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Measurements of deuterium retention and surface elemental composition with double pulse laser induced breakdown spectroscopy

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Abstract. Estimating the tritium amount retained in the plasma facing components and their surface layer composition is of crucial importance for ITER. Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique suitable for *in situ* measurements of both these quantities. For improving its sensitivity, the Double Pulse (DP) variant can be used, instead of the standard Single Pulse (SP).

In this work Mo samples coated with 1.5-1.8 μm thick W-Al (as a proxy for Be) mixed layer, with co-deposited deuterium were analyzed under vacuum ($\sim 5 \times 10^{-3}$ mbar) by SP and DP LIBS, showing enhancement of the spectral intensity for the latter. Calibration Free method was applied to the LIBS data for getting the elemental concentration of W and Al. Results are in satisfactory agreement with those obtained from preliminary, Ion Beam Analysis measurements. Deuterium concentration was tentatively estimated by accounting for the intensity ratio between $\text{D}\alpha$ and nearby WI lines.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) [1-2] is an analytical technique that is getting a growing interest in the field of spectrochemical analysis thanks to some advantages it offers compared to other similar techniques. Among these is the ability to perform analysis on both solids, liquids or gaseous samples *in-situ* without any preliminary preparation, the micro-destructiveness of the technique, leaving the sample virtually intact, the possibility to make quantitative estimations of the chemical elements detected.

LIBS technique employs a pulsed laser of low energy (up to hundreds of mJ per pulse) and focusing optics to generate a plasma that vaporizes a small fraction of the sample to be analyzed. This plasma light is collected and spectrally decomposed by a spectrometer revealing atomic and ionic species present in the plasma.

Due its versatility, which makes LIBS applicable in vacuum and a distance of many meters [2]. LIBS is nowadays considered a valuable diagnostic tool to monitor fuel retention, erosion re-deposition in the walls chamber and plasma facing components (PFCs) of the current and next generation nuclear fusion devices like ITER [3].

In this paper LIBS measurements on samples specifically made to simulate the internal walls of a fusion reactor like ITER contaminated with traces of nuclear fuel, are reported. The measurements, without plasma and under vacuum, are representative of analyses that could be done in between ITER discharges or during a short shut down cycle.

The measurements were performed by applying the double pulse LIBS technique (DP-LIBS) [4], exciting the sample with two collinear, successive laser shots, a variation which result in a significant enhancement of the LIBS intensity and an improved sensitivity of the technique. The relative concentration of each chemical species was inferred by using the Calibration-Free (CF) technique [5], without the use of calibrated samples.

2. Samples

Round shaped molybdenum samples, with a diameter of 25 mm coated with 1.5-1.8 μm thick mixed W-Al (Al as proxy for Be) layer were used in this experiment. Deuterium was co-deposited in the superficial layer by using vacuum arc deposition method [6]. The initial amount of deuterium as impurity and the relative content of W and Al were measured by using Rutherford Backscattering (RBS) [7] and Secondary Ion Mass Spectroscopy (SIMS) [8] From measurements the atomic concentration of W and Al in the mixed layer was 79 % for W and 19 % for Al, whereas D was present for about 2%. H also was detected, in a very superficial thin layer, probably from adsorbed water. The mixed sample simulates the expected PFC surface

composition [9] in some re-deposition zones of the ITER vessel, like the divertor, where probably Be eroded from the first wall will be re-deposited on the divertor tiles [9].

3. Experimental apparatus and setup

The experimental layout was fully described elsewhere [10] and here it will be briefly reviewed. The laser source is a TII LS-2131D Nd:YAG from LOTIS emitting at 1064 nm with a maximum energy of 200 mJ per pulse and a pulse duration between 9 – 12 ns, the delay between successive pulses can be set between 20 ns and 80 ms. Samples have been placed at the center of a vacuum chamber (residual pressure 5×10^{-5} mbar) on a motorized x-y stage to allow analysis of multiple points on the surface.

Laser-induced plasma light was collected by an optical collimator and directed through optical fibers to an ANDOR Mechelle 5000 spectrometer ($\lambda/\Delta\lambda = 4000$). Light was spectrally decomposed between 200 and 1100 nm and recorded by an iStar 734 intensified CCD camera (DH734/18mm). For the detailed analysis of the deuterium traces the spectral region around the D_a line at 656.1 nm was recorded by using a high resolution spectrometer ($\lambda/\Delta\lambda = 50000$) ISA 550 by Jobin-Ivon with a focal length of 550 mm. A DH520/18mm F-03 CCD camera was used with the ISA 550 spectrometer.

