Laser assisted production of plasma for analytical applications inside fusion vessels

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Outline

• Rationale: wall materials and deposited layers in fusion reactors

• Introduction to LIBS

• Set-up for LIBS stand-off measurements inside a tokamak

• Results:
  – LIBS in vacuum
  – Depth profiling on wall tiles
  – Trace detection
  – Quantitative analysis of constituents and majors impurities
Rationale

Plasma-wall interactions during a Tokamak operation may appreciably alter both the walls composition and the plasma properties.

Two noxious effects should be monitored in order to optimize the Tokamak operation:

- Walls outer layer erosion, due to the contact with the hot plasma,
- Deposition of impurities on the outer wall layers.

Both phenomena may reduce the plasma intensity and lifetime, limiting the fusion reactor performances.
Tyle-like samples with con coatings relevant to fusion vessels

from NILPRP (National Institute for Laser, Plasma and Radiation Physics) Magurele-Bucarest, Romania; size: 4x2.5x0.5 cm³ 2 different types of coatings on Titanium bulk.

<table>
<thead>
<tr>
<th>No.</th>
<th>Association</th>
<th>Number of samples</th>
<th>Identification of samples</th>
<th>GDOS profiles</th>
<th>Coating thickness (µm)</th>
<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
<td>Mo</td>
</tr>
<tr>
<td>2</td>
<td>ENEA Italy</td>
<td>10</td>
<td>IU-90-13, IU-90-14, IU-90-15, IU-90-16, IU-90-17, IU-94-5, IU-94-6, IU-94-7, IU-94-8, IU-94-9</td>
<td>IU-90-17-1, IU-90-23-1, IU-94-7-1, IU-94-18-1</td>
<td>10.8±1  11.5±1  12.8±1</td>
<td>2.0  2.2  2.4</td>
</tr>
</tbody>
</table>

1st set: multilayer W-Mo (coating W-Mo). Interlayer “Mo” to test erosion

<table>
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<tr>
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<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Thickness (µm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C    W    O</td>
</tr>
<tr>
<td>2</td>
<td>ENEA Italy</td>
<td>1+1</td>
<td>EU-567-2, EU-568-3</td>
<td>EU-567-1, EU-568-1</td>
<td>12.2, 8.5</td>
</tr>
</tbody>
</table>

2nd set: single layer C-W (coating C-W) at different percentages for quantitative analysis
Reference samples

- Growth by Combined Magnetron Sputtering and Ion Implantation (CMSII).
- Calibration by Glow Discharge Optical Spectroscopy (GDOS)

1° set
- W
- Mo
- Ti
- 10 ± 1 µm
- 2 ± 1 µm

2° set
- C-W
- Ti
- Bulk
- 8.5 (12) ± 1 µm

![Graphs showing atomic concentration depth profile for different elements.](image-url)
Laser Ablation and LIBS diagnostics

LIBS utilizes laser pulses focused at a surface to ablate a small fraction of the outer layers, ionizing the ejected material, thus generating a plasma suitable to remote optical diagnostics: stratigraphy and quantitative analysis.

In a standard LIBS set-up a portion of the radiation emitted by atomic and ionic species is collected by the receiving optics and sent to a high resolution time gated spectrometer.
LIBS Plasma expansion and relaxation

- Expansion
- Shock waves
- Deceleration of free electron (Bremsstrahlung emission)
- Collisions
- Chemical Recombination
- Radiative Recombination
- Local Thermal Equilibrium

The time scale does depend on the surrounding atmosphere

- Cooling down
- Cluster and nanoparticles ejection

Analytical applications depend on the onset of LTE

<table>
<thead>
<tr>
<th>Laser pulse</th>
<th>Continuum emission</th>
<th>LTE Ionic lines</th>
<th>Atomic lines</th>
<th>Plasma decay</th>
<th>Particles ejection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10 ns</td>
<td>500 ns</td>
<td>0.5-1 µs</td>
<td>1-3 µs</td>
<td>&gt; 5 µs</td>
<td>&gt; 10 µs</td>
</tr>
</tbody>
</table>

Water               Air (1 atm)           Vacuum
During Local Thermodinamic Equilibrium (LTE) plasma temperature and electron density are assumed to be constant: **Boltzmann statistics is suitable to describe the plasma behaviour**.
LIBS Set-up for in vessel diagnostics at reduced pressure (vacuum)

- Laser Nd:Yag $\lambda = 1064$, 532 nm
  ($E_{\text{max}} \sim 1\text{J/pulse}$, $\Delta t = 8$ ns)
- Spectrograph Triax 550
  max res. $\sim 0.1$ Å (@500 nm)
- ICCD Andor 16 bit DH532-18F
  min. time gate 10 ns
Results

Plasma parameters in vacuum: \( n_e \)

From Stark broadening
Laser fluence: 35.4 J/cm\(^2\)
Residual pressure: 5 \( \times \) 10\(^{-5}\) mbar
Instrumental broadening: 0.042 nm

\[
N_e = \frac{\Delta \omega}{w \cdot 10^{17} \text{ (cm}^{-3})} = 5 \cdot 10^{17} \text{ cm}^{-3}
\]

Sample: Titanium bulk purity > 98%
F=35.4 J/cm\(^2\)
vacuum 10\(^{-6}\) mbar

Ionic line Ti II @ 346.18 nm (parameter \( w = 0.06 \text{ nm [10}^{18}\text{ cm}^{-3}\) after taking into account instrumental broadening

Normalized LIBS intensity [AU]
Results

Plasma parameters in vacuum: $T$

Assuming a Boltzmann distribution each line emission is proportional to the species concentration and the starting energy level population:

$$I = \left( C_0 \cdot \frac{g_k A_{ki}}{\lambda_k} \right) \exp\left( -\frac{E_k}{kT} \right)$$

$g_k =$ level multiplicity, $A_{ki} =$ transition probability ($k \rightarrow i$), $\lambda_k =$ emission wavelength, $E_k =$ level energy, $k =$ Boltzmann constant, $T =$ temperature.

