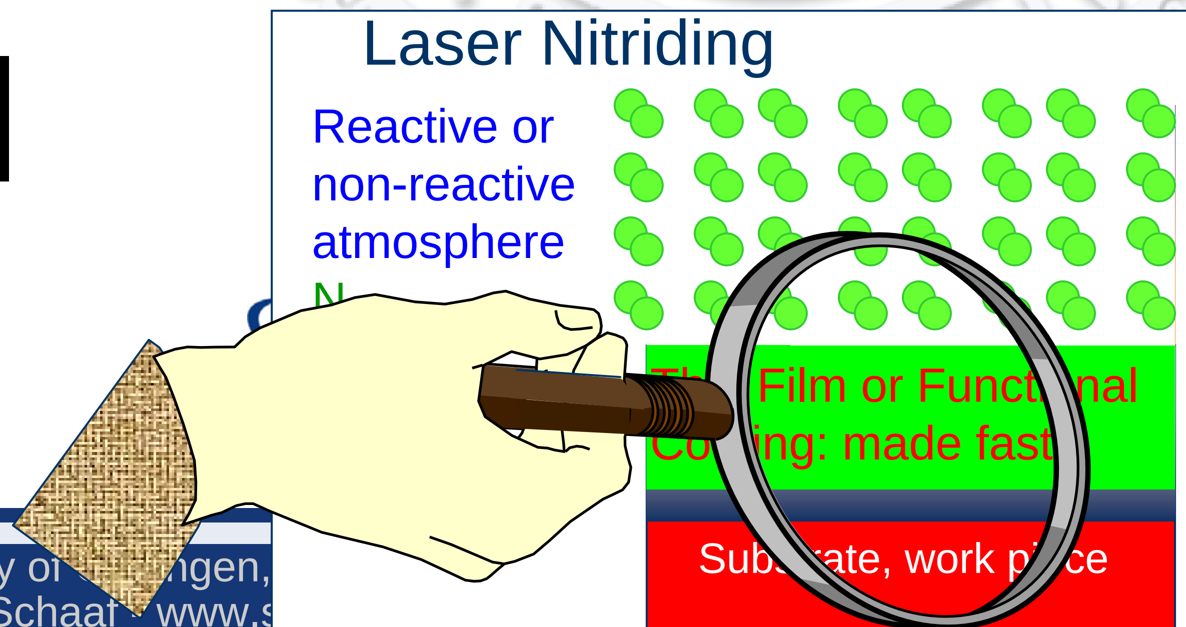
Free electron laser nitriding of metals:
from basic physics to industrial applications

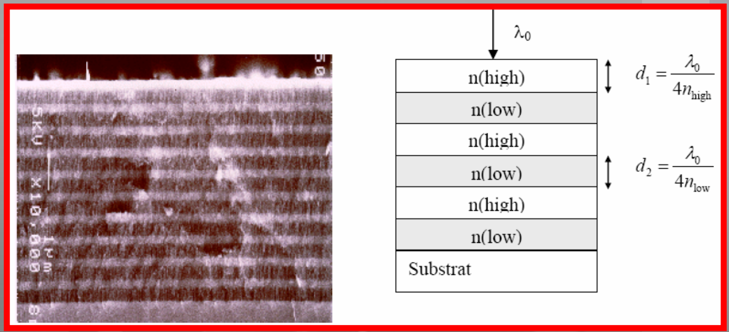
Peter Schaaf [a)], M. Shinn [b)], E. Carpene [a)], J. Kaspar [c)]

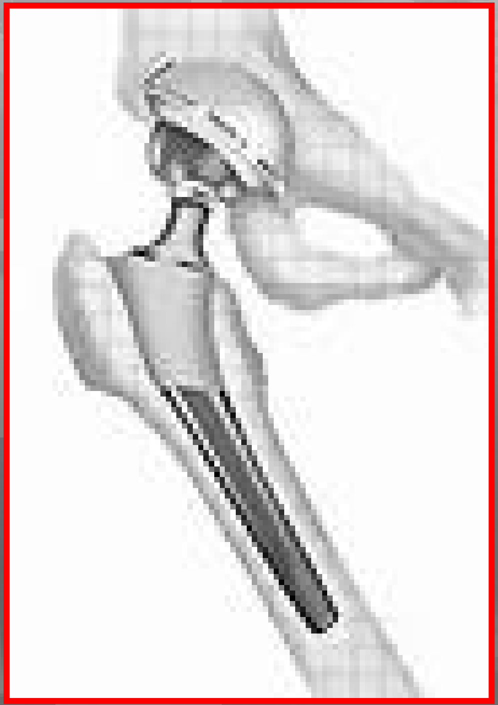
a) GEORG-AUGUST-UNIVERSITÄT GÖTTINGEN
Zweites Physikalisches Institut

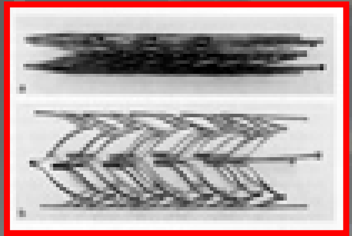
b) Jefferson Lab
Free-Electron Laser

c) Fraunhofer IWS
Institut Werkstoff- und Strahltechnik




λ0
n(high)
n(low)
n(high)
n(low)
n(high)
n(low)
Substrat
$d_1 = \frac{\lambda_0}{4 n_{\text{high}}}$
$d_2 = \frac{\lambda_0}{4 n_{\text{low}}}$





- Laser Synthesis of Thin Films and Coatings (Nitriding, Carburizing, Hydriding): experimental principles, interactions, melt, plasma, dynamics, diffusion, solidification, …
  - Fe-N and Fe-C,
  - Austenitic stainless steel
  - TiN and TiC
  - AlN and AlC
  - Si_3N_4 and SiC (IBM-Milliped)
  - Laser-Conditioning of Magnesium
  - Laser-Hydriding Ti-H
  - Production pc-a:Si(H) (TFT)
  - β-$FeSi_2$ (photovoltaics, optoelectr.)
  - Fe/Ag Multilayers by PLD (GMR, TMR)
  - Polymer-PLD (Applications)
  - Epitaxial recrystallisation (SiC, SiO_2)

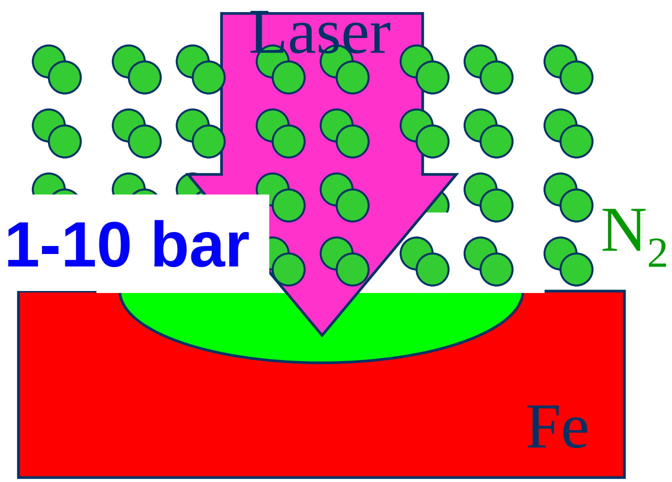
➢ Excimer Laser 55 ns
➢ Nd:YAG Laser 8 ns
➢ FEL 1 ps
➢ Ti:Sapphire 150 fs

Basic Physics

Laser Synthesis: temperature, plasma

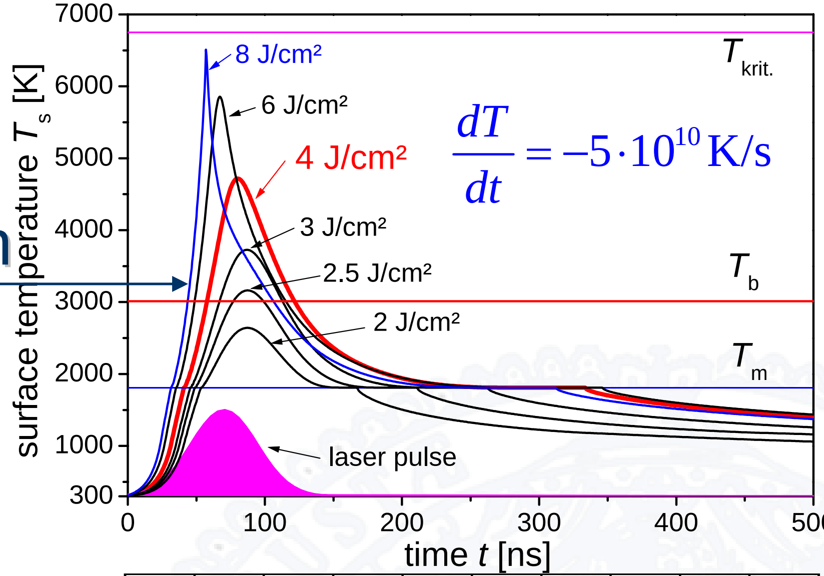
Excimer Laser: λ=308 nm (4.03 eV)
t_p=55 ns (FWHM), 5x5 mm²,
H=4 J/cm² (I_0=70 MW/cm²)

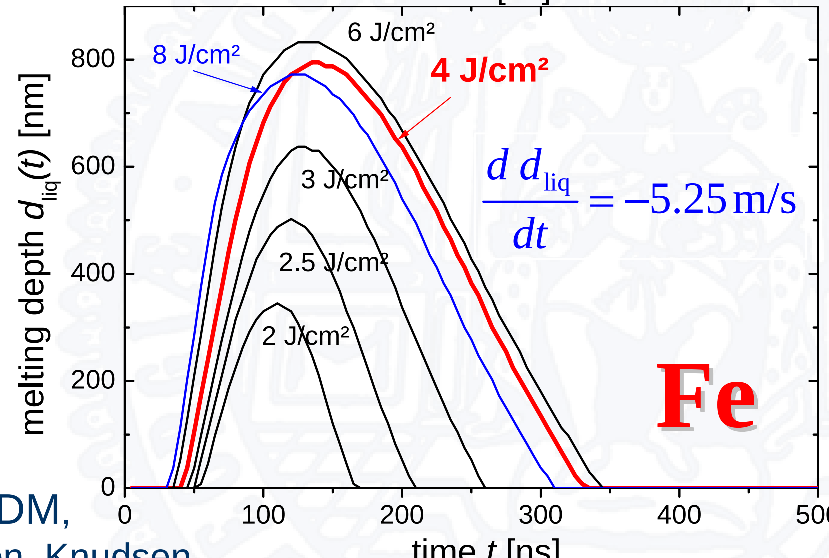
gas transparent for laser



evaporation
ablation
plasma-formation

vacuum: PLD





<u>but</u>: ambient atmosphere at high pressure **prevents ablation**, causes high pressures, chemical reactions, take-up into liquid surface, re-solidification, coating forms

