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Spectral profile of atomic emission lines and effects of pulse duration on laser ablation in liquid ☆

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ABSTRACT

The emission spectra of laser-ablated Cu atoms in water were examined, focusing on the irradiation-pulse duration effects. Spectral line profile was observed for the pulse duration of 19, 90, and 150 ns at various delay times. The line width as narrow as instrumental width was obtained by 150-ns pulse at the delay time of 800 ns. Also, long pulses result in high intensity of the emission. The spectral feature obtained by long pulses looks similar to that obtained in a gas phase. The absorption of the later part of the long pulse directly by the plume having been formed by the earlier part of the pulse may be the cause of this gas-phase-like emission. Whether the pulse heats directly the surface or the plume was investigated by the measurements of the removal volume of the ablation pit obtained by laser confocal scanning microscopy and the maximum bubble expansion size observed by shadowgraphy.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) of solid surfaces submerged in liquid has great potential in many applications, such as elemental analysis of underwater sedimentation [1] or in situ analysis of electrodeposits [2], etc. However, if a usual ns pulse with the width of 10 ns or so is used as an ablation laser, the emission spectra from the plume in liquid give intense continuum [3,4], which is not preferable for the application of LIBS to elemental analysis of solid surfaces submerged in liquid. To overcome this problem, double-pulse irradiation has been proposed [5,6]. Recently, we have published a preliminary result that the irradiation of a long nanosecond single pulse gives less-broadened emission spectral lines from the ablation plume in liquid environment without noticeable continuum from the background plasma [7]. Furthermore, the long ns pulse seems to give more intense emission than short pulses. According to these results irradiation with long ns pulses is promising in the application to in situ LIBS in water, or maybe in any transparent liquid.

Also interesting is that surface damage could be surprisingly small if the pulse width of 150 ns was used as the ablation laser. This was suggested in our previous work, in which the ablation damage of electrodeposited Cu film in water was estimated from the number of pulses required to penetrate the film, when the pulse width of 150 ns was used as an ablation laser [8]. Low damage by the irradiation with a long ns pulse is also expected for sample surfaces more solid than the electrodeposited film examined in our previous work.

The above findings can be summarized as follows: a long ns pulse gives intense emission, although the ablation efficiency is pretty low. This is an important advantage for the application to surface analysis. On the other hand, the mechanism of such improvement is not clear so far. To pursue this aspect of the phenomena further, it is important to clarify the mechanism of the laser ablation by a long ns pulse. The studies on the laser breakdown in bulk water also suggest the importance of the absorption of laser by the plasma [9–12]. Here we suppose that the most important aspect of the pulse-duration effect is the difference in the fraction of pulse energy directly deposited to the surface without being absorbed by the plume. Although we cannot directly measure this quantity, the size of the pit left after irradiation should be related to the energy given to the surface. Also, the maximum size of the cavity or bubble expansion after pulsed-laser breakdown is known to be proportional to the energy that the bubble has gained [13].

In the present paper we report on ~0.2-nm-resolution emission spectra of the plume for various pulse widths of ablation laser, namely, 19, 90 or 150 ns. The line profiles were also examined for various delay times. To have information on the energy deposited to surface, the ablation efficiency was studied in detail by examining the volume of the pit left on a Cu target. Also, to have additional information on the energy deposited to the plume, the plume expansion size or the maximum cavity size was compared for different pulse widths on the basis of the shadowgraphy of cavity expansion.

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2. Experimental

The experimental setup for the measurement of emission spectra is basically the same as our previous studies and given elsewhere [2,7]. Briefly, a home-build Q-switched Nd:YAG laser was used as an ablation laser. The laser pulse width employed in the present work was 19, 90, or 150 ns. The pulse width was measured as a full width at half maximum of the pulse profile obtained by a fast silicon-PIN photodiode. The laser beam size was 4 mm in diameter and was multimode. The laser beam was focused onto a Cu plate immersed in water. A cubic quartz cell with the sides being 40 mm long was used for lateral observation of the optical emission from the ablation plume. The emitted light was collected by a lens system and focused onto an entrance slit of the 1-m-focal-length spectrograph (Ritsu Oyo Kogaku, MC100N) equipped with an intensified charge-coupled device (ICCD, Princeton Instruments, ICCD-1024MTDGE/1) as a detector. Since the entrance slit was set to 150 μm to have good signal-to-noise ratio, the resolution of the system was ~0.2 nm. Timing of the data acquisition was controlled by the gating operation of the ICCD by a pulser (Princeton Instruments, PG200).

Fig. 1 shows a schematic illustration of the experimental setup for shadowgraph measurement. The same laser, focusing optics, target, and cell, as used in emission spectroscopy, were used. The laser-ablation region was illuminated from the back-side by a high intensity Xe lamp (Ushio, SX-UI500XQ), and photographed by the ICCD camera. A cavity or a bubble produced on the target blocks the back-side illumination, so that we can obtained a shadow image of the cavity or the bubble. The shadowgraph was obtained at various time delays for each pulse width. The time resolution of the measurement was attained by gating operation of the ICCD. The gate width was 400 ns for the measurements with the delay of 400 ns and 1500 ns, while the gate width of 2 μs was employed for the measurements with the delay of 100 μs or longer.

