Liquid-phase laser ablation

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Abstract: The irradiation of an intense laser pulse results in the explosive evaporation of a solid-state target, resulting in the production of a dense plasma with transient property. This phenomenon is called “laser ablation”. If the target is immersed in liquid, the expansion of particles ejected from the target is limited considerably by the confinement effect of the liquid, resulting in the production of a very small plasma with a high density, a high temperature, and a high pressure. We are interested in the high-pressure, high-temperature state of the laser ablation plasma. In this talk, we will show experimental results on fundamental aspects of liquid-phase laser ablation plasmas, together with some results on the application to material synthesis.

Keywords: Laser ablation, liquid phase, high-pressure plasma, cavitation bubble, nanoparticles

1. Introduction

Recently, plasmas induced by liquid-phase discharges attract much attention of many researchers. In this talk, on the other hand, we introduce another way for producing plasmas in liquids: laser-ablation plasmas. Laser ablation is a phenomenon which occurs when a solid-state target is irradiated by an intense laser beam. The intense laser beam evaporates the target explosively, and many atoms and molecules are ejected from the target. In addition, the plume also contains electrons, ions, and photons. This means that a dense plasma, which is produced from a solid, is formed in front of the target.

We are interested in laser-ablation phenomena in liquids and their applications [1,2]. Liquid-phase laser-ablation plasmas have some common features to liquid-phase discharge plasmas. However, we believe that liquid-phase laser ablation plasmas are unique, and have peculiar features which are never realized by discharges. In this talk, we will show experimental results on fundamental aspects of liquid-phase laser ablation plasmas, together with some results on the application to material synthesis.

2. Unique features of liquid-phase laser-ablation plasmas

Laser-ablation plasmas are dense even when they are produced in ambient gases, since they are produced from solid-state targets explosively. Liquid-phase laser-ablation plasmas are especially dense since the expansion of particles ejected from the target is restricted significantly because of the tight confinement effect of ambient liquid. In addition, the temperature of laser-ablation plasmas is typically $10^4$ K [3]. Therefore, liquid-phase laser ablation plasmas have high pressures of typically 1 GPa, which is never realized by discharges.

The lifetimes of liquid-phase laser-ablation plasmas with optical emissions are less than 100 ns. After the disappearance of the emissive plasma, we observe the formation of a cavitation bubble in ambient liquid, which is another unique phenomenon of liquid-phase laser ablation. Figure 1 shows snapshots of cavitation bubbles at various delay times after the irradiation of a YAG laser pulse onto a Ti target immersed in water [4]. As shown in the figure, the cavitation bubble expands with time. After reaching the maximum size, the cavitation bubble shrinks with time, and collapses at a point close to the target surface. It is known that a high-pressure state is realized at the collapse of the cavitation bubble, and the collapse of the cavitation bubble induces the formation of the second cavitation bubble. The behavior of the second cavitation bubble was dependent on the irradiation condition of the laser pulse. In the example shown in Fig. 1, the second cavitation bubble did not collapse, and it became a stable spherical bubble at a delay time of 2.4 ms.

3. Growth of nanoparticles inside cavitation bubbles

The dynamics and applications of cavitation bubbles are studied intensively in the field of sonochemistry. On the other hand, cavitation bubbles produced by liquid-phase laser ablation are unique since there is a possibility that they contain particles ejected from the target inside them. We investigated the growth of nanoparticles inside a cavitation bubble by laser light scattering. Figure 2 shows the superimposed images of the cavitation bubble and the scattered laser light. The scattered laser light is owing to the existence of nanoparticles. As shown in the figure, we observed the growth
of nanoparticles inside the cavitation bubble. The scattered laser light was intense in the region close to the interface between the liquid and the bubble. It is pretty sure that particles are ejected from the target to the liquid phase, which is before the formation of the cavitation bubble. The result shown in Fig. 2 suggests that the particles ejected to the liquid phase are transported into the cavitation bubble, resulting in the growth of nanoparticles inside it. We also observed the ejection of nanoparticles from the cavitation bubble into the liquid at specific delay times after laser ablation as shown in Fig. 2(b). In addition, Fig. 2 suggests that the cavitation bubble is going to the collapse with nanoparticles inside it. It is interesting to imagine what would happen for nanoparticles when the cavitation bubble collapses with nanoparticles inside it. Nanoparticles are in a high-pressure, high-temperature reaction field at the collapse of the cavitation bubble. It was observed that the almost entire region of the inside of the second cavitation bubble was occupied by nanoparticles as shown in Fig. 2(d).

