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## Dependence of femtosecond laser ablation for organic molecules on chosen substrate

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**Abstract.** Femtosecond laser ablation of organic molecules has been investigated to develop an elemental analysis technique for these samples. Behaviour of  $\text{Sm}^+$  emitted from organic molecules settled on chosen substrates was studied by the two-dimensional laser induced fluorescence method. Comparisons among substrates of a quartz glass, Si and Ta are presented with the parameters of a kinetic energy and a spreading velocity of  $\text{Sm}^+$ . The kinetic energy of  $\text{Sm}^+$  emitted from the sample on the quartz glass was the highest and decreased for the Si and Ta. Moreover, it is found that the spatial distribution of  $\text{Sm}^+$  on the Si substrate tends to barely spread in the transverse direction. We observed that the ablation dynamics of the organic molecules on the substrate are affected by the substrate material.

### 1. Introduction

A study of femtosecond (fs) laser ablation mechanism is rapidly progressing due to the wide use of the femtosecond laser. Applications of fs laser ablation method in combination with time-of-flight mass spectrometry for elemental analysis are also expanding for various samples from the view of ultra high power density of a fs laser pulse [1][2].

We applied fs laser ablation for organic molecules to develop an elemental analysis technique of isotopes tagged onto organic molecules. Previously, it was successfully demonstrated that the fs laser ablation method had a profound effect on simultaneous atomization and ionization for large organic molecules by using a quadrupole mass spectrometer [3]. Since then, the fs laser system has been built in a reflectron type time-of-flight mass spectrometer to realize a shot by shot quantitative analysis. It is expected that ionization processes depend on substrate material, because our target sample is solidified on a substrate which is also ionized by a fs laser single shot [4][5]. Despite versatility and wide applicability of fs laser ablation, the detailed chemical physics underlying the ablation process are still far from being fully understood. For instance, in the case of organic molecules solidified on a substrate, scarcely any knowledge and information have been accumulated. Studying the dependence of the fs laser ablation dynamics on substrate material is an important issue for a development of efficient detection technique.

In this paper, we have performed the fs laser ablation for the organic molecules on some substrate materials, a quartz glass, Si, Ta. The kinetic energy and an expansion velocity of target ions are

compared among these materials by adopting two-Dimensional Laser Induced Fluorescent (2D-LIF) method [6].

## 2. Experimental Setup

A schematic view of an experimental setup is shown elsewhere [7]. Organic molecules contained in a standard  $\text{Sm}(\text{NO}_3)_3$  solution in  $\text{HNO}_3$  (1.000 mg in 1ml) of 10  $\mu\text{l}$ , are spread in 4 mm diameter circle on substrates and slowly dried up in a vacuum chamber to be solidified on a substrate. Poly-L-lysine processing for hydrophilic property is applied to the substrates. The substrate is installed in an ablation chamber where a pressure is controlled to be less than  $1 \times 10^{-5}$  torr. Since the organic molecules are removed completely with a single laser shot, the target sample is moved through a X-Y-Z manipulator in every shot.

A generatively amplified Ti:Sapphire laser system (Spectra-Physics Hurricane) with a pulse duration of 120 fs, a typical energy of 300  $\mu\text{J}/\text{pulse}$  and a second harmonic of 398 nm were used. The single fs laser pulse was focused onto the sample from the normal direction through a quartz lens ( $f = 250$  mm) and the power density is estimated to be  $4 \text{ J}/\text{cm}^2$ . Perpendicular to the fs laser pulse direction, a probe pulse from a pulsed dye laser (Lambda Physik FL2003) pumped with an excimer laser (Lambda Physik EMG-103) irradiated onto an ablation plume with a certain delay from 0 ns to 600 ns after the fs laser ablation. The probe laser pulse was reshaped to a 1 mm thickness and 12 mm width with the combination of three cylindrical lenses ( $f = 50, 150$  and 250 mm). The produced ions,  $\text{Sm}^+$  and  $\text{Ta}^+$  (in the case of the Ta substrate) were excited resonantly by the probe laser of 422.535 nm and 540.560 nm wavelength to observe the behavior of the ion cloud from the organic molecules and the substrate, separately. Fluorescent light emitted from the ions was collected through lenses and an interference filter in the range of  $450 \pm 10$  nm and  $400 \pm 10$  nm for  $\text{Sm}^+$  and  $\text{Ta}^+$ , respectively. Behind this arrangement, an iCCD camera system was placed to visualize the spatial profile of the ions on the top of the chamber. The whole system is synchronously controlled with a combination of delay generators (Stanford Research Inc., DG535). The ion distribution image was transferred to a data taking system shot by shot.

