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Suchonova, Maria; Veis, Pavel; Karhunen, Juuso; Paris, Peeter; Pribula, Marek; Piip, Kaarel; Laan, Matti; Porosnicu, Corneliu; Lungu, Christian; Hakola, Antti

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Published in:
Nuclear Materials and Energy

DOI:
[10.1016/j.nme.2017.05.013](https://doi.org/10.1016/j.nme.2017.05.013)

Published: 01/08/2017

Document Version
Version created as part of publication process; publisher's layout; not normally made publicly available

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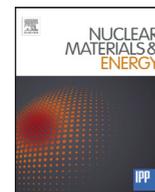
Please cite the original version:
Suchonova, M., Veis, P., Karhunen, J., Paris, P., Pribula, M., Piip, K., Laan, M., Porosnicu, C., Lungu, C., & Hakola, A. (2017). Determination of deuterium depth profiles in fusion-relevant wall materials by nanosecond LIBS. *Nuclear Materials and Energy*, 12, 611-616. <https://doi.org/10.1016/j.nme.2017.05.013>

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Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

Determination of deuterium depth profiles in fusion-relevant wall materials by nanosecond LIBS

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ARTICLE INFO

Article history:

Received 1 August 2016

Revised 21 April 2017

Accepted 30 May 2017

Available online xxx

Keywords:

LIBS

Beryllium

Aluminum

ABSTRACT

The ablation and fuel-retention characteristics of aluminum–tungsten (AlW) and beryllium–tungsten (BeW) samples have been determined using Laser Induced Breakdown Spectroscopy (LIBS) and compared to results obtained using Secondary Ion Mass Spectrometry (SIMS). The measurements have been made both at vacuum (of the order of 10^{-4} Pa) and at 50 Pa of argon to especially enhance the intensities of the spectral lines of H and D. For reliable evaluation of the ablation rate of the samples the electron density n_e and temperature T_e of the LIBS plasma have been determined with the help of selected of spectral lines of Be, Al, and W. The electron density n_e has been obtained from Stark broadening lines of Al I (308.7 nm and 394.4 nm) and Be II (457.3 nm) and T_e from the Saha–Boltzmann plot using W I and W II spectral lines having a higher value of the energy of upper states in order to prevent the influence of self-absorption on the results. The results indicate similar ablation characteristics between AlW (AlWD) and BeW (BeWD) samples but the inclusion of deuterium in the coating increases the ablation rate by a factor of 10 for both sample types. Concerning fuel retention more than one order of magnitude less D is retained in the AlWD sample than in BeWD. In the presence of background argon, the H and D lines were stronger and more easily distinguishable. This is a positive sign considering the real application in ITER where LIBS measurements are foreseen to be done during maintenance breaks. However the higher pressure gave a better signal, it is still far from the measurement conditions planned for ITER which need to be tested separately.

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1. Introduction

The feasibility of using Laser Induced Breakdown Spectroscopy (LIBS) as an analytical method for the detection of deuterium (D) in fusion-relevant materials has attracted much research interest recently [1–3]. The results obtained by LIBS have also been cross-correlated with data obtained by various ion-beam methods like Secondary Ion Mass Spectrometry (SIMS) [4]. As a part of this work the LIBS method was used for determining the composition of the deposited layers of fusion relevant materials on the samples from the inner divertor tiles of the ITER-like wall of JET. Deuterium

was detected in the deposited layers and successfully distinguished from hydrogen [4–5]. Special attention was paid to depth profiling in [6] and to ablation rate in [7] using different background gases and pressures. The so-called Calibration Free (CF) LIBS approach, which is well described in [8], was applied in [9–10], and the intensity ratio of the neighbouring H/D spectral lines was used to determine the D concentration of the studied samples. Recently we proposed to use also W III lines in the Vacuum UV / UV spectral range to evaluate T_e more precisely from the Saha–Boltzmann plot [11].

