

J. Karhunen, A. Hakola, J. Likonen, A. Lissovski, M. Laan, P. Paris
and JET EFDA contributors*

Feasibility of LIBS for In-Situ Monitoring of Deposition and Retention on the ITER-Like Wall of JET

“This document is intended for publication in the open literature. It is made available on the understanding that it may not be further circulated and extracts or references may not be published prior to publication of the original when applicable, or without the consent of the Publications Officer, EFDA, Culham Science Centre, Abingdon, Oxon, OX14 3DB, UK.”

“Enquiries about Copyright and reproduction should be addressed to the Publications Officer, EFDA, Culham Science Centre, Abingdon, Oxon, OX14 3DB, UK.”

The contents of this preprint and all other JET EFDA Preprints and Conference Papers are available to view online free at www.iop.org/Jet. This site has full search facilities and e-mail alert options. The diagrams contained within the PDFs on this site are hyperlinked from the year 1996 onwards.

Feasibility of LIBS for In-Situ Monitoring of Deposition and Retention on the ITER-Like Wall of JET

J. Karhunen¹, A. Hakola², J. Likonen², A. Lissovski³, M. Laan³, P. Paris³
and JET EFDA contributors*

JET-EFDA, Culham Science Centre, OX14 3DB, Abingdon, UK

¹*Aalto University, Otakaari 4, 02150 Espoo, Finland*

²*VTT Technical Research Centre of Finland, 02044 VTT, Finland*

³*Institute of Physics, University of Tartu, 51010 Tartu, Estonia*

* See annex of F. Romanelli et al, "Overview of JET Results",
(24th IAEA Fusion Energy Conference, San Diego, USA (2012)).

Preprint of Paper to be submitted for publication in Proceedings of the
21st International Conference on Plasma Surface Interactions, Kanazawa, Japan
26th May 2014 – 30th May 2014

ABSTRACT

The inner divertor of the ITER-like wall of JET was studied by laser-induced breakdown spectroscopy (LIBS) to show the feasibility of the method as *in situ* diagnostics in JET and ITER. The elemental depth profiles agreed with those given by earlier SIMS measurements. Deuterium was detected in the deposited layers and successfully distinguished from hydrogen. The largest amounts of deuterium were found on the apron of Tile 1 and at the bottom parts of Tile 3, whereas Tile 4 showed thin but relatively deuterium-rich layers. Beryllium, on the other hand, was mainly deposited above the inner strike point, as also suggested by SIMS. The results of these studies support LIBS as a promising *in situ* replacement for *post mortem* methods in monitoring metallic deposited layers.

1. INTRODUCTION

Formation of mixed deposited layers can significantly increase fuel retention on plasma-facing components of a tokamak and change their erosion properties [1]. This narrows the allowed operational window of the device. In ITER and future fusion reactors, where the fuel mixture will contain radioactive tritium, increased fuel retention poses a radiation safety risk and can increase the number of maintenance breaks. Hence, active monitoring of the location, composition and thickness of the deposited layers is essential.

Laser-induced breakdown spectroscopy (LIBS) [2,3], based on analyzing the spectrum emitted in a laser ablation process, is a potential method for *in situ* studies of deposition and fuel retention in ITER. Before the completion of ITER, the feasibility of LIBS with ITER-relevant material combinations is aimed to be proven with the ITER-like wall (ILW) of JET. In this contribution, the qualitative depth profiles of different elements in samples extracted from the JET ILW are measured by LIBS and the results are compared with those obtained by secondary ion mass spectrometry (SIMS) [4]. Since detection of the fuel isotopes is essential in ITER, the aim is also to reliably detect deuterium in the deposited layers by LIBS and to distinguish it from hydrogen.

2. EXPERIMENTAL SET-UP AND SAMPLES

The LIBS measurements were performed using a specific beryllium- and tritium-compatible experimental set-up at VTT. The samples are located in a vacuum chamber, and ablation is induced by focusing Nd:YAG laser pulses with energies up to 650mJ at 1064nm to the surface of the sample. The size (FWHM) of the focused laser spot is approximately 800 μ m. The emission is detected perpendicular to the laser beam by guiding the emitted light by a parabolic mirror to the tip of a 50- μ m optical fibre and further to an Andor SR-750 spectrometer equipped with an Andor iStar 340T ICCD camera. In a tokamak application, collinear measurement is required due to the challenging measurement geometry, but perpendicular detection angle was used here for practical reasons. However, the detection geometry has no significant effect on the conclusions of the analysis done in this work. Unless otherwise noted, the pulse energy was adjusted such that the fluence of the laser beam on the sample was approximately 20Jcm⁻².

