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

Peter Schaaf\textsuperscript{a)}, M. Shinn\textsuperscript{b)}, E. Carpene\textsuperscript{a)}, J. Kaspar\textsuperscript{c)}

Laser Nitriding

- Reactive or non-reactive atmosphere
- N\textsubscript{2}

Substrate, work piece

APS April Meeting 2006, Dallas, TX
Applications of Thin Films and Coatings

\[ d_1 = \frac{\lambda_0}{4n_{h1}} \]

\[ d_2 = \frac{\lambda_0}{4n_{l1}} \]
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 AIC
- Si₃N₄ and SiC (IBM-Millipede)
- Laser-Conditioning of Magnesium
- Laser-Hydriding Ti-H
- Production pc-a:Si(H) (TFT)
- β-FeSi₂ (photovoltaics, optoelectr.)
- Fe/Ag Multilayers by PLD (GMR, TMR)
- Polymer-PLD (Applications)
- Epitaxial recrystallisation (SiC, SiO₂)

- Excimer Laser 55 ns
- Nd:YAG Laser 8 ns
- FEL 1 ps
- Ti:Sapphire 150 fs
Basic Physics
Excimer Laser: $\lambda = 308$ nm (4.03 eV)
$\tau_p = 55$ ns (FWHM), 5x5 mm$^2$, 
$H = 4$ J/cm$^2$ ($I_0 = 70$ MW/cm$^2$)

gas transparent for laser

1-10 bar $N_2$

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

Evaporation

Ablation

Plasma

Formation

Vacuum: PLD

Numerical: FDM, incl. evaporation, Knudsen

$\frac{dT}{dt} = -5 \cdot 10^{10}$ K/s

$\frac{dd_{liq}}{dt} = -5.25$ m/s

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**Process: Principle of Laser Synthesis**

Plasma (600 ns):
- Laser pulse: 55 ns

Fe, 1 bar N₂, 4 J/cm²
- Plasma: expansion, but gas pressure, Laser ⇒ Laser Absorption Waves (LSAW)
- Plasma: expansion, but gas pressure, Laser ⇒ Laser Supported Combustion Wave (LSC)
- Plasma: expansion, but gas pressure, Laser ⇒ Laser Supported Detonation Wave (LSD)

Plasma (600 ns):
- Laser pulse: 55 ns

Fe, 9 bar N₂, 4 J/cm²
- Plasma: expansion, but gas pressure, Laser ⇒ Laser Absorption Waves (LSAW)
- Plasma: expansion, but gas pressure, Laser ⇒ Laser Supported Combustion Wave (LSC)
- Plasma: expansion, but gas pressure, Laser ⇒ Laser Supported Detonation Wave (LSD)

**Theory**

<table>
<thead>
<tr>
<th>Pressure</th>
<th>v_{LSD} [km/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar</td>
<td>10.4</td>
</tr>
<tr>
<td>9 bar</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Experiment**

<table>
<thead>
<tr>
<th>Pressure</th>
<th>v_{LSD} [km/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar</td>
<td>9.7 (16)</td>
</tr>
<tr>
<td>9 bar</td>
<td>6.6 (16)</td>
</tr>
</tbody>
</table>

**LSD-model**

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

Increased gas pressure ⇒ plasma expansion more slowly
- Plasma pressure higher and lasts longer!

- \(p_p\): 1 bar: 500 bar, 9 bar: 1050 bar

**Graph**

- Hom. Beam
- 0.1 MPa
- 0.9 MPa
- 310
- 120
- 0
- 0.2
- 0.4
- 0.6
- 0.8
- 0.8
- 0.7
- 0.6
- 0.5
- 0.4
- 0.3
- 0.2
- 0.1
- 0
- 0.0
- 0
- 20
- 40
- 60
- 80
- 100
- 10
- 20
- 40
- 60
- 80
- 100

**Graph**

- Pulse duration
- Plasma front position \(z_{front}\)
- Time \(t\) [ns]

**Graph**

- Raw beam
- Hom. beam
- Pulse duration
- Plasma front position


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• Irradiation of Ti in N$_2$
• Free-Electron Laser FEL
### Overview: TiN coatings

<table>
<thead>
<tr>
<th>Laser Type</th>
<th>Wavelength(s)</th>
<th>Pulse Duration</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti:Sapphire + CPA</td>
<td>750 nm</td>
<td>150 fs</td>
<td><img src="image1" alt="Ti:Sapphire Chip" /></td>
</tr>
<tr>
<td>Excimer Laser</td>
<td>308 nm</td>
<td>55 ns</td>
<td><img src="image2" alt="Excimer Laser Image" /></td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>1064 nm, 532 nm</td>
<td>6 ns</td>
<td><img src="image3" alt="Nd:YAG Image" /></td>
</tr>
<tr>
<td>FEL</td>
<td>3100 nm, 1050 nm</td>
<td>&lt; 1 ps</td>
<td><img src="image4" alt="FEL Image" /></td>
</tr>
</tbody>
</table>

