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Effects of pulse width on nascent laser-induced bubbles for underwater laser-induced breakdown spectroscopy ☆

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ABSTRACT

The reason for the significant advantage offered by long-pulse (150 ns) irradiation in underwater laser-induced breakdown spectroscopy (LIBS) is investigated from the point of view of the behavior of nascent cavitation bubbles. Shadowgraphs of nascent bubbles generated by pulsed laser irradiation of Cu targets in water were observed for two different pulse widths, 20 ns and 150 ns. It is clearly seen that the nascent bubble is formed at the leading edge of the laser pulse profile, regardless of the pulse width. Bubbles generated by a 20-ns pulse are characterized by a flat-shape filled with dense matter with intense optical emission, which is in contrast to more hemispherical low-density bubbles observed under the irradiation by a 150-ns pulse. The behavior of the nascent bubbles is consistent with the behavior of the later plasma in the bubbles, which is crucial for observation of well-defined atomic spectral lines for underwater LIBS.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) has great potential for application to in situ elemental analysis in various underwater situations [1–5]. In particular, the application to deep-sea exploration [6–8] could offer significant reductions in cost by increasing efficiency over traditional sampling-based survey methods. The main advantages of LIBS are the feasibility of remote sensing [7], high sensitivity to most elements in the periodic table, and the applicability to various states of samples [9]. However, underwater LIBS measurements suffer complications due to the confinement of the plasma to a small volume [10], i.e., it is difficult to obtain a plasma of low-density and high-temperature. The emission spectra are significantly deformed by collisions and Stark broadening [11,12] and suffer from self-absorption [13,14]. It is known that irradiation of a laser pulse underwater forms a cavitation bubble [15–20], and it is thought that the timing of bubble formation and growth relative to the plasma generation is a key factor that strongly influences the quality of underwater LIB spectra [15,21].

Attempts to control this timing have been performed by changing the irradiation scheme. It seems that the timing of the plasma formation relative to the bubble formation can be controlled by double-pulse irradiation, which is known to give high quality spectra with the broadening of atomic spectral lines being significantly suppressed [15,22,23]. We have previously demonstrated that optimization of double-pulse irradiation parameters can yield high quality spectra with non-gated detection scheme, if both the pulse interval and pulse energy are optimized [21]. Optimization of the pulse interval, in this case, is equivalent to the optimization of the timing of the plasma formation relative to the bubble generation, since in the optimized condition the first pulse takes charge in the creation of a bubble without the generation of a plasma, while the second pulse generates a low density plasma in the bubble formed by the first pulse [21].

Although the double-pulse irradiation scheme is successful in obtaining well-defined spectra for underwater LIBS, the deformation of atomic line spectra is pronounced when the hydrostatic pressure becomes more than 10 MPa [8] or 5 MPa [24] corresponding to a depth of 1000 m or 500 m, respectively. It is known that the bubble growth is restricted at even slightly elevated pressures, and does not seem to offer any advantage over single pulse irradiation when the plasma is generated by the second pulse [20,24].

The irradiation of a single long pulse (~150 ns) is also known to give clear atomic emission line spectra [25]. In this irradiation scheme a pulse energy of several millijoules gives sufficiently intense optical emission for LIBS measurements, and has an advantage of lower damage to the target [26] as well as a simpler instrumentation. On the analogy of the double-pulse irradiation, the mechanism leading to the well-defined clear spectra in this case is explained by the plasma emission lasting until the bubble becomes sufficiently developed [10]. In order to verify this explanation, and clarify the phenomena more in detail, it is important to investigate the timing of bubble formation for the long-pulse irradiation scheme. The formation mechanism of the

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bubble is also important in view of the application to a high hydrostatic pressure environment, where the bubble growth is strongly suppressed and the double-pulse mechanism no longer works, while a single pulse is essentially not affected by the external hydrostatic pressure, and a long single pulse still gives well-defined clear line spectra [6,27].

In the present work, we examine the timing of the bubble formation by shadowgraphy using monochromatic back illumination in combination with an interference filter to remove the intense emission of the plasma. Since the nascent bubble is very small, a microscope was used for the shadowgraphy. An intensified charge coupled device (ICCD) was used as the camera for the shadowgraphy to attain a 5-ns temporal resolution. The experiments were performed by irradiating the target with two different pulse widths, 20-ns pulse (short pulse) and 150-ns pulse (long pulse). The formation of the bubble takes place during the leading edge of the long, 150-ns, pulse, and later, the bubble grows sufficiently for the plasma to be entirely included in the bubble. Timing of the bubble formation was also investigated in case of irradiation with a short, 20-ns, pulse, and a comparison was made with the observations for the long pulse. We also discuss the reason why spectral features depend on the pulse width, i.e., a long pulse gives well-defined clear line spectra [25], while a short pulse usually results in a considerably deformed spectra.