The delay between the laser pulse and the onset of detection was set by a pulse generator. The optimal value to obtain maximal intensity for both atomic and ionic spectral lines with minimal line widths and background was found at 85 ns. At such a delay, the continuous spectral component due to bremsstrahlung that governs the spectrum in the beginning has decayed, while line emission is still strongly visible. The width of the measuring gate was 500ns.

Altogether 12 samples from the JET ILW were studied by LIBS. The samples were drilled from the divertor tiles 1, 3, and 4, covering poloidally the entire inner divertor, as shown in Figure 1a. Another set of 11 neighbouring samples, studied earlier by SIMS, were selected as references for comparison between the two methods. The samples had been exposed to plasma operations during the period 2010–2012.

The samples had a layered structure of tungsten and molybdenum on a CFC substrate, as presented in Figure 1b. The deeper molybdenum layer acts as a barrier preventing diffusion of carbon from the substrate to the tungsten layer, whereas the other molybdenum layer is a marker, aiding in determining the erosion of the topmost tungsten coating. On top of the tungsten coating, 0.1–10- μm thick deposited layers were found. According to previous SIMS measurements [5], the layers contained hydrogen, deuterium, beryllium, carbon, oxygen, molybdenum, tungsten, and traces of eroded Inconel components – mainly chromium and nickel.

3. ELEMENTAL DEPTH PROFILES

3.1. GENERATING THE DEPTH PROFILES

The qualitative depth profiles of different elements in the samples can be obtained by measuring the spectra emitted by several subsequent laser pulses and by plotting the integrated intensities of selected spectral lines as functions of the pulse number. In these studies, atomic spectral lines of beryllium, tungsten, and molybdenum at 457nm, 401nm, and 414nm, respectively, and an ionic carbon line at 426nm were selected due to their large intensity and minimal overlapping with the spectral lines of other involved elements. Due to strong broadening of the lines, hydrogen and deuterium could not be separated using the standard measurement settings, but the line at 656nm is a combination of both of them. This issue is revisited in the following section. For most of the samples, bright chromium lines at 393nm and 396nm were observed on the first one or two pulses, indicating the presence of Inconel traces on the surface. The depth profile of oxygen, given by the line at 777nm, was typically found to follow that of beryllium, suggesting oxidization of beryllium. The oxygen profiles were excluded from this work due to noisiness of the LIBS signal and lack of SIMS data.

Since the ablation rates of different materials can be significantly different from each other, an absolute depth axis cannot be created for the LIBS data by simply measuring the crater depth by, e.g., surface profilometry. For SIMS, instead, the sputtering rates show much less variance between different materials, enabling absolute depth analysis with the help of profilometry. The LIBS data was then fitted to the SIMS data by manually scaling the number of laser pulses by suitable ablation rates within each layer until the depth profiles coincided with those given by SIMS, thereby providing

a depth axis also for the LIBS data. In Figure 2a-b, this is done for the samples 1a (LIBS) and 2 (SIMS) as well as for 11a (LIBS) and 10 (SIMS) of Tile 1 (see Figure 1a). Within the deposited layers on the samples 1a and 11a, good matches were obtained by using ablation rates of 450nm/pulse and 2500nm/pulse, respectively. The drastic difference in the values might be explained by the significantly different thicknesses of the layers: on 1a, the deposit is less than 1µm thick, whereas the layer on the sample 11a is almost 10µm thick and probably more porous and softer than the thinner layer. For the tungsten and molybdenum layers, the ablation rates were within 120–350nm/pulse for both of the samples. Similar values were observed also for Tiles 3 and 4. The values are significantly lower than for samples from the carbon-wall era of JET for which 5–50 times higher ablation rates were determined [6], suggesting tighter structure of the metallic deposits compared to the carbon-based ones. However, for the thickest layers, the ablation rates are too high to provide a good depth resolution also in the case of the ILW samples.