4. Control of liquid-phase laser ablation
A drawback of liquid-phase laser ablation is the lack of methods for controlling plasma properties. We invented external pressurization of ambient liquid as a method for controlling liquid-phase laser ablation plasmas, and developed a special chamber which is compatible with a high pressure up to 300 atmospheres. Figure 3 shows optical emission images from laser ablation plasmas produced in water at 1 and 300 atmospheres [5]. A CCD camera with a gated image intensifier was used for taking the optical emission image, and the gate was opened from 16 to 18 ns after the appearance of the optical emission intensity. It is known from the figure that the optical emission image observed at 300 atmosphere was compressed slightly in the direction perpendicular to the target surface.

The dynamics of cavitation bubbles were also controlled by the external pressure. Figure 4 shows snap shots of cavitation bubbles observed in water at 30 atmospheres [4]. By comparing Fig. 4 with Fig. 1, it is known that the maximum size of the cavitation bubble observed at 30 atmospheres was much smaller than that at 1 atmosphere. Also, the lifetime of the first cavitation bubble at 30 atm-
Figure 3: Distributions of optical emission intensities from liquid-phase laser ablation plasmas produced in water at (a) 1 atmosphere and (b) 300 atmospheres. The gate of the ICCD camera was opened from 16 to 18 ns after the appearance of the optical emission intensity.

Another different phenomenon observed at 30 atmosphere was the dynamics of the second cavitation bubble induced by the collapse of the first cavitation bubble. As shown in Figs. 4(e) and 4(f), the second cavitation bubble observed at 30 atmosphere did not shrink, and it was extinguished into the liquid phase with a shape like a cloud. The change in the dynamics of the cavitation bubble by adding an external pressure may influence the structure and the property of nanoparticles. In addition, our theoretical analysis based on the Rayleigh-Plesset equation suggested that the pressure at the collapse of the cavitation bubble was enhanced significantly by pressurizing the ambient water.

Our ablation chamber also has an ability to heat the ambient water up to 500 °C. The super-critical state of water is obtained at a temperature and a pressure higher than 374 °C and 220 atmospheres, respectively. We are carrying out laser-ablation experiments in super-critical water.

5. Application to material synthesis
The most widely used medium in liquid-phase laser ablation is water. By ablating rare metals such as gold in water can produce nanoparticles of pure metals. Figure 5 shows an absorption spectrum of colloidal water of gold nanoparticles produced by ablating a gold target immersed in water at 1 and 300 atmospheres. The characteristic absorption at around 520 nm, which corresponds to the surface plasmon resonance of gold nanoparticles, is identified in Fig. 5. The difference between the absorbance observed at 1 and 300 atmospheres will be discussed at the conference.

Laser ablation of transition metals in water results in the formation of oxide nanoparticles. To obtain nitride nanoparticles, we carried out laser ablation in liquid nitrogen [2]. We developed a double-shelled chamber. The region sandwiched by the outer and inner shells was evacuated using a turbo molecular pump, by which we succeeded in the thermal isolation of the inside of the inner chamber. The inside of the inner chamber was filled with liquid nitrogen, and a Ti target immersed in liquid nitrogen was irradiated by YAG laser pulses. Figure 6 shows the XRD pattern and the electron diffraction pattern of nanoparticles produced by laser ablation of a Ti target in liquid nitrogen. As shown in Fig. 6, we observed the formation of crystalline nanoparticles of TiN. At the same time, a very thin nitride layer was formed on the target surface. In the case of using a Si target, we ob-
tained highly-crystalline nanoparticles of metallic silicon with negligible oxidation.

We are significantly interested in the effect of the high-pressure state, which is induced by laser ablation as well as the collapse of the cavitation bubble, on the synthesis of crystalline nanoparticles. We speculate that the rather easy syntheses of crystalline nanoparticles shown in Fig. 6 are realized with the help of the high-pressure state obtained by laser ablation (It is noted that the collapse of a cavitation bubble is not observed in laser ablation in liquid nitrogen).

5. Conclusions
Laser ablation is a method for producing a plasma in liquids, and is different from liquid-phase discharges. Liquid-phase laser ablation can produce a high-pressure state with a transient property, which is never realized by discharges. Liquid-phase laser ablation induces a cavitation bubble, which expands and shrinks in the liquid. Another high-pressure state is realized at the collapse of the cavitation bubble. We have proposed pressurization and heating of ambient liquid as a method for controlling the dynamics of the plasma and the cavitation bubble. From the viewpoint of material synthesis, the high-pressure states could be useful for promoting the formation of crystalline nanoparticles.

References