Appl. Phys. A 90, 403–409 (2008)
DOI: 10.1007/s00339-007-4341-x

Applied Physics A
Materials Science & Processing

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# Ionization in vacuum ultraviolet $F_2$ laser ablated polymer plumes

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**Received: 9 July 2007/Accepted: 15 October 2007**
**Published online: 30 November 2007 •** **© Springer-Verlag 2007**

**ABSTRACT** An experimental investigation of ion generation in the 157-nm vacuum ultraviolet (VUV) $F_2$ laser ablation of three selected polymers – glycidyl azide polymer (GAP), a triazene polymer (TP6) and polyimide – is described. An ion collector probe is used to determine the relative ion yield and white-light interferometry of ablated surfaces to ascertain mass-removal levels. The findings indicate that ions are generated under the action of the VUV laser pulse at fluences down to at least as low as the threshold for material removal. A two-photon photoionization model is proposed that provides a good description of the results.

**PACS** 52.38.Mf; 71.20.Rv; 52.25.Jm

## 1 Introduction

The 157-nm $F_2$ laser provides one of the shortest coherent wavelengths for practical applications in micromachining and nanostructuring and is of interest for processing both organic and inorganic materials [1, 2]. Its advantages include strong absorption in most materials with a concomitantly low threshold for ablative removal, and excellent spatial resolution. At this wavelength the transition to plasma formation via electron avalanche breakdown in the ablation plume [3] is expected to occur at a much higher irradiance level than used in processing polymers, so significant 'plasma' effects should not be present. Nevertheless, early studies [4] showed that the fractional ionization in the plumes of polymers ablated at 157 nm is significantly higher than under comparable conditions at longer UV wavelengths. Given that 157-nm laser photons, with energy of 7.9 eV, produce more extensive fragmentation of polymers [5] and have comparable energy to the ionization potential of many species, plasma generation is expected be driven by a significantly different mechanism to that at longer wavelengths. This is borne out by work on 351-nm-laser-irradiated metal targets where both experimental and theoretical studies confirmed that plasma ignition thresholds were strongly influenced by photoionization mechanisms [6]. As plume ionization is of potential interest in organic polymer film deposition [4], area-selective chemical plating [7], laser ablation mass spectroscopy [8] and optical spectroscopy, a further understanding of these mechanisms for the vacuum ultraviolet (VUV) laser would be beneficial.

In this paper we describe an experimental study of the 157-nm VUV $F_2$ laser ablation of three selected polymers – glycidyl azide polymer (GAP), a triazene polymer (TP6) and polyimide – placing emphasis on investigating ion formation by the laser pulse interacting with the surface. For this purpose a simple time-resolved ion collector probe has been used to measure the relative ion yield produced in the ablation regime and white-light interferometry of ablated surfaces used to ascertain mass-removal levels. The findings indicate that ions are generated with the VUV laser at fluences down to at least as low as the threshold for material removal. A two-photon photoionization model is proposed that provides a good description of the observed ion-fluence scaling.

## 2 Materials and experimental technique

The polymers selected for study exhibit very different properties. GAP (obtained from Nitrochemie Wimmis AG) decomposes highly exothermically ($\Delta H_{\mathrm{dec}} = -3.83\,\mathrm{kJ\,g^{-1}}$) and has a high absorption coefficient at 157 nm [9]. It has been suggested as a fuel for laser plasma thruster applications [9]. TP6 belongs to a class of polymers that have been specifically designed for laser ablation at 308 nm, where triazene polymers exhibit superior properties in respect of quality of ablated structures, high ablation rates and low thresholds [10]. It was synthesized according to a procedure described elsewhere [11]. The polyimide, Kapton HN, from DuPont, was included as this is a 'standard' for laser ablation studies [12] and can be ablated effectively at all UV laser wavelengths. For polyimide (Kapton HN) and TP6 the absorption coefficients at 157 nm are $\sim 1.1 \times 10^5\,\mathrm{cm^{-1}}$ [13] and $8 \times 10^4\,\mathrm{cm^{-1}}$ [5], respectively, compared with $1.6 \times 10^5\,\mathrm{cm^{-1}}$ for GAP [5]. The chemical structures of the polymers are shown in Fig. 1.

