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Collinear double-pulse laser-induced breakdown spectroscopy as an in-situ diagnostic tool for wall composition in fusion devices

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HIGHLIGHTS

- DP-LIBS is proposed as an in-situ diagnostic method for characterizing PFCs of EAST in vacuum.
- The collinear DP-LIBS configuration overcame the sensitivity shortcomings of the conventional SP-LIBS.
- Plasma emission signals are dependent on the inter-pulse delay in 3.5×10^{-3} Pa.
- Exposed divertor tiles were tested by DP-LIBS at low pressure and remotely.

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ABSTRACT

Our recent investigations have indicated the potential of double-pulse laser-induced breakdown spectroscopy (DP-LIBS) for analysis of the deposited impurity on divertor tiles in the experimental advanced superconducting tokamak (EAST). The collinear DP-LIBS configuration was suggested with the aim of overcoming the sensitivity shortcomings of the conventional single pulse laser-induced breakdown spectroscopy (SP-LIBS) technique in vacuum conditions. A systematic study of plasma emission signal dependence on the inter-pulse delay at 3.5×10^{-3} Pa was performed, and the results were compared with the ones obtained with a single laser pulse of energy corresponding to the sum of the two pulses. For a molybdenum tile, it was found that the atomic spectral lines of Mo were enhanced by a factor of 6.5 when an inter-delay time of 1.5 μs was installed. For an exposed divertor tile, significant increases in the emission line intensities of various minor elements (such as Mo, Si, Fe, Cr, Ti, Ni and Ca) were observed in DP-LIBS, while no spectra signal was achieved in SP-LIBS. This collinear DP-LIBS technique would help us to develop a more promising system to monitor the fuel retention and impurity deposition on plasma facing components of EAST.

1. Introduction

In an operating tokamak chamber, plasma–wall interactions cannot be avoided. Depending on their location, the plasma facing component (PFC) surface can be primarily influenced by erosion and deposition [1,2]. In deposition-dominated zones, these impurities would pollute the core plasma and decrease the machine performance by radiating the energy coupled to the plasma. An effective means of monitoring elemental impurities deposition and fuel retention in situ is desired.

Laser-induced breakdown spectroscopy (LIBS) is a multi-elemental analytical technique based on the atomic emission spectroscopy, in which a high-energy laser pulse is utilized as a vaporization and excitation source to create a high-temperature plasma in front of a target surface [3]. It is capable of three-dimensional chemical analysis of any sample at the micrometric scale regardless of that sample's size, shape, or other characteristics [4,5]. These advantages make it a very popular technique in many applications that include space exploration [6,7], material analysis [8–10], biological identification [11], environmental monitoring [12] and analysis of works of art [13]. In addition, an extreme application of LIBS in fusion environment has been investigated in several laboratories [14–19]. According to previous works [20], we observed that the analyte signals of single pulse (SP)-LIBS suffered from relatively poor limits of detection at low pressure (below

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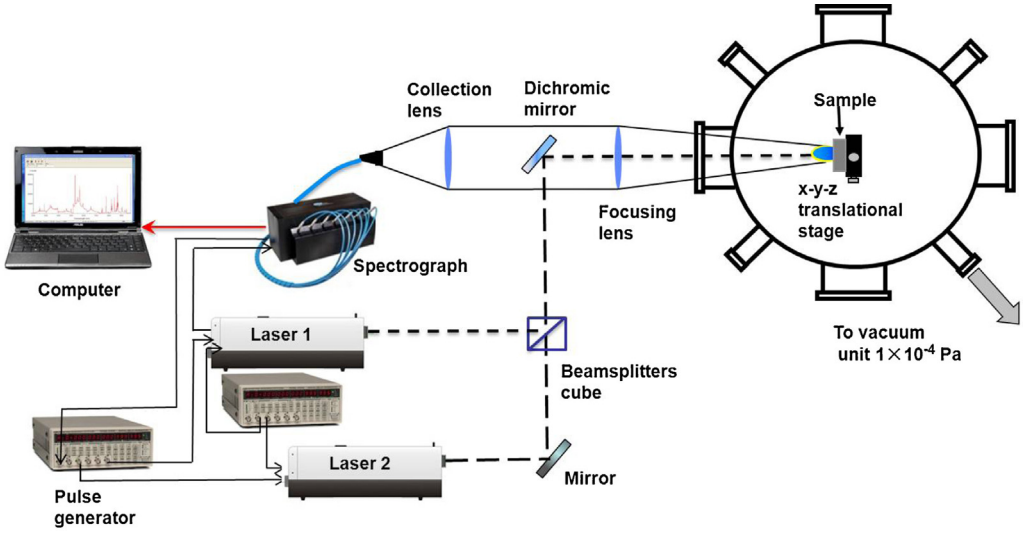

