 nm, 532 nm, 266 nm, pulse duration 40 ps, 150 ps, 5 ns, Gaussian spatial distribution

TEA CO₂ laser, wavelength 10.6 μ m, pulse duration 100 ns, multi-mode output

Pulse duration ns, ps, fs

Modes

Single-pulse irradiation, increasing pulse energy

Multi- pulse irradiation, increasing number of pulses at the constant pulse energy

Scanning regime, varying pulse energy and scanning speed

Low - fluence mode

High - fluence mode

Environment

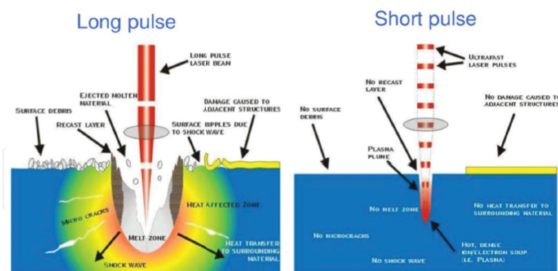
Air, vacuum, N₂, Ar, etc.

Typically used surface characterization methods

Scanning Electron Microscopy (SEM) – morphology analysis

Energy Dispersive X-ray Spectroscopy (EDS) – elemental analysis, semi-quantitative

Non - contact White Light Optical Profilometry – surface parameters and topography analysis



Source: A.H,Hamad, <http://dx.doi.org/10.5772/63892>

Long pulse and ultrafast pulse laser interaction with target material

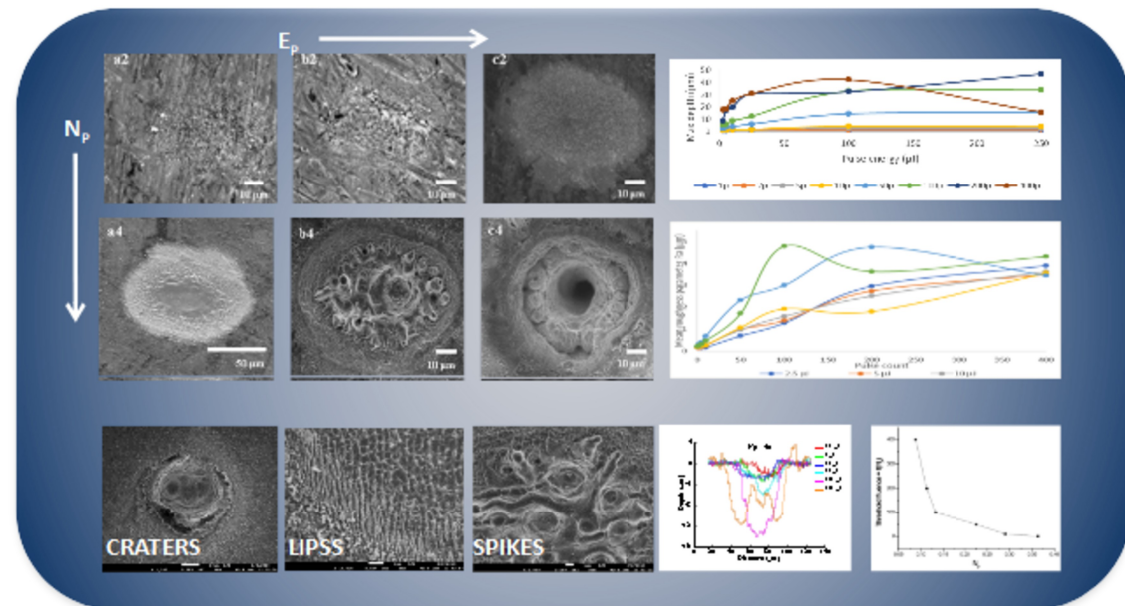
BULK MATERIAL

Femtosecond Laser Irradiation of Ti-Based Alloy

Surface structuring of Ti-based implant alloy by fs laser light

- low and high fluence mode
- ablation and surface structures

775 nm wavelength
200 fs pulse duration
Pulse count varying from single pulse to 100 pulses
Increasing output pulse energy from 0.2 μJ to 250 μJ
Energy density from 0.22 J cm^{-2} to 22.2 J cm^{-2}