Both for SP and DP-LIBS experiments the delay between the first laser pulse and the CCD gate was set to 650 ns, interpulse delay was 300 ns in the DP-LIBS experiments, whereas gate width was 500 ns in both configurations. Total pulse energy was about 170 mJ in both SP and DP experiments (for the latter this value corresponds to the sum of the two laser pulses energy). Post experiments SEM analysis of the craters was carried out to get their areas (resulting in spots of about 0.8 – 1.0 mm²). Figure 1 shows one of the examined spot on the sample surface. Laser fluence was estimated to be 17 J/cm² and power density about 1.7 GW/cm² per shot.

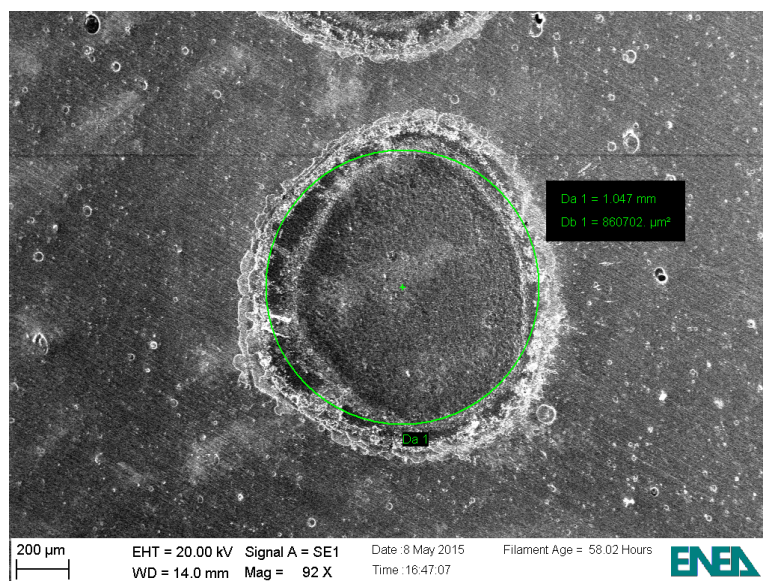


Fig. 1 SEM image of the LIBS crater after four DP-LIBS laser shots.

4. Results

4.1 DP-LIBS vs SP-LIBS

A series of four laser shots have been acquired on different points to compare SP-LIBS and DP-LIBS, keeping fixed the pulse energy. The LIBS signals obtained, with the high resolution spectrometer, from the first SP-LIBS and DP-LIBS shots in the spectral range near the D_a and H_a lines (656.2 nm) are shown in figure 2. The SP-LIBS signal intensity is lower than the corresponding DP-LIBS. Atomic W, D, H emissions from the ablated superficial layer are identified, with a higher S/N in the DP-LIBS spectra respect to the SP experiment.

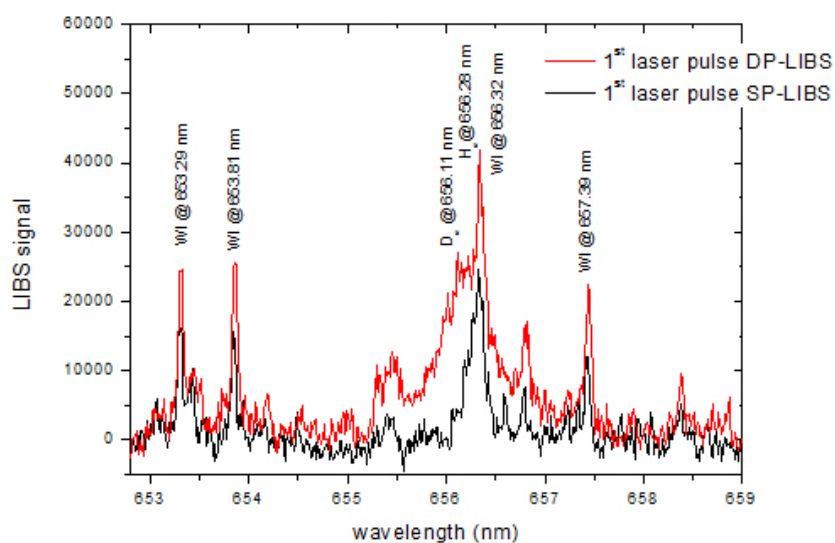


Figure 1. DP-LIBS (black line) vs SP-LIBS (red line) spectra in the D_α and H_α deuterium and hydrogen emission.