A Boltzmann Plot can be built for each species with slope $-1/kT$.

B.P. has been obtained on W in C-W coatings

$T = 18900 \pm 1200$ K
By monitoring LIBS signal intensity relevant to W, Mo, Ti, C emissions we could identify Mo interface and determine the ablation rate for each coating.

Results

Depth profiling: Time evolution of LIBS spectrum as a function of laser shot number
Results

depth profiling: ablation rate

• Sub micrometric resolution always achieved.
• Possible high sensitive detection of (re)-deposited layers.

<table>
<thead>
<tr>
<th>Fluencia laser (J/cm²)</th>
<th>Coating W-Mo (10.8 +2.0 µm) # colpi laser</th>
<th>Ablation rate (µm/shot)</th>
<th>Coating C 82%-W 15% (8.5 µm) # colpi laser</th>
<th>Ablation rate (µm/shot)</th>
<th>Coating C 70%-W 27% (12.2 µm) # colpi laser</th>
<th>Ablation rate (µm/shot)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.2</td>
<td>//</td>
<td>//</td>
<td>29</td>
<td>0.293</td>
<td>40</td>
<td>0.3</td>
</tr>
<tr>
<td>18.4</td>
<td>//</td>
<td>//</td>
<td>27</td>
<td>0.315</td>
<td>35</td>
<td>0.343</td>
</tr>
<tr>
<td>19.7</td>
<td>22</td>
<td>0.454</td>
<td>25</td>
<td>0.34</td>
<td>32</td>
<td>0.375</td>
</tr>
<tr>
<td>25</td>
<td>19</td>
<td>0.526</td>
<td>23</td>
<td>0.37</td>
<td>30</td>
<td>0.4</td>
</tr>
<tr>
<td>31.2</td>
<td>18</td>
<td>0.556</td>
<td>23</td>
<td>0.37</td>
<td>28</td>
<td>0.429</td>
</tr>
<tr>
<td>35.4</td>
<td>16</td>
<td>0.625</td>
<td>21</td>
<td>0.404</td>
<td>27</td>
<td>0.444</td>
</tr>
</tbody>
</table>
Environmental hydrogen traces detected on all samples at the first laser shot on the surface.

Contaminant Oxygen detected in C-W sample (O 3%) also detected in the innermost layers.

Results
Trace elements detection

H\(_\alpha\) @ 656, 36 nm

O I @ 777.19 & 777.42 nm
Results

Quantitative analysis by CF method

Concentration is retrieved from intercepts on the y-axis of the B.P.

On all species present the closure reaction is assumed:

\[ \sum_{i=1}^{n} q_i = 1 \]

CF has been tested on C-W Coatings in the spectral range 416-445 nm

1. Local Thermodynamic Equilibrium condition (LTE); it allows to apply Boltzmann statistics to infer chemical concentration of all detected species.

2. No saturation should occur for the considered emission lines.

3. Stoichiometric laser ablation should be verified.
Quantitative Analysis: LTE condition

McWhirther* criterion: from plasma temperature $T$, and electron density $n_e$ it is possible to have the necessary condition for LTE to occur:

$$n_e \geq 1.6 \times 10^{12} T^{1/2} \Delta E^3$$

$\Delta E$ (eV) maximum energy of the transition checked.

For current measurements: $T = 19000 \, ^{\circ}K$, $\Delta E = 2.98 \, eV$, $\rightarrow n_e \sim 6 \times 10^{15} \, cm^{-3}$.

We are well above threshold with our plasma ($n_e \sim 5 \times 10^{17} \, cm^{-3}$)

Quantitative analysis: saturation phenomena

Non linear dependence of line intensity on laser fluence at high fluences

Compromise between spectral intensity and saturation

→ remote measurements at fluence = 25 J/cm²
Quantitative analysis: stoichiometric ablation

Minimum laser intensity needed to produce vaporization

Moenke-Blakenburg* formula:

\[ I_{\text{min}} = \frac{\rho L_v k^{1/2}}{\Delta t^{1/2}} \left( W / cm^2 \right) \]

\( \rho \) = densità del materiale, \( L_v \) = calore latente di vaporizzazione, \( k \) = diffusività termica e \( \Delta t \) = durata dello shot laser.

Current measurements \( \Delta t_{\text{laser}} = 8 \text{ ns}, \Phi_{\text{laser}} = 25 \text{ J/cm}^2, I_{\text{laser}} \sim 3.25 \text{ GW/cm}^2 \), mentre \( I_{\text{minW}} \sim 1.14 \text{ GW/cm}^2 \) e \( I_{\text{minC}} \sim 0.85 \text{ GW/cm}^2 \)

CF Results
concentrazioni C-W

Good agreement with reference values (GDOS del NILPRP)

Errore dovuto a vari fattori tra cui:

- Incertezza residua su T
- Range spettrale limitato (per ridurre al minimo la distruttività della tecnica)
- Integrazione scarsa (layer sottili)

<table>
<thead>
<tr>
<th>Elemento</th>
<th>CF-LIBS</th>
<th>Valore nominale (GDOS)</th>
<th>Campione</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>70 ± 12.5</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>W</td>
<td>27 ± 12.5</td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>76 ± 12.5</td>
<td>82</td>
<td>2</td>
</tr>
<tr>
<td>W</td>
<td>21 ± 12.5</td>
<td>15</td>
<td>2</td>
</tr>
</tbody>
</table>