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Abstract

The Vacuum UV (VUV) - Near Infrared (NIR) Laser Induced Breakdown Spectroscopy (LIBS) technique was applied to investigate the composition of W-based samples with a protective carbon layer. The sample was analyzed under pressures from 5 Pa to 10^5 Pa and atmosphere (air, He). The spectra were recorded with three spectrometers at delays from *200 ns* to *10 µs* at atmospheric pressures and from *100 ns* to *500 ns* at low pressures. The electron density was determined from the measured spectra using Stark broadening and the electron temperature from the W I- W III Saha- Boltzmann plot in the VUV-NIR spectral range. The better precision was achieved due to usage W III spectral lines of tungsten. The achieved results are more reliable than results obtained without W III spectral lines. The calibration free (CF) LIBS method was then applied to determine the W and C contents of the analyzed sample.

1. Introduction

In the last few years many experiments have been conducted to find the best materials for fusion devices. Nowadays, the research focuses on tungsten and W-based compounds, especially for first-wall structures in the divertor. Divertor walls will be exposed to trace impurities (C, O, N, from injected gas), material impurities from the eroded parts of the walls (Be) as well as burning fuel (D and T resp.) which all will be incorporated in co-deposited layers on the wall structures. Knowing the composition of such deposits is important for successful operation of the fusion reactors. Laser induced breakdown spectroscopy (LIBS) seems to be suitable experimental technique for real time diagnostics of deposition and retention processes. This technique has already been used in analyzing fusion materials [1-4] and it has been proved to be a suitable technique for compositional analysis of deposited layers in the divertor region [5-7]. To find optimal conditions to produce LIBS plasma, the influence of the surrounding gas pressure and laser pulse duration on LIBS spectra was investigated [6]. For the quantification of fuel retention and the amount of impurities in the sample calibration free LIBS can be used but, to this end, accurate determination of electron temperature in laser induced plasma is necessary. The electron temperature (T) can be determined from Saha-Boltzmann (S-B) plot of different tungsten lines and from Boltzmann (B) plot [8, 9] of N I and O I lines respectively. In our previous work [10], the electron temperature was determined from the Boltzmann and Saha-Boltzmann plots of W I - W II lines without eventual correction of self-absorption and repopulation phenomena. The T evaluated from the neutral W I lines was significantly different from those evaluated from the B plot of W II lines and S-B plot of W I- W II lines respectively.

The goal of this article is to use not only W I and W II (from UV- NIR range), but also W II and W III lines (VUV range starting at 115 nm) for constructing the S-B plot. This way, electron temperature can be determined more accurately and, thus, the composition of the samples can be extracted more precisely.

The secondary goal is reliable detection of light elements (H, D, C, N, O) using VUV resonant lines [11]. Light elements have no resonant lines in the classical UV- NIR spectral range, thus VUV enables determining the impurity content of plasma-exposed samples

2. Experimental setup and measurement

The LIBS measurements were done for pure W samples with a protective carbon layer at different pressures: *1 atm* (air), *1330 P*a (He), *200 Pa* (air) and *5 Pa* (air). Our LIBS experimental setup as well as our calibration free (CF) LIBS procedure for multielemental (major, minor, trace elements) analysis is described in [12, 13]. The LIBS plasma was created by different Q- switched Nd: YAG lasers operating at the second harmonic (*532 nm*, EaZy, Quantel, pulse energy up to *300 mJ*) and the fourth harmonic (*266 nm*, CFR, Quantel, *80 mJ*). The maximal repetition rate of both lasers was *10 Hz* and laser pulse duration was *9 ns*. For the detection of lines emitted from plasma three spectrometers were used:

- Echelle spectrometer (ME5000, Andor Technology, resolution *λ/Δλ = 4000,* range *230-975 nm,*) coupled with an iCCD camera (iStar DH743, Andor Technology, Δt = 5 ns)
- UV spectrometer (THR 1500, Jobin- Yvon, *1800* gr/mm, resolution *λ/Δλ = 8500*, range *180 - 350 nm*) coupled with the iCCD (iStar DH740 for UV- VUV, Andor Technology, Δt = 5 ns)
- VUV spectrometer (234/32VM, McPherson, f = *20 cm*, *2400 gr/mm*, resolution *λ/Δλ = 1000*, range *114-295 nm*) coupled with the iCCD camera (iStar DH740 for UV- VUV, Andor Technology, Δt = 5 ns).