With the exception of the experiments presented in [4,12], most of the ITER-relevant LIBS studies have used Al as a proxy for Be due to the toxicity of the latter. Aluminum–lithium alloys, which replacing toxic beryllium–lithium alloy were used as a substitute on first wall and studied in [1] for the study of the

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<http://dx.doi.org/10.1016/j.nme.2017.05.013>

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enhancement effect of the magnetic field to LIBS spectra at various pressure. In [13] Al (as a substitute for Be) and first-wall materials tungsten and molybdenum were used to investigate the polarized continuum emission and signal-to-background ration for application polarization-resolved LIBS to reduce background continuum and enhance the resolution and sensitivity of LIBS. The samples of tungsten and molybdenum on CFC substrate, which contains hydrogen, deuterium, beryllium, carbon and oxygen were analysed using method LIBS for the determination of depth profiles of different elements in [4]. Novel processing method for quantitative depth profiles for the elemental concentration from LIBS spectra was presented in [5]. LIBS experiments on different beryllium-tungsten samples were performed to develop LIBS towards tokamak applications in [12]. However, both the LIBS analysis and fuel retention itself may be different for Be- and Al-based materials, as indicated by [14]. The goal of this article is to study the feasibility of this substitution in fuel retention studies of ITER-relevant layers by investigating the ablation characteristics and fuel retention properties of mixed BeW and AlW coatings (with and without D doping) by examining their elemental depth profiles using LIBS and SIMS. In addition, the effect of background pressure on the distinguishability of closely lying spectral lines of different H isotopes was investigated.

2. Experimental setup and measurement

The measurements were carried out using the beryllium-compatible LIBS set-up at VTT Technical Research Centre of Finland [4]. Ablation was induced by an Nd: YAG laser operating at 1064 nm with pulse duration of 5 ns and fluence of approximately 4.3 J/cm² on the sample surface. The laser beam has Gaussian profile. The spectra were recorded with an Andor SR-750 spectrometer equipped with an Andor iStar 340T camera (Resolution $D = 0.03$ nm with 40 nm window, $D = 0.01$ nm with 20 nm window for H and D α line recording). The light was collected by a special bundle (transformation from round to linear bundle) of 50 optical fibers of 0.125 mm in diameter in the lateral direction to the sample surface. Two different pressures were used in the measurements: 10⁻⁴ Pa and 50 Pa of argon. In the latter case, the intensities of H α and D α lines were enhanced due to increased collisional excitation which enabled improved observations of their changes from shot to shot. The samples were produced in Romania in the National Institute for Laser, Plasma, and Radiation Physics using reactive magnetron sputtering method [15] on Mo substrates. The thickness of the AlWD and BeWD coatings were approximately 1.2 and 3.1 μ m respectively.

3. Results and discussion

In the experiments, fuel retention in ITER-relevant layers was studied by determining depth profiles of D and H in coatings with different compositions, with and without D doping. Two mixed BeW with 67 at.% of Be and 33 at.% of W and AlW samples with 67 at.% of Al and 33 at.% of W, further denoted as Be67W33 and Al67W33, have been analysed using LIBS and SIMS.

For the determination of the depth profiles from the LIBS measurements, a group of representative non-interfering W, Mo, Al and Be spectral lines were chosen and their intensities were studied for depth profile evaluation (Al I 394.40 nm, Al I 396.15 nm, Be I 457.26 nm, W I 410.27 nm, W I 401.52 nm, Mo I 379.82 nm, Mo I 386.41 nm). Examples of experimental spectra are shown in Fig. 1. (Al67W33D and Be67W33D). Recording parameters, which were optimized to obtain the strongest signal for H and D and the best signal-to-noise ratio for neutral and ionic spectral lines of other elements, were as follows: recording gate 500 ns, delay time between the laser shot and the onset of spectral recording for vac-

uum conditions 80 ns and 150 ns for the acquisition at 50 Pa of Ar background pressure.