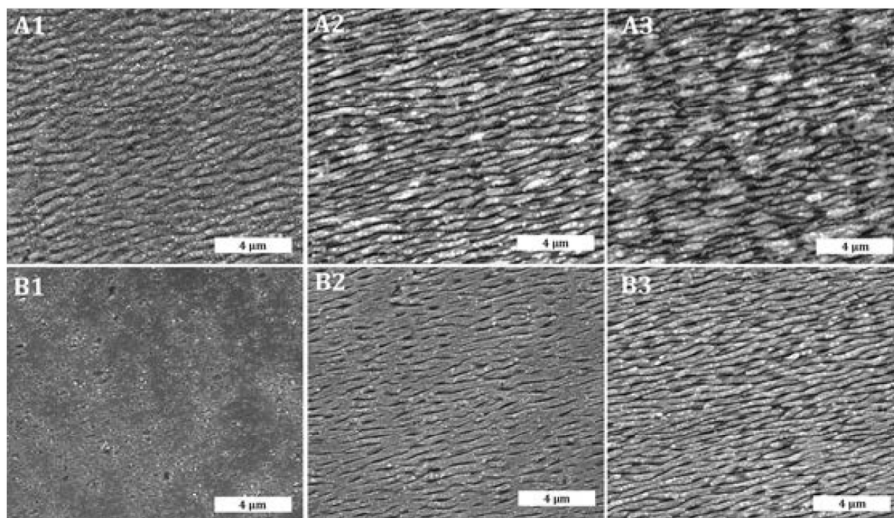
Laser action induced **ablation** of the surface material, hydrodynamic effects, the appearance of laser induced periodical surface structures and micro-/nano-particles.

- Considering periods of LIPSS emerging from this work (530 – 700 nm), there is a good comparison to experiments by other authors and literature; periods of LIPSS structures are below the laser wavelength, around 0.75 λ . The observed LIPSS periods are not significantly affected by surface deformations/irregularities.

Laser modification of Ti alloy by fs laser light – Scanning regime

Laser-induced periodic surface structures (LIPSS, other term “ripples”) are a laser-induced phenomenon which can be generated on a various materials – metals, semiconductors, dielectrics under different processing conditions, in a wide range of pulse durations, from continuous wave irradiation down to a few femtoseconds.

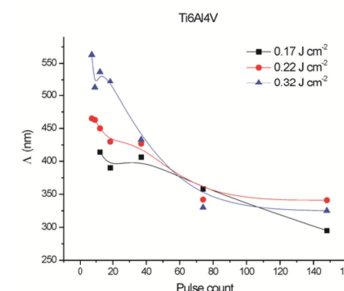
775 nm wavelength
200 fs pulse duration
pulse energy 0.5 - 3.6 μJ
scanning speed 0.5 - 10 mm s^{-1} .
modified area 0.5 mm $\times$ 0.5 mm



SEM of Ti6Al4V alloy after 200 fs laser action: at fluence 0.32 J cm^{-2} , after 7 (A1), 37 (A2), and 74 (A3) pulses, and at fluence 0.17 J cm^{-2} after 7 (B1), 37 (B2), and 74 (B3) laser pulses.

Generally accepted explanation of LIPSS formation:

Wavelength dependent LF-LIPSS, are typically attributed to the interference between the incident laser radiation and scattered or excited surface waves [2]. The HF-LIPSS can be the result of interaction of the focused fs laser beam with surface plasmons



Periods of **LF-LIPSS** decrease with pulse count and range from an average of $\sim 500 \text{ nm}$ (Fig. A1 and B1) to an average of 300 nm .

Generally, with the increase of accumulated pulses:

LF-LIPSS

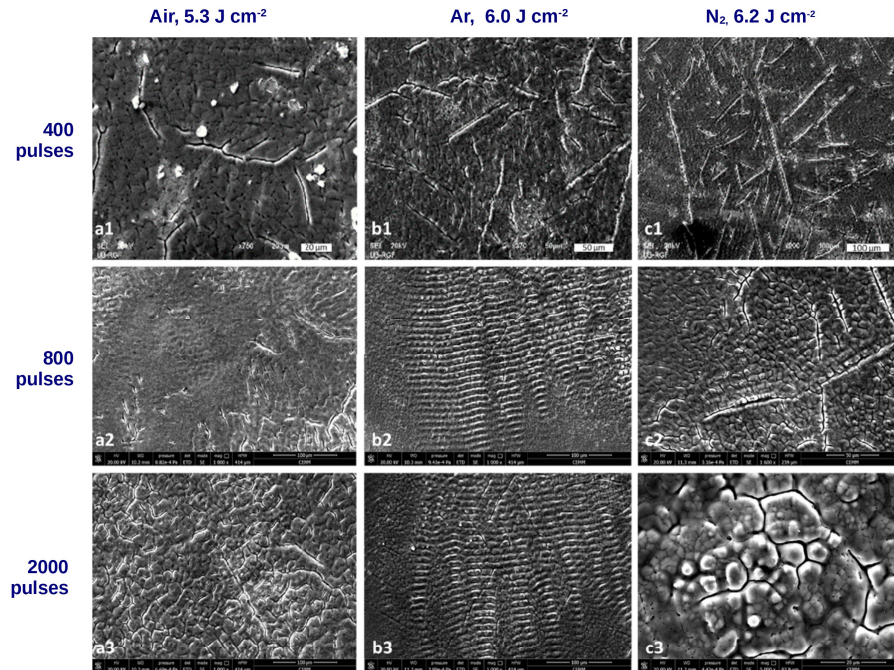
(i) the periods tend to get smaller

(ii) stop changing the period size $\sim \lambda/2$, regardless of energy

HF-LIPSS

$\Lambda \sim \lambda/5 \text{ to } \lambda/9$

Nanosecond Laser Irradiation of a Ti-Based Alloy under Controlled Atmospheric Conditions



SEM microphotographs of the Ti6Al4V surface after TEA CO₂ laser irradiation with 100 ns pulse duration and 175 mJ pulse energy

LIPSS period is proportional to the laser irradiation wavelength and, therefore, LIPSS formed as a result of TEA CO₂ laser action should have values of $\sim 10.6 \mu\text{m}$, which corresponds to the obtained experimental values of LIPSS periods of $\sim 10 \mu\text{m}$ and, the ripples are preserved even at higher pulse count.

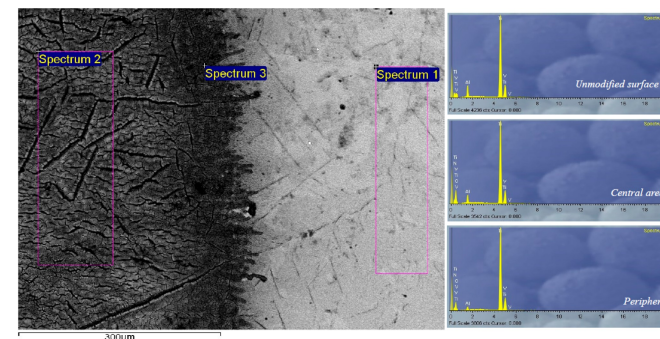
LIPSS formation theory – hydrodynamical origin.

TEA CO₂ laser
Multi-mode intensity profile
Pulse duration 100 ns
Wavelength $10.6 \mu\text{m}$
Different ambient conditions: **air** and **argon-** and **nitrogen-rich** atmospheres.

The observed surface features: resolidified pool of molten material, craters, hydrodynamic effects and parallel periodic surface structures.

N-rich atmosphere – **nitriding achieved**
Ar-rich atmosphere – **subdued hydrothermal effects**
LIPSS formed by multi-mode-beam nanosecond laser action and, uniformly distributed over the spot surface.

Elemental analysis of the surfaces indicated **nitrogen presence** on the surface after the laser irradiation in the nitrogen-rich ambient conditions.



Locations and EDS spectra of unmodified and Ti6Al4V area modified by nanosecond laser in nitrogen-rich atmosphere; $E_p = 175 \text{ mJ}$, $N_p = 2000$.