Despite the general match on the samples 1a and 2, some deviations between the two methods can be seen in Figure 2a. The beryllium profiles were fitted to match within the deposited layer, while deeper in the tungsten coating the strong matrix effect in SIMS changes the behaviour of the signal. The same applies also for the deuterium signal, but here the mismatch is observed already in the deposited layer. This can be due to lower sensitivity of LIBS to the small amounts of deuterium and thermal desorption induced by the heating effect of the laser pulses [7] – but also due to the 20-mm difference in the poloidal locations of samples 1a and 2. For tungsten, LIBS suggests far higher content on the surface than SIMS. The peak probably originates from tungsten that has been ablated from a crater used in earlier measurement and deposited on the nearby surface. The deviation of the tungsten signals at the deeper end of the coating can be explained by the Gaussian energy distribution of the laser beam, as will be discussed in Section 3.2. For the samples 11a and 10, the match is also generally good, although the matrix effect of SIMS induces differences in the beryllium profiles on the surface and in the tungsten profiles when entering the molybdenum layer.

With decreased fluences, the depth resolution of the LIBS measurements is improved due to the roughly linearly decreasing ablation rate. This way, at a fluence of 5 Jcm^{-2} , the layered structure of the samples (see Figure 1b) was observed also by LIBS, as shown in Figure 2c. In the deeper tungsten and molybdenum layers, the materials might be mixed, which could explain the coexistence of the two signals.

3.2. IMPROVING THE QUALITY OF THE DEPTH PROFILES

The Gaussian energy distribution of the laser beam produces unfavourable features in the depth profiles. The energetic central part of the beam ablates material deeper in the sample than the main part of the beam such that the observed spectrum is a combination of contributions from different layers in the sample. Moreover, the edges of the beam continue ablating material long after the central part has propagated further, producing slowly decaying tails into the profiles. A laser beam

with a flat-top energy profile [8] would not produce these features, but such beams are not suitable for tokamak applications due to the demand of a fixed measurement geometry.

Another feature seen in the profiles in Figure 2b (solid lines) is the remarkable decrease of the intensity levels at large numbers of laser pulses. For example, the tungsten profile decreases throughout the entire coating and reaches a significantly lower level within the second tungsten layer beneath the molybdenum marker than in the coating. While mixing of tungsten and molybdenum could partly explain the behaviour in the deeper layer, another possible reason is the partial shadowing and confinement of the plasma plume by the deepening crater, which weakens the perpendicularly observed signal and, thus, has a direct effect on the depth profiles determined from the line intensities.

The sensitivity of the depth profiles to variations in the general intensity level can be eliminated by studying correlations between the spectra recorded for different laser pulses, as suggested in [9], instead of examining the evolution of line intensities. By definition, the correlation coefficient between two signals is independent of any constant scaling of the signals themselves. Hence, the method registers only the changes in the shape of the spectrum, neglecting variations in the intensity level. The dashed depth profiles in Figure 2c have been obtained by selecting spectra from different layers of the sample and studying their correlation with all the spectra measured from the same crater. Compared to the depth profiles determined from line intensities (solid lines), the resulting curves are flatter within the different layers and show clearer interfaces between them, improving thus the resolvability of the depth distribution of the elements in the sample. However, the tail effect due to the Gaussian laser beam still exists, which can be seen, e.g., as the persistence of the molybdenum profile in the deeper tungsten layer.

4. DETECTION OF DEUTERIUM

To overcome the overlap of the hydrogen and deuterium lines in the measured spectra, the detection system was re-designed by replacing the single 50- μm optical fibre by a bundle of 50 such fibres. After this, more light was transmitted to the spectrometer and the entire active area of the CCD cell was used, which led to an improvement in the intensity and signal-to-noise ratio of the H/D line by an order of magnitude. This enabled using longer measurement delays to narrow the observed lines without significant loss of the signal. At delays of 235–335ns, the density- and temperature-driven broadening of the observed spectral lines had decreased such that the spectral lines of hydrogen and deuterium at 656.3nm and 656.1nm, respectively, and, thereby, their depth profiles were clearly distinguishable from each other, as presented in Figure 3a-b. To avoid excessive ablation of the layer, these measurements were done at a fluence of 10Jcm^{-2} .

