Non-thermal ablation of expanded polytetrafluoroethylene with an intense femtosecond-pulse laser

M. Hashida,[1,*] **H. Mishima,**[2] **S. Tokita,**[1] **and S. Sakabe**[1]

[1] *Institute for Chemical Research, Kyoto University, gokasho, Uji, Kyoto 611-0011, Japan*
[2] *Sumitomo Electric Industries, 1-1-3 Shimaya, Konohana-ku, Osaka 554-0024, Japan*

hashida@laser.kuicr.kyoto-u.ac.jp

Abstract: Ablation of expanded polytetrafluoroethylene without disruption of the fine porous structure is demonstrated using an intense femtosecond-pulse laser. As a result of laser-matter interactions near ablation threshold fluence, high-energy ions are emitted, which cannot be produced by thermal dissociation of the molecules. The ion energy is produced by Coulomb explosion of the elements of $(\text{-}CF_2\text{-}CF_2\text{-})_n$, and the energy spectra of the ions show contributions from the Coulomb explosions of the ions rather than those of thermal expansion to generate high-energy ions. The dependence of ion energy on the laser fluence of a 180-fs pulse, compared with that of a 400-ps pulse, also suggests that the high-energy ions are accelerated by Coulomb explosion.

OCIS codes: (140.3390) Laser materials processing; (160.5470) Polymers; (310.6628); Subwavelength structures, nanostructures; (240.6670) Surface photochemistry; (140.7090) Ultrafast lasers; (020.2649) Strong field laser physics.

References and links

1. Y. Masuda, F. Hayashi, T. Fujita, M. Uenoyama, Y. Idomoto, Y. Okuda, "Development of anisotropic conductive film for semiconductor chip testing," SEI technical review **166,** 24-27 (2005).
2. T. Katoh, D. Yamaguchi, Y. Ikeda, Y. Aoki, M. Washio, Y. Tabata,"Microfabrication of crosslinked polytetrafluoroethylene using synchrotron radiation direct photo-etching," Appl. Surf. Sci. **186,** 24-28 (2002).
3. T. Gumpenberger, J. Heitz, D. Bäuerle, T. C. Rosenmayer "Modification of expanded polytetrafluoroethylene by UV irradiation in reactive and inert atmosphere," Appl. Phys. A **80,** 27-33 (2005).
4. A. A. Serafetinides, M. I. Makropoulou, C. D. Skordoulis, A. K. Kar, "Ultra-short pulsed laser ablation of polymers," Appl. Surf. Sci. **180,** 42-56 (2001).
5. M. Rauh, J. Ihlemann, A. Koch, "Laser surface roughening of PTFE for increased bonding strength," Appl. Phys. A **88,** 231-233 (2007).
6. M. Hashida, A. F. Semerok, O. Gobert, G. Petite, Y. Izawa, J. F. Wagner, "Ablation threshold dependence on pulse duration for copper," Appl. Surf. Sci. **197-198,** 862-867 (2002).
7. Yu. Izawa, Y. Setsuhara, M. Hashida, M. Fujita, Y. Izawa, "Ablation and amorphization of crystalline Si by femtosecond and picosecond laser irradiation," Jpn. J. Appl. Phys. **45,** 5791-5794 (2006).
8. S. Guizard, A. Semerok, J. Gaudin, M. Hashida, P. Martin, F. Quere, "Femtosecond laser ablation of transparent dielectrics: measurement and modelisation of crater profiles," Appl. Surf. Sci. **186,** 364-368 (2002).
9. M. Lenzner, J. Kruger, S. Sartania, Z. Cheng, C. Spielmann, G. Mourou, W. Kautek, F. Krausz, "Femtosecond optical breakdown in dielectrics," Phys. Rev. Lett. **80,** 4076-4079 (1998).
10. S. Kuper and M. Stuke, "Ablation of polytetrafluoroethylene (Teflon) with femtosecond UV excimer laser pulses," Appl. Phys. Lett. **54,** 4-6 (1989).
11. H. Kumagai, K. Midorikawa, K. Toyoda, S. Nakamura, T. Okamoto, M. Obara, "Ablation of polymer films by a femtosecond high-peak-power Ti:sapphire laser at 798nm," Appl. Phys. Lett. **65,** 1850-1852(1994).