The size of the pit formed by ablation was systematically measured. Again, Cu was employed as a target. Confocal laser scanning microscopy was employed to observe 3-dimensional image of the pits and the volume of the material removal was calculated by the software installed in the confocal laser scanning microscope system (Olympus, OLS1000). The volume removal was measured as a function of the laser pulse shot number.

3. Results

The emission spectra of the ablation plume obtained by the irradiation of a Cu target in water are given in Fig. 2 for various pulse widths. The spectral lines observed in this spectral range are assigned to the $3d^{10}4s^1\ ^2S$–$3d^{10}4p^1\ ^2P^o$ transition of atomic Cu [14]. Note that the lower state has a configuration of the ground state, i.e., [Ar core] + $3d^{10}4s^1$. The upper state has a configuration of [Ar core] + $3d^{10}4p^1$.

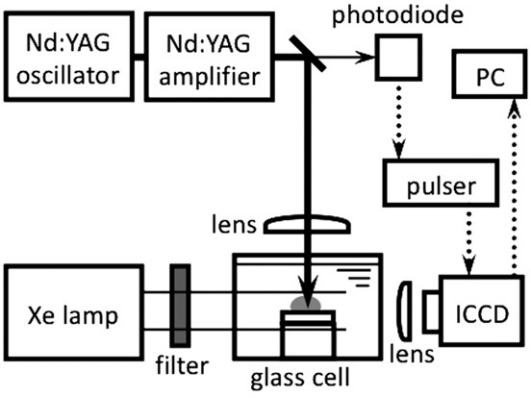

Fig. 1. Experimental setup for shadowgraph measurements.

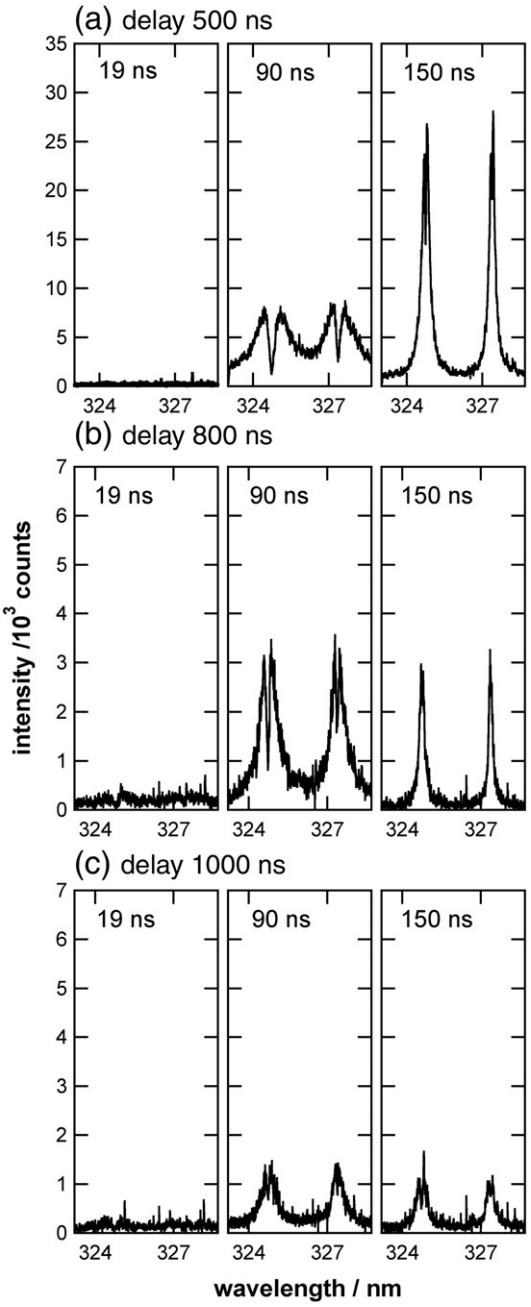

Fig. 2. Emission spectra of Cu atoms in the ablation plume in water at the delay time of (a) 400 ns, (b) 800 ns, and (c) 1000 ns after the laser irradiation. Pulse widths of 19, 90, and 150 ns were compared. The laser pulse with the pulse energy of 1.7 mJ was used. The laser beam was focused onto the target by a 32.7-mm focal-length lens.

This configuration has a fine structure, i.e., a doublet, $^2P^o_{3/2}$ and $^2P^o_{1/2}$, with a splitting of 248 cm^{-1}. Therefore, two transition lines appear, at 324.8 nm ($^2S_{1/2}$–$^2P^o_{3/2}$) and 327.4 nm ($^2S_{1/2}$–$^2P^o_{1/2}$). These lines were expected to give strong self-absorption, because of the high population of the lower state, which is the ground state. We selected these lines to demonstrate clearly the effects of the pulse width and the advantage of the long pulse. For all the delay times employed in the measurement, the intensity of emission was high enough to evaluate the spectral line width when the pulse width of 90 ns or 150 ns was employed, while we could not obtain clear spectral feature by the irradiation with a 19-ns pulse. This agrees with our previous work based on lower-resolution spectral measurements [7]. The spectral width of the line depends on the delay time. We obtained the narrowest width of 0.18 nm at the delay time of 800 ns, which