The main aim of tokamak-relevant LIBS studies is to determine the fuel content in the deposited layers. The poloidal distribution of the deuterium content on the inner divertor of JET was calculated by integrating the depth profile of deuterium over the thickness of the deposited layer. To eliminate the effect of possibly changing intensity levels between different samples, this integral was then

normalized to the peak value of the tungsten profile which also had been integrated over an equally wide depth interval to cancel out the effect of the layer thickness. The resulting qualitative profile, presented in Figure 3c, agrees well with the one obtained by SIMS: both methods suggest the largest amounts of fuel at top part of Tile 1 and the bottom part of Tile 3. Similar results could be obtained also for the Be/W ratio, implying the thickest deposits at the aforementioned locations.

To study the relative amount of fuel in the deposited layers, the ratio of the deuterium and beryllium signals was examined. Again, the resulting profiles between the two methods agree, as seen in Figure 3d, indicating thin but relatively D-rich layers on Tile 4 which is partly shadowed from the plasma (see Figure 1a). Elsewhere, the D/Be ratio remains approximately constant, suggesting that beryllium, eroded from the main chamber wall, does not reach the bottom of the divertor to as large extent as deuterium but is mostly deposited above the inner strike point on Tiles 1 and 3, which agrees with the SIMS depth profiles.

5. CONCLUSIONS

The feasibility of LIBS on detecting ITER-relevant deposited layers and fuel retention in them was studied by performing LIBS measurements on a set of samples from the inner divertor tiles of the ITER-like wall of JET and comparing the results to those obtained from neighbouring samples by SIMS.

The depth profiles detected by LIBS were found to agree qualitatively with those given by SIMS, when the LIBS profiles were scaled with ablation rates of 100–2500nm/shot which are 1–2 orders of magnitude lower values than those observed for the carbon-era samples from JET. Hence, LIBS is a promising *in situ* replacement for *post mortem* methods in monitoring metallic deposited layers, although the ablation rates are rather large for the thickest layers. The depth resolution of LIBS can be improved by decreasing the fluence of the laser beam and the representativity of the depth profiles by studying correlations between spectra instead of integrated line intensities.

By replacing a single optical fibre with a bundle of 50 fibres and by increasing the measurement delay, the spectral lines of hydrogen and deuterium could be separated. Thus, LIBS is also principally capable of detecting the different fuel isotopes. However, it has to be noted that the isotopic shift between deuterium and tritium is smaller than that between hydrogen and deuterium – of the order of the line width ($\approx 0.1\text{nm}$) [10] – so measurements with samples containing both deuterium and tritium are required to confirm the distinguishability of the fuel isotopes.

By studying the ratios of integrated deuterium signal to tungsten and beryllium, the largest amounts of deuterium were found on the top part of Tile 1 and the bottom part of Tile 3, while thin but relatively D-rich layers were found on Tile 4. Fairly similar profiles were given by SIMS, suggesting migration of deuterium deeper into the divertor than beryllium.

In the future studies, the aim is to detect deuterium reliably also quantitatively using, e.g., calibration-free LIBS [11] to determine the concentrations of different elements. However, reference samples and cross correlation with ion beam analysis data are still required to convert the concentrations to absolute amounts.

ACKNOWLEDGMENTS

This work was supported by EURATOM and carried out within the framework of the European Fusion Development Agreement. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

REFERENCES

- [1]. R.A. Pitts et al., *Plasma Physics and Controlled Fusion* **47** (2005) B303–B322
- [2]. R.E. Russo et al., *Talanta* **57** (2002) 425–451
- [3]. A. Huber et al., *Physica Scripta* **T145** (2011) 014028
- [4]. J.P. Coad et al., *Nuclear Fusion* **46** (2006) 350–366
- [5]. J. Likonen et al., *Physica Scripta* **T159** (2014) 014016
- [6]. J. Karhunen et al., 40th EPS Conference on Plasma Physics (2013)
- [7]. V. Philipps et al., *Nuclear Fusion* **53** (2013) 093002
- [8]. V. Kekkonen et al., *Journal of the European Optical Society* **6** (2011) 110135
- [9]. M.P. Mateo et al., *Surface and Interface Analysis* **38** (2006) 941–948
- [10]. D.A. Tate et al., *Journal of Physics B: Atomic, Molecular and Optical Physics* **21** (1988) 421–430
- [11]. A. Ciucci et al., *Applied Spectroscopy* **53** (1999) 960–964