#111560 - $15.00 USD Received 18 May 2009; revised 9 Jul 2009; accepted 10 Jul 2009; published 16 Jul 2009

12. S. Nakamura, K. Midorikawa, H. Kumagai, M. Obara, K. Toyoda, "Effect of pulse duration on ablation characteristics of tetrafluoroethylene-hexafluoropropylene copolymer film using Ti:sapphire laser," Jpn. J. Appl. Phys. **35,** 101-106 (1996).
13. Z. B. Wang, M. H. Hong, Y. F. Lu, D. J. Wu, B. Lan, T. C. Chong, "Femtosecond laser ablation of polytetrafluoroethylene (Teflon) in ambient air," J. Appl. Phys. **93,** 6375-6380 (2003).
14. K. P. Adhi, R. L. Owings, T. A. Railkar, W. D. Brown, A. P. Malshe, "Femtosecond ultraviolet (248nm) excimer laser processing of Teflon (PTFE)," Appl. Surf. Sci. **218,** 17-23 (2003).
15. T. Lippert and J. T. Dickinson, "Chemical and spectroscopic aspects of polymer ablation: Special features and novel directions," Chem. Rev. **103,** 453-485 (2003).
16. M. Womack, M. Vendan and P. Molian, "Femtosecond pulsed laser ablation and deposition of thin films of polytetrafluoroethylene," Appl. Surf. Sci. **221,** 99-109 (2004).
17. T. Lippert, "Interaction of photons with polymers: From surface modification to ablation," Plasma Process Polym. **2,** 525-546 (2005).
18. S. Oga, "Fabrication of porouspolytetrafluoroethylene," Jpn. Patent No.S42-13560(67/13560), Aug.(1967).
19. S. Sakabe, S. Shimizu, M. Hashida, F. Sato, T. Tsuyukushi, K. Nishihara, S. Okihara, T. Kagawa, Y. Izawa, K. Imasaki, T. Iida, "Generation of high-energy protons from the Coulomb explosion of hydrogen clusters by intense femtosecond laser pulses," Phys. Rev. A **69,** 023203 (2004).
20. S. Okihara, T. Z. Esirkepov, K. Nagai, S. Shimizu, F. Sato, M. Hashida, T. Iida, K. Nishihara, T. Norimatsu, "Ion generation in a low-density plastic foam by interaction with intense femtosecond laser pulses," Phys. Rev. E **69,** 026401 (2004).
21. M. Hirokane, S. Shimizu, M. Hashida, S. Okada, S. Okihara, F. Sato, T. Iida, S. Sakabe, "Energy distributions of ions emitted from argon clusters Coulomb-exploded by intense femtosecond laser pulses," Phys. Rev. A **69,** 063201 (2004).
22. S. Sakabe, K. Shirai, M. Hashida, S. Shimizu, S. Masuno, "Skinning of argon clusters by Coulomb explosion induced with an intense femtosecond laser pulse," Phys. Rev. A **74,** 043205 (2006).
23. B. N. Chichkoh, C. Momma, S. Nolte, F. von Alvensleben, A. Tunnermann, "Femtosecond, picosecondand nanosecond laser ablation of solids," Appl. Phys. A **63,** 109-115 (1996).
24. The Chemical Society of Japan, 5*thKagakubinranII* (Maruzen,2004), Chap.16.1.
25. T. Seideman, M. Yu. Ivanov, P. B. Corkum, "Role of electron localization in intense-field molecular ionization," Phys. Rev. Lett. **75,** 2819-2822 (1995).
26. J. H. Posthumus, J. Plumridge, M. K. Thomas, K. Codling, L. J. Frasinski, A. J. Langley, P. F. Taday, "Dynamic and geometric laser-induced alignment of molecules in intense laser fields," J. Phys. B: At. Mol. Opt. Phys. **31,** L553-L562 (1998).
27. E. Constant, H. Stapelfeldt, P. B. Corkum, "Observation of enhanced ionization of molecular ions in intense laser fields," Phys. Rev. Lett. **76,** 4140-4143 (1996).
28. J. Jandeleit, G. Urbasch, H. D. Hoffmann, H. G. Treusch, E. W. Kreutz, "Picosecond laser ablation of thin copper films," Appl. Phys. A **63,** 117-121 (1996).
29. S. Preuss, M. Spath, Y. Zhang, M. Stuke, "Time resolved dynamics of subpicosecond laser ablation," Appl. Phys. Lett. **62,** 3049-3051 (1993).
30. S. B. Dake, N. R. Rajopadhye, S. V. Bhoraskar, "Evaluation and characterization of chemically modified polymers as secondary electron emitters," J. Phys. D: Appl. Phys. **20,** 1631-1636 (1987).
31. J. P. Jog, S. J. Walzade, S. V. Bhoraskar, "Study of localized states in FEP by space-charge limited current measurements," Polymer **23,** 1622-1626 (1982).

