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in ITER relevant samples**

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Deuterium detection and quantification by laser-induced-breakdown-spectroscopy and calibration free analysis in ITER relevant samples

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Tritium (T) inventory in Plasma Facing Components (PFCs) will be one of the critical issues for ITER because of the impact tritium can have on the machine operation and safety. Laser Induced Breakdown Spectroscopy (LIBS) is a promising technique to accomplish this task, providing both qualitative and quantitative composition of the chemical elements retained in PFCs. LIBS does not require sample pretreatment or manipulation, it can work *in-situ* between fusion discharges or during maintenance periods, it is suitable for measurements at different residual pressures, with different background gases. It can detect all the chemical elements through their spectral emission. This paper presents the results of LIBS measurements at 100 mbar nitrogen pressure on metallic coating (W-Al-D) simulating the superficial composition of ITER divertor PFCs contaminated with nuclear fuel and material eroded from the first wall.

LIBS spectra showed clear W, Al, D emission lines. A quantitative estimation of their relative concentration was performed by applying the Calibration Free (CF) analysis. CF does not require reference samples, so it's particularly suitable for this purpose. CF results were compared with the nominal concentrations and were found in good agreement with the latter.

Keywords: LIBS, PFC, D-T retention, ITER divertor tiles , calibration free (CF)

1. Introduction

The detection, localization and quantification of unburned nuclear fuel (Deuterium and, in particular, Tritium) and materials eroded from the first wall will be one of the main issues in ITER, because of safety and administrative limits to accomplish in case of accidental release in the environment [1-2]. The major concerns related to T in ITER is its retention, diffusion and/or hydrides formation in PFCs. Concerns related to other materials are the localization of the eroded and re-deposited species, to determine how much fuel and/or dust is retained and generated in wall components. Among the eligible methods to accomplish this tasks and characterize PFCs, LIBS [3] is an analytical technique gaining increasing interest, because it does not require sample pretreatment or manipulation, it can work *in-situ* between fusion discharges or during maintenance periods, it is suitable for measurements at different residual pressures, with different background gases. Moreover LIBS can detect all the chemical elements through their spectral emission. In LIBS a small fraction of the sample (of the order of μg) is vaporized by focusing a high power laser pulse on it. A short-lived but highly luminous plasma is formed and the ejected material is dissociated into excited ionic and atomic species emitting characteristic spectral lines from which they can be detected and identified. LIBS can provide not only a qualitative but also a quantitative estimation of the detected chemical elements by applying the calibration free (CF) approach [4]. CF is based on the knowledge of the plasma parameters and line integrated intensities, provided that the LIBS plasma is close to the local thermodynamic equilibrium (LTE) [5]. The results of a LIBS analysis of thin metallic layers simulating PFCs are here presented. Measurements were performed

at 100 mbar nitrogen atmosphere to investigate the effect of pressure on the measurement performance. The CF approach allowed a quantitative estimation of the detected elements.

2. Experiment

2.1 Samples

Samples were rectangular molybdenum tiles (10 x 15 mm²), coated with 3 μm thick mixed W-Al-D layer by using the Combined Magnetron Sputtering and Ion Implantation technique [6]. After production, the relative content of W, Al, D was measured by Glow Discharge Optical Emission Spectrometry [7] resulting in W 85% , Al 10%, D 5% atomic concentration. This mixed layer was designed to simulate contamination of the ITER divertor tungsten tiles [8], where Be, eroded from the first wall (represented by Al in these samples, due to Be toxicity) and unburned D+T (represented by D and environmental H) will be re-deposited and implanted on W [9].

2.2 LIBS system

The LIBS system is composed of a Nd:YAG laser HANDY-YAG (wavelength 1064 nm, pulse width 10 ns, repetition rate 10 Hz, spot diameter 1 cm) focused by a 1 inch, 500 mm focus plano-convex lens (BK7) into a vacuum chamber (350 mm diameter) through a 2", 1064-AR coated window. Pulse energy is 250 mJ, The focus point of the lens is set a few centimeters behind the target surface to prevent breakdown of air in front of the sample. In this way the spot diameter at the sample surface is 1.5 mm. Laser fluence and power density are 14 J/cm² and 1.4 GW/cm² per shot. LIBS plasma is collected collinearly to the laser beam in order to reduce the influence of the outer regions of the plasma which

are known to be at lower temperature and electron density than the central area [10]. This was accomplished by posing an holed aluminum mirror tilted 45° in front of the vacuum window. The focused laser beam passes through this hole towards the sample. Plasma light emitted collinearly to the laser is reflected by this mirror to a 2" diameter collection lens ($f = 200$ mm), focusing the light in an optical fibers bundle (2 mm total diameter, $200 \mu\text{m}$ core diameter for each fiber, NA 0.12).

