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The laser-induced plasma persistence time extension in low pressures using the ablated mass confinement method☆

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ABSTRACT

The laser-induced plasma characteristics are strongly dependent on the surrounding pressure. Confining of the rapidly expanding plasma at low pressure conditions has shown that it is possible to perform the laser-induced breakdown spectroscopy (LIBS) detection by using a long gate width CCD detector. The acrylic window is placed above the sample for adjusting the plasma confining height for optimally extending the plasma persistence time. At 1 mm confining height at 1 torr, the signal intensity of Al III emission (452.8945 nm) was enhanced up to 5.5 times the free expansion case. The signal intensity was markedly lower at 760 torr as thickness of the window became larger, whereas it was constant at 1 torr. It is suggested that optimum detection scheme as opposed to generation of strong plasma is more important in the low pressure LIBS study. The laser energy required for aluminum detection was only 3.664 mJ/pulse at 1 torr. The key aspect of this successful detection is the combined ablated mass confinement and the low pressure detection. This method has the potential to lead the detection of minor elements in metals at an increased sensitivity.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) allows chemical component analysis of the material based on the plasma generated when laser light ablates the sample surface. The plasma light emission consists of the unique wavelengths of sample components. LIBS also allows for real-time analysis without the preprocessing of samples, stand-off detection, and no loss or contamination of sample by chemical reagent. In principle, samples in any phase (solid, liquid or gas) can be detected.

LIBS plasma characteristics such as temperature, density, and persistence time tend to vary by the local pressure [1]. At low pressure, detection of the plasma by a CCD with its long gate width and low sensitivity is a daunting task because of the short persistence time of the vanishing plasma and low particle density in the focal volume. CCD has long gate width in the order of ms while an intensified CCD (ICCD) can enhance time resolution using an MCP intensifier (Micro-Channel Plate Image Intensifier) which has electronically fast shutter function. The persistence time of plasma is typically in the order of μs. Thus, the background signal is collected for an extended time, resulting in lower signal to noise ratio. In low pressure, relatively more background signal is integrated while the persistence time is rapidly decreased. Furthermore the effect of low particle density at low pressure is also significant, which makes it even more difficult to detect signals using the CCD. Therefore, ICCD with a shorter gate width has been used for the low pressure detection, which would also increase the cost of the LIBS system over all.

Nonetheless, many researchers have worked in the low pressure because signal to noise ratio is known to increase due to a lower continuum and the background signal [2]. Cowpe et al. compared LIBS spectra taken at atmospheric and vacuum (~10^{-6} torr) conditions [3]. Though the intensity of the LIBS spectrum at vacuum is lower, it showed much higher resolution. Dreyer et al. observed maximum spectral intensities of Ca, Mg, and Fe near 7 to 5 torr while the values decreased near 5 to 1 torr, suggesting a rapid decrease in the electron density [4]. Delgado et al. visualized laser-induced plasmas from TNT and Pyrene samples at different pressures ranging from 1000 to 10^{-3} mbar [5]. At 1 mbar, the plume from TNT and Pyrene reached the maximum size of 3 mm and 7 mm respectively, such that one can anticipate an effective detection by the ablated mass confinement method at the low pressure condition.

The present study focuses on several advantages of the low pressure measurements in LIBS study. First of all, the plasma shielding effect caused by the inverse bremsstrahlung process decreases at low pressure due to the reduction of the number of species within the plasma by a rapid expansion [2]. Also obstructions along the beam path such as dust or airborne particles are less likely than those in an atmospheric pressure. Both of these two effects effectively increase the resultant laser energy delivered to the sample because more photons can then be reached at the sample surface. Thus the detection of the highly ionized atoms as well as the challenging minor elements such as Cl

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and S is presumed possible at the low pressure condition where the loss of laser intensity diminishes. For this reason, the present low pressure LIBS research is aimed at developing a novel detection scheme to significantly enhance the signal intensity.

In this study, we tried to overcome the difficulty of the low pressure detection by the ablated mass confinement. In the early time right after the plasma initiation, the strong continuum disturbs the obtaining of a meaningful spectrum. After several tens or hundreds of nano seconds, we can then start to obtain LIBS spectra. However at low pressure, the plasma persistence time is too short to be detected while signal to noise ratio is high when using a CCD. Thus in our setup, the acrylic window is placed above the sample to prevent rapid extinction because the expansion of the ablated mass is then confined in an optimally limited space.

Shen et al. produced the plasma between two parallel walls and in cylindrical pipe with different diameters [6] for confining the plasma, and showed that the cylindrical pipe for plasma confinement was better than the parallel walls. The aluminum emission line in cylindrical pipe was enhanced by nine times relative to the free expansion case. Guo et al. used aluminum hemispherical cavity to enhance the LIBS signal intensity [7]. Particular emission lines of Cr and Co were enhanced using the combination of spatial and magnetic confinements. The accuracy of a quantitative analysis was improved by using the hemispherical cavity [8], and the combined effect of the spatial confinement and dual-pulse irradiation was discussed [9]. Popov et al. used a small cylindrical chamber with 4 mm in diameter and 4 mm in height to confine the plasma [10], which resulted in the improvement in both signal intensity and the limit of detection (LOD). Ding et al. used metal disks with 2 mm hole in its center to investigate the plasma confinement effect by the reflected shock wave [11]. The reflected shock wave allowed the secondary enhancement of signal intensity from CN molecules during several microseconds following the initial sharp increase by the plasma generation. After the secondary enhancement, CN emission decayed faster than that in the free expansion case. Tao et al. performed numerical analysis of a confinement effect using a microhole in Ar atmosphere and suggested that the plasma temperature, pressure, and thrust are enhanced [12]. Zeng and Mao studied the effect of cavity with various aspect ratios in a fused silica sample [13,14]. The plasma temperature and electron number density were at maximum in the case of a largest aspect ratio. Hou et al. measured the plasma temperature, electron number density, and RSD (Relative Standard Deviation) according to laser energy and delay when a cavity wall is used [15,16]. They reported on the enhancements of spectral line intensity and the reduction of shot-to-shot fluctuation. Corsi et al. drilled the craters of different depths on a copper sample to create cavity for the signal enhancement [17]. Xiu et al. tested the plasma confinement by using a thin gel layer in Ar atmosphere [18] and showed an improvement.