1. Introduction

High-polymer materials in a foam or sponge state are available for many applications. Expanded polytetrafluoroethylene (ePTFE) is a dielectric material that possesses superior heat, chemical, and weather resistances, and was developed for applications in medical and industrial fields such as artificial blood vessels, substrates for three-dimensional integrated circuits, and probe guides for integrated circuits [1]. In general, processing soft porous materials such as foams and sponges requires precise processing technology. Various techniques have been proposed and investigated for the micromachining of ePTFE, including mechanical processing, synchrotron radiation [2], and nanosecond laser ablations [3, 4]. However, sufficiently precise processing has not been realized due to the low melting temperature of ePTFE (T_m = 327 °C) and its non-uniform bond strength due to its surface roughness [5]. Lasers are generally available and widely used for precise processing. When matter is irradiated with nanosecond-pulse laser, the laser energy is absorbed by the matter, that is, the energy of the photons is trans-

#111560 - $15.00 USD Received 18 May 2009; revised 9 Jul 2009; accepted 10 Jul 2009; published 16 Jul 2009

ferred to the electrons in the matter. The electron temperature increases instantaneously, and the electron energy is gradually transferred to ions by electron-phonon coupling, depending on the thermal conductivity of the material. Finally, the matter becomes sufficiently hot to melt (to form a plasma) and to expand into free space (isothermal expansion occurs during the pulse and adiabatic expansion occurs after the pulse). This process is referred to as laser ablation. For the duration of the laser pulse, the absorbed energy diffuses over the matter. Therefore, even with pinpoint laser irradiation, the affected area includes a larger area than that irradiated by the laser due to thermal conduction. As a result, nanosecond lasers are not feasible for the processing of soft porous materials because the fine porous structure is damaged by thermal melting. The recent remarkable progress in the development of short-pulse laser technology, such as mode-locked laser oscillators and chirped pulse amplifications, has led to new methods of laser processing, and femtosecond laser material processing has been studied intensively for metals [6], semiconductors [7], and transparent materials [8, 9]. Low-energy and intense short-pulse lasers would be useful for processing soft materials. With femtosecond-pulse lasers, intense fields with lower energy can be applied to materials, and as a result, field processing can be expected rather than thermal processing. Femtosecond laser ablation of PTFE has been reported by several authors [10]-[17]. However, to our knowledge, there have been no reports regarding the processing of porous materials with femtosecond-pulse lasers. To design efficient and sophisticated processing techniques, the interactions between femtosecond-pulse lasers and porous materials must be well understood. In this study, the ablation of ePTFE with femtosecond-laser pulses was investigated by energy spectroscopy of the ions emitted from the interactions, and it was demonstrated that ePTFE was ablated not thermally, but by an intense field.

2. Experimental

The polymer used in the present experiment was porous ePTFE ($(\text{-CF}_2\text{-CF}_2\text{-})_n$) stretching in one dimension with a nominal thickness of 50 μm and a porosity of about 60%. The ePTFE was fabricated by stretching and annealing pressed PTFE powder. Figure 1(a) shows the cross-sectional view of an ePTFE bulk sample. The ePTFE has a textile structure consisting of PTFE fibers 10 - 100 nm in diameter[18]. The experiments for laser ablation were performed with a Gaussian-transverse laser beam (wavelength: 800 nm, pulse duration: 130 - 1000 fs and 400 ps, repetition rate: 10 Hz) from a Ti:sapphire chirp pulse amplification laser system. The laser beam was focused onto the ePTFE surface with a lens (f = 10 cm) in normal incidence. At the focal position, the laser beam was circular with a diameter of $\sim$ 50 μm at an intensity of 1/e. The laser energy was varied with an energy attenuator from 10 μJ to 350 μJ for pulses of 130 - 1000 fs and from 600 μJ to 4 mJ for pulses of 400 ps . The laser-ablated ePTFE surface was observed with a scanning electron microscope (SEM) and an optical microscope. The emitted ions were measured by a time-of-flight mass spectrometer with a micro-channel plate (MCP). For ion measurements, the laser was irradiated with an incidence angle of 45°relative to the surface normal. The TOF axis was normal to the ePTFE surface. The distance from the ePTFE sample to the MCP detector was 1.58 m, and the pressure was maintained at 10^{-7} Torr.