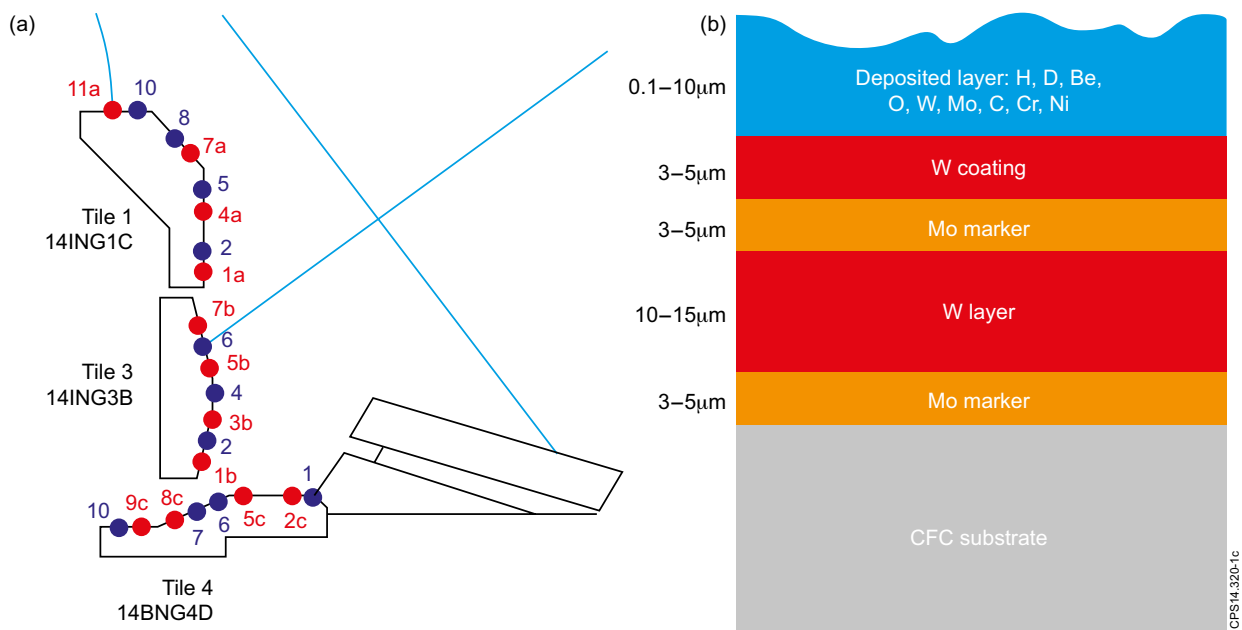


Figure 1: a) The locations of the samples selected for LIBS (red) and SIMS (blue) studies in the inner divertor of JET; b) The layered structure of the studied samples.