A TRIAX550 Czerny-Turner spectrograph with a 2400 gr/mm grating ($\lambda/\Delta\lambda = 50000$) complete the optical chain. The resolution ($\Delta\lambda = 0.013$ nm at 656 nm) is sufficient for the spectral analysis of the nearby deuterium D_α (656.1 nm) and hydrogen H_α (656.28 nm) Balmer alpha emission lines (hydrogen is expected as

environmental contaminant). An Andor ICCD camera DH534-18F, (1024×256 pixels) records the LIBS signal, covering a spectral window of 12 nm. Samples have been placed in the vacuum chamber on a motorized x-y stage at residual air pressure of 100 mbar. Time delay from laser pulse and ICCD gate was set to 1500 ns, ICCD gate width was set to 1000 ns.

For the detection of D traces the spectral region around the $D_\alpha - H_\alpha$ lines is recorded, including also some atomic tungsten emission. For the simultaneous detection of W and Al the spectral region between 391 and 402 nm is recorded, where strong Al I lines (394.4 and 396.15 nm) and many well resolved atomic and ionic W lines are present.

Fig. 1 shows a scheme of the LIBS setup.

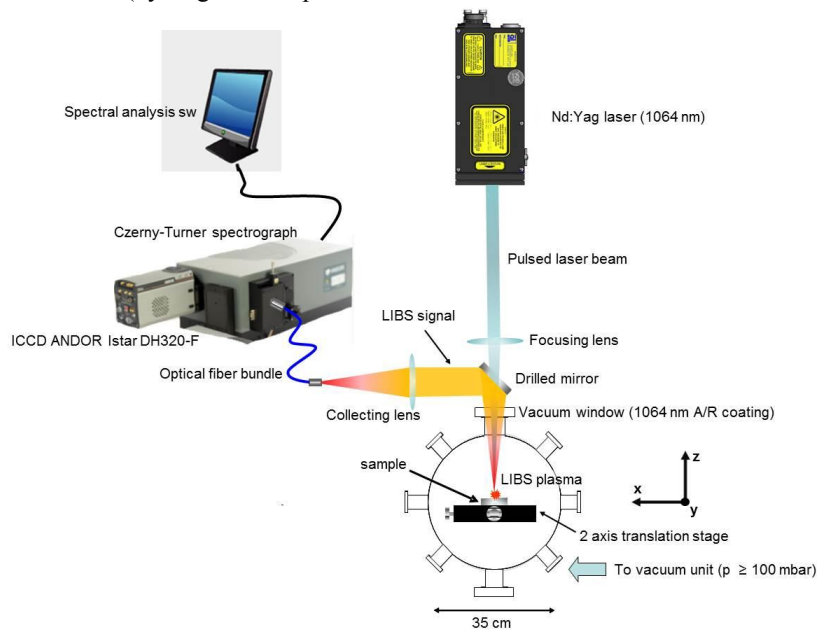


Fig. 1. Scheme of the LIBS apparatus with collinear detection.

3. Results and discussion

3.1 LIBS In-depth stratigraphy

The stratigraphy of the coating was studied recording the emission intensity of W and Al emission lines as a function of the laser shot number. A sequence of 20 laser shots was applied on the same point of the sample and the corresponding spectra recorded one-by-one, as shown in Fig. 2. Apart for the first shot, whose enhanced intensity is due to the superficial contamination by material previously ablated from other closeby points, the W and Al line intensities appear to be quite stable until the 12th laser shots (in red in Fig. 2) after which the signal decrease abruptly. From these results an average ablation rate (AAR) was estimated to be about 250 nm, showing the high sensitivity of the technique for thin layers, meaning detection of low level of contamination.