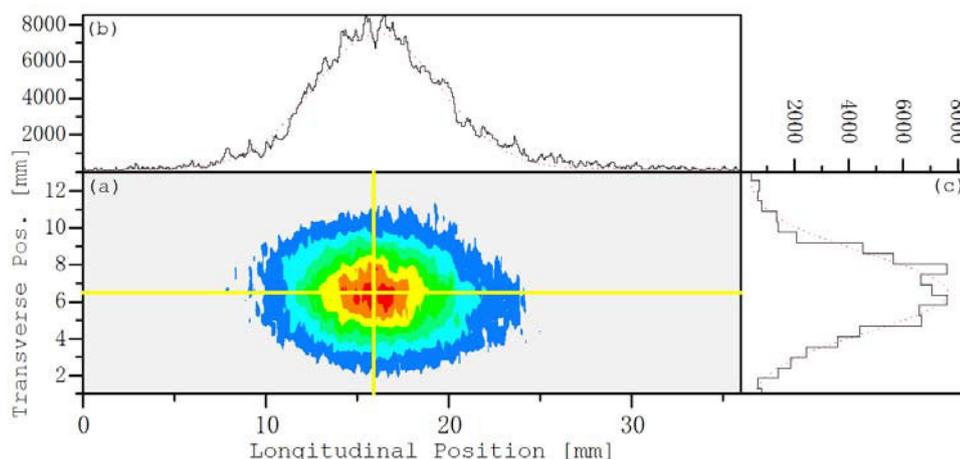


Figure 1. (a) Intensity contour plot of  $\text{Sm}^+$  emitted from a sample on Si substrate. A space profile in the longitudinal and transverse directions at the maximum intensity is shown in (b) and (c), respectively. The dotted lines indicate a Gaussian function fitted to the data.

### 3. Results and Discussions

An intensity contour plot of  $\text{Sm}^+$  produced from the sample on Si substrate is pictured in figure 1(a). The spatial profiles in the longitudinal and transverse directions at the maximum intensity are also plotted in figure 1(b) and (c), respectively. This data is fitted with a Gaussian function to determine a centroid position and a cloud size, as is shown by dotted lines. The centroid position for the longitudinal direction is plotted against the delay time of the probe laser in figure 2(a). The kinetic energy of the target ion is determined from the slope of linear fitting to that data. Expansion velocities of the  $\text{Sm}^+$  cloud are obtained from figure 2(b) where the cloud size in both directions is plotted as a function of the delay time and fitted with a linear function.

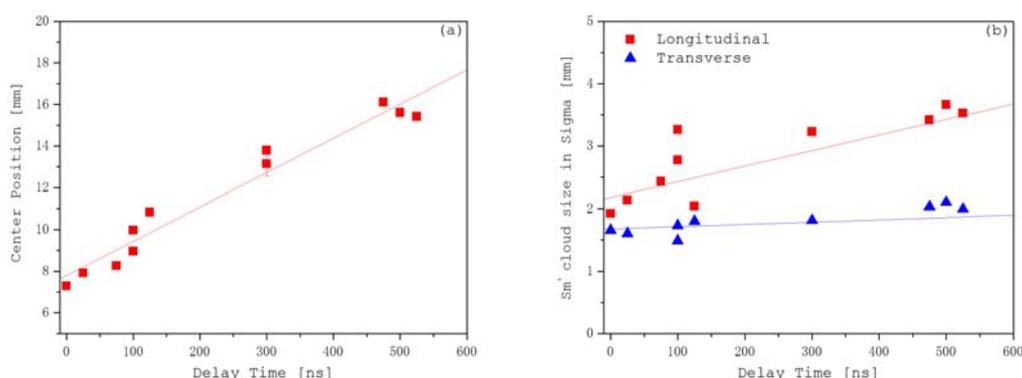


Figure 2. (a) Centroid position for longitudinal direction of  $\text{Sm}^+$  plotted against to the delay time of the probe laser. (b) Cloud size in longitudinal (closed square) and transverse (closed triangles) direction plotted as a function of the delay time. The solid lines in both figures show linear fits to the data.

