Kinetic energy of ions produced with first-, second-, and multi-shot femtosecond laser ablation on a solid surface

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Abstract. We report that the kinetic energy of samarium (Sm) atom and Sm⁺ ion produced by femtosecond laser ablation of solid samarium is strongly dependent on the number of ablation laser shots in the range from 1 to 10. By ablating the fresh surface (i.e. 1st shot), we find the kinetic energy of both Sm and Sm⁺ ion to be the largest (24 and 250 eV, respectively). Almost 10 times larger kinetic energy of Sm⁺ ion than that of Sm clearly indicates the contribution of Coulomb explosion in the acceleration process. From the second shot, kinetic energies of Sm and Sm⁺ ion are lower than those of the first shot and almost constant (ca. 12 and 80 eV, respectively). This behaviour suggests the change in the nature of the solid surface after femtosecond laser ablation, which can be explained by the amorphization of ablated sample surface reported in recent studies.

1. Introduction
Femtosecond laser ablation has been a promising technique for producing clear, well-defined cutting edge of solid materials. This characteristic of material processing with a femtosecond laser has been believed coming from the fact that the heat conduction during femtosecond laser irradiation is negligible [1]. However, in the recent studies, the residual thermal energy [2] and the amorphization of heat-affected zone [3-7] have been reported in the femtosecond laser ablation of solid materials. These new findings imply that the change must be observed not only in morphological features but also in physical properties of solid surface after the femtosecond laser ablation.

In the present study, we observe the change in physical property of ablated solid surface mentioned above by the time-of-flight (TOF) measurement. As a typical physical property of solid material, kinetic energies of atoms and ions produced by laser ablation are obtained by 2-dimensional laser induced fluorescence (2D-LIF) technique [8].

Kinetic energy of atoms and ions produced by laser ablation has been intensely studied since the invention of pulsed lasers. In 2000, Stoian and coworkers reported TOF analysis of Al⁺ and O⁺ ions produced by ablating a sapphire (Al₂O₃) substrate with a femtosecond laser [9]. Their main interest was, however, in the cross-over of etch-phases which took place between 25 and 30 laser shots and only data after the second shots were shown.
We choose a polished samarium (Sm) substrate as a sample because both Sm and Sm$^+$ ion can be selectively excited to the electronically excited states with a pulsed dye laser for the 2D-LIF measurement. By comparing kinetic energies of Sm and Sm$^+$ ion, contribution of the Coulomb explosion for particle acceleration at the ablation spot [10] is expected to be revealed.

2. Experimental
Laser ablation from a polished samarium substrate has been carried out with a second harmonic ($\lambda$ = 398 nm, 0.3 mJ) of the femtosecond laser system (Spectra-Physics Hurricane) operated at a repetition rate of 500 Hz. We obtain a single femtosecond laser pulse by synchronously operating an electromagnetic mechanical shutter (Uniblitz LS6) with a temporal aperture of 2.5 ms. Ablation laser is focused on the sample with a lens of 250 mm focal length and the power density is estimated to be 4 J/cm$^2$. The pressure of vacuum chamber is kept below 5.0x10$^{-4}$ Pa during experiments.

To obtain 2D-LIF images of Sm and Sm$^+$ ion in the expanding ablation plume, we have resonantly excited Sm and Sm$^+$ ion to electronically excited states by a pulsed dye laser (Lambda Physik FL2003) pumped with an excimer laser (Lambda Physik EMG-103) at various delay time after the femtosecond laser ablation. The output of dye laser (436.291 nm for Sm and 422.535 nm for Sm$^+$, respectively) is focused on the ablation plume with a combination of 3 cylindrical lenses ($f$=-50, 150, and 250 mm) in order to obtain images of wide area (10 mm long). The 2D-LIF images are captured with an ICCD camera (Oriel Instaspec V) through an interference filter in order to avoid intense plasma emission. The temporal gate width of ICCD camera (50 ns) is comparable with the fluorescence lifetimes of Sm and Sm$^+$.

