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Loading of deuterium and helium by Pilot-PSI plasma and their detection by *in-situ* LIBS

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Monitoring of fuel retention and helium (He) content in plasma-facing components will be mandatory task from point of view of safety during ITER operation. Laser-induced breakdown spectroscopy (LIBS) is a promising method to quantify the fuel content in-situ and after cleaning activities. Fuel retention in tungsten (W) by implantation is strongly dependent on the W surface morphology and the surface temperature during the plasma exposure. The aim of the present study is to identify suitable plasma/temperature regimes for the loading of W samples with deuterium (D) and He at the linear plasma machine Pilot–PSI and to test the applicability of LIBS for in-situ detection of D and He.

After 1000 s of exposure to He plasma during which the temperature increased up to 720 ºC in the samples' centre, at 10^{-2} mbar residual pressure of the device the He I line at 587.6 nm that decreased to the detection limit after 2-3 first shots was seen with LIBS.

D loading was performed during ~1000 s plasma exposure at low (200-300 ºC) surface temperatures. Regardless of low intensity and noisy LIBS spectra, H and D lines fitted with Lorentzian contours were reliably resolved.

We demonstrated that in-situ LIBS is a reliable method for detection of He and D retention in ITER-relevant materials. Nevertheless, to measure the absolute concentrations of D and He further research is needed.

Introduction

Monitoring of hydrogen (H) isotopes as well as helium (He) accumulation in plasma-facing components will be mandatory tasks during the ITER operation. The tritium (T) retention in the reactor walls is from the viewpoint of safety the main concern, while He induced structures at the wall surface cause enhanced erosion and dust formation [1]. To develop the diagnostics for the fuel retention in the plasma facing components, deuterium (D) is used instead of the radioactive T.

Several works have demonstrated that during the plasma exposure the retention of fuel in tungsten (W) is strongly dependent on the W surface morphology and the surface temperature [2], [3],[4], [5], [6], [7]. At lower (10^{22} $m^{-2}s^{-1}$) D fluxes the retention rate is more efficient at

lower (200-300 ºC) surface temperatures [7]. At higher fluxes (10^{23} $m^{-2}s^{-1}$) the situation is somewhat different, because blisters are formed on the surface.
Studies of He-caused fuzz-like structure [8] have revealed that the concentration of the retained He is 1-2 atomic %.
Laser-induced breakdown spectroscopy (LIBS) is a promising method for remote *in-situ* monitoring of the fuel retention in the reactor walls. Both the signal-to-noise ratio and width of spectral lines corresponding to a laser shot depend on delay time between the laser pulse and the beginning of the spectral recording t_d and the width of the recording time-gate Δt and thus time–resolved LIBS spectra should be recorded. Presently most of fusion related LIBS studies have been done in *ex-situ* conditions.
Experience shows that in case of D detection the using of background gas (Ar or He at ~ 1mbar pressure) improves the signal-to-noise ratio [9]. However, compared with vacuum the background gas increases the electron density in the laser-produced plasma plume. As a result, the broadening of spectral lines by Stark effect increases which leads to a bigger overlapping of H isotopes spectral lines. It means that the value of t_d and Δt have to be carefully chosen to resolve H and D spectral lines [10], [11], [12]. As described, He is widely [13], [14], [15] used as background gas in LIBS experiments.
He as an analyte is much less studied [16] and according to our knowledge the studies related to the detection of He content in solid samples by LIBS are nearly missing.
The aim of the present study is to ascertain plasma/temperature regimes at the linear plasma machine Pilot–PSI suitable for He or D implantation into W and to test the applicability of LIBS for *in-situ* detection of accumulated D and He.

Samples and procedure

The samples with 1.5 μm thick W coatings on molybdenum (Mo) were prepared, using the DIARC® plasma coating method [17]. The thickness and diameter of the samples was 2.5 mm and 30 mm, respectively.

