Determination of elemental depth profiles by multi-spot averaging technique of LIBS spectra

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The paper deals with the development of the laser induced breakdown spectroscopy (LIBS) into an in situ method for studying of erosion/deposition processes at the first walls of fusion reactors. Because of fluctuations in the signal-to-background ratio of single-shot LIBS spectra, an averaging procedure has been used to reliably determine depth profiles of different elements at the surface, including that of deuterium. In the present study the averaging was carried out over LIBS spectra recorded from different sites of the studied sample. The set up allowed the characterization of nth laser shot by spectra recorded from N different sites. Deuterium-doped and Al-coated Ti samples were tested. The required ablation was produced by a UV (λ = 248 nm) laser. LIBS results for the depth profiles of D, Al, and Ti were compared with the data obtained by three different ion-beam techniques. Comparison of the averaged intensity of elemental spectral lines of an element versus laser shot number curves with depth profiles obtained by other methods showed a good qualitative match.

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1. Introduction

Erosion studies of plasma-facing components and depositions on them are important research areas in tokamak-type fusion reactors [1]. So far, erosion and deposition have been largely studied by post mortem surface-analysis methods, i.e., by removing samples from the reactors after long-term experimental campaigns and studying them using various ion-beam techniques including Rutherford backscattering (RBS), nuclear reaction analysis (NRA), and secondary ion mass spectrometry (SIMS) [2–4]. The studied samples are typically wall tiles with different marker coatings. However, an inherent limitation of all post-mortem techniques is that the data is obtained from tiles exposed to numerous plasma discharges including different plasma configurations and even regular openings of the vacuum vessel of the fusion reactor.

Laser induced breakdown spectroscopy (LIBS) can be used as a straightforward in situ technique for the determination of elemental composition of the material deposited on fusion reactor walls. In addition, with the help of information about ablation rate of materials, recording LIBS spectrum as a function of laser shot number opens the possibility to determine depth profiles of different elements on the surface layers. In future fusion reactors, a particularly interesting application area would be determination of the amount of tritium accumulated in the deposited layers.

Fusion-related applications of LIBS have certain limitations. The main one is a long recovering distance, which leads to a low signal-background ratio in the recorded spectra. Moreover, the long recovering distance rules out the detection of spectra in directions, other than that of the incident laser beam. The need to analyze shot-to-shot spectra precludes taking ensemble averages of the recorded data, a method usually used for improving the signal-to-background ratio. Thus, more sophisticated data processing methods have to be applied [5]. Promising applications of LIBS for characterization of plasma facing components are described in [6,7].

At the present bench-scale stage of studies, we have tested coating materials, which are representative for ITER and are thus important candidates for plasma–surface interaction studies inside the reactor. In our earlier studies [8,9] we have observed that only time-resolved recording of the LIBS spectra allows a reliable identification of metal elements. Both the width of the data acquisition time-gate Δt and the delay time τd between a laser pulse and opening of the gate for data acquisition were varied and the optimum values corresponding to the best signal to background ratio were found.
Fig. 1 presents the results of studying a sample which has a multilayer (W + Mo) coating on a Ti substrate. The sample was prepared using combined magnetron sputtering and ion implantation technology [10]. The figure shows that from shot to shot the intensity of a single spectral line of W fluctuates remarkably but the correlation between the fluctuations of different lines of W is missing. The average of normalized intensities of several spectral lines (see Table 1) gave intensity profiles which correlate well with the depth profiles obtained by glow discharge optical spectrometer.

In Fig. 1, only averages of normalized intensities of Mo and Ti lines are presented. However, this averaging method is not applicable when only one spectral line is detectable or results are influenced by the roughness of the surface.

The aim of the present study was to elaborate a technique which allows the averaging of LIBS signals recorded from different sites of a sample.

2. Set up and procedure

Fig. 2 presents a sketch of the device for recording of LIBS spectra from different sites of a sample. Samples were mounted in a testing chamber which was equipped with quartz window. The residual pressure in the chamber was ≈1 Pa. Ablation was produced by a KrF laser (wavelength—248 nm, pulse halfwidth—35 ns, maximum pulse energy—200 mJ). The fluence on the sample surface was smoothly varied by an attenuator (Att). The laser radiation was focused on the sample surface by a lens (L) with a focal length of 50 cm. The laser beam was directed to the sample by dichroic (DM) (reflective at 248 nm and transparent within 280–850 nm) and scanning (SM) mirrors. The area of the crater produced by the laser ablation on the surface of the samples was ≈0.7 mm × 1.4 mm.

A concave mirror (CM) with a 5 cm focal length collected the light emitted from the plasma plume that ablation produced. The mirror focused the light into the fiber (F) with a diameter of 50 μm, which guided the light into a Mechelle 5000 (Andor Technology) spectrometer. The near-surface area from where the light was collected had ca 0.5 mm diameter. An intensified CCD camera recorded the spectrum at fixed values for the delay-time, t₀, and time gate width, Δt. Using deuterium and tungsten lamps, the spectral response of the whole recording system was determined.

The scanning mirror SM was rotated by a stepper motor. Because of a small angle between the mirror’s axis of rotation and the normal of the mirror, the rotation of the mirror led to changing of the laser beam position at the sample surface. Thus, if a full turn (cycle) is divided into N steps of the motor then the laser beam hits the sample surface at N different sites. The N spectra recorded during the first cycle characterize the effect of the first laser shot. During the next cycle the laser beam hits the same sites and again spectra are recorded etc.

A photo of a sample surface with 16 craters is presented in Fig. 3. Craters at each site are formed from the exposure of the surface to 10 laser shots.

To test the multisite recording technique, samples with deuterium-doped Al coating on Ti substrate were used. Al coating was used assuming that its response to laser irradiation should be rather similar to that of Be. The samples were prepared, using the DIARC® plasma coating method [11].