Picosecond Laser Irradiation of a Ti-Based Alloy under Controlled Atmospheric Conditions

Nd:YAG laser

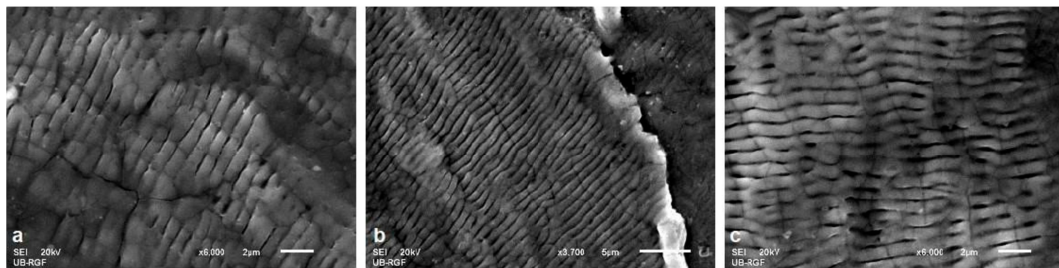
Near Gaussian intensity profile

Pulse duration 150 ps

Wavelength 1064 nm

different ambient conditions: air and argon- and nitrogen-rich atmospheres.

The observed surface features similar after the nanosecond laser irradiation, with LIPSS – at the periphery of the spots.



LIPSS on picosecond laser modified Ti6Al4V surface after: a) 400 pulses at 6.10 J cm^{-2} in **air**; b) 200 pulses at 5.40 J cm^{-2} in **nitrogen-rich atmosphere**; c) 400 pulses at 23.5 J cm^{-2} in **argon-rich atmosphere**.

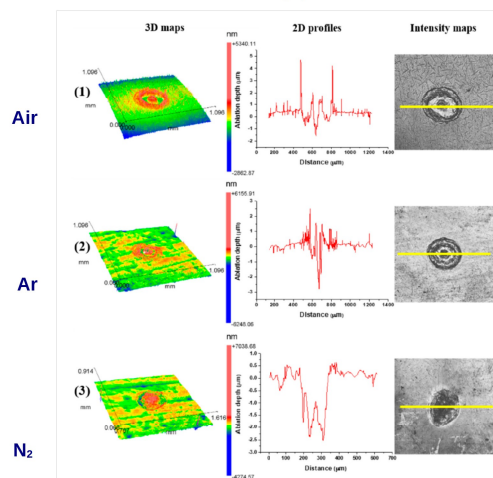
Fluence increase - decrease of Λ LIPSS.

In **air**, ripples with $\Lambda \sim 630 \text{ nm}$ are visible at the periphery of the modified area, at energy density value of 6.1 J cm^{-2} and 400 accumulated pulses (Figure a).

The most regular formed in **N-rich** atmosphere, at 5.4 J cm^{-2} fluence, 200 accumulated pulses (Figure b), period value $\sim 900 \text{ nm}$.

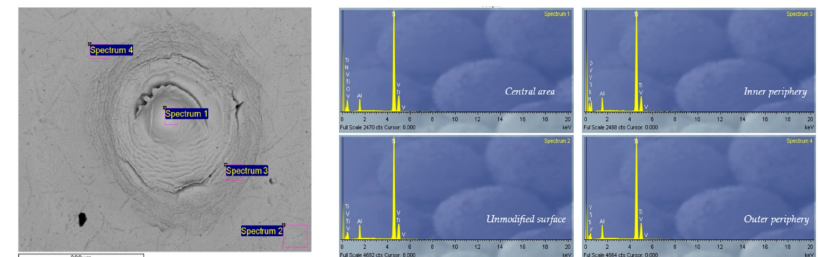
In the **Ar-rich** atmosphere, LIPSS structures are observed after 400 accumulated pulses, energy density 23.5 J cm^{-2} , LIPSS period $\sim 685 \text{ nm}$ (Figure c).

Ti6Al4V surface, pulse count 10.



N-rich atmosphere – nitriding achieved
Ar-rich atmosphere – subdued hydrothermal effects

Elemental analysis of the surfaces indicated nitride compound formation at the modified area, in the nitrogen-rich ambient conditions.