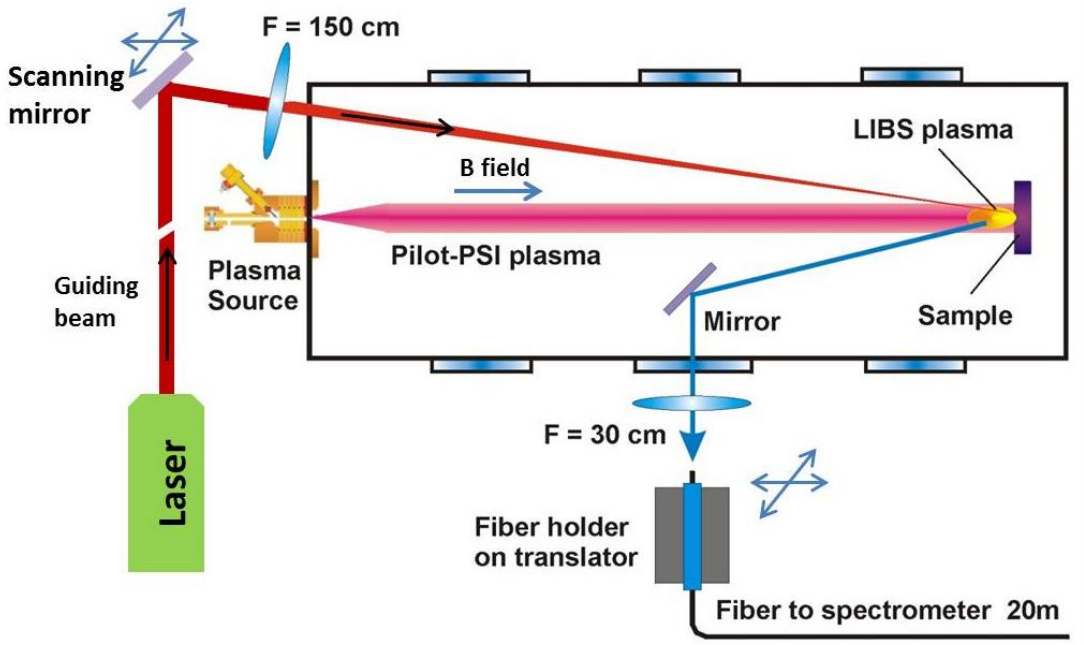

Figure 1. Pilot-PSI with the *in-situ* LIBS setup

The samples were exposed to plasma on the Pilot-PSI linear plasma machine in FOM Institute DIFFER (The Netherlands). A detailed description of the device and the regularities of the formed plasma flux are available in [18]. A spectral pyrometer measured the peak temperature of the sample surface (T_s). Temperature spatial distribution was observed by IR camera. Thomson scattering was applied to determine the electron density (n_e) and temperature (T_e) in the plasma near the sample surface.

T_e and n_e were around 1 eV and $5 \cdot 10^{20}$ m^{-3}, respectively. Peaking particle and heat fluxes were 10^{24} $s^{-1}m^{-2}$ and 10 MW m^{-2}, respectively. The targets were biased with -40 V, resulting ion energy at the target around 30 eV. Plasma conditions specific to samples are described in the Table 1. The axial magnetic field determined the full width at half maximum (FWHM) of the Gaussian plasma beam: at 0.4 T FWHM was 25 mm and at 0.8 T 12 mm. The temperature profile followed the particle flux and thus had also Gaussian profile.

The exposure procedure was similar to that described in our previous work [19]. As the Pilot-PSI device was operated with plasma shots of ≈100 s duration, 10 plasma shots result to the ≈1000 s total exposure. With 1000 s exposure particle fluence in the range of 10^{27} m^{-2} was achieved.

In addition to the standard diagnostics *in-situ* LIBS setup was installed (Figure 1). Nd:YAG laser (λ=1064 nm, pulse duration 8 ns) with the guiding laser was applied for the LIBS measurements. The laser was at approximately 20 m distance from the Pilot-PSI device. The laser beam was focused with a lens of 1.5 m focal length to the sample. Laser pulse energy at the sample surface was 170 mJ and the area of the laser spot was approximately 1 mm^2 corresponding to the average fluence 17 J/cm^2. The radiation of the laser-produced plasma was directed to the end of a fiber of 0.8 mm diameter, using a plane mirror and a lens of 30 cm focal length. The magnification of the plasma image at the fiber end was close to unity. The fiber of approximately 20 m length delivered the radiation to the spectrometer. The output end of this long fiber was coupled to a round-to-linear fiber optics bundle consisting of 50 fibers each 120 μm in diameter. The linear end of the bundle was used as an entrance slit of 1 meter Czerny-Turner spectrometer with 1200 lines/mm line grating [20].