The sample was first analyzed under atmospheric pressure (excitation by the second harmonic) with different gate delay times and spectral gate width which were set always to the same value (*200 ns - 10 μs*) in order to find conditions where lines from different ionization states have the largest signal to noise ratio. The LIBS or CF LIBS analysis of W based material is very complicated due to a great number of neutral and singly ionized spectral lines and also due to strong self- absorption of the lowest lying states Even with the greater spectral resolution of the THR 1500 spectrometer it was hard to identify all the individual lines. In addition, at atmospheric pressures, spectral lines of tungsten are wider than under lower pressure because there is strong Doppler broadening at atmospheric pressure.

Due to this reason the next series of measurements were done at low pressures. The spectral lines became narrower due to the decrease of the Stark broadening effect on the spectral lines. Analysis of time evolving spectra shows big differences between the electron temperatures obtained from the Saha- Boltzmann plot of W I and W II and Boltzmann plots of W I and W II lines (approx. 30%). This led to the idea of using doubly ionized lines of tungsten which are situated in the VUV spectral range to obtain more precise results.

For these investigations, the laser excitation was changed (Nd: YAG laser operating at the fourth harmonic*)* to obtain more stochiometric ablation and less thermal heating by the laser pulses. Only the Echelle (accumulation of 200 shots) and VUV (accumulation of 100 shots) spectrometers were used. Measurements were done with different gate delay times and spectral gate widths (*100 - 500 ns*). These values were chosen on the basis of previous measurements. At *100 ns* the intensity of W III spectral lines was the greatest and at *500 ns* the lines were still detectable. The first test measurements were done under the lowest achievable pressure of about *5 Pa* to test the possibility to detect elements under such conditions. Finally, LIBS analyses were done at the pressure of *1 330 Pa* under helium atmosphere in order to achieve a state in which the so-called McWhirter criteria is met::