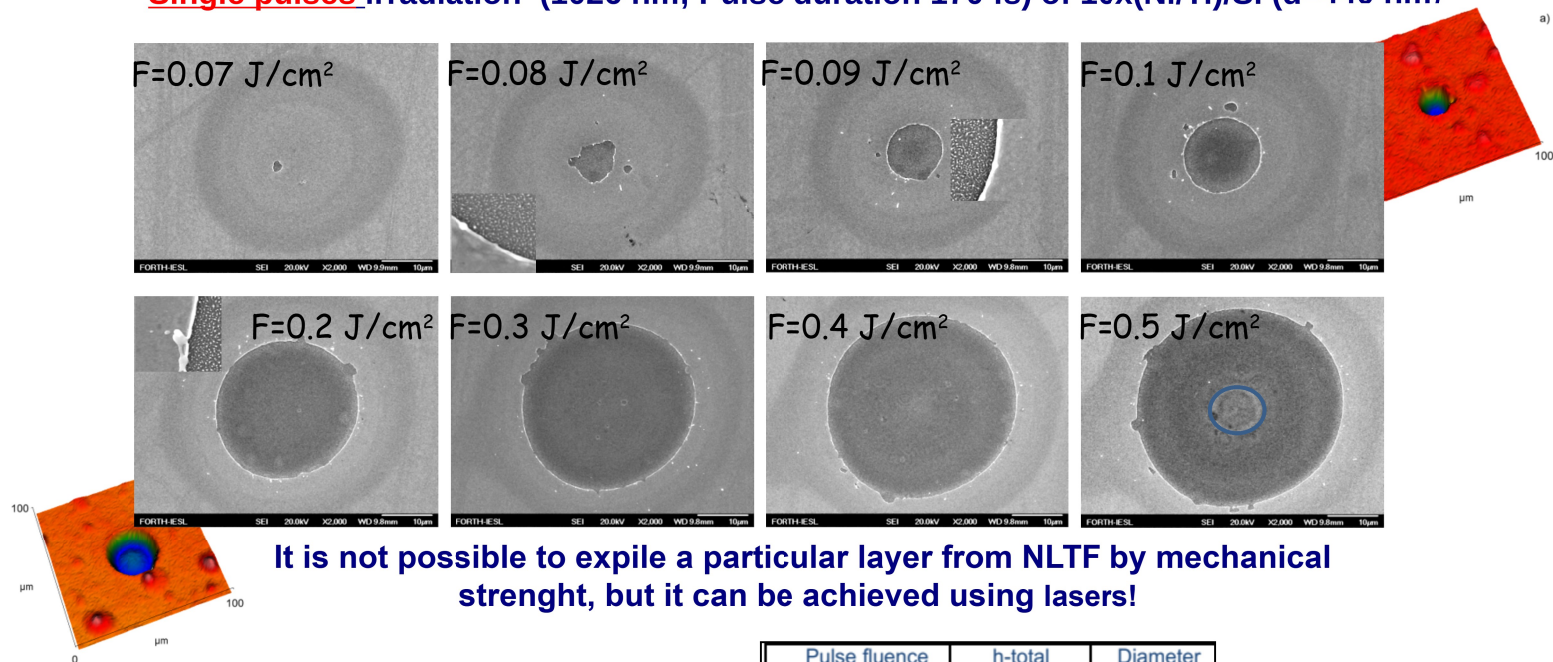


Locations and EDS spectra of unmodified and Ti6Al4V area modified by picosecond laser in nitrogen-rich atmosphere; $E_p = 15 \text{ mJ}$, $N_p = 100$.

THIN FILM

Femtosecond laser surface nano structuring of titanium nickel – multilayer thin film

Single pulses irradiation (1026 nm; Pulse duration 170 fs) of 10x(Ni/Ti)/Si (d=440 nm)



It is not possible to expile a particular layer from NLTF by mechanical strenght, but it can be achieved using lasers!