4.2 Determination of the elements concentration in the deposited layer

To get the elemental composition of the surface layer in the DP-LIBS experiments the CF method [5] has been applied to the spectral lines intensities recorded by the less sensitive monochromator (not able to separate H_α and D_α emission lines but recording the LIBS spectrum in all the visible range with a single laser shot), the wavelength range of the high resolution spectrometer not allowing the detection of Al lines. The first step was the estimation of the temperature and electron density of the plasma plume. The electron density has been calculated from the Stark broadening [10, 11] of the ionic Al emission lines at 281.6 nm and 466.3 nm, whose spectral parameters are known [11] and was $1.13 \cdot 10^{17} \text{ cm}^{-3}$ for DP-LIBS. The plasma temperature was calculated from the Boltzmann plot [11] of the stronger and not-saturated tungsten and aluminum atomic and ionic lines, to get an average value of 15000 °K. Applying the CF procedure the results shown in Table 1 were obtained for the superficial concentration of W and Al:

Element	W (atomic %)	Al (atomic %)
CF (in-situ)	73 ± 6	27 ± 6
RBS (nominal)	79 ± 12	19 ± 12

Table 1 CF vs RBS concentration measurements of W and Al

from which it is shown that the obtained concentrations results in good agreement, within the experimental errors, with those obtained from preliminary RBS measurements.

The presence of residual deuterium was evaluated from the intensity ratio between the D_α line at 656.1 nm and the nearby W I line at 657.39 nm (not overlapped, like the 656.32 line, to the H_α line at 656.28 nm), with a procedure similar to that reported in [10]. The concentration of tungsten was known from the results reported in table 1. After background subtraction all the emission lines were tentatively fitted with Lorentzian lineshapes as shown in figure 4.

With the calculated plasma density and average temperature, under the hypothesis of local thermodynamic equilibrium the deuterium concentration was estimated to be about 1.5% atomic, in satisfactory agreement with the nominal concentration found with SIMS. On the other hand it is to be taken into account that the D_α line results not very well separated from the H_α line and that the concentration of species to be quantified depends on the evaluation of spectroscopic quantities, like ionic and atomic partition functions of the chemical species in turn, strongly depending on the assumed plasma temperature and electron density.

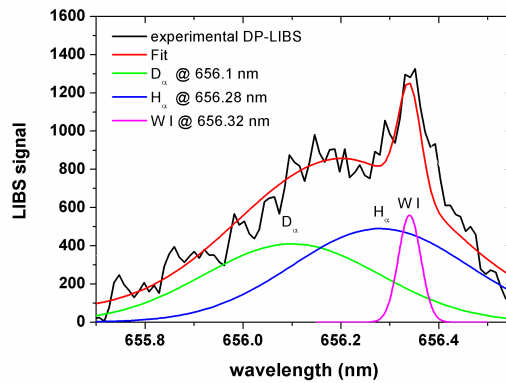


Figure 4 Lorentzian fit of the DP-LIBS signal near the D_{α} emission of deuterium.

5 Conclusion

LIBS is capable of detecting hydrogen and its isotopes as well as plasma facing materials like Al (as proxy for Be) and W co-deposited in a thin superficial layer of about $1.5 \mu\text{m}$. DP-LIBS exhibit a higher S/N ratio, compared with SP-LIBS. CF was applied for quantitative estimation of the main constituents the superficial layer showing results in good agreement with the preliminary RBS measurements. The estimation of deuterium concentration, carried out by analyzing the intensity ratio between the D_{α} line at 656.1 nm and the W I line at 657.39 nm, resulted in a value in satisfactory agreement with SIMS measurements. Nevertheless the presence of hydrogen line not well resolved with respect to the deuterium one (that could be less problematic in ITER environment in between shots) and, above all, the critical dependence of elemental concentrations on plasma plume parameters, need new efforts in the choice of the DP experiment parameters.

Acknowledgements

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