Reaction between laser ablation plume and ambient gas studied by laser-induced fluorescence imaging spectroscopy

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Abstract. We visualized the density distributions of $\text{C}_2$ (plume), NO (ambient gas), and CN (reaction product) when a graphite target was ablated by irradiating YAG laser pulses at wavelengths of 1064 and 355 nm in ambient gas mixture of NO and He. It has been shown by the density distributions of $\text{C}_2$ and NO that the expansion of the plume removes the ambient gas and the plume and the ambient gas locate exclusively in both the cases at 1064 and 355 nm. A high CN density was observed at the interface between the plume and the ambient gas at 1064 nm, which is reasonable since chemical reactions between the plume and the ambient gas may occur only at their interface. On the other hand, in the case at 355 nm, we observed considerable CN inside the plume, indicating that the chemical reaction processes in the laser ablation at 355 nm is different from that expected from the density distributions of the plume and the ambient gas.

1. Introduction
Reactive laser ablation is widely used for synthesizing new materials. In this technique, new materials are synthesized with the help of chemical reactions between species ejected from the target (the laser-ablation plume) and the ambient gas. Hence the mixing between the plume and the ambient gas is important in reactive laser ablation. In a previous work [1], we examined the transient dynamics of both the laser-ablation plume and the ambient gas by measuring the temporal variations of their density distributions using laser-induced fluorescence (LIF) imaging spectroscopy [2, 3, 4, 5]. As a result, it has been found that that the expansion of the plume removes the ambient gas and that the ambient gas and the plume locate exclusively. According to the above results, chemical reactions between the plume and the ambient gas may occur only at their interface. To obtain better understanding of reactive laser ablation, we measured the density distribution of the reaction product in addition to the laser ablation plume and the ambient gas. In addition, we compared the density distributions observed in laser-ablation experiments at 1064 and 355 nm.

2. Experimental
In previous work, we installed a C$_4$F$_8$ discharge cell near the observation space, and we employed CF$_2$ (a dissociation product of C$_4$F$_8$) as the tracer of the ambient gas since the detection of CF$_2$
by LIF is highly sensitive. In this work, we used a simpler method for visualizing the ambient gas. The experimental apparatus is schematically shown in Fig. 1. The vacuum chamber was filled with a mixture of He (950 mTorr) and NO (50 mTorr) after evacuating it using a turbomolecular pump. A graphite target installed on a rotating holder was ablated by Nd:YAG laser pulses at wavelengths of 1064 and 355 nm from the normal direction. The fluences of the YAG laser pulses on the target surface were approximately 3 J/cm$^2$.

We measured the density distributions of C$_2$, NO, and CN, which were considered to be representative of the plume, the ambient gas, and the reaction product, respectively. The observation area was illuminated by a tunable laser beam generated by an optical parametric oscillator (OPO) at a delay time $t_D$ after the irradiation of the YAG laser pulse. The OPO laser beam was arranged to be a planar shape. When the wavelength of the OPO laser beam was tuned to resonances, the images of LIF were formed on the planar laser beam. A gated CCD camera with an image intensifier was used for taking the pictures of the LIF images which represented two-dimensional distributions of the C$_2$, NO, and CN densities. The excitation and observation wavelengths for detecting C$_2$, NO, and CN by LIF are in the literature [6, 7].

### 3. Results and discussion

Figure 2 shows the distributions of the C$_2$, NO, and CN densities observed at 5 μs after the irradiation of the YAG laser pulse at 1064 nm. The YAG laser pulse irradiated the graphite target at the position of $(r, z) = (0, 0)$ in the figure. Since the excitation wavelength of NO (226.19 nm corresponding to $X^2Π_{1/2}(v'' = 0) → A^2Σ^+(v' = 0)$) was located at the edge of the tunable range of the OPO laser, it was difficult to obtain fine oscillation at this wavelength. The perturbation in the density distribution of NO was caused by the nonuniformity of the OPO laser beam. Apart from the perturbation caused by the nonuniformity of the OPO laser beam, as shown in Fig. 2(b), the distribution of the NO density had a deep dip, which corresponded to the location of the C$_2$ density shown in Fig. 2(a). As described in the previous paper, this means that the high pressure of the plume removes the ambient gas. The plume and the ambient gas locate exclusively. Hence, chemical reactions between the plume and the ambient gas are expected at interface. The CN density had a distribution similar to a crescent moon as shown in Fig. 2(c), and had a high density at the interface between the C$_2$ and NO densities. This result reveals that chemical reactions between the plume and the ambient gas mainly occur at interface.

We repeated the same experiment at an ablation wavelength of 355 nm. The distributions of the C$_2$, NO, and CN densities at 5 μs after the irradiation of the YAG laser pulse are shown in Fig. 3. We can find several differences between Figs. 2 and 3. A difference is the peak position

![Schematic drawing of the experimental apparatus.](image_url)
Figure 2. Distributions of (a) C\textsubscript{2}, (b) NO, and (c) CN densities observed at 5 μs after the irradiation of the YAG laser pulse at 1064 nm.

in the density distribution of C\textsubscript{2}. As shown in Figs. 2(a) and 3(a), the peak position in the case of ablation at 1064 nm was located near the leading edge of the plume, while in the case at 355 nm, the peak of the C\textsubscript{2} density was adjacent to the target surface. Another difference is found in the distribution of the NO density. In the case of laser ablation at 1064 nm, the dip in the NO density was surrounded by a high-density layer which was formed by the compression of the ambient gas by the expansion of the plume. In the case of ablation at 355 nm, a deep dip was also observed in the distribution of the NO density, but we did not observe the formation of the compressed layer. The most important difference between 1064 and 355 nm is seen in Figs. 2(c)
and 3(c). In the case of 355 nm, the peak CN density was adjacent to the target surface, and the CN density decreased steeply with the distance from the target. This result is rather mysterious since the NO density in the plume is close to zero as shown in Fig. 3(b). These three differences were observed similarly at various ambient gas pressures from 0.1 to 10 Torr.

A possible explanation for the distribution of the CN density shown in Fig. 3(c) is that CN is not the reaction product in the gas phase and is produced from the nitrided target directly. To examine this explanation, we evaluated the temporal evolution of the total number of CN by integration the density distribution. As shown in Fig. 4, the total number of CN increased with the delay time $t_D$ significantly. This result indicates clearly that CN is really a reaction product in the gas phase, and the distribution of the CN density shown in Fig. 3(c) is not the direct result of the formation and expansion of the plume but is due to chemical reactions. Accordingly, at the moment, we have no reasonable explanation for the production process of CN in the plume with the negligible NO density.

4. Conclusions
In this work, we examined the distributions of the laser-ablation plume, the ambient gas, and the reaction product to obtain a better understanding of reactive laser ablation. It has been shown experimentally that the plume and the ambient gas locate exclusively. Therefore, chemical reactions between the plume and the ambient gas may occur at their interface. The density distribution of the reactive product was consistent with this expectation in the case of ablation at 1064 nm. However, in the case of ablation at 355 nm, the density distribution of the reaction product was not compatible with the distributions of the plume and the ambient gas. The present experimental results provide us with helpful insight into reactive laser ablation, but further investigation is necessary to obtain complete understanding of the reaction kinetics.

5. References
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