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LIF observation of neutral atoms and ions produced by femtosecond laser ablation of Sm on a substrate

Yukari Matsuo¹, Tohru Kobayashi¹, Mizuki Kurata-Nishimura¹, ², Toshiyuki Kato¹, ², Tohru Motobayashi¹, Jun Kawai¹, ², and Yoshihide Hayashizaki¹, ²

¹Discovery Research Institute, RIKEN, Wako, Saitama 351-0198, Japan
²RIKEN Genomic Sciences Center, RIKEN Yokohama Institute, Yokohama, Kanagawa 230-0045, Japan

E-mail: ymatsuo@riken.jp

Abstract. We have studied the behavior of atoms and ions out of sample on a substrate ablated by femtosecond laser with one-dimensional (1D) and two-dimensional (2D) laser induced fluorescence (LIF) measurement. The sample of samarium standard solution spread and solidified on a Si (111) substrate was ablated by a femtosecond laser. Approximately half of the atomized samarium particles appeared to be neutral atoms and the other half did singly charged ions. It is found that the ablated Sm atoms and Sm⁺ ions have rather strong orientation to the surface normal, and the kinetic energy of Sm⁺ ions is larger than that of Sm atoms. Moreover, the kinetic energies of ablated Sm and Sm⁺ particles are similar to those obtained for the first-shot ablation of Sm solid sample, and are much larger than those of Sm and Sm⁺ after multi-shots.

1. Introduction

Trace atom analysis using laser ablation technique is one of the important topics among various applications of laser ablation in combination with mass spectroscopic techniques such as time-of-flight (TOF) spectrometry. The method should be widely applicable to the detection of trace atoms, the dating of diogenite, and the analysis of inorganic and organic molecules labeled with isotopes even when a tiny volume of the sample is ablated. We have so far demonstrated the simultaneous atomization and ionization of organic molecules labeled with stable isotopes by femtosecond laser ablation using a quadrupole mass spectrometer. The result shows that the femtosecond laser ablation is very effective for the atomization and ionization of soft materials like bio-molecules and liquid samples [1].

In the trace atom analysis of the soft materials these samples might be often placed on a substrate and subjected to the femtosecond laser ablation combined with TOF spectrometry. In order to improve the detection efficiency of trace atoms, the knowledge on the behavior of ablated target atoms is required. However, the study of such double-layered samples is quite limited [2], in particular, from the point of view in detecting target atoms contained in the upper-layer material.

In this paper we report the motion of ablated atoms and production ratio of neutral atoms and mono-atomic ions out of Sm sample on a Si substrate ablated by femtosecond laser with one-dimensional (1D) and two-dimensional (2D) laser induced fluorescence (LIF) measurement. Since the material in the upper-layer is vaporized at the first shot, all the measurements need to be carried out...
for fresh surface. Hence, the common rotating target cannot be used in our experiment. We set a XYZ-stage as a sample mount to the ablation chamber and maintained the ablation spot to be a fresh surface. Our results have revealed that the behavior of ablated particles out of sample spread on a substrate is quite different from that of continuous ablation of a solid sample.

2. Experiment

Figure 1 shows the experimental setup for 1D- and 2D-LIF measurement. It consists of a vacuum chamber, a femtosecond laser for ablation, a pulsed dye laser as a probe laser, and a detection system either with a photo-multiplier through a monochromator or with an ICCD camera through an interference filter. The output of the second harmonics of Ti:Sapphire laser (400nm, pulse energy 150μJ/pulse) is focused onto a sample on a XYZ-stage with a lens of focal length 250mm. The diameter of the spot is approximately 100μm and the fluence is estimated to be 1.5J/cm². After a delay time (0 – 1000ns) controlled by a delay generator, a pulsed dye laser (approximately 10μJ/pulse) whose wavelength is resonant to the transition line of Sm or Sm⁺ is fired.

![Figure 1. Experimental setup for (a) 1D- and (b) 2D-LIF.](image)

For the 1D-LIF experiment a probe laser beam of 4mm in diameter, which is either 5mm or 28mm apart from the sample surface, is irradiated onto the produced plasma and fluorescence is detected with a photo-multiplier tube through a monochromator. On the other hand, the 2D-LIF experiment is carried out with a probe laser in a sheet shape of 15mm in width and a combination of an ICCD camera and an interference filter. The sample was prepared by spreading 1μL of samarium standard solution (Sm(NO₃)₃, 1mol/L) on a Si (111) substrate in the area of 20mm² and further dried in vacuum condition. The number of Sm is calculated to be 10¹² atoms/spot in the laser spot size of 100μm in diameter, all of which are removed upon ablation.