Before LIBS experiments, the properties of the samples were studied using three different ion-beam techniques: RBS, NRA, and SIMS. The RBS and NRA measurements were carried out at the Max-Planck-Institut für Plasmaphysik, Garching, Germany, while the SIMS analyses were made at VTT in Finland. In the RBS analyses, 3.0 MeV protons were used and from the energy spectrum of the backscattered particles the modeling gave crude depth profiles for the different elements. The NRA measurements were performed by bombarding the samples with 3He+ ions and measuring emitted protons at 150°. The energy of the helium ions was varied between 690 keV and 4000 keV to extract the deuterium content of the samples at different depths. It was found that the average concentration of deuterium in Al coating was 1.8 at%.

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
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<tbody>
<tr>
<td>W</td>
<td>407.44</td>
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<tr>
<td></td>
<td>426.93</td>
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<tr>
<td></td>
<td>434.81</td>
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<tr>
<td></td>
<td>459.99</td>
</tr>
<tr>
<td>Mo</td>
<td>470.73</td>
</tr>
<tr>
<td></td>
<td>550.65</td>
</tr>
<tr>
<td></td>
<td>557.05</td>
</tr>
<tr>
<td></td>
<td>724.25</td>
</tr>
<tr>
<td>Ti</td>
<td>430.06</td>
</tr>
<tr>
<td></td>
<td>550.65</td>
</tr>
<tr>
<td></td>
<td>557.05</td>
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<td></td>
<td>724.25</td>
</tr>
</tbody>
</table>
Detailed depth profiles for D, Al, and Ti were measured with SIMS (Fig. 4). For these analyses, we used a double-focusing magnetic sector instrument (VG Ionex IX-70S). The main regularities of profiles did not differ from those determined by the help of RBS. The most remarkable exception was a bump around 1 μm, which was missing from the RBS results.

Our LIBS tests were carried out at a repetition rate of 0.5 Hz. Two Al–Ti samples were tested, using almost the same value $\Phi \approx 10 \text{ J cm}^{-2}$ for the laser fluence. In the case of both samples, LIBS spectra were recorded from 16 different sites during 10 cycles of the stepper motor work, i.e., the samples were characterized by 160 spectra.

3. Results and discussion

LIBS spectrum in Fig. 5 was recorded at optimal values for $t_d$ and $\Delta t$. The intensity of the analytic lines exceeded considerably that of the background and the Stark widening did not cause overlapping of analytic lines. The example in Fig. 5 was obtained during the fifth laser shot and it shows that the Al coating was not totally removed: both Al and Ti lines are detected.

Intensities of spectral lines belonging to the same cycle (i.e., the sites were exposed to the same number of laser shots) fluctuated considerably. Fig. 6 shows that the intensity of a spectral line varies with the site by a factor of 2–3.

As the correlation between fluctuations in the intensities of different spectral lines of a certain element was missing, it was concluded that shot-to-shot stability of laser pulses as well as spatial fluctuations of ablation-formed plasma plume were not the reasons of fluctuations. Our analyses showed that there are three main reasons for the fluctuations. The first one is related to the noise caused by the recording system and photon statistics of signals at low intensities. The second reason is the fluctuations in the continuous component of the spectrum. The third reason is related to the surface roughness: on sites where cavities are present, the laser radiation is absorbed more efficiently, which finally leads to higher intensities of spectral lines.

Fig. 7 gives the dependence of the intensities of analytic lines of Al and Ti both on the site and on the laser shot number. The comparison of site-to-site fluctuations corresponding to different cycles showed that that an apparent correlation between the intensity and the site number was missing. Averaging over sites gave considerably smoother intensity versus laser shot number profiles and the difference between the averaged profiles of two samples was negligible.

For Al and Ti there is a good correlation between the averaged LIBS profiles (Fig. 7) and depth profiles obtained by SIMS (Fig. 4). However, the transition from Al coating to Ti substrate is steeper for SIMS than it appeared from LIBS recordings. A likely reason for the discrepancy is related to the intensity distribution along the laser beam cross-section, i.e., the distribution was not a flat-top one. Comparison of SIMS and LIBS profiles allows us to estimate that the ablation rate of the Al coating is $\approx 1 \mu$m per laser shot.
Fig. 8. Intensity of Dα line versus laser shot number n and spectrum number R; points connected with thinner lines present the intensities of different sites of sample S1; thick lines give the averaged intensities of samples S1 and S2.

Only the Dα line (λ = 656.1 nm) of deuterium was detectable. Because the intensity of this line was at least an order of magnitude lower than that of Ti and Al lines, the relative variations in its intensity were remarkably large. In spite of big site-to-site intensity fluctuations, averaging over sites gave rather smooth profiles (Fig. 8). Furthermore, LIBS profiles from two different Al–Ti samples with identical coatings practically coincided. Like the depth profile of deuterium obtained with the help of SIMS (Fig. 4), the LIBS signal for the Dα line had the same growing trend towards the Al–Ti interface. However, the bump recorded by SIMS was missing.

4. Conclusions

The main results concluded in this work, indicate that shot-to-shot time-resolved LIBS spectra can be used to obtain the elemental depth profiles. Fluctuations in the signal-to-background ratio are the main factor, which determines the reliability of the LIBS profiles. Applying the multi-spot shot-to-shot technique for recording of LIBS spectra leads to a considerable improvement in the signal-to-background ratio. The recorded LIBS profiles matched with the depth profiles obtained with the help of ion beam techniques. Compared with the averaging procedure described in Section 1, the multisite averaging requires recording the spectrum in a reasonably narrow wavelength range and the data processing demands comparatively less time. Finally, the method damps the role of surface imperfections which could exist on a single site.

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References