The thicknesses of the coatings have been determined by surface profilometry by measuring the depth of craters produced in such SIMS measurements that were stopped immediately after penetrating the coating. In order to determine the ablation rate by dividing the thickness of the coating by the number of laser shots required to reach the substrate, we should be sure that ablation is constant throughout the coating. Ablation rate depends on many factors like heat conduction, heat capacity, melting/evaporation temperature, the laser fluence as well as the composition, structure and optical properties of the coating. Higher ablation of material using the same laser fluence is mainly for the material with lower melting point and lower ionization potential of presented elements. Comparing Be and Al (as a proxy of Be), Al has both parameters lower than Be (melting point: Be–1287 °C, Al–660.3 °C and ionization potential Al I–5.98 eV, Be–9.32 eV). Due to the higher efficiency of melting and ionization of Al, at the beginning of the laser pulse the first electrons are created more effectively (quickly and in higher quantity). Consequently, these electrons are heated longer by inverse bremsstrahlung process than in the case of the Be. It means that for the Al based samples created plasma should have a higher temperature and electron density.

Having the same material composition and the plasma parameters (T_e , n_e) practically unchanged from shot to shot suggests that the generated plasmas are most likely as identical as possible and the amount of removed material is the same. Then we can also assume the coating to be uniform and homogeneous and thus the ablation rate remain constant, which was verified by SIMS depth profiles.

The electron density of the LIBS plasma has been determined from Stark broadening using equation

$$n_e = \frac{\Delta\lambda_{1/2}}{2w} 10^{16} \quad (1)$$

Where $\Delta\lambda_{1/2}$ is the Full Width at Half Maximum (FWHM) of the analysed spectral line, w is a tabulated collision parameter and n_e is the electron density in cm⁻³. We have used here the Al I (308.7 nm and 394.4 nm, sample Al67W33/ Al67W33D) and Be II (457.3 nm, sample Be67W33/ Be67W33D) spectral lines. The evaluated average electron densities from the first ten shots as well as the spectral parameters of the transitions and the Stark widths of the studied lines [16–17] are listed in Table 1.

We assume that the energetic distribution and the density of the particles in plasma (characterized by T_e and n_e) is related on the ablation rate so we verified the stability of the electron temperature T_e for each shot from the Saha-Boltzmann (SB) plot [18] of the W I-II lines (see Fig. 2).

The measured spectra have been corrected by the spectral response function of the spectrometer and after that the integrated intensities of the identified tungsten lines were evaluated for the construction of the SB plot. The ratio of ions and neutral atoms required for the SB plot was calculated from the Saha equation:

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

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 the aforementioned Be II and Al II spectral lines, m_e is the mass of the electron, k is the Boltzmann constant, h is the Planck constant and ϵ_i is the ionization energy. The electron temperature is given by the slope of the fitted line in the SB plot. Finally, the obtained average electron temperatures (T_e) are listed in Table 1. Neither electron temperature nor electron density changes signifi-