The kinetic energy of  $\text{Sm}^+$  is compared among the substrates in figure 3(a). The highest energy of  $268 \pm 25$  eV is obtained for the quartz glass substrate and decreases for the Si and Ta substrates. Furthermore, the kinetic energy of  $\text{Ta}^+$  from the Ta substrate is analyzed to be 64 eV/ion, while 180 eV/ion for  $\text{Sm}^+$  is observed. The comparison of the expanding velocity in both directions for each substrate is shown in figure 3(b). Amazingly, it is found that the  $\text{Sm}^+$  on the Si substrate tends to spread in the longitudinal direction while it barely spreads in the transverse direction. This may relate to the fact that  $\text{Si}^+$  is more likely to compose clusters [8].

We found that the ablation dynamics obviously depend on the substrate material. From the aspect of achieving sensitive ion detection with a time-of-flight system, production of ions having less kinetic energy and not spreading in the transverse direction are favorable; that is, the Si substrate is the best of three.

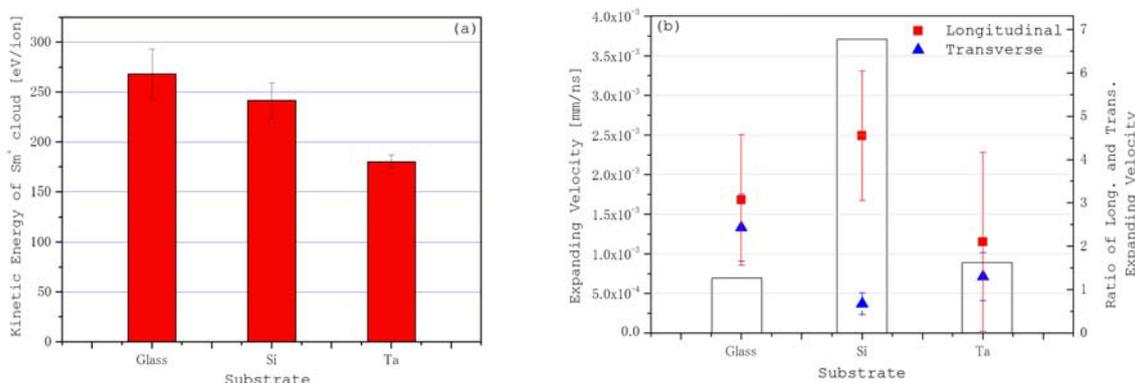


Figure 3. (a) Comparison of kinetic energy for  $\text{Sm}^+$  compared among substrates. (b) Comparison of expanding velocity in longitudinal (closed squares) and transverse (closed triangles) for each substrate. A bar chart shows ratio of them on the right vertical axis.

#### 4. Summary

We have studied the behavior of the  $\text{Sm}^+$  emitted from the organic molecules settled on the chosen substrates using a 2D-LIF system. The kinetic energy and the spreading velocity of  $\text{Sm}^+$  are compared among the quartz glass, Si and Ta substrate. The kinetic energy of  $\text{Sm}^+$  emitted from the organic molecules on the quartz glass is the highest and decreased toward the Si and Ta substrate. It is observed the kinetic energy of  $\text{Ta}^+$  is a half time as large as that of  $\text{Sm}^+$ . It is also found that the  $\text{Sm}^+$  on the Si substrate tend to spread in the longitudinal direction while barely spread in the transverse direction. We found that the ablation dynamics obviously depend on the substrate material. The preferable features for the time-of-flight system are observed on the Si substrate.

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