Fig. 1. Schematic of the experimental setup.

10 Pa). Double pulse (DP)-LIBS is a promising method for improving the detection sensitivity of LIBS [21–23]. DP-LIBS is different from SP-LIBS as fellows; two laser pulses used for LIBS excitation, which are separated in time by a period of few nanoseconds to several microseconds. Investigations of collinear double pulses interacting with aluminum samples showed higher line intensities lasting longer than corresponding emissions generated by single laser pulses [24]. A significant improvement in detection limits was achieved using double pulse excitation, and electron temperatures in the laser-induced plasma determined spectroscopically were higher by 1000–1500 K using double pulses [25]. In this paper, a collinear double pulse laser configuration is proposed to improve LIBS sensitivity in vacuum environment for the first time. The present investigations are designed to check the chemical analytical capability of the DP-LIBS technique as an in-situ diagnostic method for the determination of deposition layer on PFCs.

2. Experimental set-up

2.1. LIBS experimental set-up

A schematic diagram of the collinear DP-LIBS experimental set-up is depicted in Fig. 1. Basically, it consists of two lasers, a spectroscopic system, pulse generators, a vacuum chamber and a target holder. Two Q-switched Nd:YAG lasers (Brilliant Eazy, Quantel), each one emitting a pulse lasting 5 ns at 1064 nm, were combined into the same beam path with a beam splitter. Both laser beams were directed normal to the sample surface by reflective dichroic mirror and focused by a 500 mm focal length lens. The focus of the lens was set a couple of millimeters under the target surface. Samples were mounted on an *XYZ* translation stage inside a vacuum chamber which was equipped with ultraviolet grade fused silica windows. The vacuum chamber was pumped down to a pressure of 3×10^{-3} Pa to simulate the pressure condition in the fusion vessel. The energy of both laser beams was fixed at 45 mJ, which was accurately measured by a laser power meter (842-PE, Newport). During the measure phase the detector head was put in the laser path in vacuum chamber. The operation of the lasers was externally controlled by two programmable pulse generators (DG645, Stanford Research System) which allowed firing laser pulses simultaneously or at different inter-pulse delays ranging from 0.1 to 100 μs. The delay between the laser pulses was monitored using a fast rise detector and oscilloscope. The system of SP-LIBS was the common for the DP-LIBS, In the SP-LIBS regime two laser pulses emitted simultaneously, which provided the total energy of 90 mJ. With this configuration the diameter of the crater was about 1.1 mm and the instantaneous power density was 1.84×10^9 W/cm^2.

LIBS emission from the sample plasma was collected along the laser axis through the dichroic mirror with a 250 mm focal length lens and was guided into an optical fiber bundle coupled to a spectrometer. The applied spectrometer, LIBS2500+ (Ocean Optics Inc, US) detection system with seven linear silicon CCD array detectors, made it possible to analyze the plasma emission of wavelength range from 200 to 980 nm at the optical resolution of 0.1 nm with a single laser pulse. All spectra were collected at an integration time of 1 ms.