**16. Juni 2006**
Faster and better with FEL?

**Jefferson Lab**
Newport News, Virginia, USA

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Time (µs)</th>
<th>Time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 ms</td>
<td>250 µs</td>
<td>1 ps</td>
</tr>
<tr>
<td>Macropulse</td>
<td>Micropulse</td>
<td>27 ns</td>
</tr>
<tr>
<td>37.4 MHz</td>
<td>37.4 MHz</td>
<td>10 mm</td>
</tr>
</tbody>
</table>

FEL

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

**3.1 µm**
**2 kW**

flexible in timing

10 mm
FEL: TiN Synthesis

Line scan: velocity $u=0.5$ mm/s, line width $D=0.4$ mm, shift $\delta (50, 100, 200 \mu m)$

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Macro $t_m$ ($\mu$s)</th>
<th>Macro $f_m$ (Hz)</th>
<th>shift $\delta$ ($\mu$m)</th>
<th>Fluence $\phi_m$ (J/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-a1</td>
<td>250</td>
<td>60</td>
<td>200</td>
<td>123</td>
</tr>
<tr>
<td>Ti-a2</td>
<td>250</td>
<td>60</td>
<td>100</td>
<td>123</td>
</tr>
<tr>
<td>Ti-a3</td>
<td>250</td>
<td>60</td>
<td>50</td>
<td>123</td>
</tr>
<tr>
<td>Ti-b1</td>
<td>500</td>
<td>30</td>
<td>100</td>
<td>246</td>
</tr>
<tr>
<td>Ti-c1</td>
<td>750</td>
<td>30</td>
<td>100</td>
<td>369</td>
</tr>
<tr>
<td>Ti-d1</td>
<td>1000</td>
<td>10</td>
<td>200</td>
<td>492</td>
</tr>
<tr>
<td>Ti-d2</td>
<td>1000</td>
<td>10</td>
<td>100</td>
<td>492</td>
</tr>
<tr>
<td>Ti-d3</td>
<td>1000</td>
<td>20</td>
<td>200</td>
<td>492</td>
</tr>
<tr>
<td>Ti-d4</td>
<td>1000</td>
<td>30</td>
<td>200</td>
<td>492</td>
</tr>
<tr>
<td>Ti-d5</td>
<td>1000</td>
<td>30</td>
<td>100</td>
<td>492</td>
</tr>
</tbody>
</table>

FEL - Ti in 1 bar N$_2$

Always TiN
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

Jörg Kaspar, IWS Dresden

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

Rocking curve

Strong texture for long macropulses and small overlap
no texture for short macropulses and large overlap

no texture (polycryst.)
fully textured (single cryst.)

Hardness [GPa]
depth [µm]

1000 µs, 10 Hz, 200 µm
1000 µs, 30 Hz, 100 µm
250 µs, 60 Hz, 100 µm

Textured material

Texture parameter η

\[ η = \frac{D^2 \cdot f}{V \cdot σ} \]

0 = perfect (200) texture

FEL TiN: Pole Figures

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

Ti-d3 (Ti-25)
scan: 5° × 5°
φ: 0-360°
χ: 0-80°
Simulation of Melting and Solidification

Strong dependence of the melting temperature on the nitrogen content.

Nitrogen concentration gradient:
- Re-solidification starts at surface.
- Free (200) surface is most favorable.

$t_{\text{macro}} = 750 \, \mu s$

Surface temperature [K], melting depth [\mu m]

Time [\mu s]
Comparison: Simulation and cross section

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

**Graph**

- Untreated Titanium
- Femtosecond Pulses
- Excimer Laser
- Nd:YAG
- FEL

**Equations**

- Excimer = “smooth“ ($R_a < 0.5 \ \mu m$)
- Nd:YAG: $R_a \sim 1-2 \ \mu m$
- FEL: smooth (cracks)
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.

Real Human Implant (hip joint)

3D image of a laser structured hip joint (drilling holes of D=200 µm)

Aim: durable osseo-integration and implant stability

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

chemical modification for chemical resistivity
Femtosecond pulses (Ti:sapphire laser)

Ti:Saphir mit CPA, $t_p = 150$ fs, $\lambda = 800$ nm

nitrogen gas ($N_2$)

150 fs laser pulse

plasma

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

- affected depth $\sim 10$ nm
- plasma only after laser pulse
- highly ionized vapor

$t_p << t_e \Rightarrow T_{\text{elec}} >> T_{\text{latt}}$
Industrial Applications
Applications: Cylinder Liners

J. Lindner, AUDI AG
In series production: V6 engine

Treatment: mirror inside cylinder; rotating engine block, in series production, 5 Excimer simultaneous, 2 min/engine
Application: Cylinder liners (grey cast iron)

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
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- Prof. J. Wilden, TU Ilmenau, 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
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  IWT Dresden: J. Kaspar
  FH Amberg: A. Emmel, R. Queitsch

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You are welcome to visit Göttingen

New Physics building