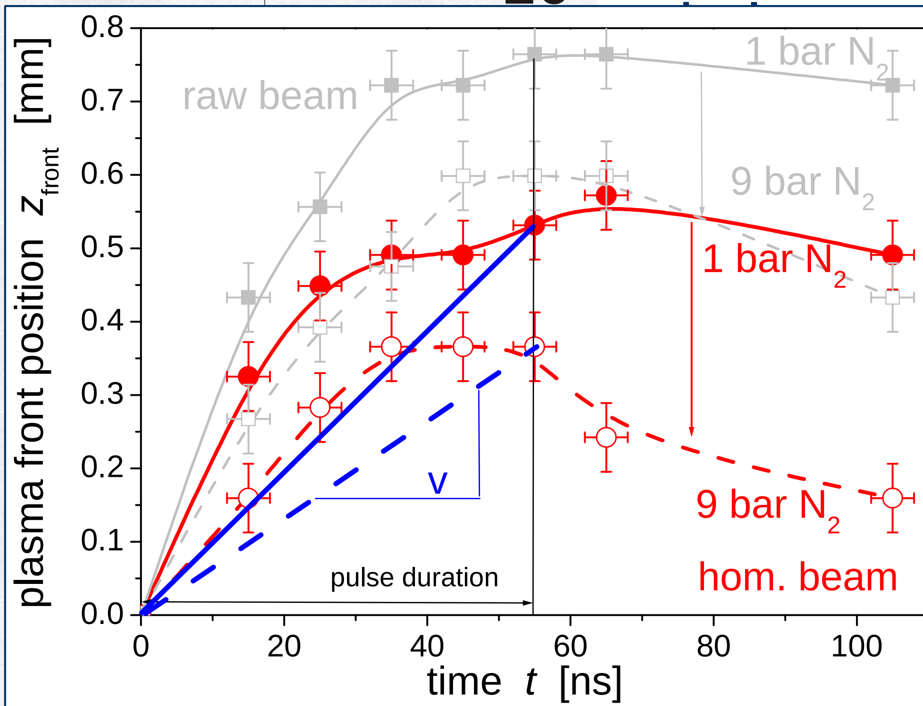
Numerical: FDM,
incl. evaporation, Knudsen

…cess: Principle of Laser Synthesis

Hom. Beam

0.1 MPa | 0.9 MPa

10



… dynamics
… sure,
…s (LSAW)
…tion Wave
…on Wave

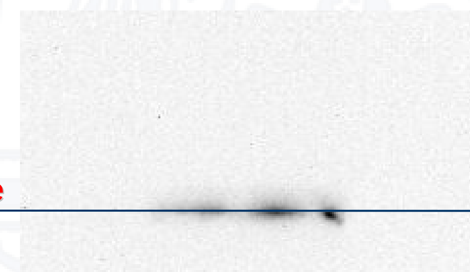
Plasma (600 ns) :

Laser pulse: 55 ns

Fe, 1 bar N_2, 4 J/cm²

surface

Fe, 9 bar N_2, 4 J/cm²



surface

150

350

Theory	Experiment
1 bar : v^{LSD} = 10.4 km/s	1 bar : v^{LSD} = 9.7(16) km/s
9 bar : v^{LSD} = 5.0 km/s	9 bar : v^{LSD} = 6.6(16) km/s

LSD-model

$$= \left[2\left(\gamma^2 - 1\right) \cdot \frac{I_0}{\rho_0} \right]^{1/3}$$

increased gas pressure ⇒ plasma expansion more slowly –Plasma pressure higher and lasts longer!

p_p: 1 bar : 500 bar – 9 bar : 1050 bar

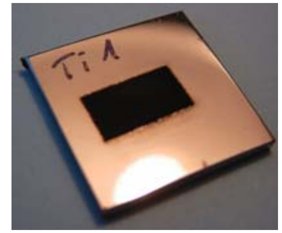
TiN

TiN

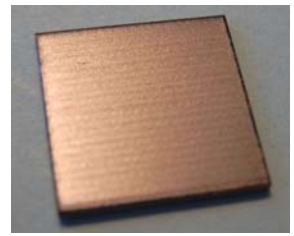
- Irradiation of Ti in N_2
- Free-Electron Laser FEL

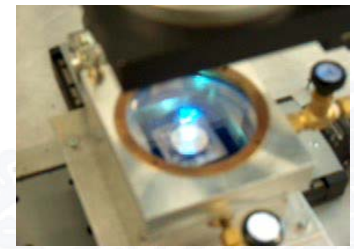
Overview: TiN coatings

Ti:Sapphire+CPA
750 nm
150 fs

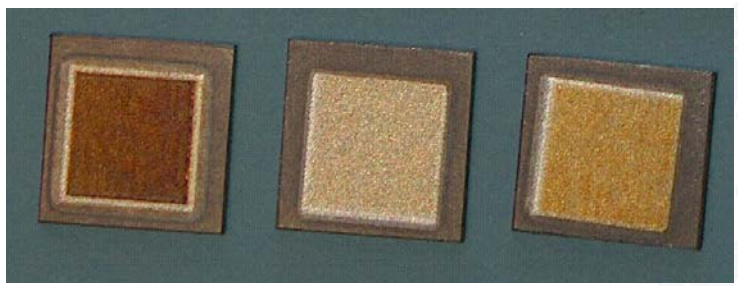


Excimer Laser
308 nm
55 ns

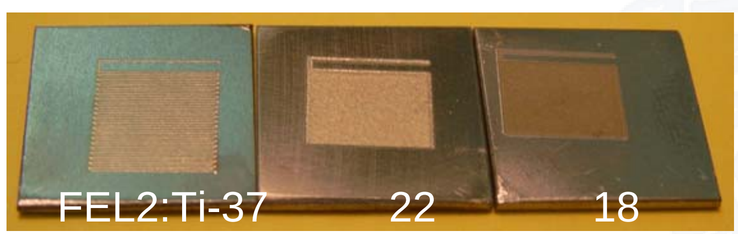




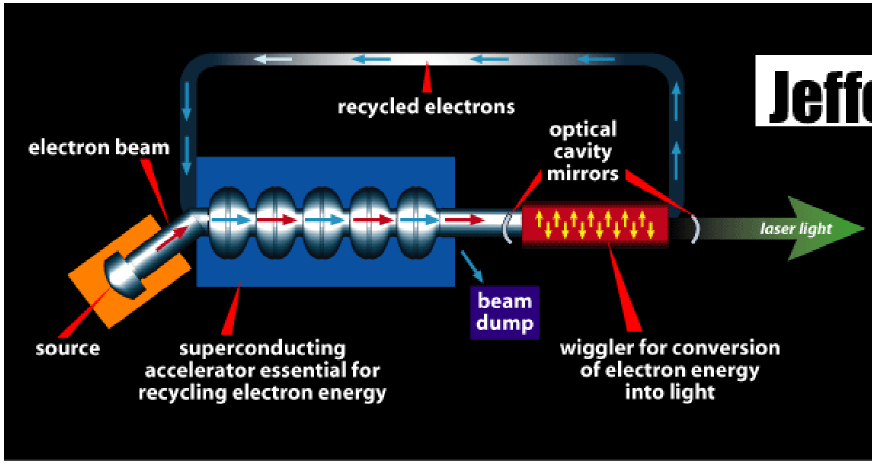
Nd:YAG
1064 nm, 532 nm
6 ns



FEL
3100 nm, 1050 nm
< 1 ps

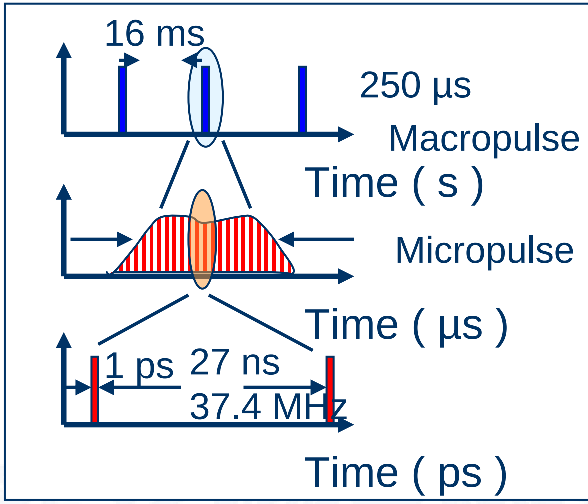


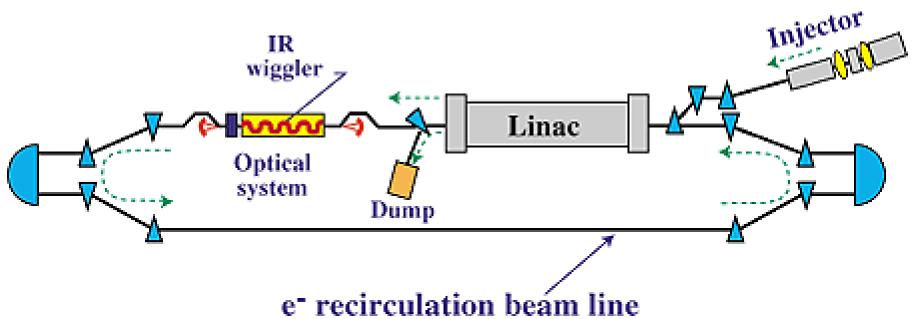
Faster and better with FEL ?