2.2. Sample description

Samples used in the parametric study were high purity polycrystalline molybdenum tiles as a substitute for the first wall tile of EAST. The samples were mechanically polished with silicon carbide (SiC) papers of different grades and then ultrasonically cleaned using alcohol. Furthermore, an exposed divertor tile of EAST was employed for the characterization of deposited impurities on the plasma facing component at low pressure and at stand-off distances. The original divertor tiles were made of multi-element doped graphite GBST1308 (1% B_4C, 2.5% Si, and 7.5% Ti) with about 100 μm thick SiC gradient coatings [26]. These tiles were used to cover all of the divertor panels and were designed to endure high heat flux without large erosion or damage. One typical sample (named DM2-2012) was prepared for our LIBS experiments, which was installed on the dome of the upper divertor and exposed to plasma discharges during the whole 2012 campaign.

3. Results and discussion

3.1. Effect of pressure on the emission intensity

According to previous works on LIBS analysis of the co-deposited layers on the first wall in vacuum [20], we observed that the signal intensity decreased significantly at lower pressure. The effect of surrounding atmosphere on the SP-LIBS signals of Mo was investigated with high purity polycrystalline molybdenum tile. Fig. 3 shows the results for the emission line of Mo I (550.65 nm) and

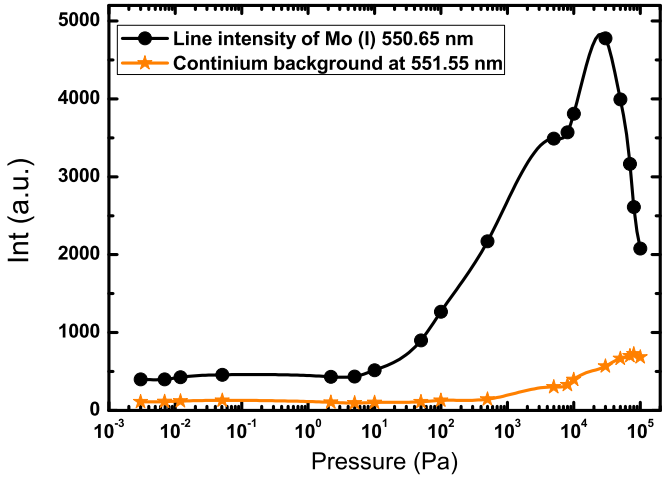

Fig. 2. Variation of the LIBS signal of line intensity of Mo I (550.65 nm) and continuum emission (bremsstrahlung) as a function of the pressure.

the background emission at 551.55 nm. There were no observed changes in the emission intensities of Mo with pressure increases from 3×10^{-3} to 10 Pa. However, at pressure above about 10 Pa, as the background pressure increases the line intensity of Mo I first increases, peaks around 3×10^{4} Pa, then decreases as the pressure further increases. The behavior can be explained by the competing processes of collisional excitation of species in the plasma and ablation of the tile [27]. As the pressure decrease, the number of elastic and inelastic collisions per unit time decreases whereas the mass of material ablated increases because of reduced plasma shielding above the sample [28–31]. As shown in Fig. 3, for pressure above about 3×10^{4} Pa, increased mass ablation more than makes up for a loss in analytic signals due to decreased pressure. For a pressure decrease from 3×10^{4} Pa to 10 Pa, the mass ablated showed a much smaller increase with decreasing pressure. Therefore, strong decrease in the intensities of emission lines was found due to the decrease in the collisions between vapor and ambient gas species. For pressure below about 10 Pa, collisions become infrequent and material is readily ejected from the surface into the surrounding free space so that pressure changes no longer affect emission signals. In Fig. 2 the continuum background intensities increase with ambient gas pressure. This continuum emission is proportional to the forth power of plasma temperature [32]; therefore, reduction of electron temperature at lower pressure is responsible for the lower level of background continuum obtained at a lower pressure.