3. Results and discussion

Figure 1(b) and (c) are SEM images of the surfaces ablated for 400 ps and 130 fs, respectively, where a clear difference is observed between the craters produced by laser ablation on the two surfaces. The laser fluence corresponding to Fig. 1(b) and (c) is 8 J/cm^2. For the 400-ps pulses, the fine structure is destroyed, while following the 130-fs pulse, the fine porous structures can still be seen. This suggests that molecules or their ions are ablated from the surface without thermal melting.

The energy spectra of ions emitted from ePTFE are shown in Fig. 2. For the pulse of 400 ps

#111560 - $15.00 USD Received 18 May 2009; revised 9 Jul 2009; accepted 10 Jul 2009; published 16 Jul 2009

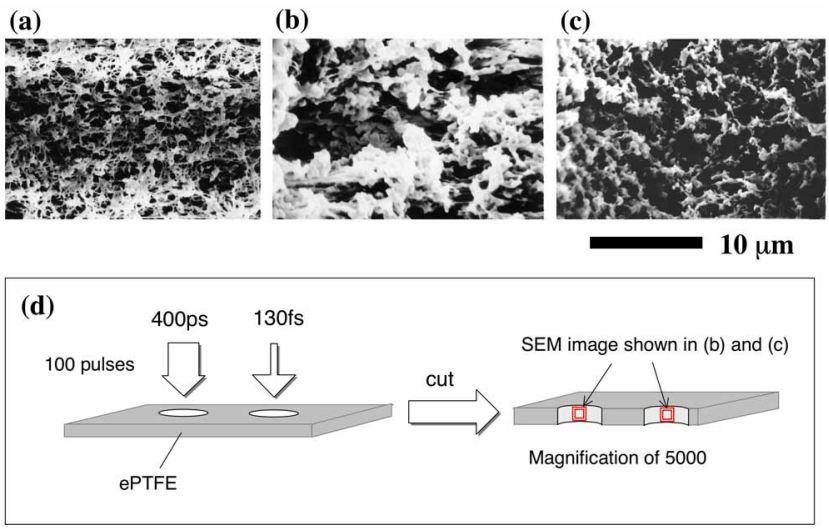

Fig. 1. SEM images: (a) cross-section of an ePTFE bulk sample; surfaces containing holes drilled by pulse irradiation of (b) 400 ps and (c) 130 fs. For pulses of 400 ps, fine structure is destroyed and aggregated ePTFE having a size of $\sim 2\ \mu$m is produced. Holes for SEM imaging were produced by irradiation with 100 laser pulses having laser fluence of 8 J/cm^2; produced holes were cut as shown in (d).

(40 J/cm^2), the spectrum shows an exponential distribution at high energy, while for the pulse of 180 fs (0.78 J/cm^2), the spectrum is relatively flat and truncated around 70 eV. This difference is possibly due to the exposure of the porous structure to an intense laser light. The porous structure can be regarded as an aggregate of elements that are smaller than the wavelength of the laser; thus, the interaction between the laser and the bulk material is reduced to the interaction between the laser and the small elements, which is analogous to laser-cluster interactions [19]-[22]. The intense laser can ionize the elements instantaneously by non-resonant multi-photoionization or optical-field ionization (barrier-suppression ionization) and can produce elemental ions, which induces Coulomb explosions emitting energetic ions. The generation of ions from laser-element interaction can be identified in the energy distribution of ions emitted through the process. When the element changes to a plasma as a result of laser irradiation, it expands adiabatically (the laser pulse is too short to be isothermal), and the emitted ions generally exhibit a Maxwellian distributions of energies, $\mathrm{d}N/\mathrm{d}E \sim \exp(-E/k_B T_e)$, where T_e is the electron temperature and k_B is the Boltzmann constant. Consequently, the energy distribution is quite broad, with a maximum energy E_{max} of about $10T_e$. On the other hand, when many electrons are expelled instantaneously from an element, it becomes highly ionized. Atomic ions generated by Coulomb explosion exhibit the energy distribution of $\mathrm{d}N/\mathrm{d}E \sim E^i$ (i =1/2 for spherical elements, i = 0 for cylindrical elements, and i = -1/2 for planar elements) having a finite maximum E_{max}. The results shown in Fig. 2(b) tend to be the Maxwellian distribution corresponding to the expansion of heated plasma elements, while the result of shown in Fig. 2(a) is much closer to the distribution expected as a result of Coulomb explosion since i = 0 for cylindrical elements. The maximum energy of the emitted ions, 70 eV, also supports this interpretation as discussed later in this section.