3. Results and Discussions
Figure 1 shows typical 2D-LIF images of Sm and Sm$^+$ ion after femtosecond laser ablation of fresh surface of samarium (first shot). In the figure, a samarium substrate is placed at 3.6 mm and ablation

![Figure 1](image)

**Figure 1.** 2D-LIF images of Sm (1)-(2) and Sm$^+$ ion (3)-(4) from the fresh samarium surface. Delay times after laser ablation are (1) 150 ns, (2) 250 ns, (3) 100 ns, and (4) 150 ns, respectively.
plume expands to the right-hand side. As shown in the figure, image of \( \text{Sm}^+ \) ion is longer than that of \( \text{Sm} \), which reflects the larger velocity of \( \text{Sm}^+ \) ion during the gate width of ICCD camera. By measuring the peak position of these species at various delay time, we can calculate center velocities of these species and thus kinetic energies of them.

In figure 2, kinetic energies of \( \text{Sm} \) and \( \text{Sm}^+ \) observed at 1st, 2nd, 5th, and 10th ablation laser shots are plotted. The figure clearly shows two distinct features for the kinetic energies of \( \text{Sm} \) and \( \text{Sm}^+ \) ion. First, the kinetic energy of \( \text{Sm}^+ \) (250 eV) from the fresh surface is almost 10 times larger than that of \( \text{Sm} \) (24 eV). Second, kinetic energies of \( \text{Sm}^+ \) and \( \text{Sm} \) from second shot (96 and 11 eV, respectively) decrease sharply from those at first shot. After the second shot, the kinetic energy is almost constant for both species until 10th shots.

![Figure 2. Kinetic energies of Sm atom and Sm$^+$ ion after 1, 2, 5, and 10 shots of laser ablation at the same spot.](image)

Difference in kinetic energies between \( \text{Sm} \) and \( \text{Sm}^+ \) ion is the direct evidence of contribution of Coulomb explosion in the acceleration process at the initial stage of laser ablation. Femtosecond laser induced Coulomb explosion from \( \text{CaF}_2 \) below the single-pulse ablation threshold has been reported by Costache and Reif [10]. In their study, kinetic energy of only 8 eV is reported for \( \text{Ca}^+ \) ion. The value is much smaller than that of \( \text{Sm}^+ \) in our study and we attribute such a small kinetic energy of ion to the lower ablation fluence and multi-shot condition in their experiment.

Distinct decrease in kinetic energy at and after second shot suggests the change in physical property of ablated surface. Only the difference between the fresh surface and the surfaces after first shot is whether the surface has ever been ablated or not. The formation of amorphous layer by picosecond and femtosecond laser ablation on the solid surface has been reported [3-7]. Bonse and coworkers observed amorphization for every fluences above the melting and below the ablation threshold of sample material [6]. In our experiment, fluence of ablation laser is much higher than the ablation threshold. However, low kinetic energy of ablated atom and ion indicates the presence of rigid amorphous material on the surface of ablated substrate. Further work is necessary to clarify the nature of amorphous surface and its effect on the engineering of solid materials.

4. Conclusions

The two-dimensional LIF technique is applied to investigate kinetic energies of \( \text{Sm} \) and \( \text{Sm}^+ \) ion after femtosecond laser ablation of a samarium substrate. We find the kinetic energies of both \( \text{Sm} \) and \( \text{Sm}^+ \)
ion from the fresh surface are the largest. Kinetic energy of Sm$^+$ ion is almost 10 times larger than that of Sm, which indicates directly the contribution of Coulomb explosion in the acceleration process. From the second shot, the kinetic energy is found almost constant at around half and one-third of those at first shots for Sm and Sm$^+$, respectively. This result indicates that the nature of sample surface is changed by femtosecond laser ablation and we suggest the amorphization of sample surface may well explain the present result.

The result also implies that any physical quantities derived from the average of measurements after many shots of femtosecond laser on the same spot may not reflect the true physical properties of sample material. Including the effect of amorphization must be indispensable for the model calculation of mechanism and dynamics of femtosecond laser ablation of solid materials.

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