In all previous plasma confinement attempts, the purpose was the enhancement of a signal intensity or repeatability, and the key concept was to utilize the secondary pressure waves or reflecting shock waves from the confining walls. To maximize the strength of the reflecting shock wave, they used metal object as a confinement material. These studies were performed at a standard pressure or 760 torr, and the laser beam was irradiated directly on a sample. On the other hand, the purpose of our study is the prevention of a rapid plasma extinction at varying low pressures to maximize the detection efficiency. The key concept is the confining the ablated mass within the limited space. The transparent window such as an acrylic window was used as a confinement material. Also the laser beam passes through the window to reach the sample surface at a pressure range between 760 and 0.35 torr all of which are by contrast to those of earlier attempts.

Here, we successfully prevented rapid plasma extinction at low pressure conditions by confining the expanded ablated mass as opposed to the previous efforts based on the secondary pressure waves within the confined space. As a result, a significant amplification to the LIBS signals is achieved using a low laser energy and a CCD detector.

2. Experimental Setup

A LIBS system (RT250-Ec, Applied Spectra Inc.) that uses Q-switched Nd:YAG laser operating at 1064 nm with 5–7 ns pulse duration at pulse energy of 50 to 3.664 mJ at 10 Hz is focused onto the surface of a sample placed inside of a vacuum chamber. The laser beam is perpendicular to a surface of aluminum alloy plate. A high resolution 6 channel-CCD spectrometer covers the spectrum ranging from 196.466 to 970.528 nm. The spectral resolution of the spectrometer is less than 0.1 nm for UV to VIS and 0.12 nm for VIS to NIR range. The emission from the plasma was detected through the side-view window. To collect the plasma, uncoated quartz lens of 100 mm focal length was used. The gate delay is varied from 0.1 to 0.5 μs to obtain high signal to noise ratio (0.1 μs at 0.35 and 1 torr, 0.3 μs at 10 and 100 torr, 0.5 μs at 760 torr) while gate width is set to 1.05 ms.

Sample is mounted on a XYZ stage inside a chamber, de-pressurized from 760 to 0.35 torr where a rotary pump is used to evacuate the chamber to provide low pressure test conditions for the laser-induced plasma. A carefully selected confining material for plasma was acrylic window of 1, 3, 5 mm thicknesses and 12.7 mm diameter. The transparency of the acrylic window at 1064 nm wavelength beam is about 92% and the cost of acryl is not so high as such replacement cost is low. The damage threshold of the acrylic window caused by Nd:YAG laser at 1064 nm wavelength is about 200 J/cm^2 [19]. The irradiance at sample surface in our setup is about 70 J/cm^2 which is lower than the damage threshold of the acrylic window. The confining window was placed and spaced about 1, 2, 3 mm above a sample (Fig. 1). The sample used for the experiments was aluminum alloy. The laser beam was focused on the sample surface and fired on 3 locations with 5 shots for each location.

3. Results and discussion

Fig. 2 shows the effect of plasma confinement for the doubly ionized aluminum. The ionization energy of aluminum is 1816.7 kJ/mol, which is too high to be detected from the plasma at ambient pressure as such Al III emission line at 760 torr is not detected. At 1 torr, Al III emission lines were detected. The plasma shielding effect decreases with pressure decrease thus more energy can reach the sample surface. As a result, mass of the ablated material is increased [2]. Besides, the mean free path for collision at low pressure is not short enough to convert the ionized atom to the neutral atom immediately. Thus particularly highly ionized atom may appear at low pressure condition. For an unconfined case at 1 torr, Al III is shown as a broad peak at a very weak signal intensity. On the contrary, the signal intensity (short dashed line) and the signal to noise ratio (SNR) increased significantly when the plasma confinement is used. The use of 1 mm thick acrylic window placed at 1 mm confining height and the delay time of 0.1 μs resulted in the successful detection of a strong signal at 1 torr. The rapid

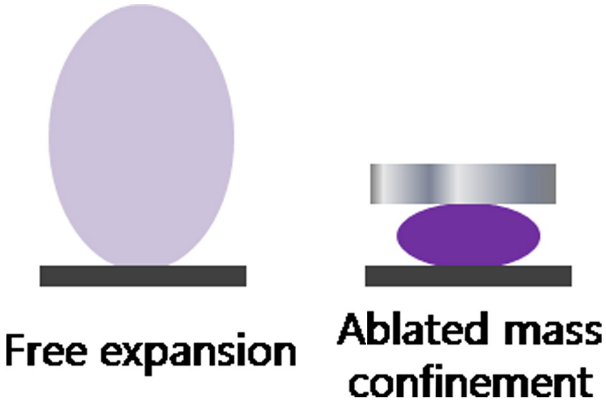

Fig. 1. Schematic of the position of the acrylic window.