Figure 3 shows the dependence of maximum ion energy on laser fluence. The ablation thresholds of ePTFE were 0.60 J/cm^2 for a pulse of 180 fs and 3.87 J/cm^2 for a pulse of 400 ps. The thresholds were estimated by the fitting function of experimental data shown in Fig. 4(b). The

#111560 - $15.00 USD Received 18 May 2009; revised 9 Jul 2009; accepted 10 Jul 2009; published 16 Jul 2009

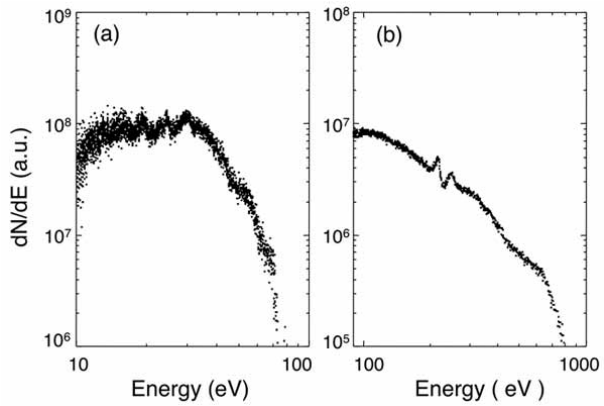

Fig. 2. Energy spectra of ions emitted from laser-ePTFE interactions. (a)180 fs, 0.78 J/cm^2, (b) 400 ps, 40 J/cm^2.

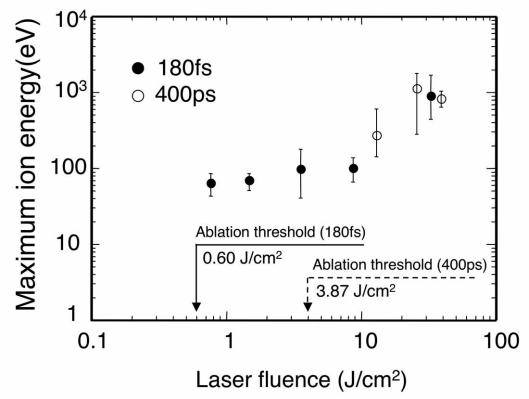

Fig. 3. Dependence of maximum ion energy on laser fluence.

details of the ablation threshold measurements are discussed below. The maximum ion energy E_{max} is defined as the energy at which the ion signal in Fig. 2 is ten times larger than the noise level. For 400 ps, the ion energy is approximately proportional to the laser fluence in the range of 10 - 40 J/cm^2. For thermal expansion, the ion energy E_{max} is proportional to the electron temperature T_e, which is proportional to the laser fluence F_L[23] if the absorption process is assumed to be unchanged. Therefore, the ions emitted as a result of the 400-ps pulse are possibily produced by thermal ablation.

On the other hand, for the pulse of 180 fs, the maximum energy is about 70 eV and does not depend on the laser fluence in the range of 0.75 - 8 J/cm^2. Furthermore, the ion species were measured by time-of-flight mass spectroscopy, and the ions of C^{Z+} (Z = 1, 2, 3), F^{Z+} (Z = 1, 2), and $C_jF_l^+$ were observed. The ePTFE has a chain structure of (- CF_2 - CF_2 -)$_n$ and the atomic distance of two carbons, r, is 1.31 Å[24]. If the carbons are ionized to C^{Z+} in the initial configuration, the carbon ions repel each other as a result of the Coulomb force. The ion energy obtained by Coulomb explosion is expressed as $E_{coul} = Z_1Z_2e^2/(4\pi\varepsilon_0 r)$, where Z_1 and Z_2 are the charges of the ions and e is the elementary electric charge. For carbon ions of maximum charge Z = +3, the ion energy of E_{coul} is 99 eV, which is of the order of the experimental results, since the energy is reduced by the initial extension of a two atom interval[25]-[27].