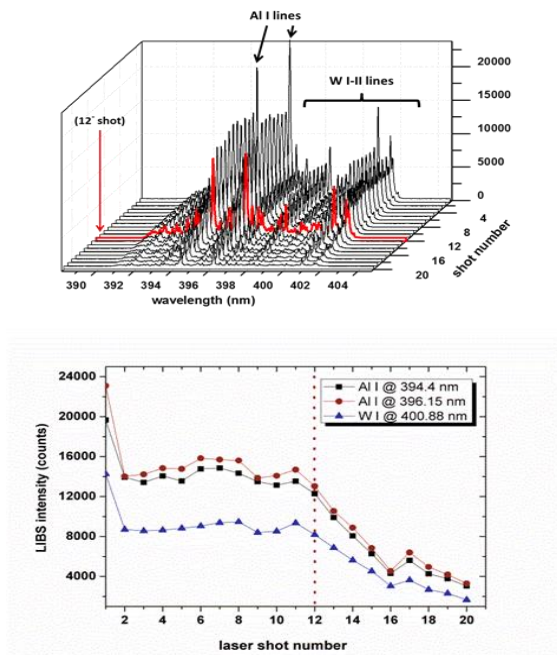


Fig. 2. (up) sequence of LIBS spectra on the W-Al-D superficial coating in the 391-402 spectral region. (bottom). Selected Al I – WI line intensities as a function of laser shot number; the vertical dotted line marks the 12° laser shot where the intensity abruptly decreases

3.1 D detection

Fig. 3a shows the LIBS spectrum of the W-Al-D coating around the D_α - H_α lines. Nearby W I lines are also detected in this spectral region. Al is not detected lacking of strong atomic and ionic emission lines.

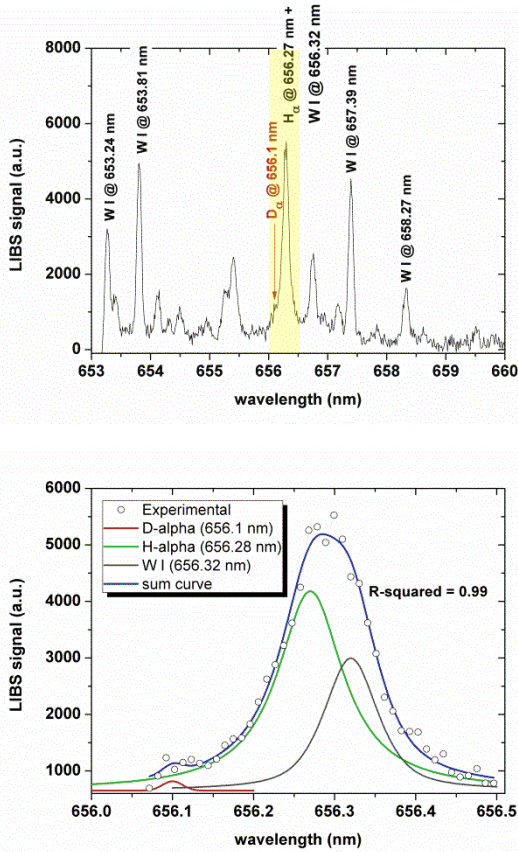


Fig. 3a. LIBS spectrum of the coating in the Balmer alpha emission region. 3b magnification of the central region of the spectrum (in light yellow in Fig. 3a) with the D_α - H_α – W I lines and their deconvolution.

Although partially overlapping with the more intense H_α emission at 656.27 nm and WI emission at 656.32 nm, a weak D_α emission at 656.1 nm was observed. In Fig. 3b a magnification of the central region of the spectrum is shown, where the experimental signal was fitted with Pseudo-Voigt analytical functions [11] to obtain the three components.

3.2 CF quantitative analysis

The CF quantitative analysis assumes the LTE condition for the LIBS plasma. In this condition the line integral intensity I_{ki} corresponding to a specific transition between two levels E_k and E_i can be expressed as [12,13]:

$$I_{ki} = C^S A_{ki} \frac{g_k e^{-(E_k/K_B T)}}{P_S(T)} \quad (1)$$

where C^S is the species concentration, A_{ki} is the transition probability for the specific line, g_k is the k -level degeneracy, K_B is the Boltzmann constant, T the plasma temperature and $P_S(T)$ the partition function. The LIBS plasma is also considered to resemble the sample stoichiometric composition and to be optically thin. To check if stoichiometric ablation occurred in our LIBS plasma an estimate of the minimum power density required to produce vaporization of all the considered elements was performed through the following relation [14]:

$$I_{min} = \rho L_v k^{1/2} / \Delta t^{1/2} (W/cm^2) \quad (2)$$

where I_{min} is the minimum power density required to produce vaporization of the target material, ρ is the material density, L_v is the latent heat of vaporization, k is the thermal diffusivity and Δt is the laser pulse length. For a pulse length of $1 \cdot 10^{-8}$ s I_{min} is about $0.69 \cdot GW/cm^2$ for W and $0.29 GW/cm^2$ for Al, negligible for D, well below the experimental power density. To check if the plasma was optically thin we compared the intensities ratios of W I-II emission lines in both spectral region with theoretical values from NIST database [15] finding a good agreement. The LTE condition was checked estimating the fulfillment of the McWhirter criterion [16] which is expressed as the lower limit of electron density (n_e) that plasma should have to be considered in LTE (although this criterion is a necessary but not sufficient condition for LTE). This criterion is expressed through the following equation:

$$n_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3 (cm^{-3}) \quad (3)$$

where T is the plasma temperature and ΔE is the largest energy gap between adjacent levels of the considered elements [16]. For a plasma largely dominated by W and Al atoms and ions ΔE is maximized for Al II ($\Delta E = 4.64$ eV) [17]. The electron temperature was calculated through the Saha-Boltzmann Plot (BP) [18] of tungsten atomic an ionic lines (Fig.4) and a value of $T = 8400 \pm 500$ K was found. Consequently, for our plasma, the McWhirter criterion is fulfilled when $n_e \geq 1.36 \cdot 10^{16} cm^{-3}$.

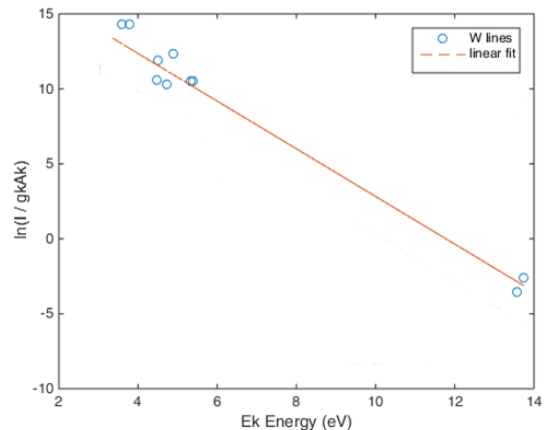


Fig. 4. BP of W atomic and ionic lines.

The experimental electron density can be obtained from the Saha–Boltzmann [18] equation by using the intensity ratio of neutral and singly ionized optically thin spectral lines of tungsten [19]. By applying this procedure an electron density $n_e = 6 \pm 1 \cdot 10^{16} \text{ cm}^{-3}$ was estimated for our plasma, more than four times above the McWhirther limit. In conclusion LTE was reasonably considered to occur and CF was applied.

The CF procedure states that the concentration C^S of each species (atomic and ionic species are treated as different species) present in the plasma is related to the intercept q^S of his BP through the following relation [12]:

$$C^S = \frac{P_S(T)}{F} e^{q^S} \quad (4)$$

where F is an instrumental factor equal for each species. If all the species present in the plasma are experimentally detected it is possible to calculate all the C^S from (4) and their sum can be normalized to 1 getting the relative concentration [12]. Otherwise, if one species (atomic or ionic) is not detected, the LTE condition ensures that its relative concentration can be calculated from the Saha-Boltzmann equation:

$$\frac{n_{iom}}{n_{atom}} = 2.4 \cdot 10^{15} \frac{T^{3/2}}{n_e} \cdot \frac{P_{ion}(T)}{P_{atom}(T)} \cdot \exp\left[\frac{E_{ion}}{k_B T}\right] \quad (5)$$

where n_{ion} and n_{atom} are the concentrations of the atomic and ionic species of a particular element, P_{atom} , P_{ion} their partition functions, E_{ion} is the ionization energy of the chemical species and k_B the Boltzmann constant. In the case of the present measures no Al II lines were detected in the investigated ranges, so its concentration was retrieved from (5).

Table 1 summarizes the obtained results by applying the CF procedure on W, Al, D, neglecting the H contribution (due to environmental hydrogen).

Table 1. CF results .

Element	Nominal conc.	CF conc.
W	85	87 ± 2
Al	10	12 ± 2
D	5	4 ± 2

The errors being estimated as propagation of the errors on temperature and electron density on the values of the intercepts q^S of the species.

Conclusions

In this paper we have shown the LIBS potentialities as innovative diagnostic to monitor PFCs in the next generation fusion devices. LIBS do not need samples manipulation from the fusion vacuum vessel and can work in air or in vacuum conditions, with different residual gases (Ar, N₂, He), it allows the simultaneous detection of all the hydrogen isotopes, even in traces, and can provide a quantitative estimation of the detected

chemical elements. The errors on the quantitative estimation depends on the uncertainty on the values of the LIBS plasma parameters (temperature and electron density) and on the uncertainty associated with some spectroscopic quantities (partition functions, transition probabilities) and on the full achievement of the LTE condition of the LIBS plasma. The careful selection of experimental conditions (integration time, geometry of signal collection) can help to reduce these errors and it is also needed for the presently under-discussion LIBS measurements on ITER by using a robotic arm during machine maintenance periods [20].

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