The experiments used a Lambda Physik model LPF 202 $F_2$ laser providing a maximum output energy of $\sim 35$ mJ in a pulse of duration $\sim 11$ ns FWHM (full width at half maximum). The polymer samples were placed in an evacuable chamber that was connected to the laser with a 2-m-long beam delivery tube and irradiated under vacuum at a pressure of $\sim 10^{-5}$ mbar. The samples were mounted on a rotary

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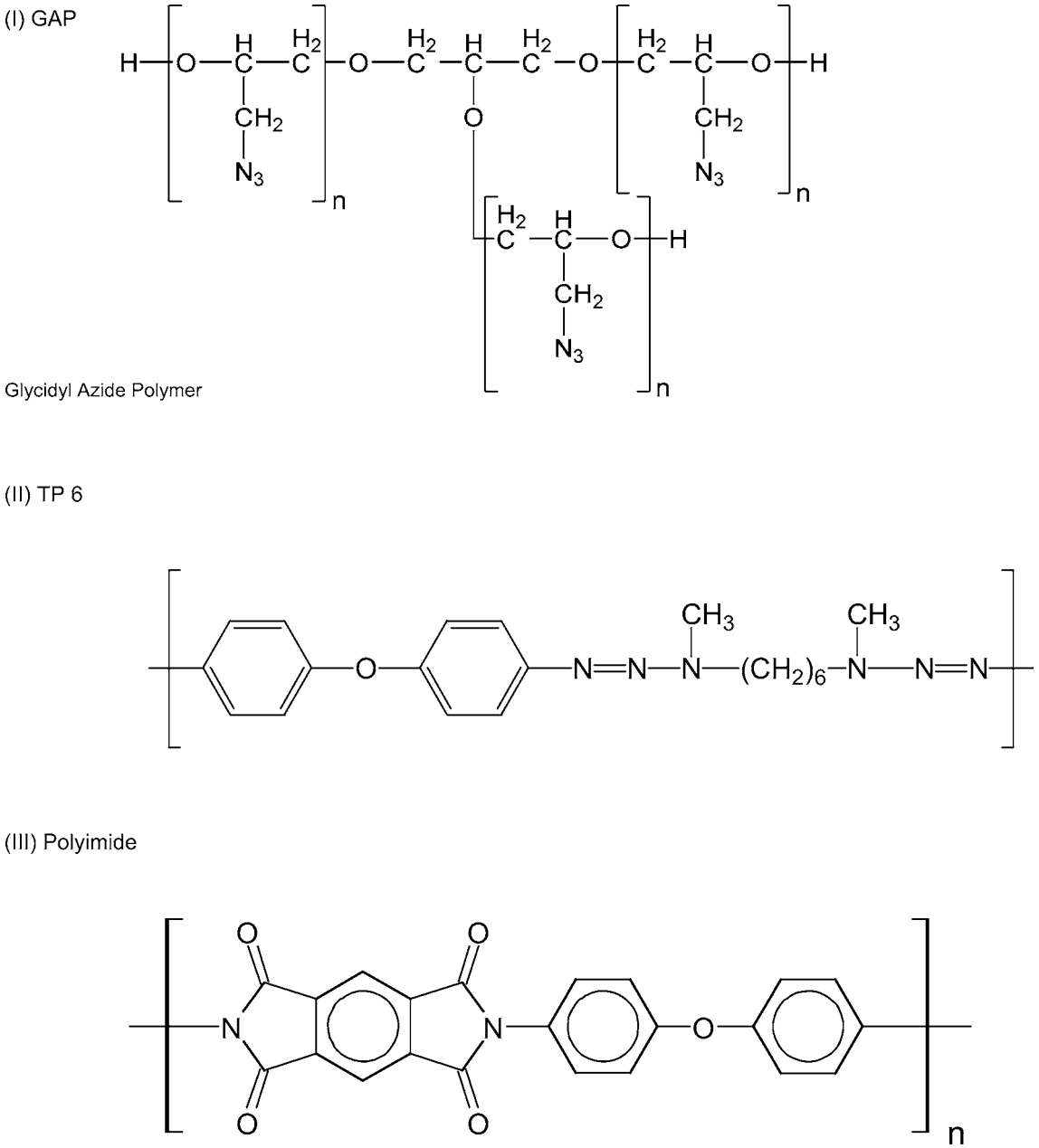