Jefferson Lab

FEL
Newport News,
Virginia, USA

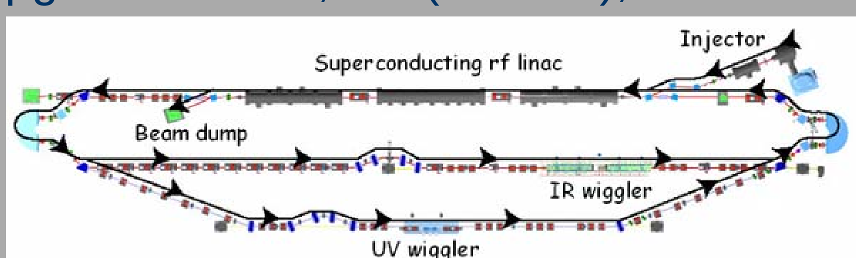


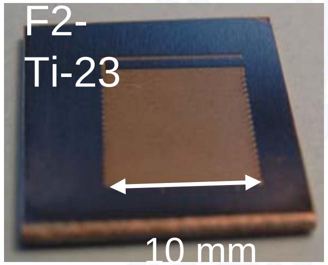


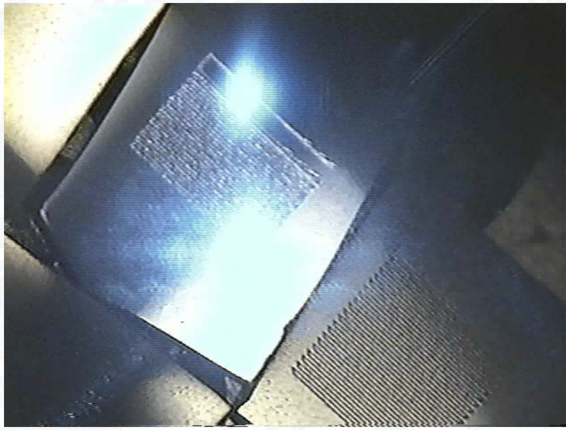
3.1 µm
2 kW

flexible in timing

upgrade: 10 kW, UV (300 nm), 2005

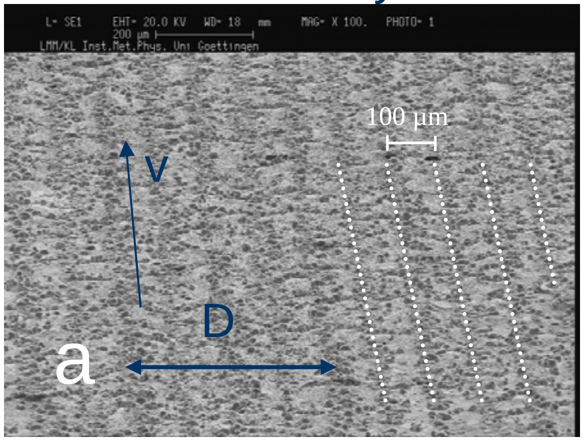


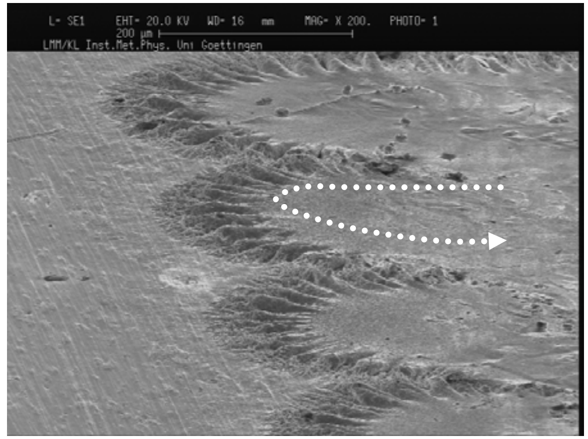




FEL: TiN Synthesis

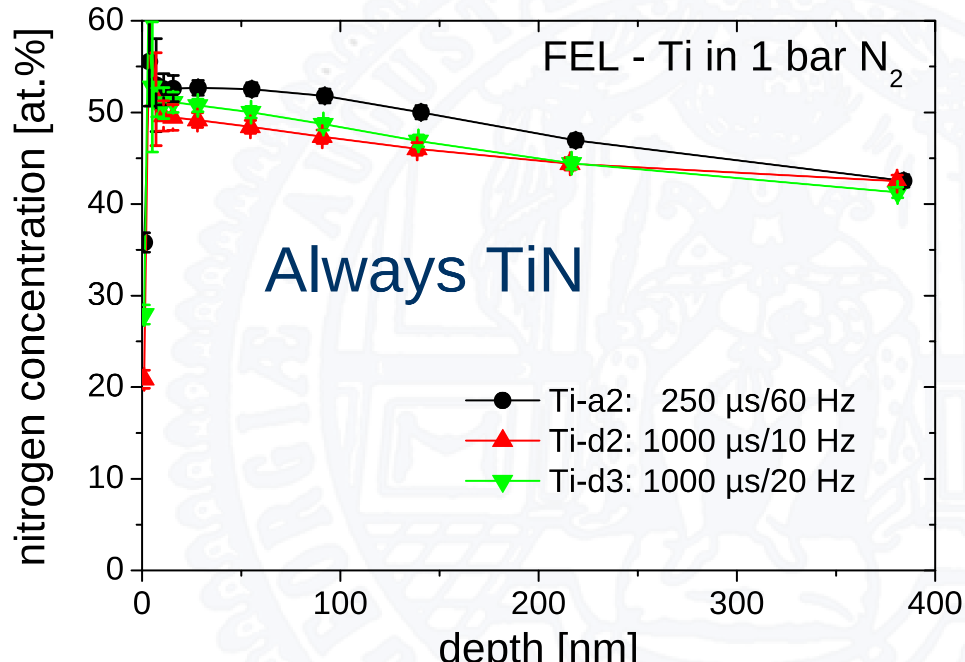
Line scan: velocity u=0.5 mm/s, line width D=0.4 mm, shift δ (50, 100, 200 µm)



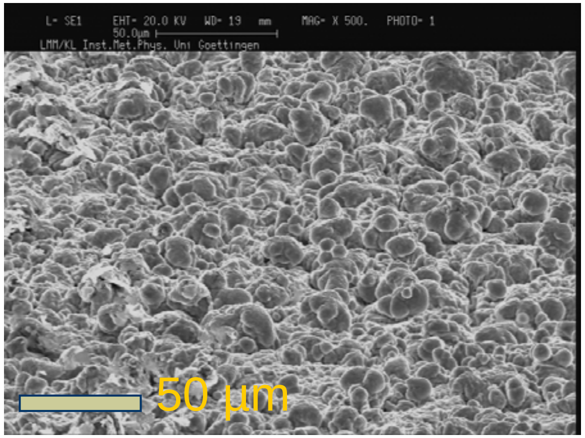


- formation of TiN
- concentration gradient
- independent of parameters
- structure of surface?

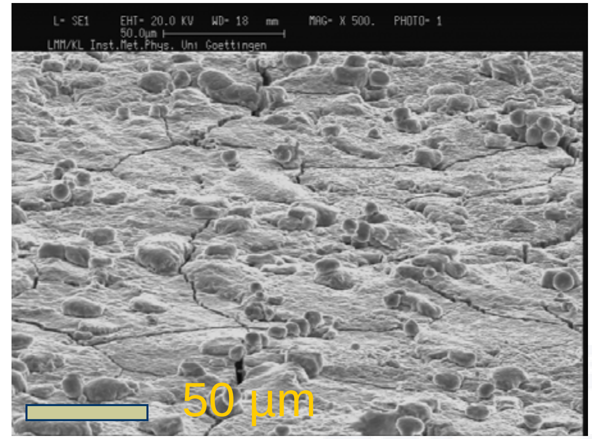
Sample	Macro t_m (µs)	Macro f_m (Hz)	shift δ (µm)	Fluence ϕ_m (J/cm^2)
Ti-a1	250	60	200	123
Ti-a2	250	60	100	123
Ti-a3	250	60	50	123
Ti-b1	500	30	100	246
Ti-c1	750	30	100	369
Ti-d1	1000	10	200	492
Ti-d2	1000	10	100	492
Ti-d3	1000	20	200	492
Ti-d4	1000	30	200	492
Ti-d5	1000	30	100	492