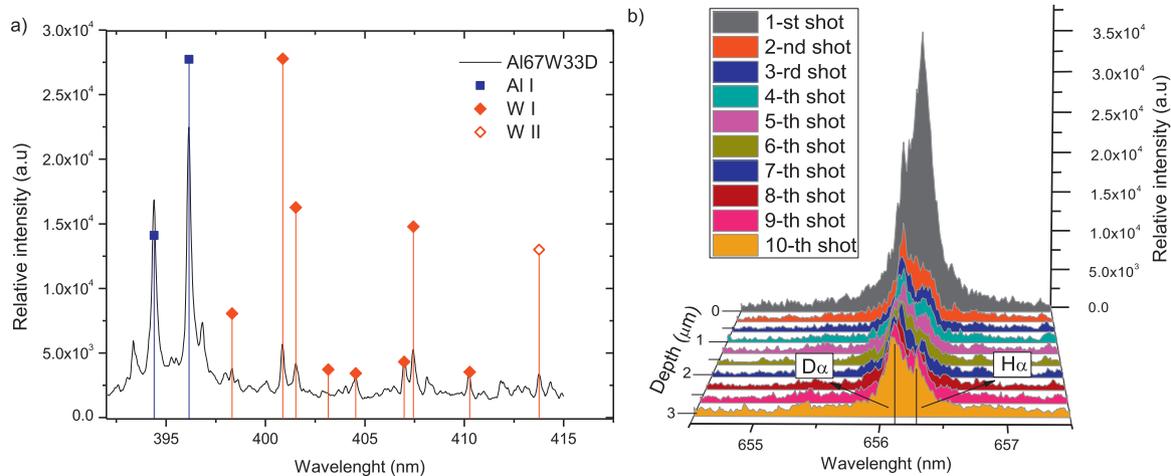


Fig. 1. (a) Examples of experimental spectra for Al67W33D sample (b) Evolution of Be67W33D LIBS spectra from 1st to 10th shot showing the decaying tendency of the D_{α} and H_{α} lines.

Table 1

Spectral parameters of selected spectral lines, n_e determined using Stark broadening of Al I and Be II spectral lines and T_e determined using the SB plot.

Sample	Spectral line	λ [nm]	Aik [s ⁻¹]	Ei [eV]	Ek [eV]	Stark width [nm]	N_e [cm ⁻³]	T_e [eV]
Be67W33	Be II	457.27	7.26E+07	5.28	7.99	6.33E-03	1.68E+17	0.96 ± 0.12
Be67W33D	Be II	457.27	7.26E+07	5.28	7.99	6.33E-03	2.12E+17	1.03 ± 0.12
Al67W33	Al I	308.70	5.87E+07	0	4.021	2.61E-03	5.50E+17	1.16 ± 0.14
Al67W33D	Al I	394.40	4.99E+07	0	3.14	1.54E-03	5.40E+17	1.31 ± 0.15

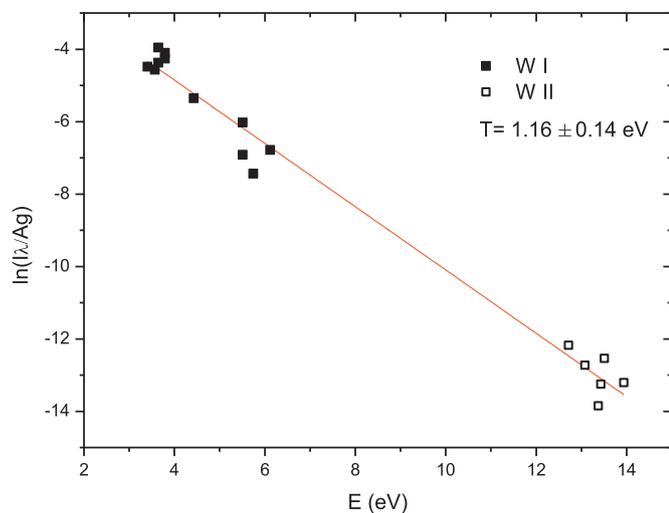


Fig. 2. Saha-Boltzmann plot used for the electron temperature determination (Al67W33, average of first 10 shots).

cantly from shot to shot, suggesting that the ablation rates are constant throughout the coatings (Fig. 3).

After this we calculated the ablation rate by dividing the thickness of the coating by the number of laser shots required to penetrate the coating. The calculated LIBS ablation rates are shown in Table 2. Comparison of ablation rate and evaluated electron densities and electron temperatures are presented in Fig. 4.

The results of ablation rates agree within uncertainties between the AlW and BeW coatings, while the ablation rates increase almost by an order of magnitude for the D-doped coatings. The higher ablation rate of D-doped coatings could be due to the fact that D has changed the structure and composition of the coating-

Table 2

Ablation rates for the Al/ Be- W samples with/without D.

Ablation rate [nm/shot]	Al67W33	Be67W33
w/o D	45 ± 8	39 ± 10
with D	330 ± 80	275 ± 35

sample has softer and less crystalline character. This coating is easier to ablate and also has decreased heat conductivity leading to lower diffusive heat losses into the sample (allowing more laser energy for the ablation process). Similar behaviour has been observed also earlier in [12].