3.2. Influence of the delay between the two laser pulses

In a vacuum environment, the main challenge of the future LIBS diagnosis for tokamaks is the high precision determination of the impurity deposition on PFCs. A systematic study of LIBS signal enhancement was carried out in our laboratory using the collinear DP-LIBS. Two different lasers were used to provide the two pulses for DP-LIBS; therefore, SP-LIBS experiments were performed with an inter-pulse delay of 0 μs. The time between the two laser pulses plays a key role in the double-pulse scheme, and it is adjusted by means of a delay generator. The emission line intensity of Mo(I) at 550.65 nm as a function of the inter-pulse delay time (up to 100 μs) is shown in Fig. 3a. The signal increases as a function of inter-pulse delay time until reaching a maximum value at 1–2 μs. This delay time is the best condition for energetic coupling between the first laser-induced plasma and the second laser pulse. From this time, the intensity is progressively reduced. Fig. 3b shows the emission LIB spectra of a molybdenum tile in both SP and DP-LIBS

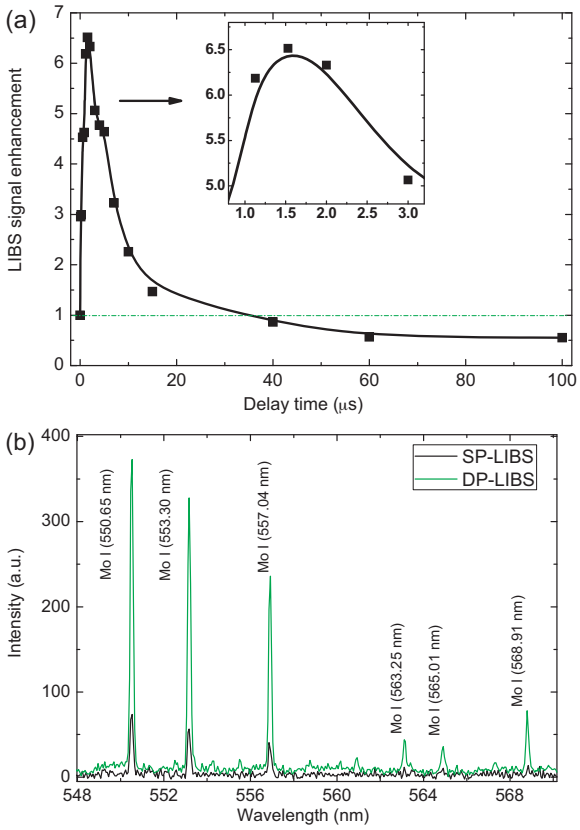

Fig. 3. (a) LIBS signal enhancement for the Mo I line at 550.65 nm, as a function of the inter-pulse delay time at 3.5×10^{-3} Pa. (b) DP-LIBS spectra in 3.5×10^{-3} Pa air with a 1.5 μs inter-pulse delay compared to SP-LIBS.

configuration in 3.5×10^{-3} Pa. DP-LIBS with an inter-pulse delay of 1.5 μs is ~6.5-fold greater than SP-LIBS for the 550.65-nm Mo line. According to these results, an inter-pulse delay time of 1.5 μs is selected as the best condition for the following chemical analysis of the exposed divertor tiles. With this delay time, all the materials ablated from the surface is still around the target area and able to interact with the second laser pulse.