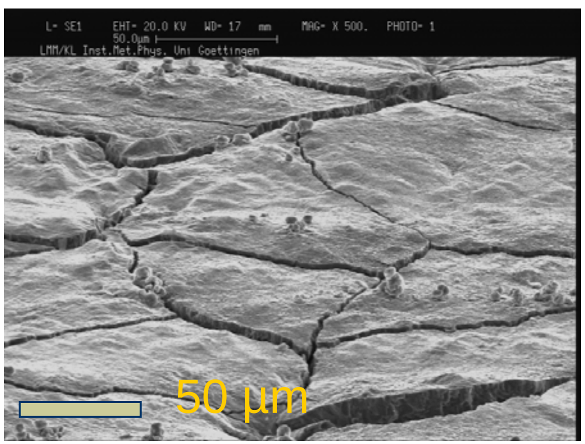
FEL TiN: Surface by SEM



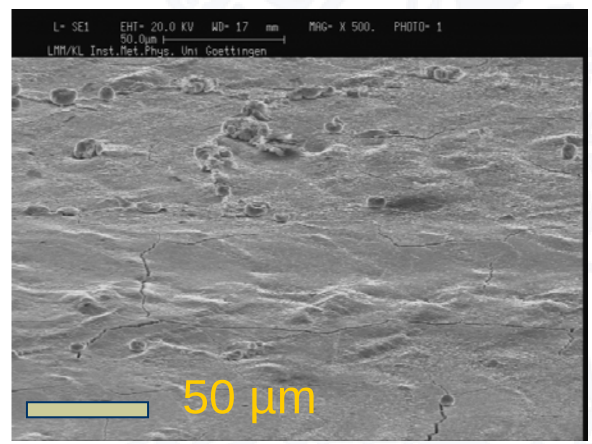
a2: 250 µs, 60 Hz, 100µm



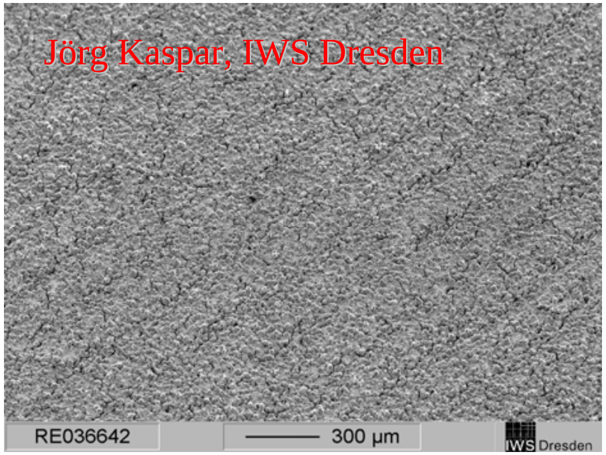
c1: 750 µs, 30 Hz, 100µm

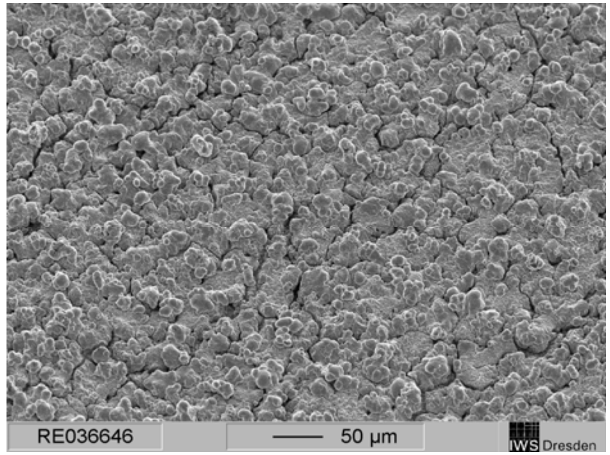


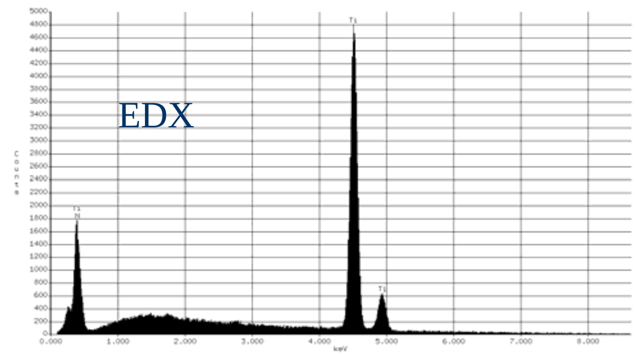
d5: 1000 µs, 30 Hz, 100 µm

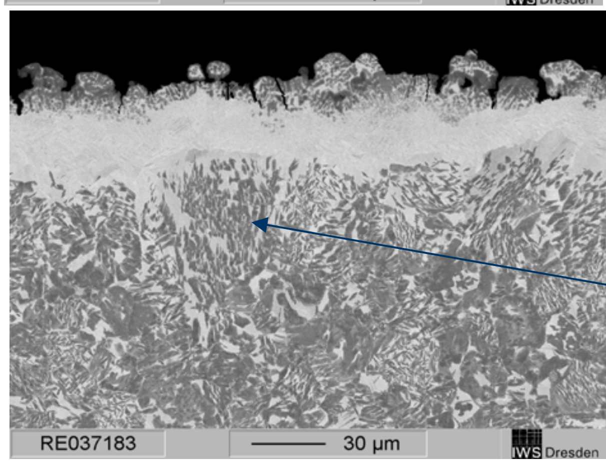


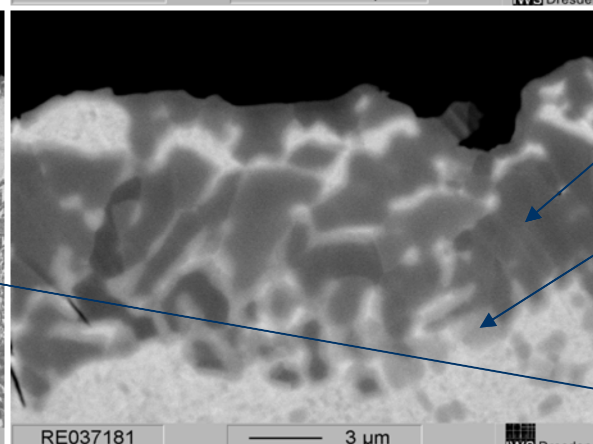
d1: 1000 µs, 10 Hz, 200µm





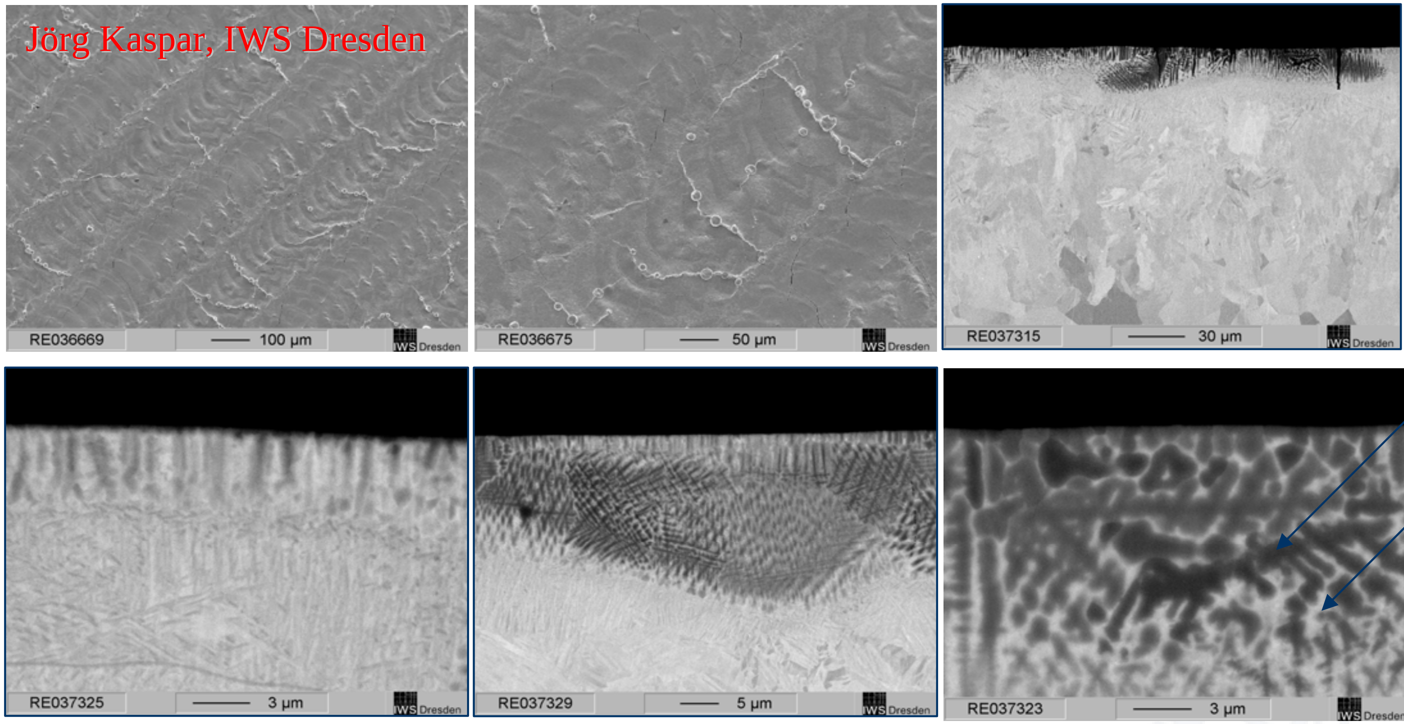






Surface very rough, melting pearls, network of fine cracks, melting depth 30-40 µm, TiN 5-15 µm, primary solidification of TiN at the surface, TiN has a nitrogen rich kernel and less nitrogen cover, α‘-Martensite in between

Ti23: 1000µs, 10 Hz, 200µm, (100) Texture



EDX: ~30 at% N

EDX: ~10 at% N

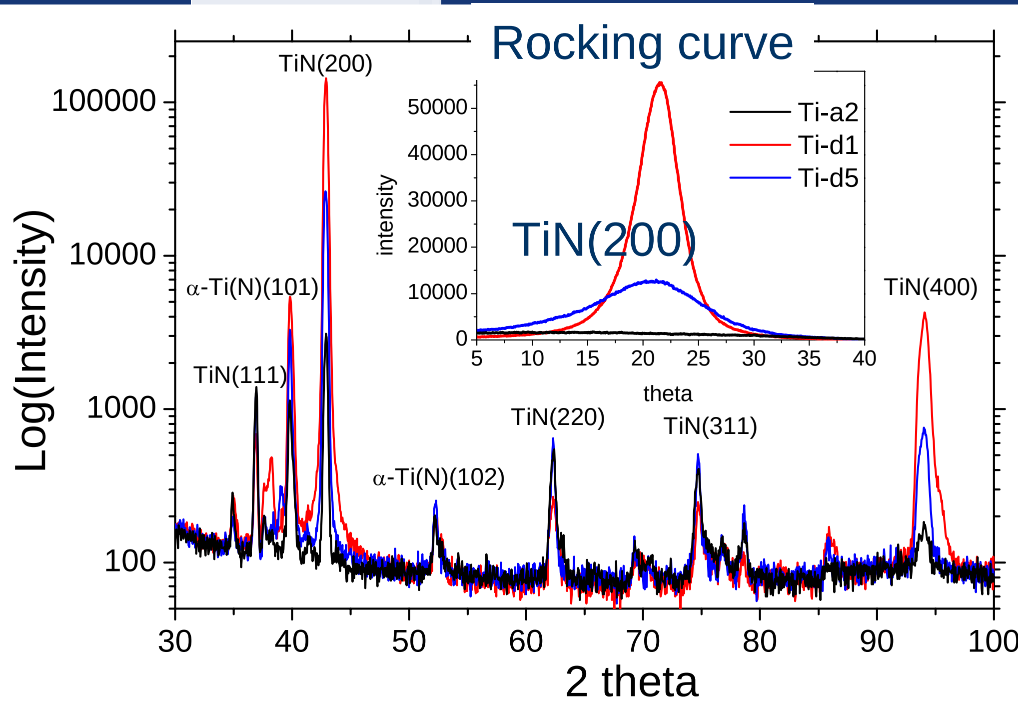
melting zone 20-30µm, TiN 0-25µm,

Very smooth surfaces, very few melt pearls, significant solidification lines, fine cracks.

cracks only within TiN. TiN cover smaller.

TiN perpendicular to the surfaces, dendritic solidification

GIXRD: Texture, Rocking curves



1000 µs, 10 Hz, 200 µm

1000 µs, 30 Hz, 100 µm

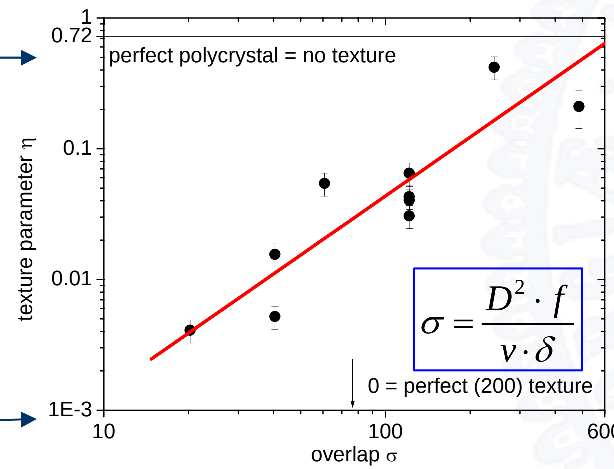
250 µs, 60 Hz, 100µm

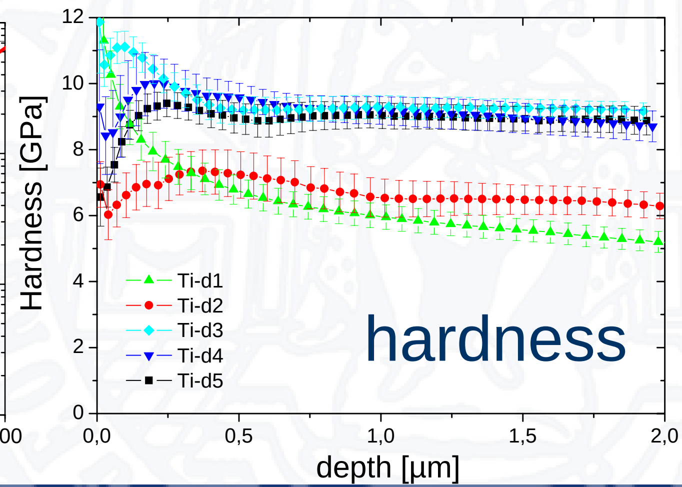
Strong texture for long macropulses and small overlap

no texture for short macropulses and large overlap

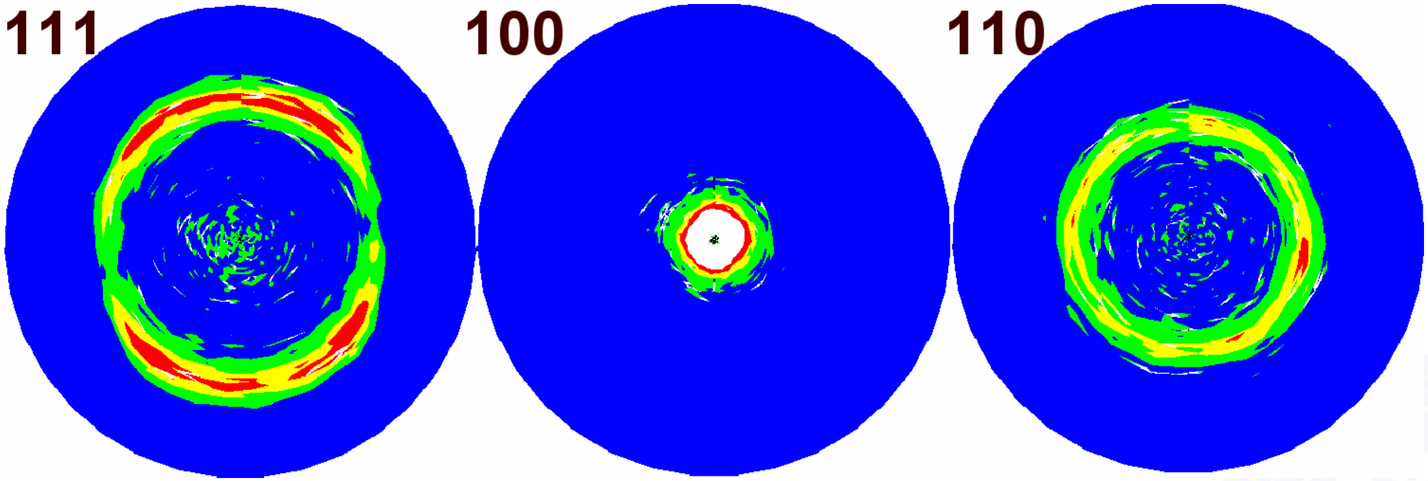
no texture (polycryst.) →

fully textured (single cryst.) →





FEL TiN: Pole Figures

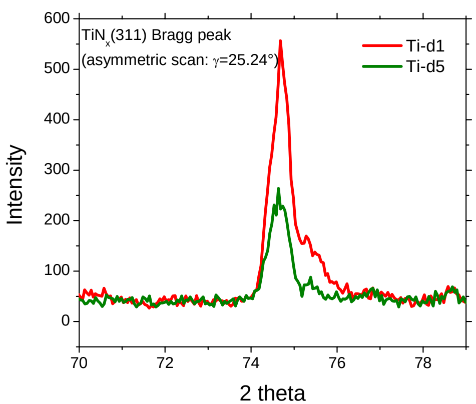


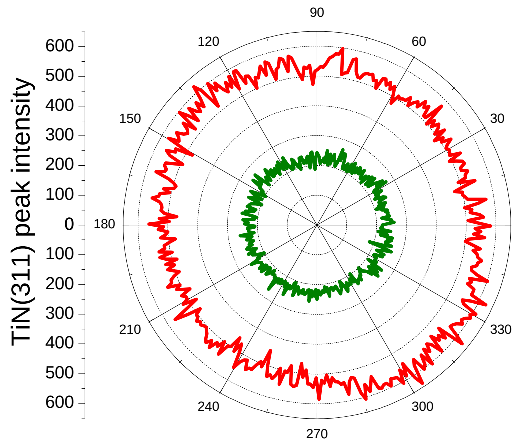
Ti-d3 (Ti-25)