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

This is one of the necessary conditions for applying the CF LIBS analysis [14,15] since it guarantees local thermodynamical equilibrium for the LIBS plasma. Examples of tungsten LIBS spectra measured under helium atmosphere at the pressure of *1 330 Pa* (delay time = gate width = *100 ns – 500 ns*) are shown in Figure 1. The left part shows the VUV spectra measured by the McPherson spectrometer while in the right part, the UV spectra measured by the Echelle spectrometer is visible.
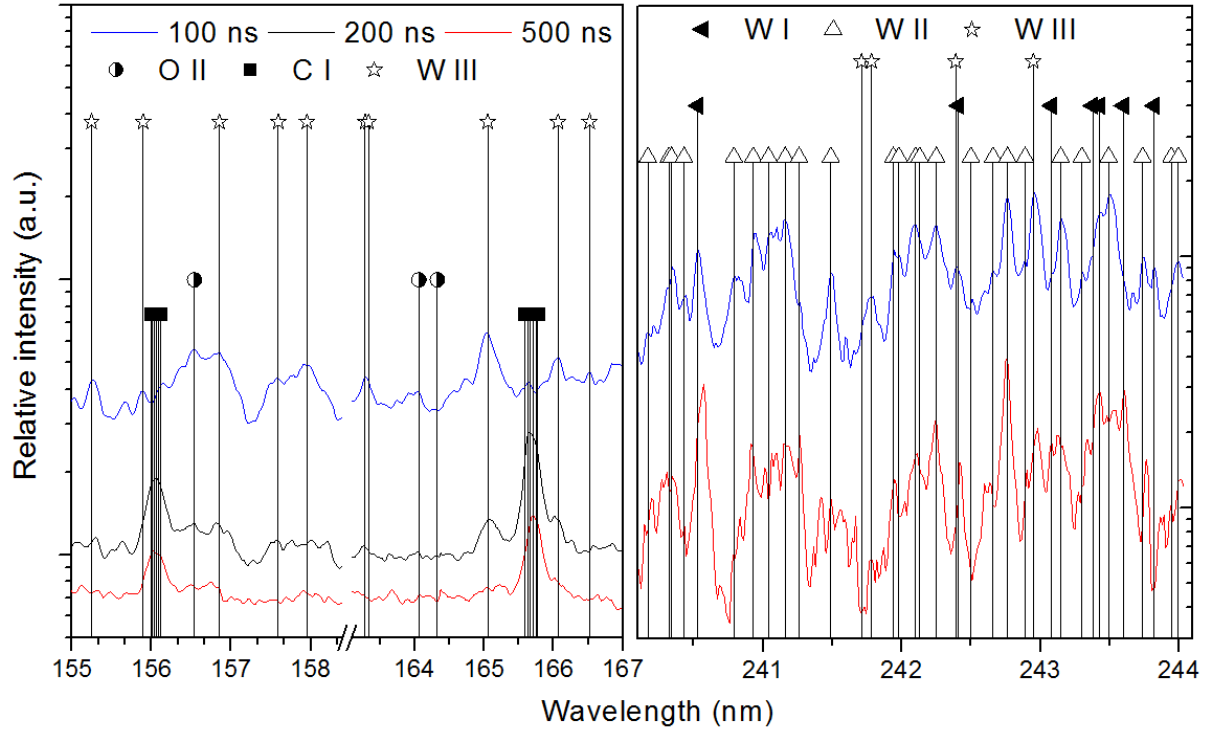
Figure 1. Examples of experimental spectra of tungsten in VUV (left part of the figure, gate delay time was *100 ns - 500 ns,* accumulation of 100 shots, laser energy per pulse *80 mJ*) and UV (right part of the figure, gate delay time *100 ns* and *500 ns*, accumulation of 200 shots, laser energy per pulse different up *300 mJ*) spectral range, He atmosphere at *1 330 Pa*. W III, O II and C I spectral lines are visible each at the different gate delays. W III and O II spectral lines are visible in earlier delays (from *100 ns*) and then very quickly evanescent (at *500 ns* the intensity decrease rapidly about one order). C I spectral lines are visible in greater delays (from *200 ns*).

3. Results

3.1 Determination of the electron density

The electron density, n_e, was calculated from Stark broadening of hydrogen alpha (*656.25 nm*) spectral line (measurements by the Echelle spectrometer):

$$FWHA = 0.549nm \left(\frac{n_e}{10^{17}cm^{-3}}\right)^{0.67965} \tag{2},$$

where FWHA is the full width at half area [16].

The spectral line of W I (*430.21 n*m) (measurements by the THR 1500 spectrometer) can also be used for the determination of electron density from equation:

$$\Delta\lambda = 2w\frac{n_e}{10^{16}} \tag{3},$$

$$w(T) = 4,8767x10^{-4} + 1,6385x10^{-8}T - 1,8473x10^{-13}T^2 \tag{4},$$

where $\Delta\lambda$ is the full width of the line at half area, w is the electron impact width parameter, and T is electron temperature [17]. The evaluated electron densities for LIBS plasma under helium atmosphere at *1 330* Pa and for time delays of *100 n*s and *500 ns* resp. are summarized in Table 1. The impact of the electron temperature in equation (4) is very small. Thanks to this fact was used the most common temperature in CF-LIBS measurements: *1eV ± 20%*.

