Quasi Nondestructive Elemental Analysis of Solid Surface in Liquid by Long-pulse Laser Ablation Plume Spectroscopy

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Emission spectroscopy of laser ablation plume can be applied to in situ elemental analysis of solid surface in liquid, especially if the laser pulse with the pulse width of 150 ns is used. The long nanosecond pulse not only suppresses the disadvantageous broadening and deformation of spectral line profiles usually observed when short nanosecond pulses are used but also greatly suppresses the material removal from analyte surfaces. The latter is also an important advantage for the application to surface analysis.

Emission spectroscopy of laser ablation plume can be used for surface elemental analysis. The method is generally called "laser-induced breakdown spectroscopy" or LIBS and is known as a promising method for surface elemental analysis, since it does not require any bulk sample preparation. The sampling is done merely by pulsed laser irradiation of the surface to be analyzed.[1] On the other hand, there is not any established method for in situ elemental analysis of solid surface in liquid. If emission spectra of the laser ablation plume, or the laser ablation plume spectroscopy (LAPS), be applicable to the solid surface analysis in situ in liquid, it would be used for a wide variety of applications such as monitoring of electrodeposited films or corrosion of the inner wall of piping, environmental monitoring of the bottom of a lake or sea.

However, emission spectra of the plume in liquid usually show broadened and deformed spectra due to a high density and steep temperature gradient in the plume.[2,3] Such broadening and deformation make it difficult for these spectra to be applied to elemental analysis of the solid surfaces in liquid.

In our previous study,[4] we reported that the irradiation of long nanosecond pulses, such as pulse width of 150 ns, gives sharp and narrow line spectra which are clear enough to be applied to the surface elemental analysis. We could not obtain such clear spectra by using short pulses such as 20-ns pulses, even though we optimized experimental conditions, such as laser focusing condition.

In this article, we report that the use of long nanosecond pulse gives not only the sharp clear line spectra but also very limited damage to the analyte surface, and the method can be regarded as a quasi nondestructive method.

The 1064-nm radiation of home-build Q-switch pulsed Nd:YAG laser was used as an irradiation source. In a usual operation the pulse width of the laser was ca. 20 ns.[5] By the low power operation near the lasing threshold the pulse width becomes longer. We obtained 150 ns as the longest pulse width by this method.[4] The beam was multimode and was ca. 4 mm in diameter. The laser pulse was amplified and focused down onto a sample surface by a lens. The target was immersed in pure water of which the thickness above the target was 5–10 mm. The emission from the plume was collected by a lens system and focused onto an entrance slit of the spectrograph (Acton, SpectraPro275). The spectrograph has the focal length of 275 mm and is equipped with an intensified charge coupled device (ICCD, Princeton, ICCD-1024/MTDGE1). The time-resolved measurement was done by the gated mode of the ICCD detector. The spectral resolution of the system was ca. 0.1 nm. The 324.75- and 327.40-nm lines of atomic Cu were measured.

Figure 1 shows the intensity of the emission lines with consecutive irradiations to the same spot of the copper plate immersed in water. The gate of the ICCD was set to open at the delay time of 500 ns from the pulse irradiation, and the gate width was set to be 5 µs. This avoids the initial intense continuous spectrum and gives seemingly the best spectral line feature for the analytical purposes. Note that the pulse energy was adjusted to be 1.0 mJ for three experimental runs with different pulse widths, which means the peak power of a long pulse is low compared with a short pulse. It is clearly seen in the figure that the long pulses always give intense emission throughout the pulse repetition. In any pulse width, the intensity decreases with increasing the pulse number. This is due to the deformation of the irradiation spot of the target surface by hole drilling effect by the surface ablation and also to the debris formation in the bulk liquid accompanying the ablation of surface layers, resulting in the following pulses to be absorbed in the bulk. Both effects are related to the destructive nature of the pulsed laser irradiation. The decay of the intensity is gradual in case of the use of long pulses. The results mean that the use of long nanosecond pulses gives less damage to the analyte surface.

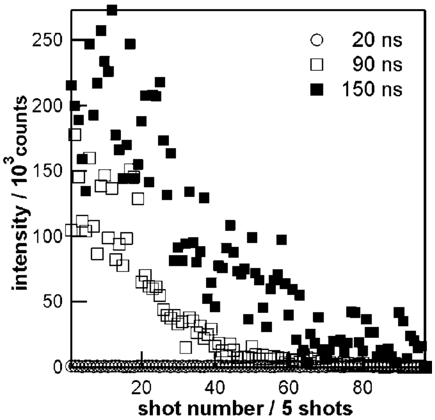

Figure 1. Intensity of emission spectral lines of Cu atoms (324.75 nm) from the ablation plume in water plotted as a function of pulse shot. The target was a metal Cu plate. Each point is an average of consecutive 5 shots. Each symbol represents a different pulse width; solid square: 150 ns, open square: 90 ns, and open circle: 20 ns. Note that the emission intensity was always indistinguishable from the continuous spectrum in the case that the 20-ns pulse was used.