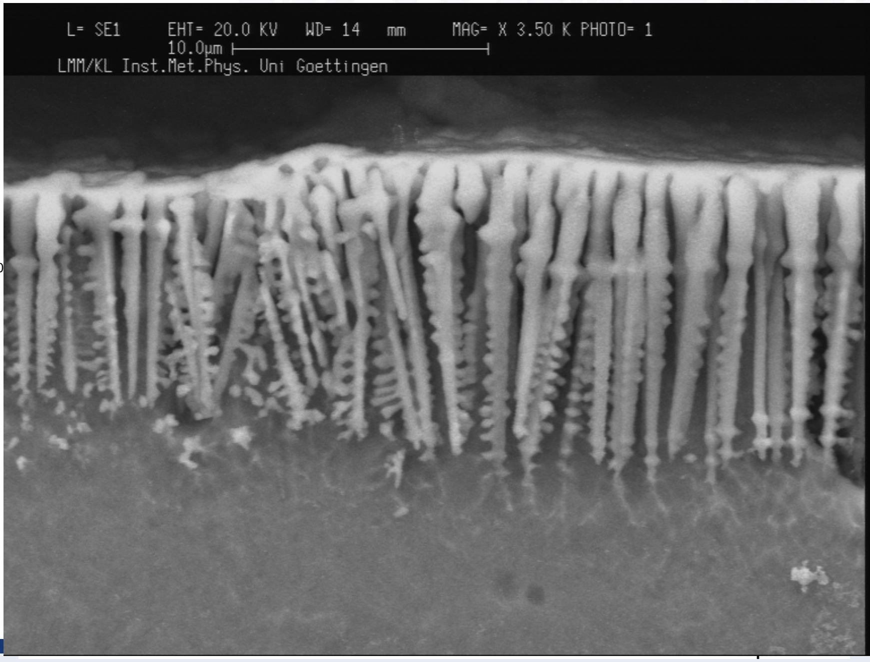
scan: 5° × 5°

φ: 0-360°

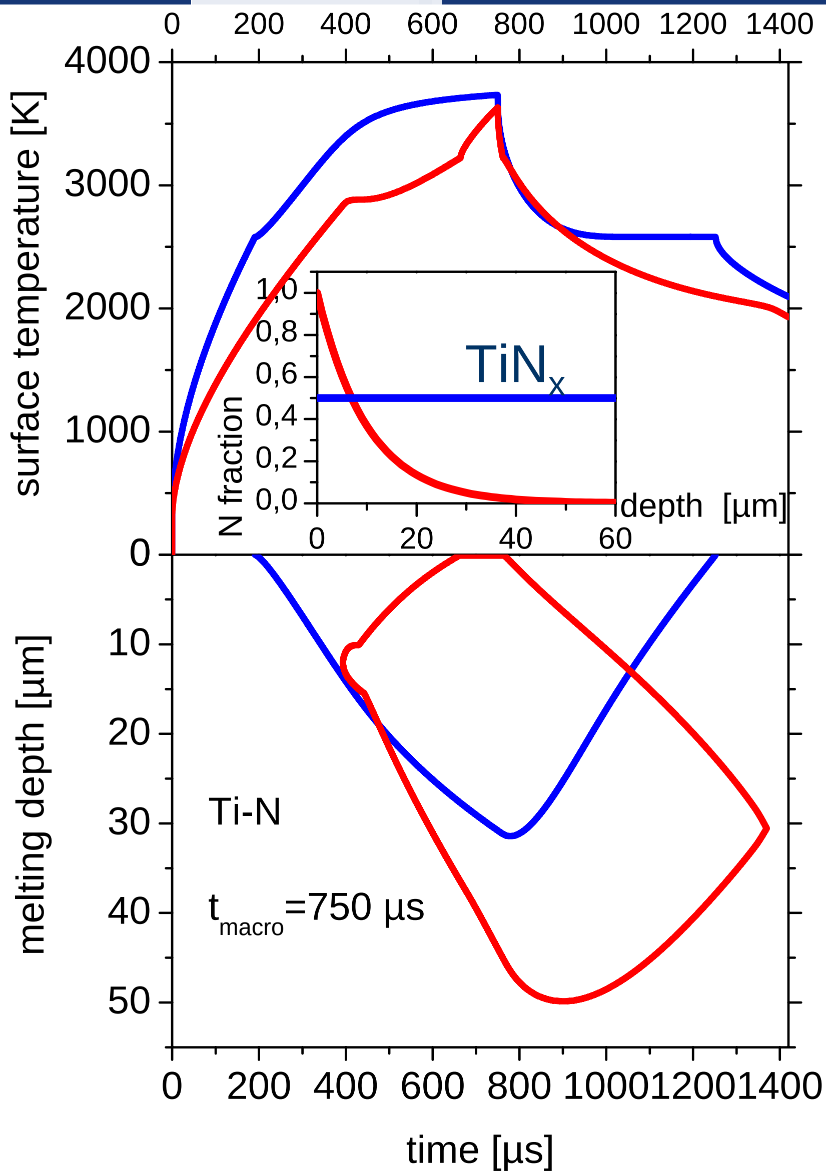
χ: 0-80°

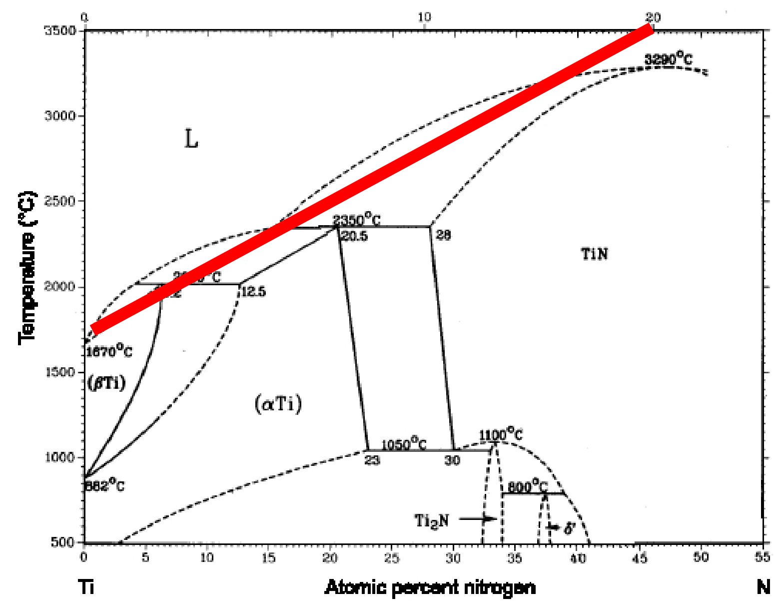






Symmetric -> columnar growth, fiber texture
very strong texture, well aligned columns





Strong dependence of the melting temperature on the nitrogen content

nitrogen concentration gradient:

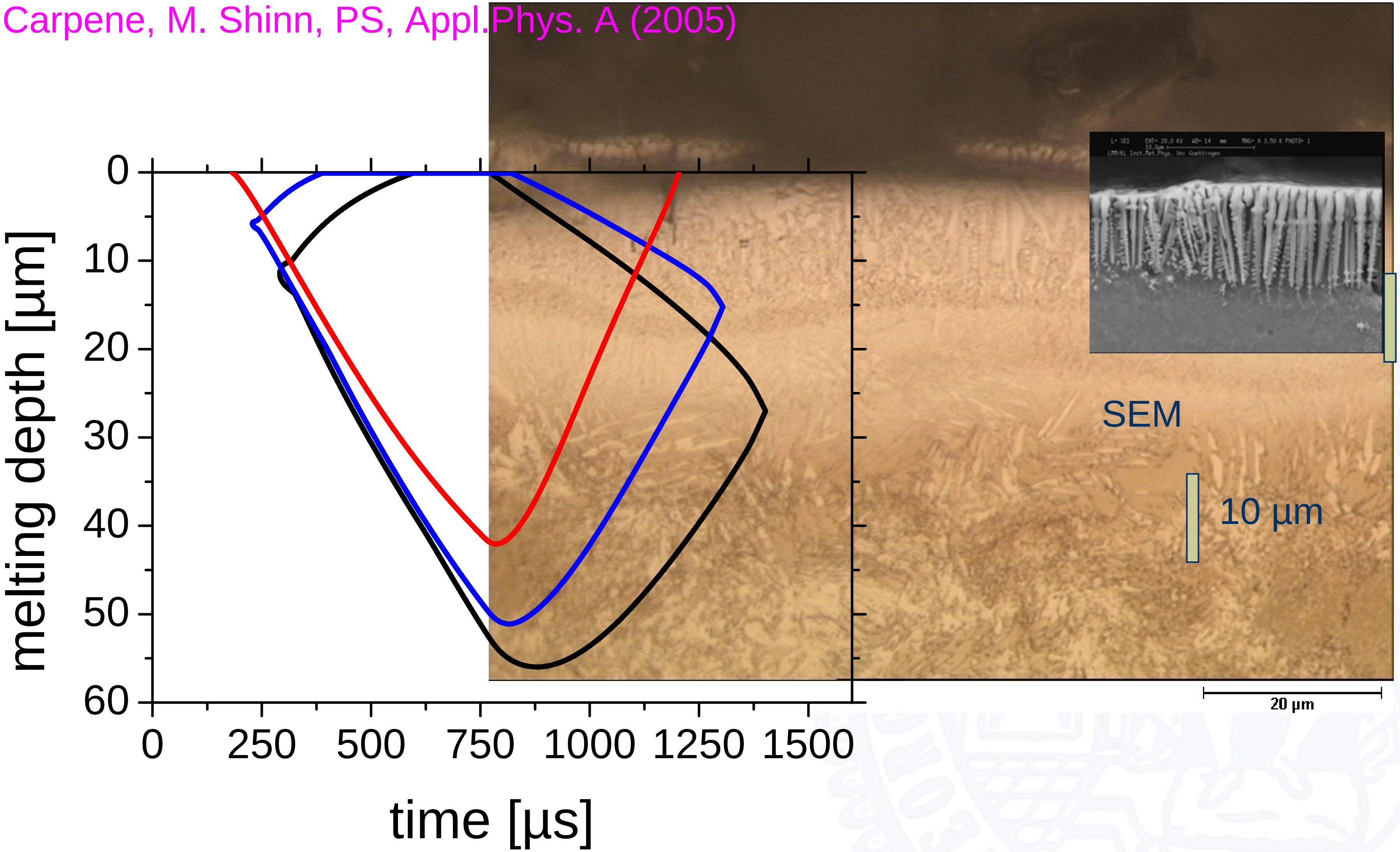
re-solidification starts at surface

free (200) surface is most favorable

Comparison: Simulation and cross section

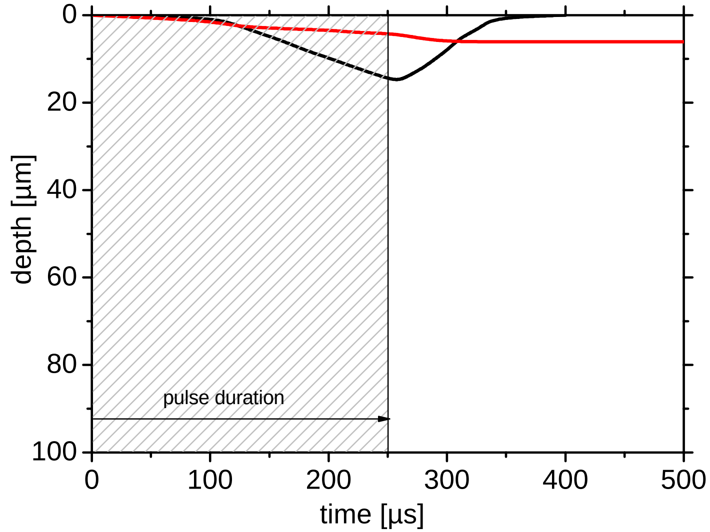
E. Carpene, PS, *MRS Proc.* **780** (2003) Y5.8.1