Comparing the Al and Be containing coatings the Al-based coating has little bit higher ablation rate which correlates with slightly higher T_e and n_e , and relates to the fact about the ionization potential of coating elements mentioned before.

Elemental depth profiles of the D-doped BeW and D-doped AlW coatings, given by SIMS and LIBS, are presented in Figs. 5 and 6, respectively.

When determining the LIBS depth profiles by studying the intensity of the spectral lines as a function of the laser shot number, the intensities were normalized by the ablation rate to consider the effect of the ablated volume on the emission intensity.

When evaluating the D/H ratio, the central wavelengths of the two spectral lines have to be determined accurately as D_{α} and H_{α} lines are only partially separated due to broadening of the lines in the measured spectra. After that the D_{α} and H_{α} ratio was evaluated by fitting the lines with Lorentzian profiles. Optimal fitting was possible when the intensities of both lines were comparable while the fitting turned out to be impossible in the case of one of the spectral line being more than 10-times weaker than the other. This is for instance the case of D in Al67W33D sample after the fifth shot (corresponding to the depth of approximately 2 μm).

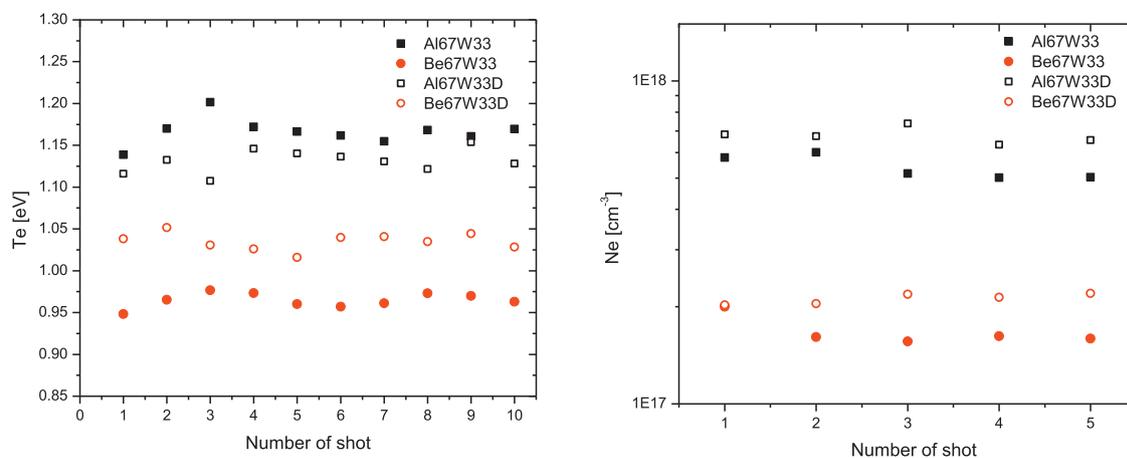


Fig. 3. Example of the electron temperature and electron density evolution as a function of the laser shot number for the measured samples, measured at vacuum pressure (of the order of 10^{-4} Pa).