The advantage of using samarium as a sample element is the availability of multiple lines both for neutral Sm atom and singly charged Sm⁺ ion. Transition lines from low-lying levels of Sm and Sm⁺ observed in this work are listed in Table 1 together with energy levels.

| Table 1. Sm and Sm⁺ transition lines. |
|--------------------------------------|
| wavelength of transition line (nm) | energy of lower level (cm⁻¹) | electronic configuration | wavelength of transition line (nm) | energy of lower level (cm⁻¹) | electronic configuration |
|--------------------------------------|-------------------------------|--------------------------|-----------------------------------|-------------------------------|--------------------------|
| 436.291                              | 0.00                          | ⁴f⁶ 6s² F₀               | 422.535                           | 0.00                          | ⁴f⁶ 6s F⁴/₂               |
| 441.933                              | 292.58                        | ⁴f⁶ 6s² F₁               | 418.377                           | 326.64                        | ⁴f⁶ 6s F⁵/₂               |
| 442.965                              | 811.92                        | ⁴f⁶ 6s² F₂               | 421.034                           | 838.22                        | ⁴f⁶ 6s F₅/₂               |
3. Results and Discussion

First, we observed 1D-LIF signals of Sm and Sm⁺. Time-resolved LIF signals from ground states of Sm and Sm⁺ for several delay times were taken by one shot of ablation and detection. The integrated LIF intensity of each signal is plotted against velocity and kinetic energy of particle at the detection region in Figure 2(a). The results for the first-shot of Sm bulk sample and continuous ablation of Sm sample on a conventional rotating-target are also shown in Figure 2(b) and (c). The velocity of Sm and Sm⁺ from Sm solution on Si substrate is as large as that for Sm and Sm⁺ from Sm fresh surface, which is much larger than the velocity of atomized and ionized particles after many shots [3]. The kinetic energy of Sm⁺ is 3 to 4 times larger than that of Sm in all cases probably due to the Coulomb explosion effect in the acceleration process at the initial stage of laser ablation.

![Figure 2. Integrated LIF intensity against velocity and kinetic energy at the detection region for (a) Sm(NO₃)₃ on Si substrate, (b) first shot of Sm bulk sample, and (c) continuous ablation of Sm sample.](image)

Second, snap shot of ablated Sm and Sm⁺ was taken with 2D-LIF. Figure 3 shows the 2D-LIF view of Sm and Sm⁺ on Si substrate. It is seen that the ablated Sm atoms and Sm⁺ ions have rather strong orientation to the surface normal, in particular, the orientation of ablated ions is very strong. It should be noted that Si substrate causes much stronger orientation than the other substrates [4].

With the results of 1D- and 2D-LIF we have estimated the ratio of Sm atoms and Sm⁺ ions vaporized during the ablation. Since the LIF signal observed so far in this work is obtained by excitation from the ground states, it does not represent the total number of atoms and ions. In order to estimate the population of atoms and ions in each electronic state, we observed 1D-LIF signal for low-lying levels and estimated the electronic temperature. Figure 4 shows the LIF intensities of Sm and Sm⁺ for three low-lying levels against the internal energy of those levels divided by multiplicity. The electronic temperatures of Sm and Sm⁺ are deduced from the slope to be 880K and 960K, respectively, at delay time 500ns. By calculating partition functions of Sm and Sm⁺ at above temperatures we have estimated that 5 times and 4 times larger amount of Sm atoms and Sm⁺ ions, respectively, exist in the observation area than those observed only with ground state LIF. Taking into account the factor of partition function, solid angle of collection lens, efficiency of monochromator, quantum efficiency of photo-multiplier tube, excitation and detection efficiency of transition lines used for the LIF observation, we have estimated that approximately half of the atomized samarium particles appeared
to be neutral atoms and the other half did singly charged ions. We consider that the high ionization efficiency (nearly 50%) is a consequence of the nature of ablation using femtosecond laser, namely, high energy density in short period of time.

Figure 3. 2D-LIF view of Sm\(^+\) from Sm sample on Si substrate.

Figure 4. Electronic temperature of Sm and Sm\(^+\) deduced from 1D-LIF intensity of Sm sample on Si.

The temperature we obtained is about one order of magnitude smaller than typical temperature of plasma cloud measured by emission spectroscopy [5]. Note that the electronic temperature we measured by LIF corresponds to the distribution of atoms and ions among low-lying fine structure levels, whereas temperature deduced from emission spectroscopy is related to the population of upper levels. Therefore, low electronic temperature obtained in this work does not necessarily mean low temperature of the whole system because the system might not be in equilibrium in terms of electronic state.

The results of 1D- and 2D-LIF also reveal that the ion detection by femtosecond laser ablation combined with TOF spectrometer out of sample spread on a substrate can be performed with high efficiency because (1) the efficiency of atomization and ionization is large and (2) the orientation of ablated atoms and ions is strong.

4. Conclusion
We have studied the behavior of ablated atoms and ions out of Sm sample on a Si substrate ablated by femtosecond laser with 1D- and 2D-LIF measurements. Our result shows that the ablated Sm atoms and Sm\(^+\) ions have rather strong orientation to the surface normal, and the ratio of the produced Sm atoms and Sm\(^+\) ions is approximately one to one. It is also found that the kinetic energy of Sm\(^+\) ions is larger than that of Sm atoms. More interestingly, kinetic energies of ablated Sm and Sm\(^+\) particles are similar to those obtained for the first-shot ablation of Sm bulk sample, and they are much larger than those of Sm and Sm\(^+\) after multi-shots.

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