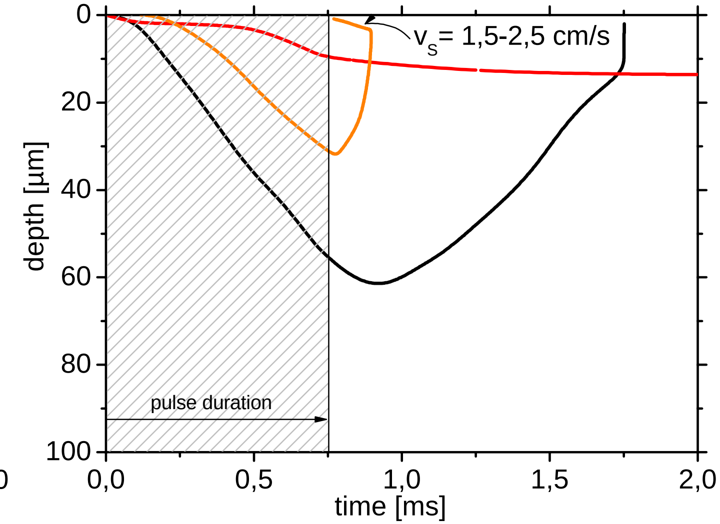
E. Carpene, M. Shinn, PS, Appl. Phys. A (2005)



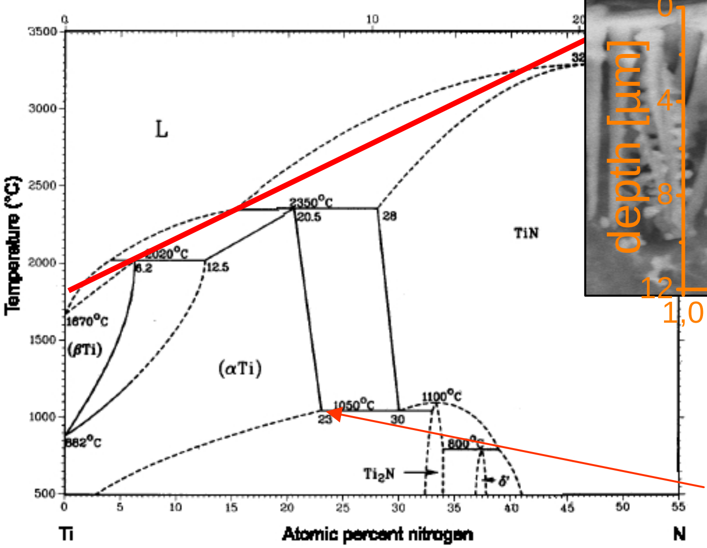
melting depth:
- Ti
- TiN

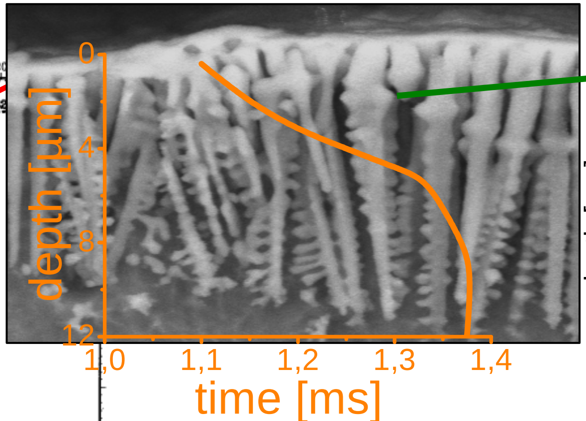
diffusion depth (1/e):
- 1 Pulse
- 2 Pulses
- 2 Pulses (corr.)





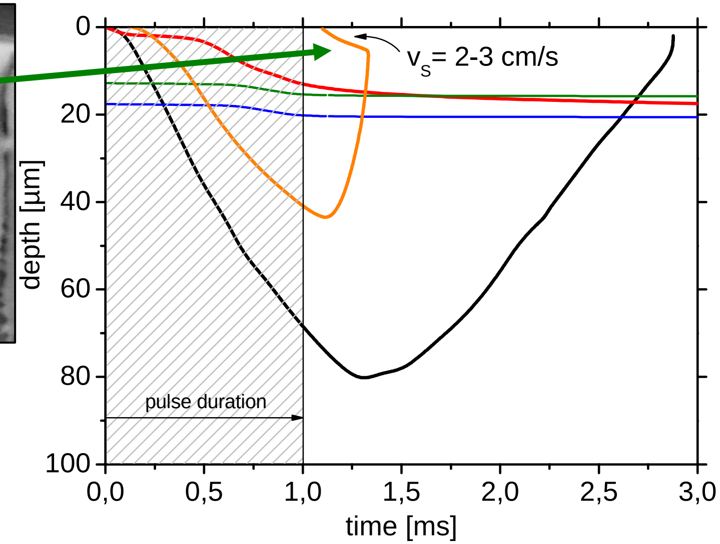
Phase diagramme:



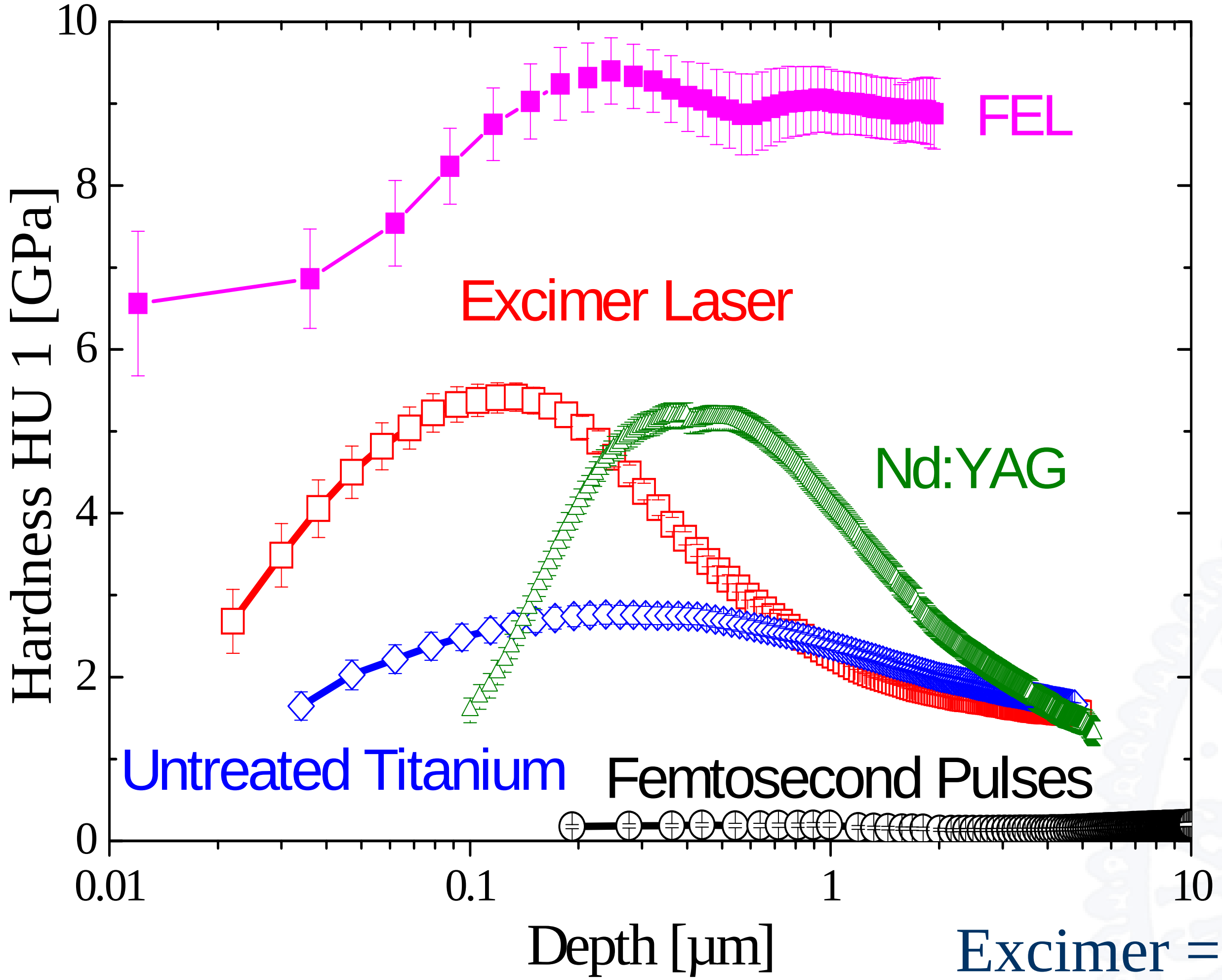


$T_m = f(N\%)$

23% solubility



TiN: hardness – comparison laser

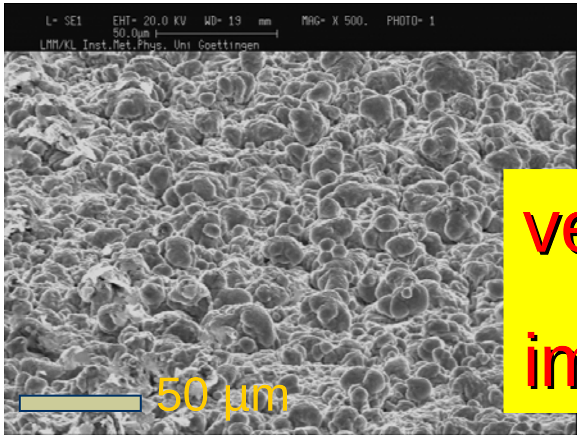


Femtoseconds – very soft (nanocluster)

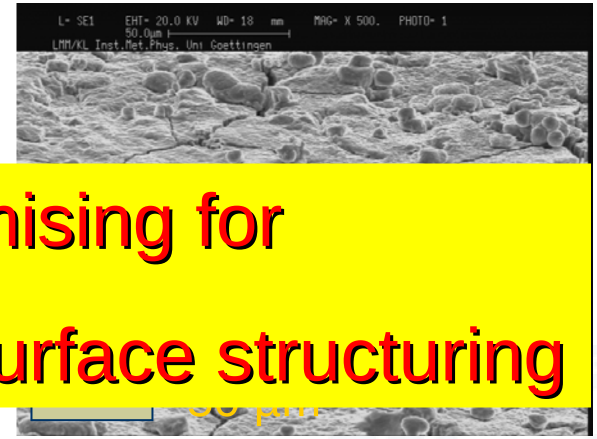
FEL highest hardness and thickest coating

Excimer = „smooth“ (R_a < 0.5 µm)
Nd:YAG: Ra ~ 1-2 µm
FEL: smooth (cracks)

FEL TiN: Surface by SEM



a2: 250 µs, 60 Hz, 100µm



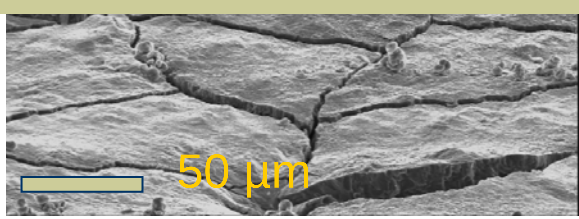
c1: 750 µs, 30 Hz, 100µm

very promising for implant surface structuring

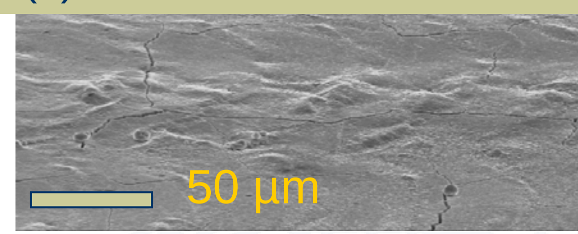
Kieswetter K, Schwartz Z, Hummert TW, Cochran DL, Simpson J, Dean DD, Boyan BD.