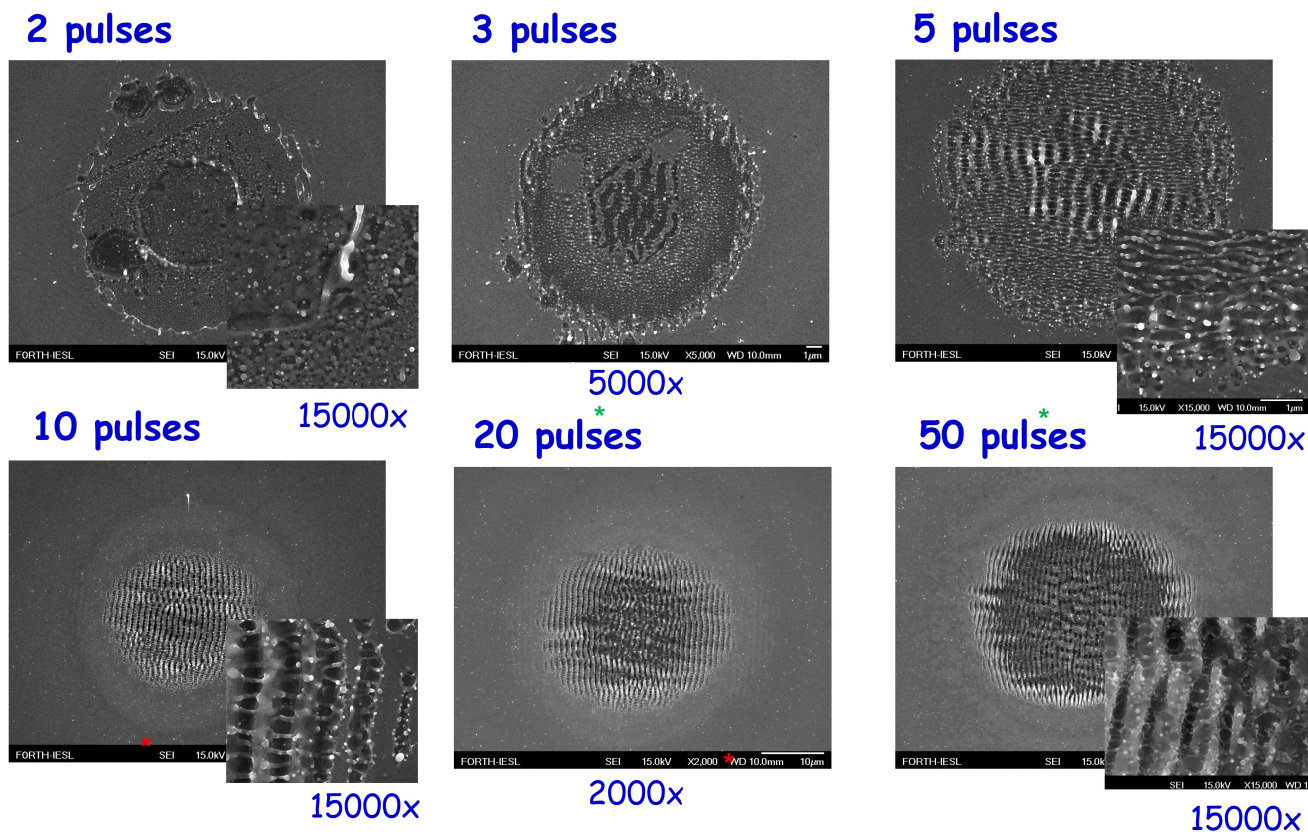
Layered thin films - **selective ablation** of the singular layers from the NLTFs.

Achievable in the specific range of fluences for certain materials.

Pulse fluence [J/cm ²]	h-total depth (nm)	Diameter 2R (μm)
0.08	23	7
0.09	23	11.1
0.1	24	15.6
0.2	25	28.5
0.3	26	34.0
0.4	26	37.5
0.5	23/59	41.0
1.0	≥ 440	~56

LIPSS formation on the nanolayer thin film with femtosecond laser pulses

Multi-pulses irradiation of 10x(Ni/Ti) with N=2-50 pulses ($F=0.08 \text{ J/cm}^2$).



LIPSS evolution as number of successive pulses increasing.

LF-LIPSS: $\Lambda_L = 900 \pm 30 \text{ nm}$, and **HF-LIPSS:** $\Lambda_H = 460 \pm 25 \text{ nm}$