For adjustment of the recording system to the spot of the sample surface where the LIBS signal was planned to record, we used a visible guiding laser beam which spot at the sample surface coincided with that of the Nd:YAG laser beam. Next the fiber end was shifted to the position corresponding to the maximum response to the guiding laser radiation. Nevertheless, there was a noticeable uncertainty (about 0.5 mm) in the fiber position and thus the sensitivity for the different spots might alter. To overcome this problem, the spectral lines of the Mo (the substrate of the samples) were used. It was assumed that after 40 subsequent laser shots the W coating is totally removed and the intensity of these lines is independent of the sample and spot. This was checked and sensitivity corrections were introduced, if needed.

The spectrum was detected in a preselected 20 nm wavelength range by Andor ICCD DH340T-18F-03 (512 x 2048 pixels) camera where to a certain wavelength corresponded nearly 500 vertically binned ICCD pixels. For D detection the range was centered near 656 nm wavelength and for He detection near 587 nm. The instrumental half width of the recording system was less than 0.05 nm.

Since D and He measurements were carried out at different background pressures of Ar gas (Table 1), the optimal parameters for recording of time-resolved spectra were also different. D was detected at $t_d \approx 200$ ns and $\Delta t = 3000$ ns, while for He the values $t_d \approx 100$ ns and $\Delta t = 400$ ns were used.

LIBS measurements were carried out at *in-situ* conditions right after the plasma exposure. As the plasma-caused surface modifications were different at different sites at the sample surface, spectra as a function of the laser shot number were recorded from various spots. At every spot spectra for 40 subsequent laser shots were recorded.

To characterize the sample surface, scanning electron microscopy (SEM) measurements were carried out using the Helios^{TM} NanoLab 600.

Results and discussion

In our previous unpublished experiments we have successfully used Ne/D plasma flux to prepare the W coatings for efficient D loading (Previous study in Table 1). Ne ions were used to simulate heavy impurities in the tokamak plasma. In this study it was confirmed that the efficient D loading took place during 2nd step of the described regime (exposure with pure D plasma at low surface temperature). To gain more insight into the D loading process in this regime, we also tested the regime 1, which does not include the low temperature step; in this case no D signal was detected. Thus it was confirmed that loading took place during the 2nd, 1st step was needed to prepare the W surface for loading.

Table 1 Plasma regimes used in the experiments and parameters and results of the LIBS measurements

Regime	Plasma	Surface temp. T_s, ^{0}C	FWHM, mm	Exposure, s	Background pressure & gas	Result of LIBS detection
Previous study	2-step: Ne/D & D	1100 & 200-300	12 & 25	300 & 370	1.2 mbar Ar	Reliable D-line detection
1	Ne/D	1100	12	300	1.2 mbar Ar	No reliable D-line detection
2	2-step: He & D	770 & 400-500	12 & 25	600 & 640	1.2 mbar Ar	No reliable D-line detection
3	D	200-300	25	910	1.2 mbar Ar	Noisy but resolved D & H lines
4	He	720	25	1010	Both 10^{-2} mbar & 1.2 mbar Ar	He 587 nm line is easily detectable

In the present study other, less severe plasma regimes for D loading of W coatings were tested (Table 1 regimes 2-4).

In regime 2 the sample surface was pretreated by He plasma. Exposure to pure He plasma lead to the formation of fuzz-like structure on the sample surface. After the pretreatment the sample was exposed to pure D plasma. Using of this regime did not allow to detect D by LIBS, only the H_α line was recorded. Appearance of H_α is discussed below. This result is consistent with other results: in some cases pre-treatment with low energy He ions even reduced D retention [21].