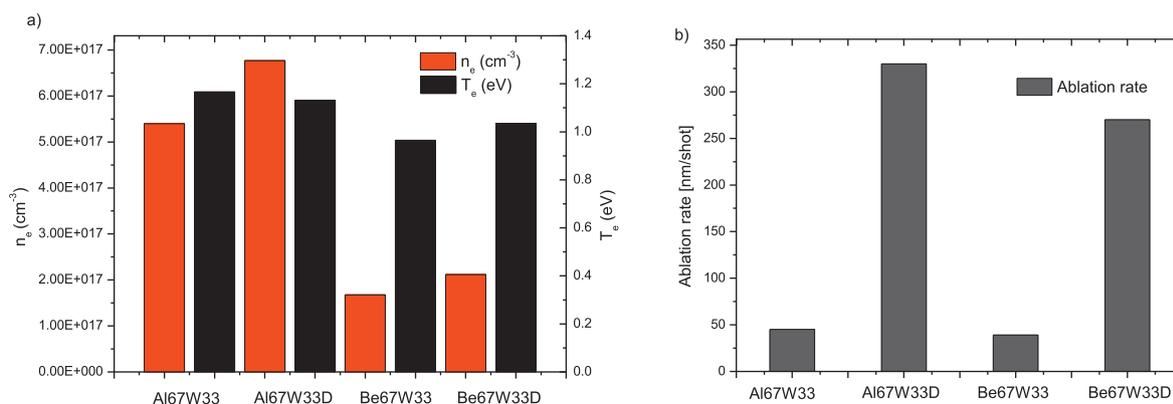


Fig. 4. (a) Electron density n_e and electron temperature T_e (b) Ablation rate of the studied samples.

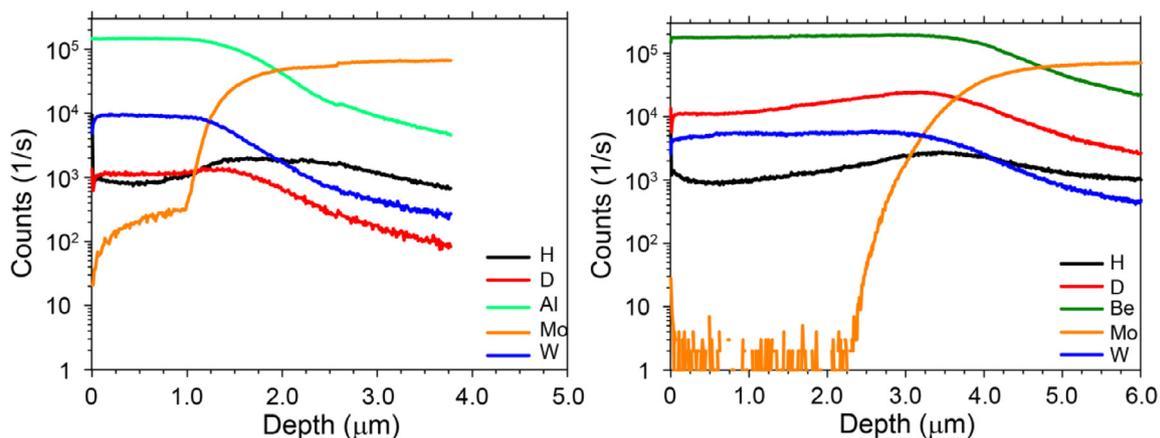


Fig. 5. SIMS depth profiles of different elements in D-doped Al67W33 (left) and Be67W33 (right) coatings.

The D content of the D-doped Be67W33 samples is clearly higher than their H content according to the SIMS measurements and confirmed by the LIBS measurements. Both SIMS and LIBS show similar depth evolution of H and D content, so they give the comparable results.

In contrast, in the case of D-doped Al67W33 samples their D content is much lower than the H content. In the LIBS measurements, the D content quickly decreases after few laser shots with the analysis depth while the H content stays at approximately the same level throughout the depth profile with the exception of the first laser shot. SIMS, however, indicates that the D and H contents

stay at the same constant level in the coating. In the substrate, the D content decreases and the H content stays rather constant. The quick decay of D signal in LIBS measurements of AlWD coating could be due to the easier outgassing of probably more porous AlWD coating, as mentioned above.