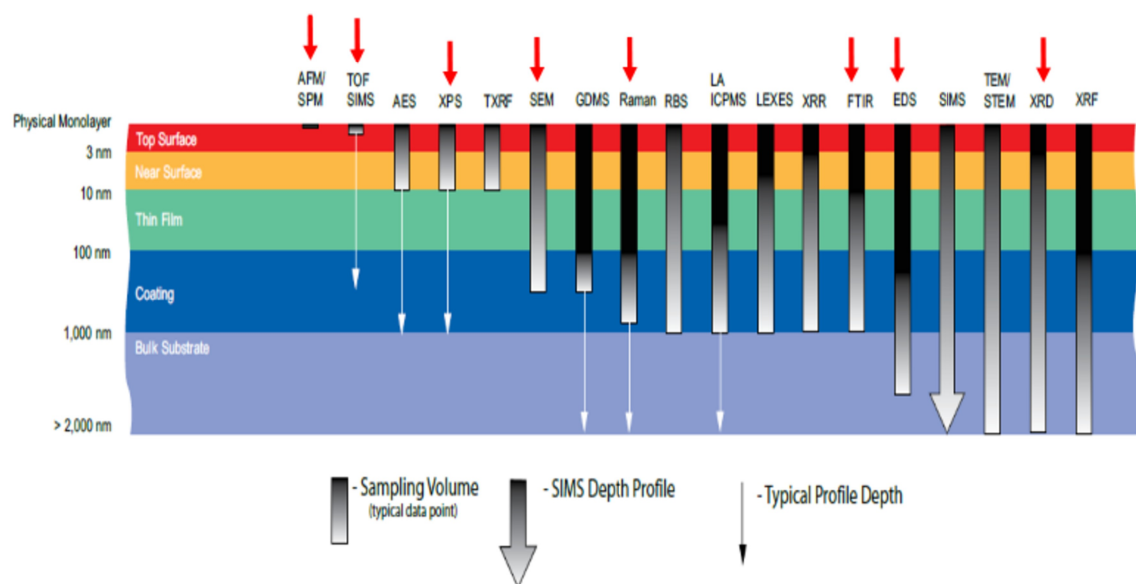
N	2	3	5	10	20	50
Depth (nm)	37	61	82	297	507	1000

LIPSS formed on the TF

LIPSS formed on the Si substrate

Physico-chemical techniques in surface characterization / longevity studies

- Set of complementary analytical techniques which give a detailed characterization of deposits accumulated on particle detector electrodes.
- **Multi-layered nature** of deposit demands combination of analytical techniques with **different penetration depths**:



Typical values of analyses depths by different characterization technique

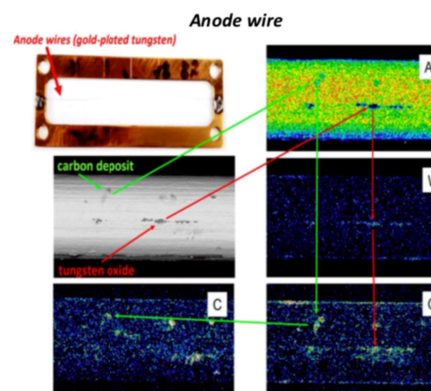
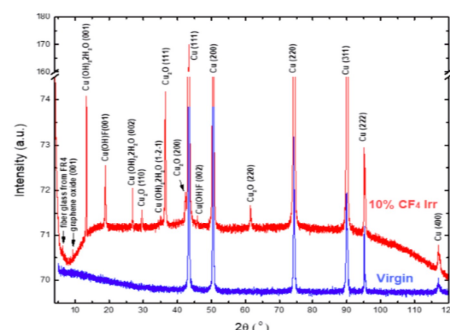
- Atomic Force Microscopy (**AFM**): No penetration
- Time of Flight Secondary Ion Spectroscopy (**ToF-SIMS**): 1-2 nm, depth profiling up to several hundred nm
- X-ray Photoelectron spectroscopy (**XPS**): ~ 5 nm, depth profiling up to 1 μ m
- Scanning Electron Microscopy (**SEM/EDS**): < 2 μ m
- Fourier Transform Infrared (**FTIR**) and Raman Spectroscopy: < 2-3 μ m
- X-ray Diffraction (**XRD**): < 15 μ m

LONGEVITY STUDIES

Characterization is the application of various analytical techniques in order to fully understand the nature of the material from different aspects. Analytical techniques are used to determine physical and chemical properties of the material – **identify (qualitative) and quantify (amount) chemically, measure physical parameters (electrical properties etc.).**

Combining various analytical techniques operating at different scales (nano, micro and meso), provide complementary results comprising: surface morphology and roughness, elemental composition and, structural information (middle range ordering at the molecular level (functional groups, e.g. O-H, C-H, etc.) and long range ordering (crystal or amorphous structure))

Comparison of XRD patterns of virgin and aged 10% CF₄ cathode



To determine a degree of deterioration of the electrode's surface (**physical aspect**) and to analyse the deposit formed (**chemical aspect**) in plasma chemical reaction, analytical techniques well established in the field of materials science were used.

*5th International Workshop on Proton-Boron Fusion Belgrade, Serbia
September 8th - 11th 2025.*

Thank you for your attention!