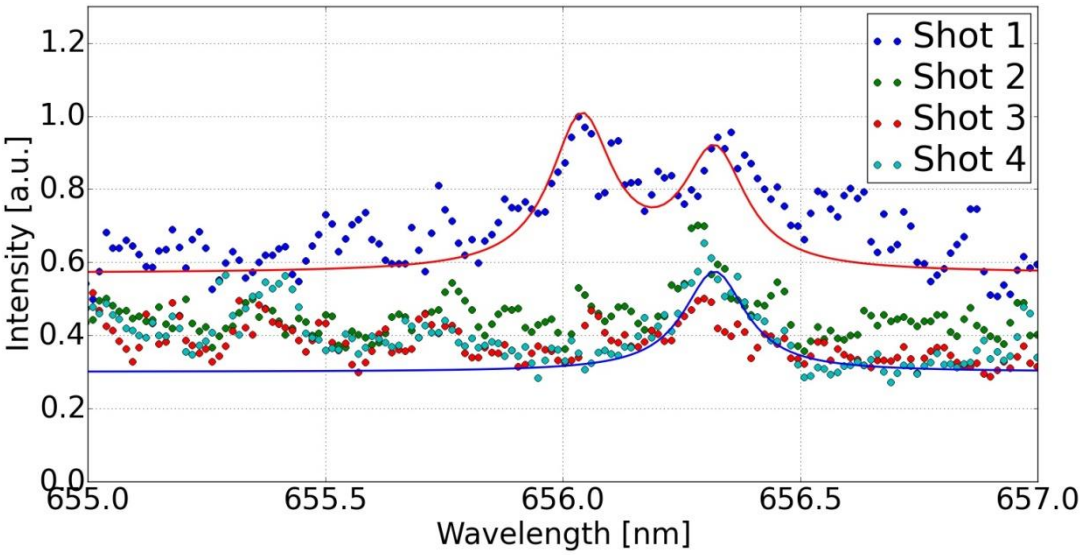

Figure 2. D LIBS signal during the four first laser shots. Data fitted with Lorentzian contours. The uncertainty of obtained FWHM and peak intensities is approximately 10 %.

Using the regime 3 the sample was exposed to pure D plasma at low surface temperature and a noisy D signal was observed (Figure 2). Despite of the low surface temperature D plasma caused noticeable surface modifications (Figure 3 b) compared to the unexposed sample (Figure 3 a). The noisy signal was fitted with two Lorentzian contours. In the fitting procedure equal FWHM was assumed for both H_α and D_α lines. The uncertainty of the FWHM and peak intensities obtained by fitting is approximately 10 %. Fitting H_α and D_α lines with Lorentzian contours shows the D presence during the first laser shot. Thus, most of the D is retained near the surface (in less than 100 nm depth). Besides there is a possibility that the outgassing may decrease the D signal intensity for the next shots: the first shot heats the sample near the LIBS crater and D may be released. At the same time H_α line at 656.3 nm existed during all laser shots. The intensity of this signal was nearly constant for all the 40 laser shots, therefore it is not caused by the water vapor on the surface, that is reported in several works [9]. So it seems very likely that hydrogen originated as a contamination from the background Ar gas.

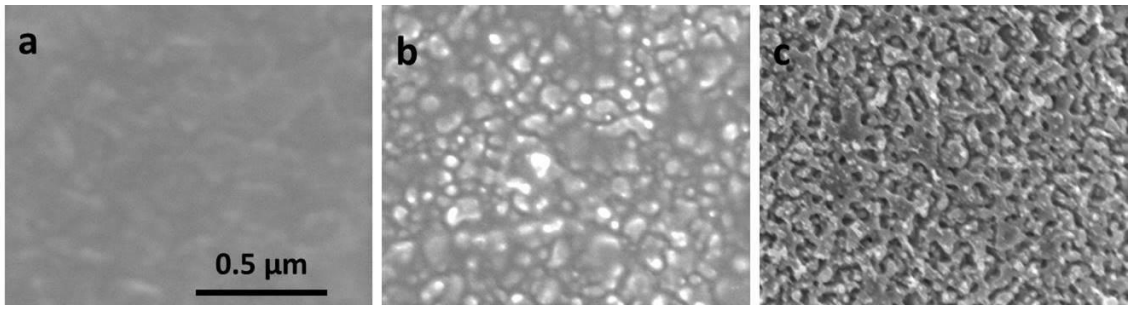

Figure 3. SEM images of the W coated samples: a) unexposed b) exposed to D plasma (regime 3) c) exposed to He plasma (regime 4)