Surface roughness modulates the local production of growth factors and cytokines by osteoblast-like MG-63 cells.

Journal of Biomedical Material Research 1996; 32 (1): 55-63.

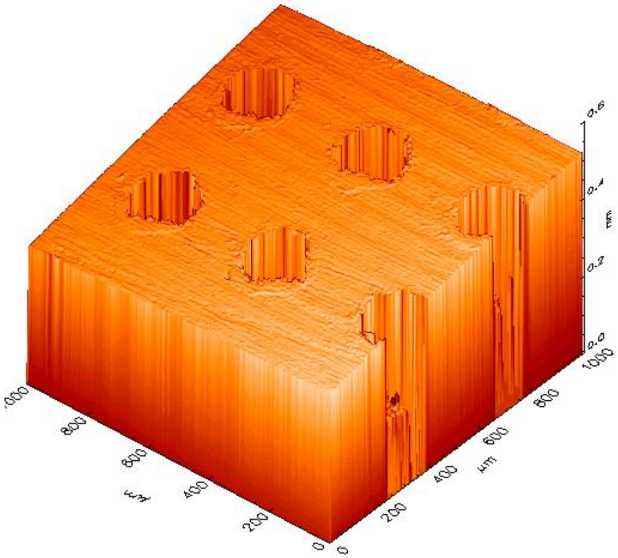


d5: 1000 µs, 30 Hz, 100 µm



d1: 1000 µs, 10 Hz, 200µm

Real Human Implant (hip joint)



3D image of a laser strcutured hio joint (drilling holes of D=200 µm)

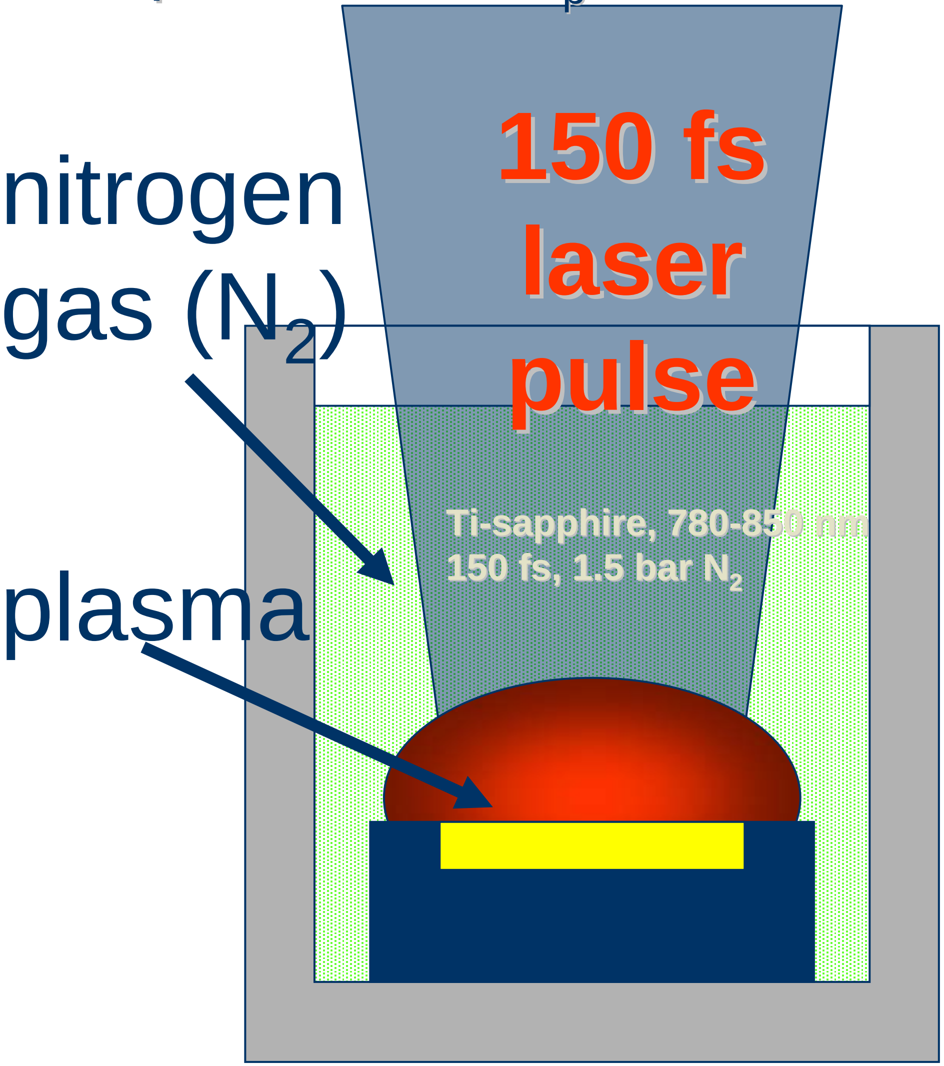
<u>Aim</u>: durable osseo-integration and implant stability

<u>Way</u>: Surface must be a good stimulus for bone ingrowth (good microcontacts=osseo-integration) very stable bone-implant-connection

chemical modification for chemical resistivity

Laser-Structuring of an hip-joint

Ti:Saphir mit CPA, t_p=150 fs, λ=800 nm



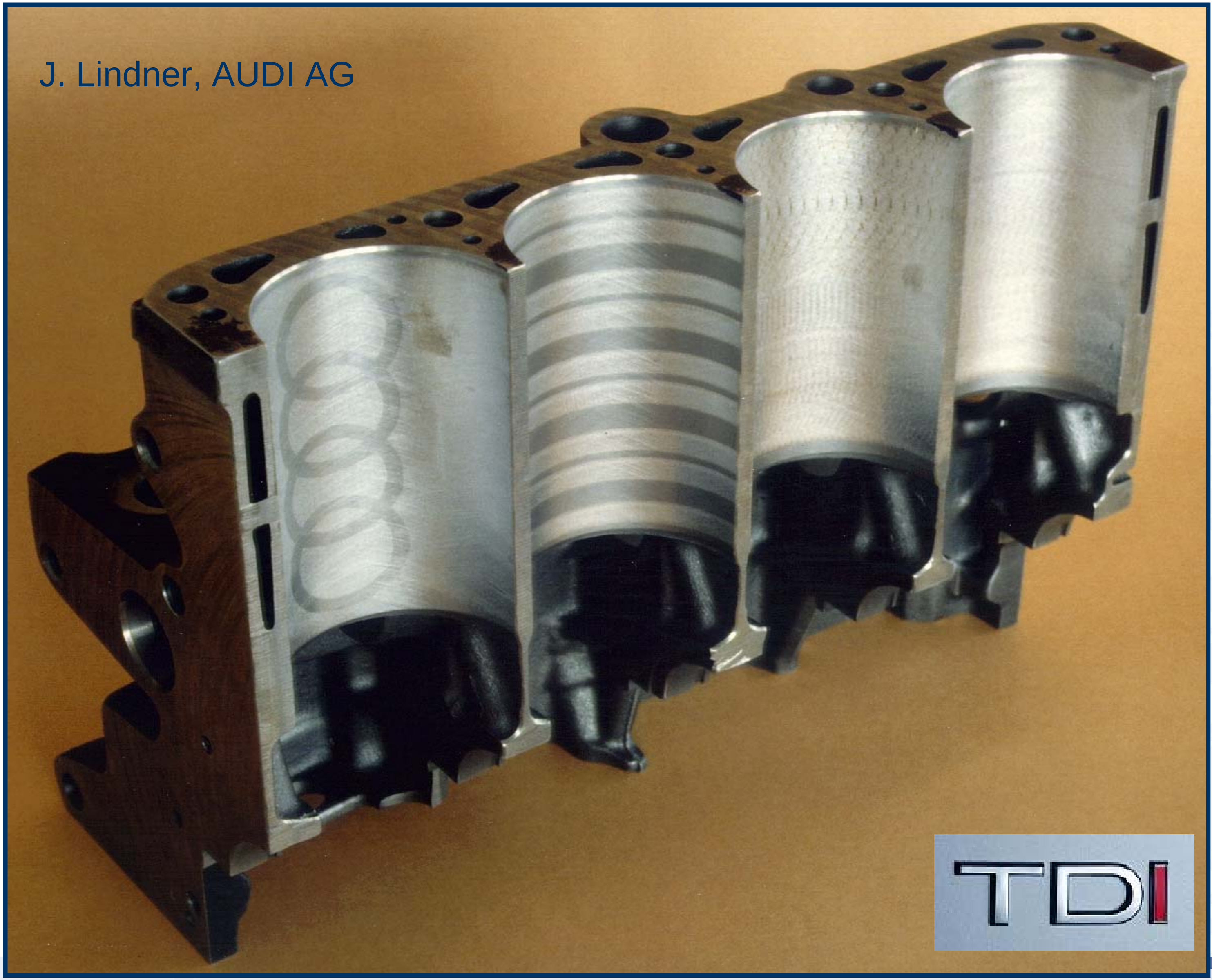
t_p=1.5·10^{-13} s (pulse duration):
⇒ non-thermal treatment (Coulomb explosion)

$$t_p << t_e \Rightarrow T_{elec} >> T_{latt}$$

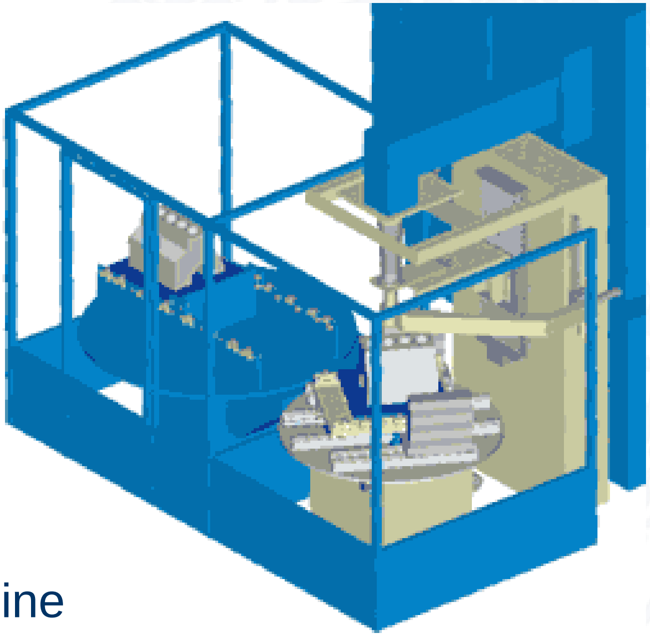
- affected depth ~ 10 nm
- plasma only **after** laser pulse
- highly ionized vapor