#111560 - $15.00 USD Received 18 May 2009; revised 9 Jul 2009; accepted 10 Jul 2009; published 16 Jul 2009

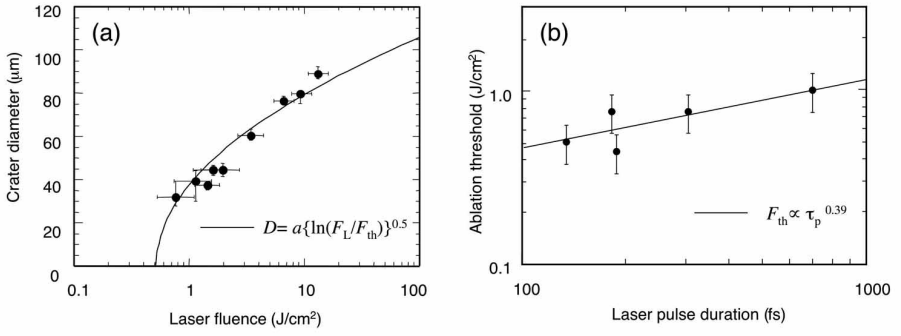

Fig. 4. (a) Dependence of ablated crater diameter on laser fluence for a pulse duration of 130 fs, and (b) dependence of ablation threshold on laser pulse duration.

The ablation threshold of the ePTFE was derived from the dependence of the ablated crater diameter on the laser fluence [28]. For the Gaussian transverse laser beam, the crater diameter D can be expressed as

$$D = a\sqrt{ln(F_L/F_{th})} \tag{1}$$

where F_{th} is the ablation threshold, F_L is the incident laser fluence, and a is the laser beam diameter on the sample surface. The experimental results of a crater diameter for a pulse of 130 fs are shown in Fig. 4(a). The experimental data agree well with Eq. (1). Assuming $D = 0$, the ablation threshold can be estimated as F_{th} = 0.50 J/cm^2 for a pulse of 130 fs. For different pulse durations under otherwise identical conditions, the ablation thresholds of ePTFE were reduced to 0.75 J/cm^2 for a pulse of 183 fs, 0.44 J/cm^2 for a pulse of 189 fs, 0.75 J/cm^2 for a pulse of 305 fs, 0.99 J/cm^2 for a pulse of 700 fs, and 3.87 J/cm^2 for a pulse of 400 ps. In Fig. 4(b) the ablation threshold dependence on the laser pulse duration (τ_p) is plotted. The ablation thresholds obtained experimentally were in good agreement with the function $\tau_p^{0.39}$. The pulse duration dependence is similar to the experimental results reported by *Nakamura* et al. regarding tetrafluoroethylene-hexafluoropropylene copolymer (FEP) [12]. For m-photon absorption and an incident laser pulse of rectangular temporal shape, the ablation threshold F_{th} can be analytically obtained and expressed[29] as

$$F_{th} = \left(\frac{E_{th}}{\xi_m}\right)^{\frac{1}{m}} \tau_p^{\frac{m-1}{m}} = \beta_m \tau_p^{\frac{m-1}{m}} \tag{2}$$

where ξ_m is the m-photon absorption coefficient, E_{TH} is the ablation threshold energy per unit volume, and τ_p is the duration of the incident laser pulse. PTFE has a band gap of 6 eV and an electron affinity of 2.2 eV. [30, 31] Therefore, six photons are necessary for multi-photon absorption at 800 nm (= 1.55 eV). Thus, the ablation threshold for the ePTFE is expected to depend on the pulse duration as $\beta_6 \tau_p^{5/6}$. The experimentally obtained threshold dependence of the pulse duration for the ePTFE cannot be interpreted as a multi-photon absorption process for bulk PTFE. The absorption process in the porous structure requires further study.

4. Conclusion

It was demonstrated that an expanded polytetrafluoroethylene (with porous foam structure) material can be ablated with an intense femtosecond-pulse laser without disrupting the fine structure. The ablation is not driven by thermal expansion, but mainly by Coulomb explosion of ionic elements produced instantaneously by a femtosecond laser pulse.

#111560 - $15.00 USD Received 18 May 2009; revised 9 Jul 2009; accepted 10 Jul 2009; published 16 Jul 2009