3.3. Analysis of the co-deposition layer on the divertor tile

The surface compositions of the divertor tile (DM2 2012) were characterized using X-ray photoelectron spectroscopy (XPS) and

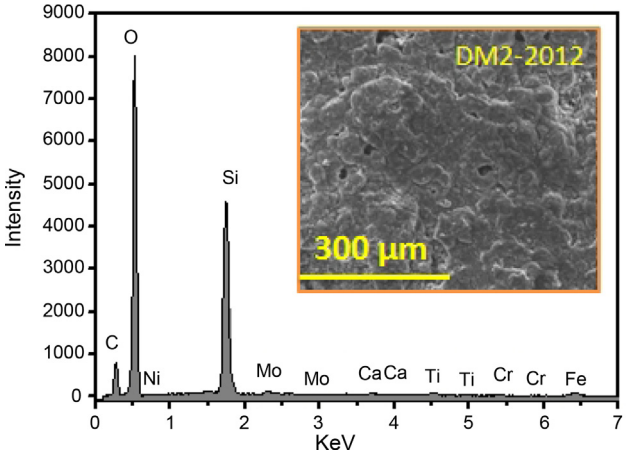

Fig. 4. EDX analysis of the exposed divertor tile of DM2-2012.

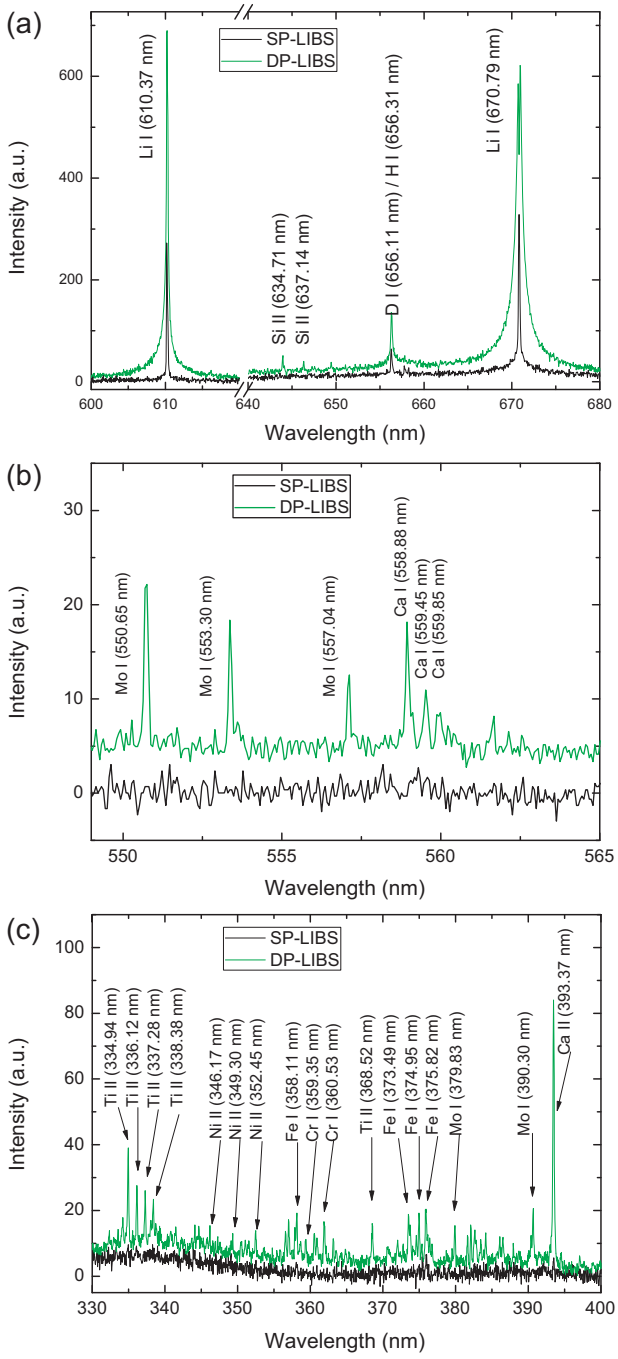

Fig. 5. Comparison of LIB spectra obtaining in 3.5×10^{-3} Pa for the exposed divertor tile (DM2-2012) in the range of (a) 600–680 nm, (b) 549–565 nm and (c) 330–400 nm in both SP-LIBS and DP-LIBS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