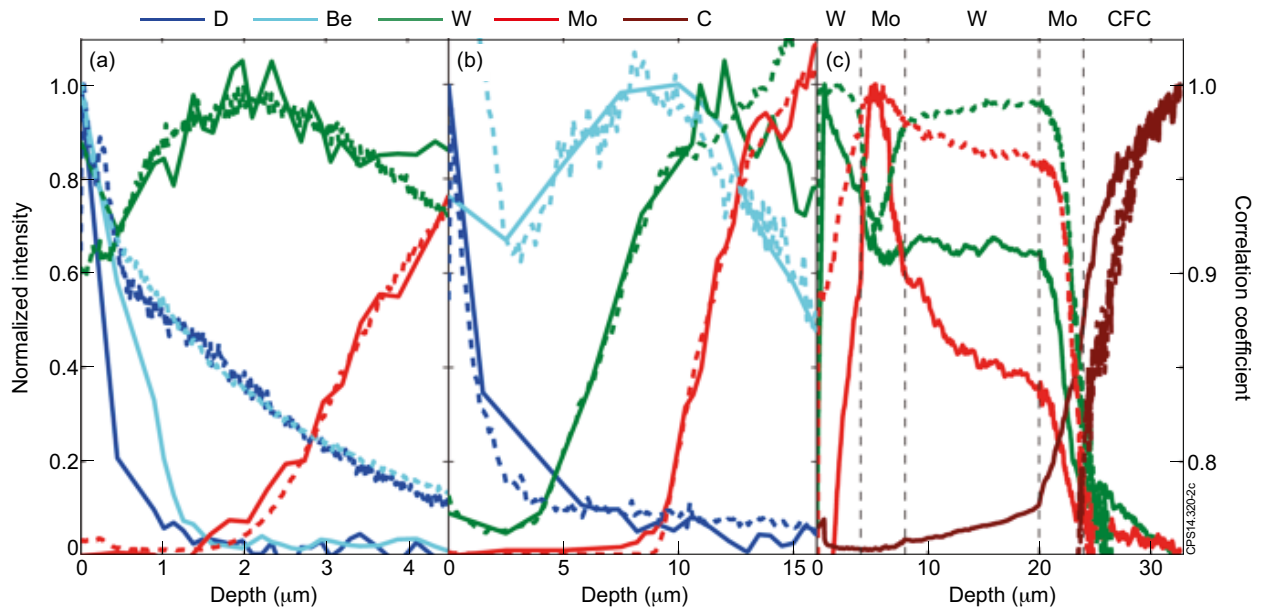


Figure 2: a) The elemental depth profiles detected for samples 1a (LIBS, solid line) and 2 (SIMS, dashed line) and b) 11a (LIBS, solid line) and 10 (SIMS, dashed line) on Tile 1; c) The layered structure of the sample 5c on Tile 4 measured by LIBS at a fluence of 5Jcm^{-2} . The solid profiles are determined directly from the normalized line intensities, whereas the dashed profiles represent the correlation coefficients (right y axis) between spectra from different layers.

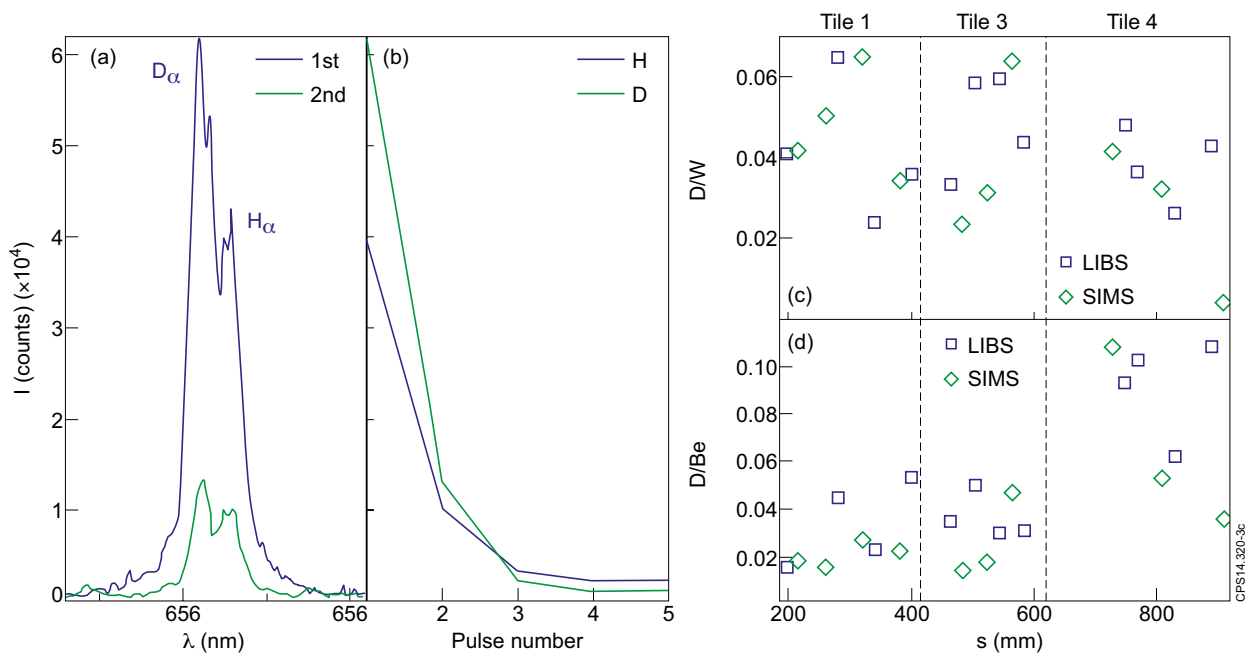


Figure 3: a) The separated spectral lines of hydrogen and deuterium at 656.3nm and 656.1nm, respectively, on the first two laser pulses and b) their depth profiles; c) The integrated deuterium profiles normalized to the tungsten signal, indicating largest amounts of deuterium on the upper part of Tile 1 and the lower part of Tile 3; d) Ratios of integrated deuterium and beryllium profiles in the deposited layer, suggesting relatively deuterium-rich layers on Tile 4.