3.2 Determination of the electron temperature

The electron temperature, T, was determined from the Saha-Boltzmann plot [8, 9] using the Saha equation:

$$\frac{N_{i+1}}{N_i} = \frac{2Z_{i+1}}{n_e Z_i}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-\varepsilon_i/kT} \tag{5},$$

where N_i and N_{i+1} are the populations of the ionization states i and $i+1$, respectively, Z_i and Z_{i+1} are the partition functions of these states, n_e is the electron density calculated from Stark broadening of h alpha spectral line, m_e is mass of the electron, k is the Boltzmann constant, h is the Planck constant and ε_i is the ionization energy. The temperature was determined for two different delays of *100 ns* and *500 ns*. The neutral and singly ionized lines were taken from the spectra recorded by the Echelle spectrometer while the VUV spectrometer was used to extract singly and doubly ionized tungsten lines. The spectral lines for the Saha- Boltzmann plot were selected such that no interference with neighboring spectral lines occurred. Spectral data were taken from the NIST [18] and Harvard [19] databases. The Saha-Boltzmann W I- W III plots for the delays *100 ns* and *500 ns* are shown in Figure 2 and the resulting electron temperatures are summarized in Table 1. For the verification of the obtained results, the electron temperature also from the N I and O I lines was calculated using the Boltzmann plot (measurements by Echelle spectrometer in UV- NIR range) (see Table 1). After obtaining final electron temperature the method of CF LIBS was used for determination of W and C concentration in the sample, where the series of C I lines at *156* and *165 nm* were used [14]. The major element of the sample was W, which represent 99.7 % of composition of the sample. The C content in the sample was 0.3 %.

Table 1. The electron temperature, electron density and ionization degree composition for tungsten LIBS under He (*1 330 Pa*), for delay *100 ns* and *500 ns* resp.

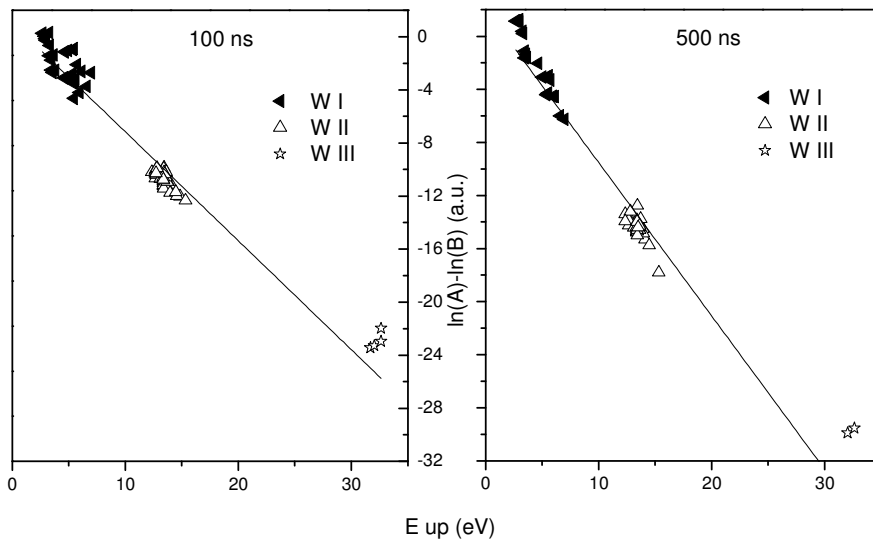| Delay [ns]	T [eV] W I-III	T [eV] N I, O I	n_e [m³]	Ion abundance		
				W I [%]	W II [%]	W III [%]
100	1.22	1.21	2.21x 10²³	2.1	94.8	3.1
500	0.87	0.85	1.06x10²²	1.9	97.9	0.2

Figure 2. Saha- Boltzmann plot of neutrals (circles), singly (triangles) and doubly (pentagons) ionized spectral lines of tungsten. Gate delay time was *100 ns* and *500 ns*, pressure was *1 330 Pa*. Calculated temperature from the Saha- Boltzmann plot is *1.22 eV* (*100 ns*) and *0.87 eV* (*500 ns*).