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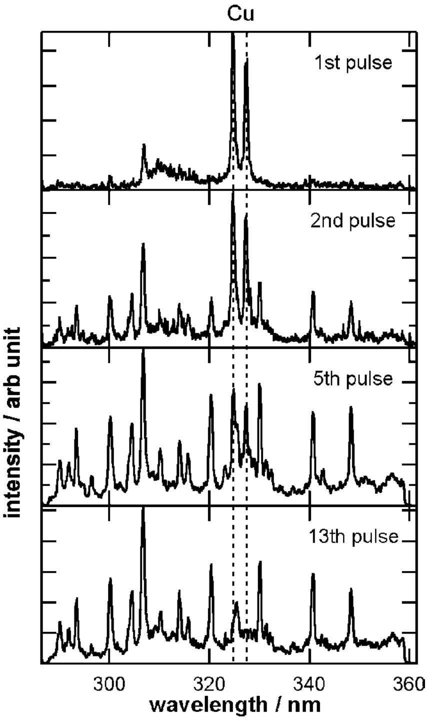

Figure 2. Spectrum obtained by consecutive irradiation of the same spot on the Cu thin film electrodeposited on a Pt plate. The intensity is normalized to the highest peak in the spectrum. The spectral lines other than 324.75 and 327.40 nm are all assigned to atomic Pt.

In Figure 2 we demonstrate the spectra obtained by consecutive irradiations of 150-ns pulses to the same spot on an electrodeposited copper film on a platinum plate. The average thickness of the original Cu film estimated by coulometry during the electrodeposition was 164 nm. The pulse energy was adjusted to 1.7 mJ and a 100-mm focal length lens was used to focus the laser pulse down to the target surface. The gate of the ICCD detector was set to be open from 800 ns from the ablation pulse, and the gate width was set to be 5 µs. The first pulse shot gives clear and intense Cu lines with very low intensity of the lines originated from Pt atoms. In the spectra obtained by the following consecutive irradiations to the same spot, the emission lines assigned to Pt atoms appear in addition to the Cu lines. By continuing the irradiation to the same spot the intensity of the Cu lines decreases, and finally the spectrum is dominated by the emission lines from Pt atoms, suggesting that the Cu film was penetrated by the hole drilled by the laser pulse irradiation. If we assume that the disappearance of the Cu lines corresponds to the complete Cu film removal at the irradiation spot, the material removal rate is estimated to be ca. 13 nm/pulse in the present experimental condition. The damages of 2–10 nm/pulse have been reported, depending on the experimental condition, for minimized damages in LIBS studies in gas phase or in vacuum.[6,7] The present results are comparable to these results and promising for “quasi non-destructive” analysis in liquid.

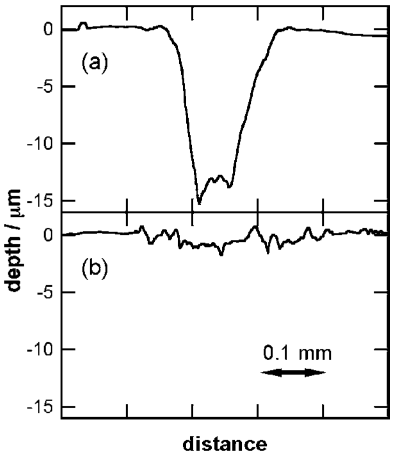

Figure 3. Typical profiles of an irradiation spot after the irradiation of 10 shots of (a) 19-ns pulse and (b) 150-ns pulse. The target was a metal Cu plate.

The depth profiles of the surface spot left after the irradiation of a Cu plate were measured by a line scan using a pin-type profilometer (Tencor P-10). The pulse energy was 10.7 mJ and a 70-mm focal length lens was used to focus the ablation pulse to the target surface. The typical results are shown in Figure 3. The irradiation of 19-ns pulse gives a deep and sharp profile. On the other hand, the irradiation of 150-ns pulse shows only a very small amount of material removal from the surface, although it results in a small roughness of the surface at the irradiation spot. These results also support that a long nanosecond pulse is suitable for the surface elemental analysis.

In conclusion, the irradiation of a long nanosecond pulse such as 150 ns to solid surface immersed in liquid gives very limited damage to the surface compared with the use of short nanosecond pulses such as 20 ns. The use of a long nanosecond pulse for LAPS as an in situ surface elemental analysis in liquid is advantageous not only because it gives clear line spectral feature which cannot be attained by using a short nanosecond pulse, but also for its less destructive nature.

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