Both LIBS and SIMS measurements show that the D content in the AlWD layer is lower than in the BeWD layer, suggesting significantly different retention properties of Al and Be under similar deposition conditions. As mentioned before, the precision for evaluating the ratio of the D and H signals by LIBS is limited by the mutual fitting of the closely lying lines in cases where the

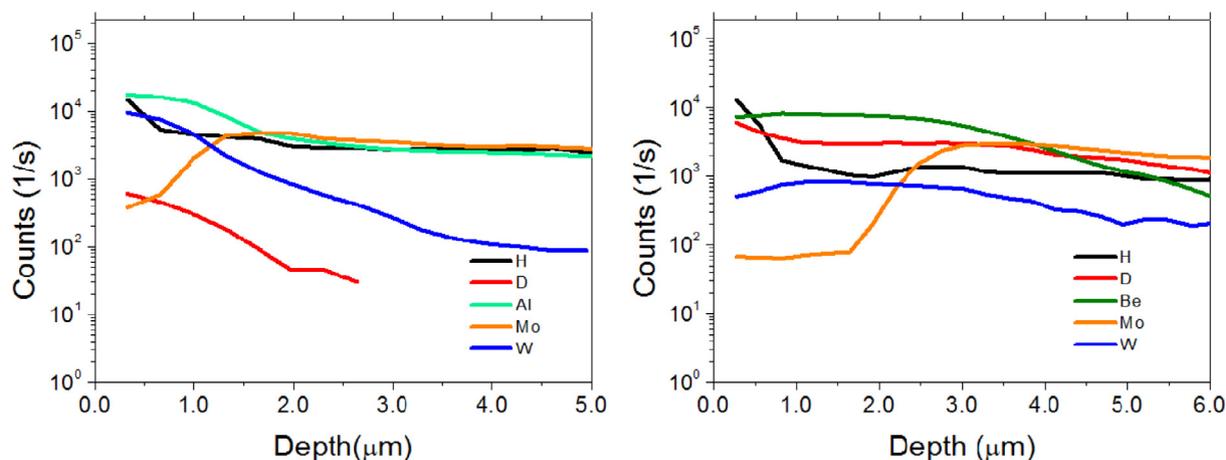


Fig. 6. LIBS depth profiles of different elements in d-doped Al67W33 (left) and d-doped Be67W33 (right) coating.

intensity of either of the lines is 1–2 orders of magnitude lower than that of the other isotope, e.g., in the case of the D content in Mo substrate of the AlW–D sample).

4. Conclusion

Aluminum has been used in many studies as the nontoxic proxy for beryllium. Thanks to the similar electronegativities of Be and Al the formation of compounds, especially the oxides and possibly the hydrides can be studied by replacing Be with Al [19]. In the present study we have compared the laser ablation rates and deuterium retention properties of Al and Be mixture layers with W.

The parameters n_e and T_e of the laser-induced plasma together with the laser ablation rate have been determined for the samples Al67W33 and Be67W33 both with and without D doping. D-containing samples show considerably larger ablation rates, and furthermore, the measurements indicate the ablation rate being slightly larger for Al than for Be, while still agreeing within the relatively high error bars. Different ablation rates of samples with and without D can be caused by different structures of the coatings. The electron temperature is almost the same for both doped and undoped samples. The electron density more than three times higher for Al than for Be samples.

The depth profiles of the studied samples have been determined using SIMS and LIBS. The D_α depth profile has been clearly detectable only in the case of Be sample, while both methods showed significantly lower D contents in the Al sample. Since the coatings were manufactured under similar deposition conditions, this indicates that the retention properties of Al are different from Be, potentially leading to significant underestimation of D retention, if Al is used as a proxy for Be in plasma exposure experiments. From these results we conclude that Al can be used as a substitute for Be in ablation experiments, but for fuel retention experiments this substitution is not suitable. In the presence of background argon, H and D lines were stronger and more easily distinguishable. This is a positive sign considering the real application in ITER where LIBS measurements are foreseen to be done during maintenance breaks.

Acknowledgement

The authors thank for financial support from the Scientific Grant Agency of the Slovak Republic (VEGA) under the contract no. 1/0925/14 and also Slovak Research and Development Agency under the contract No DO7RP-0021-12. This work has been carried out within the framework of the EUROfusion Consortium and

has received funding from the Euratom research and training programme 2014–2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. Work performed under EUROfusion WP PFC.

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