X-ray spectroscopy (EDX). XPS analysis was carried out using a ThermoVG Scientific XPS Escalab 250, and the results of XPS revealed that the surface layer of the exposed tile was mainly composed of Li, C and O. The surface compositions tested by EDX (Quanta 450, FEI) as Fig. 4 were: 22.88% C, 68.91% O, 7.26% Si, 0.10% Ca, 0.15% Ti, 0.25% Cr, 0.29% Fe, 0.05% Ni, and 0.11% Mo. The acceleration voltage of EDX is continuously adjustable from 0.2 to 30 kV. The results demonstrated that the exposed divertor tile was quite different from the original tile, which was nearly as the stoichiometric composition of SiC (52.74% C, 47.26% Si). In the exposed tile, Li was used as wall conditioning material, and the other metal elements were found to originate from the sputtering of the in-vessel component materials. Oxygen came from plasma wall interaction and exposure to air [18,20]. These techniques are mostly used in off-site laboratories and they require preparational steps to present the sample in a physical state necessary for the respective method. The sample preparation steps such as cutting, or grinding are time consuming and require high maintenance efforts to avoid contamination. LIBS has been regarded as a promising in-situ diagnostic technique due to its unique features such as no sample preparation required, remote (stand-off) sensing capability, rapid analysis and simultaneous multi-element detection.

The LIBS spectra of the exposed divertor tile were measured using both SP-LIBS and DP-LIBS configuration in 3.5×10^{-3} Pa. Fig. 5a shows the Li, D and Si lines in the SP-LIBS (black curve) and in the DP-LIBS (green curve) in a spectral range from 600 to 680 nm. The spectral lines of Li I (610.37 and 670.79 nm), D I (656.11 nm) and H I (656.31 nm) are clearly observed. It is clear that the atomic spectral lines of Li, D and H are enhanced by a factor of 2.3 (±0.3) when an inter-delay time of 1.5 μs is installed. Moreover, the DP-LIBS spectra of the exposed divertor tile show the line emissions from various minor elements, such as Si (in Fig. 5a), Mo, Ca (in Fig. 5b), Fe, Cr, Ti and Ni (in Fig. 5c), that are present in the co-deposition layer on the divertor tile. This is consistent with the results of EDX analysis. In contrast, no LIBS signal is obtained in the SP-LIBS regime. The collinear double pulse approach increases LIBS system performance through better coupling of laser energy to the target, leading to a more efficient production of analyte atoms in an excited state [33]. The spectra clearly indicate that DP-LIBS is useful in identifying the trace elements on the plasma facing component (PFC) surface in a vacuum environment.

4. Conclusion

The main results concluded in this work indicate that DP-LIBS can be an effective way of significantly enhancing detecting sensitivity and reducing the limits of detection (LOD) of LIBS in vacuum environments, which are the mimic environment of tokamak operation. The data for both samples show the following: (1) the analyte signals increased significantly as the inter-pulse delay time was increased from 0 to 1.5 μs; (2) as the inter-pulse delay time increased more than 1.5 μs, the analyte signals decreased significantly and then appeared to level off at the longer inter-pulse delay time used here. It was found that signal intensity of DP-LIBS with an inter-pulse delay of 1.5 μs was ~6.5-fold greater than that of SP-LIBS for Mo lines in a molybdenum tile. For an exposed divertor tile, significant enhancements in the signal line intensities of various minor elements (such as Mo, Si, Fe, Cr, Ti, Ni and Ca) have been observed using DP-LIBS, while no spectral signal was measured by SP-LIBS. The ultimate goal of our LIBS analysis technique is to provide a quantitative analysis, to determine the concentration of a species with adequate precision and accuracy. In the next work, we will investigate quantitative analysis approaches in DP-LIBS based on the different calibration models. The present results would be helpful for optimizing a LIBS system which can be used for in-situ monitoring of the impurity deposition and D retention processes in an extreme environment for the next generation fusion device.

Acknowledgments

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