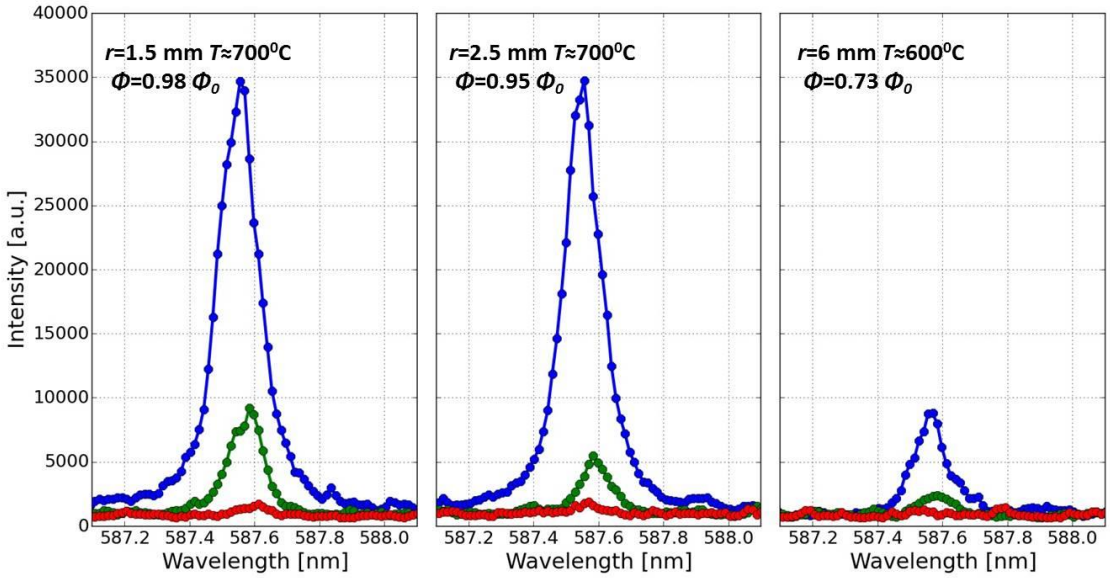

Figure 4. He LIBS signal during the three first laser shots. a) centre b) near centre c) away. Distance from the centre *r*, surface temperature *T*, maximum fluence $\Phi_0 \approx 10^{27}$ m^{-2}.

Regime 4 exposed for 720 s the sample at a high temperature to pure He plasma. With the applied regime we noticed the start of the fuzz [22] growth in the central region of the sample. SEM pictures (Figure 3 c) show a fuzzy structure which is more raised in the central part of the sample. First LIBS measurements were performed at 1.2 mbar Ar background pressure, giving a clear and strong He signal at 587.6 nm wavelength. Further LIBS testing was carried out at a lower pressure (10^{-2} mbar). He signal was still easily detectable in parts of the sample where stronger fuzz structure existed (Figure 4 a and b). Further away from the center the He signal was almost missing (Figure 4 c). He signal was detectable for the first two laser shots; whereby the line intensity of the second shot was nearly 10 times lower. It could be assumed that He is retained in the fuzz structure and not much deeper in the coating.

Comparing with the results presented in [8] we can say that He concentration of 1-2 at. % in W samples is easily detectable with *in-situ* LIBS even at low (less than 10^{-2} mbar) background pressure. This result is somewhat unexpected since the calculated (assuming excitation temperature in LIBS plasma around 1 eV) intensity for D 656.1nm line should be orders of magnitudes greater than for the He 587.6 nm line. The energies for the upper states of the transitions are 12.1 eV and 23.7 eV for D and He, respectively. The D_α line consists of 7 transitions with probabilities ($g_k A_{ki}$) in the range of 10^7-10^8 s^{-1}, He lines consists of 5 transitions with similar probability [23].

Several reasons for that result could be pointed out. First straightforward reason could be that the He concentration in the sample is much higher than for D. Our previous studies have showed that typical and LIBS detectable D concentrations are in the range of 10^{17} at/cm^2 [9]. He concentration reported in [8] is comparable or even less than this value. In current experiments the absolute concentrations of D and He are not known, but they could be assumed to be similar. Another reason could be difference in the temporal and spatial development of D and He laser induced plasma. In the further research the D and He concentrations have to be measured with quantitative *ex-situ* methods, such as nuclear

reaction analyzes (NRA). If the concentrations of D and He are confirmed to be comparable, more fundamental aspects of the He and D excitation and LIBS plasma development have to be studied.

Conclusions

In this study we loaded tungsten coatings with deuterium and helium on Pilot-PSI linear plasma machine. After the plasma exposure we carried out *in-situ* LIBS measurements to detect D and He from the samples. As previous studies suggest, the efficiency of deuterium loading depends strongly on the sample surface temperature. For the plasma fluxes used in this work the loading was efficient at low surface temperature. In this case we reliably detected D signal at 1.2 mbar background pressure. He retention was efficient at regions were fuzz-like structure was formed or had begun to form. He signal was easily detectable at 10^{-2} mbar background pressure.

Thus we demonstrated that LIBS is a suitable *in-situ* tool for deuterium and helium detection from tungsten samples. In this study we describe suitable LIBS setup and measurement procedure for linear plasma machines. We suggest installing LIBS as a permanent *in-situ* diagnostic method for linear plasma machines to monitor the samples during the plasma exposure on the one hand and gather more data to develop LIBS for ITER-like conditions on the other hand.

Further study is needed to obtain quantitative deuterium and helium concentration from LIBS measurements.

Acknowledgements

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