Industrial Applications

Applications: Cylinder Liners



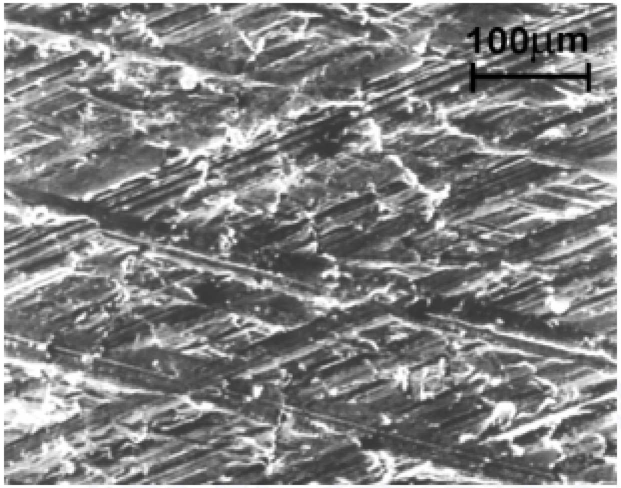
In series production: V6 engine



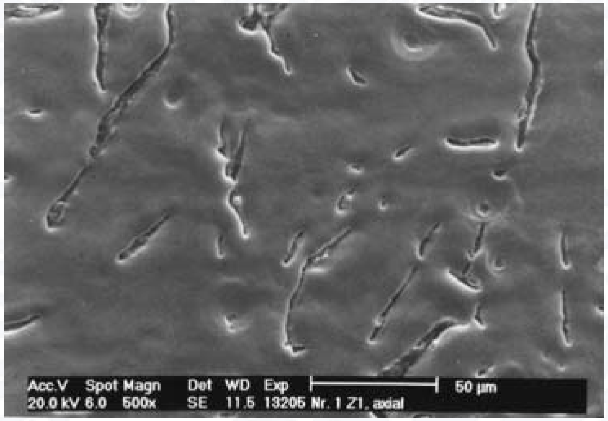
Treatment: mirror inside cylinder;
rotating engine block,
in series production, 5 Excimer simultaneous, 2 min/engine

Audi

Application: Cylinder liners (grey cast iron)



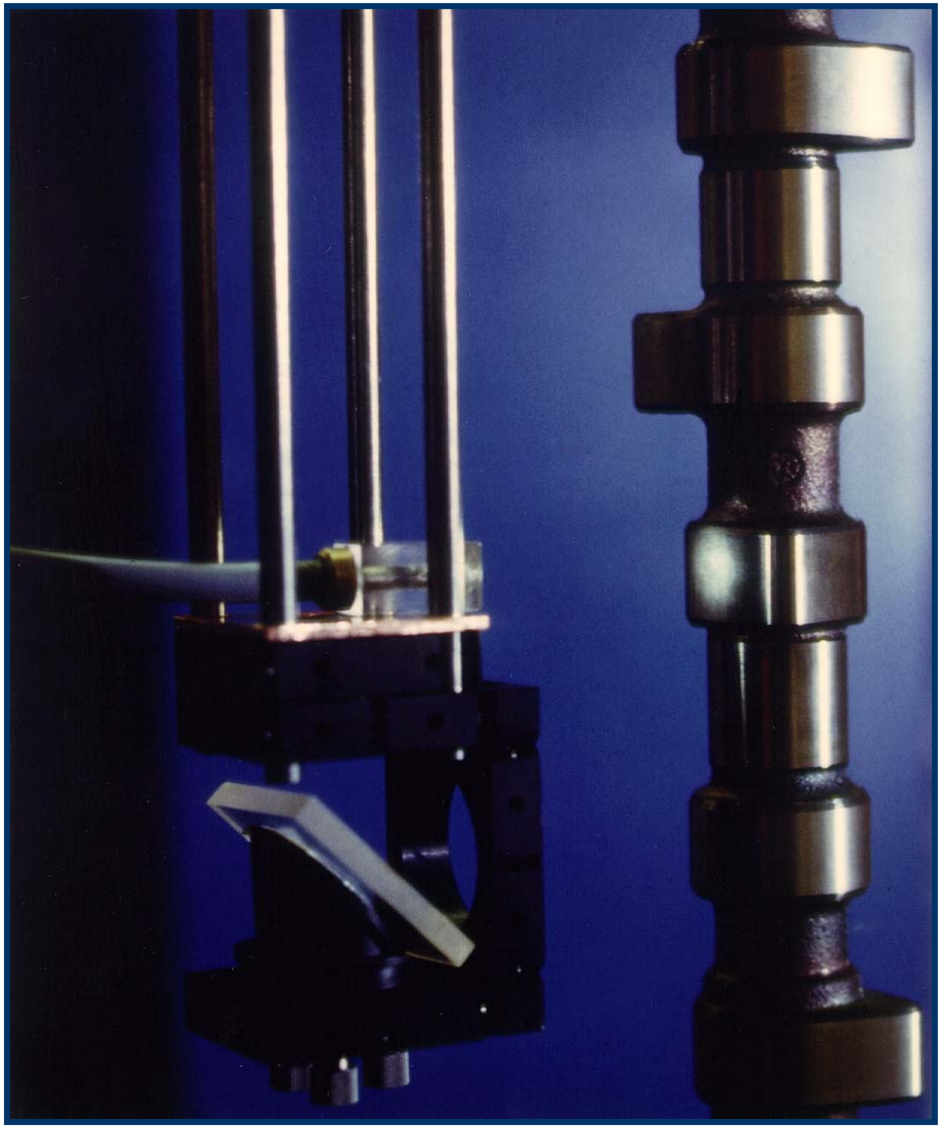
After honing

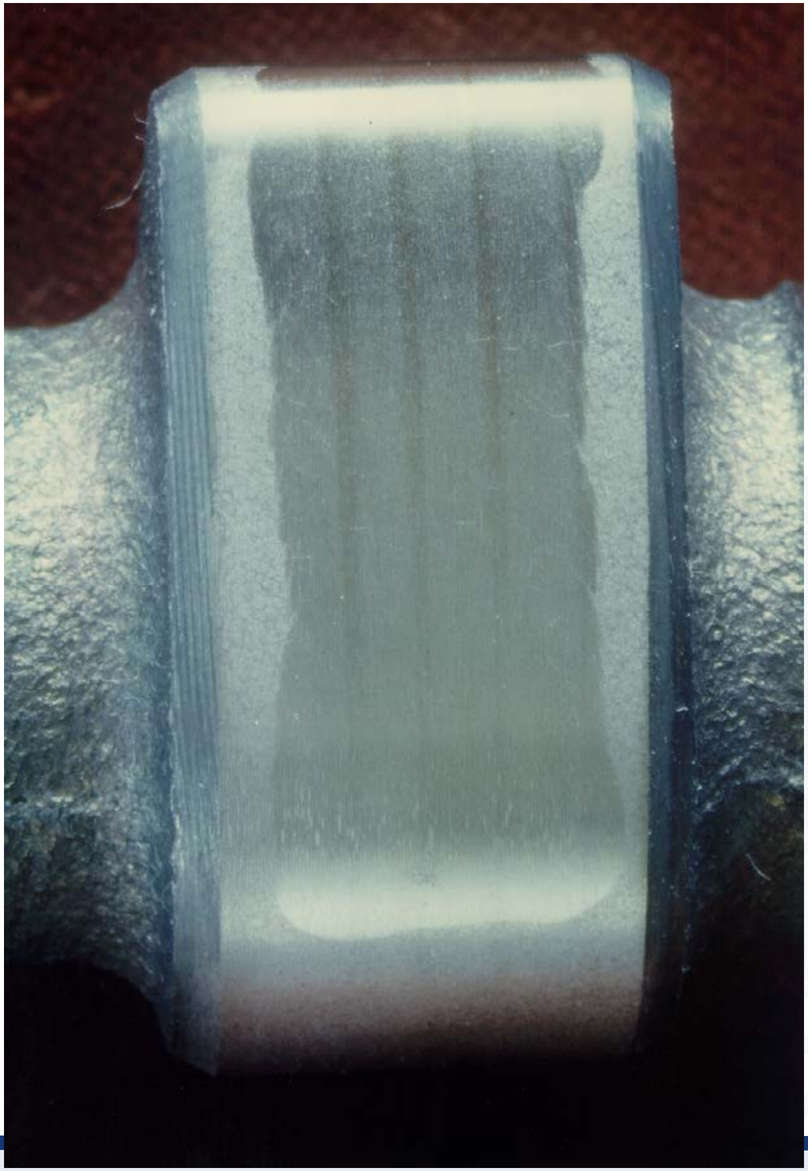


After laser treatment

Reduction of oil consumption (30x)
increase in efficiency and power

Application: Cam Shafts





Summary

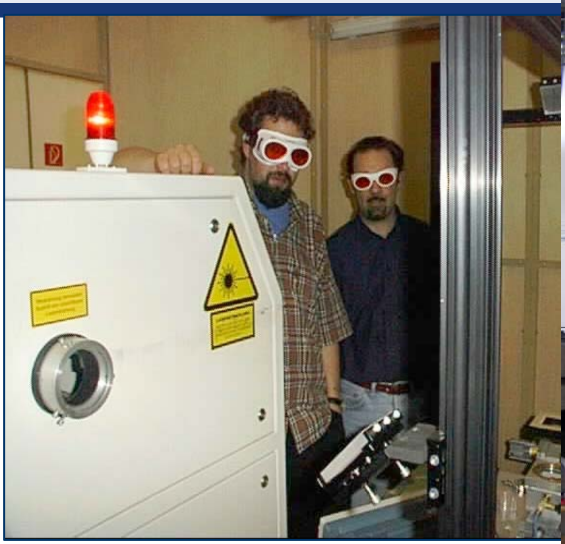
Summary

- Reactive Laser treatments enable flexible, clean and fast ways for the production of new materials, thin films and coatings
- Easy and fast modification and functionalizing of thin films and coatings by laser beams.
- But: sensitive adaptation of material, laser, and laser treatment for the specific application.
- Combination of several methods for resolving complicated processes and optimization of processing necessary.
- FEL is very attractive for fast (competitive) surface treatments
- Nanostructuring, Pulse tailoring
- Many Perspectives for thin films

Cooperations

- FEL, Jefferson Lab, Newport News, Virginia, USA
- AUDI AG, Daimler Benz, INA Wälzlager, IBM, Stihl
- Prof. H.-W. Bergmann (†), Uni Bayreuth, Metall. Werkstoffe
- Prof. A. Emmel, FH Amberg-Weiden, FB Maschinenbau
- Prof. M. Bamberger, Dr. W.D. Kaplan, Technion Haifa, Israel
- Prof. J. Wilden, TU Illmenau, Fertigungstechnik
- BIAS Bremen, LZH Hannover
- Fraunhofer ILT, IPT, RWTH Aachen
- IWT, IWS Dresden, MPI Halle
- LURE Paris, ESRF, Grenoble, BESSY, ANKA
- Prof. H.-J. Spies, TU Freiberg, Werkstoffkunde
- Prof. M. Somers, TU Kopenhagen, Materials Science
- Prof. E. Mittemeijer, Dr. G. Dehm, MPI Stuttgart
- Uni München, Nancy, Leuven, Krakow, Padova, Trento, Jena, Durban, Dortmund, Bratislava, Brno, Budapest, Helsinki, Erlangen, Belgrad, …

Thanks to ….



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- Co-workers and Group:

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  C. Illgner, S. Dhar, S. Cusenza,

  IWT Dresden: J. Kaspar

  FH Amberg: A. Emmel, R. Queitsch
- FEL@Jefferson Lab:

  Fred Dylla, Gwyn Williams, Jo Gubeli,
  Kevin Jordan

- Your interest and patience

You are welcome to visit Göttingen