The repartition of neutral, singly ionized and doubly ionized tungsten atoms calculated for measured electron density as a function of electron temperature is shown in Figure 3. We can conclude that the relative fractions of neutral and singly ionized atoms practically do not change between two different delays (*100 ns* and *500 ns*). On the other hand the fraction of doubly ionized atoms decreases more than one order of the magnitude (see Table 1) which is observable also in the spectra by strong intensity decrease of the W III lines. Because of high abundance of singly ionized atoms of tungsten (more than 95%) the Saha- Boltzmann plot is significantly influenced by the effect of self-absorption in case of ionized atoms (the points representing singly ionized lines in S-B plot are underestimated). The recombination of singly ionized atoms with electrons leads to the repopulation of neutral lines. This process is very significant due to very high abundance of W^+ (the points representing neutral lines are overestimated- that leads to the lower temperature in the comparison with the temperature evaluated from the S-B plot. As a conclusion, W III spectral lines are more suitable for determining electron temperature since they are not prone to self-absorption. However, because of their small number in the S-B plot, we have used not only W III but all the available W I - W III lines in the analyses.
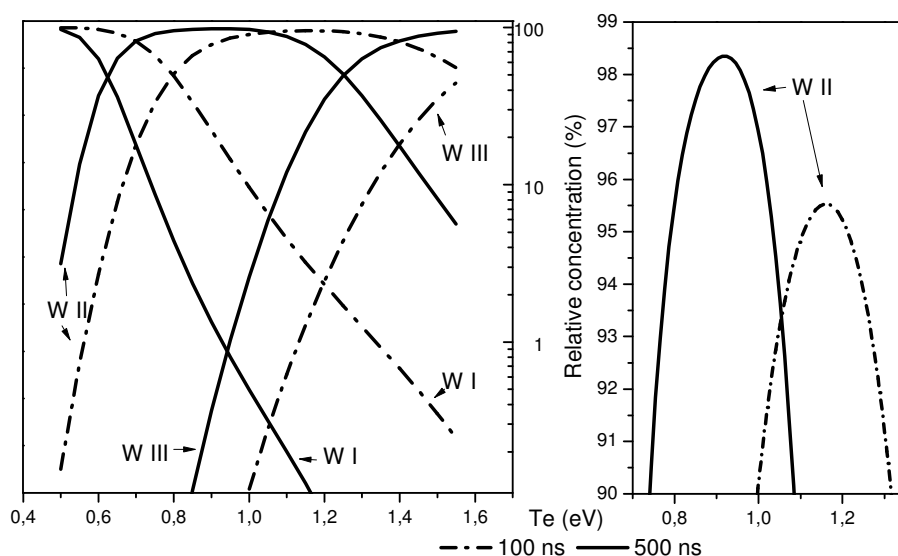

Figure 3. Relative density of different ionization states of tungsten as a function of temperature for electron densities corresponding to *100 ns* and *500 ns* delay.

4. Discussion and conclusion

This study dealt with using VUV spectral range for the analysis of W-based materials by LIBS. The main part of this work was focused on precise determination of the electron temperature. The electron temperature along with the electron density represent important parameters for calibration free LIBS using for the quantification of fuel retention and incorporation of impurities in the divertor wall.

We proved that the evaluation of electron temperature of Saha- Boltzmann plot from neutral, singly and doubly ionized lines of tungsten is possible for short delays up to several hundreds of nanoseconds and is more accurate compared to the evaluation of electron temperature from simple Saha- Boltzmann plot of neutral and singly ionized ions only. In this case it is not necessary to correct for self-absorption.

More precise electron temperature evaluation by VUV-NIR LIBS from W I– W III S-B plot enabled to determine W and C content in the analyzed sample by CF LIBS method. This method could be used in future also for N, O, D quantification by CF LIBS using their VUV resonant lines.

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