2. Experiment

The experimental setup is schematically shown in Fig. 1. The fundamental wavelength (1064 nm) of a flash-lamp-pumped Q-switched Nd:YAG laser (home built) was used as the ablation laser. The pulse width is 20 ns under normal operating conditions. A pulse width as long as 150 ns is obtained by lowering the power of the flashlamp to near the lasing threshold [25]. Since only a low energy pulse can be achieved when operating the laser in this manner, the output from the laser oscillator is passed through an optical amplifier to give a pulse energy sufficient for ablation. A pulse energy of 12 mJ was used for the 20-ns pulse, while 2 mJ was used in the case of the 150-ns pulse width. Different pulse energies were used since they are the energies giving the highest quality spectra. A small portion of the laser pulse was introduced into a fast photodiode (PD1) to trigger the ICCD (Princeton, PI-MAX:1K) for shadowgraphy. The remaining part of the laser passed through a 50 ns optical delay. The laser beam was then focused with a 60-mm focal-length lens, and a target in a water cell was irradiated at the focal point. Just before the irradiation, a portion of the pulse was introduced into a fast photodiode (PD2), the signal of which gives the temporal profile of the laser pulse, and was recorded by an oscilloscope. Although the pulser to drive the ICCD has an internal delay of ~50 ns from the trigger to the output of an electrical pulse which drives the ICCD gate, the optical delay of the laser pulse enables us to capture a shadowgraph image at the very beginning of the pulse. The high-voltage electrical pulse from the pulser, which determines the time-gate of the measurement, was monitored by the same oscilloscope as used to monitor the pulse profile.

The shadowgraph was observed by the ICCD detector via a water immersion type microscope objective lens with a magnification of 40× (Olympus, LUMPlanFL), together with an imaging lens. The objective lens was dipped in water through a hole made in the side of the irradiation cell. The ICCD detector was operated with a gate width of 5 ns. A frequency doubled Nd:YAG laser (home built) was used for the back illumination. The pulse width of this laser was ~20 ns. The intensity of the laser was regulated with a variable neutral-density (ND) filter, and then the laser was scattered by a diffuser made of acrylic resin. An interference filter (532 nm) was placed in front of the ICCD detector in order to block the spontaneous emission from the plasma, and only 532 nm light was detected. The timing of the illumination laser with respect to the ablation laser was controlled by a delay generator (Stanford Research Systems, DG535).

The cell was rectangular and made of polytetrafluoroethylene resin. It has two windows in the sides, one for ablation laser and the other for the back illumination for shadowgraphy, and one hole to attach a microscope objective lens. The target was a Cu plate (Nilaco) polished using emery paper. It was placed in the cell, and the cell was filled with pure water.

Atomic lines of the Cu I $^2S_{1/2}$–$^2P^o{}_{3/2}$ ($^2P^o{}_{1/2}$) fine-structure doublet were observed after irradiation with three different pulse widths, i.e., 20 ns, 50 ns, and 100 ns. The same target Cu plate used for

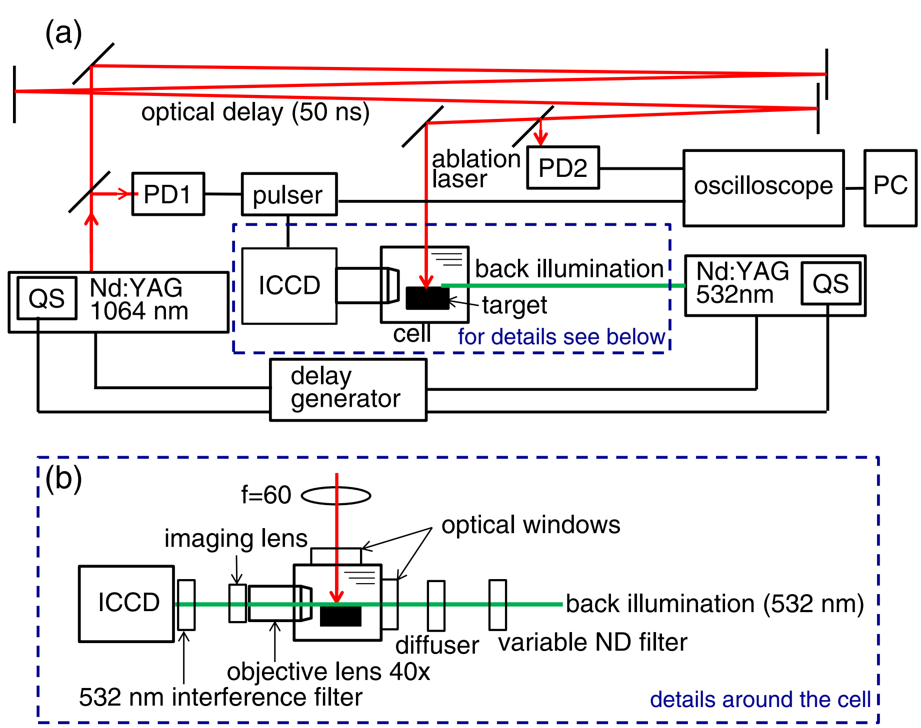

Fig. 1. Experimental setup.