**FIGURE 1** Chemical structures of (I) GAP (glycidyl azide polymer), (II) TP6 and (III) polyimide (Kapton HN)

stage and positioned with their normal at a fixed angle of $\sim 26°$ to the incident laser beam direction, so that an ion collector probe could lie in the direction of the target normal without obscuring the beam. The probe was formed by a 3-mm-diameter collector plate of platinum–10% rhodium alloy that lay beneath a grounded fine mesh of Au-coated nylon. The probe was biased at $-64$ V to collect positive ions and was positioned with its collection surface at a distance of 12–14 mm from the target and, except for when making angular distribution measurements, was oriented along the target normal. The voltage output from the probe was taken from a 240-Ω load resistor that in combination with the connecting cable capacitance gave an electrical response time of approximately 20 ns. The ion probe sensitivity was $4.16 \times 10^{-3}$ A/V for a 240-Ω load corresponding to $2.6 \times 10^{16}$ (singly charged) ions/V. Assuming a limiting detectable voltage of 0.5 mV this corresponded to a minimum number of $1.3 \times 10^{13}$ ions or $3.3 \times 10^{14}$ ions/steradian based on the probe solid angle. Alternatively, a 3-kΩ load was used to increase sensitivity albeit at the expense of response time. The signal was recorded using a Hewlett-Packard Infinium oscilloscope, and averaged over typically 5–10 pulses with the laser operating at a pulse-repetition frequency of 1 Hz. The probe was occasionally cleaned between sets of experiments by ablation using a 308-nm XeCl laser to minimize the effects of any build up of re-deposited polymer ablation products on its surface.

The quasi-uniform central region of the laser output beam was selected by passing it through a rectangular aperture in a metal plate. This aperture was imaged onto the polymer surface with a demagnification factor of about 13 × using an 83 mm focal length $CaF_2$ lens so as to produce a relatively uniform exposure fluence. The rectangular spot dimensions

varied slightly depending on the experiment but were typically 170 μm × 350 μm. A white-light interferometer (Wyko NT1100 optical profiling system) was used to perform surface depth profiling of the ablation sites in the exposed polymers.

## 3 Experimental results

Results obtained using the white-light interferometer for 10-pulse exposure of GAP at 1510 mJ cm$^{-2}$, five-pulse exposure of TP6 at 980 mJ cm$^{-2}$ and single-pulse exposure of polyimide at 1130 mJ cm$^{-2}$ are shown in Fig. 2a–c, respectively. The quality of the ablation sites provides indirect evidence that the spatially filtered optical projection arrangement provided good fluence uniformity. The nanometric depth resolution of the white-light interferometer enabled a sensitive determination of material removal in the low-fluence regime. In this way the threshold fluence, $F_T$, for significant material removal was found to be ≈ 30 mJ cm$^{-2}$ for TP6, ≈ 21 mJ cm$^{-2}$ for GAP and ≈ 20 mJ cm$^{-2}$ for polyimide (Kapton HN) based on the lowest fluence at which a resolvable depth (∼ 0.5 nm) could be measured with a single-pulse exposure.

Figure 3 shows the ion probe signal obtained by averaging 10 pulses when polyimide was ablated at a fluence of 1100 mJ cm$^{-2}$. The initial short-duration spike is attributed to the photoelectric signal generated by scattered 157-nm laser radiation that falls on the probe surface. This provides a useful reference marker for timing the broad voltage signal produced by the current of positive ions that start arriving after approximately 530 ns. The ion signal has a width of 570 ns (FWHM) and is seen to be smooth and devoid of substructure, a feature that was preserved when single pulses were recorded and is thus not simply a result of multi-pulse averaging. The variation of the peak ion signal (which is proportional to the maximum ion current) is shown in Fig. 4 as a function of fluence. Also shown is the time integral of the ion probe signal excluding the photoelectric pulse, which gives a measure of the total ion charge collected by the probe. Both exhibit a similar variation, with an initially slow rise followed by a faster upturn as the fluence is increased.

The ion probe signal in Fig. 3, and the ion-fluence scaling seen in Fig. 4, are typical of the data obtained over the entire range of conditions investigated for polyimide, GAP and TP6 and did not change significantly when a somewhat different

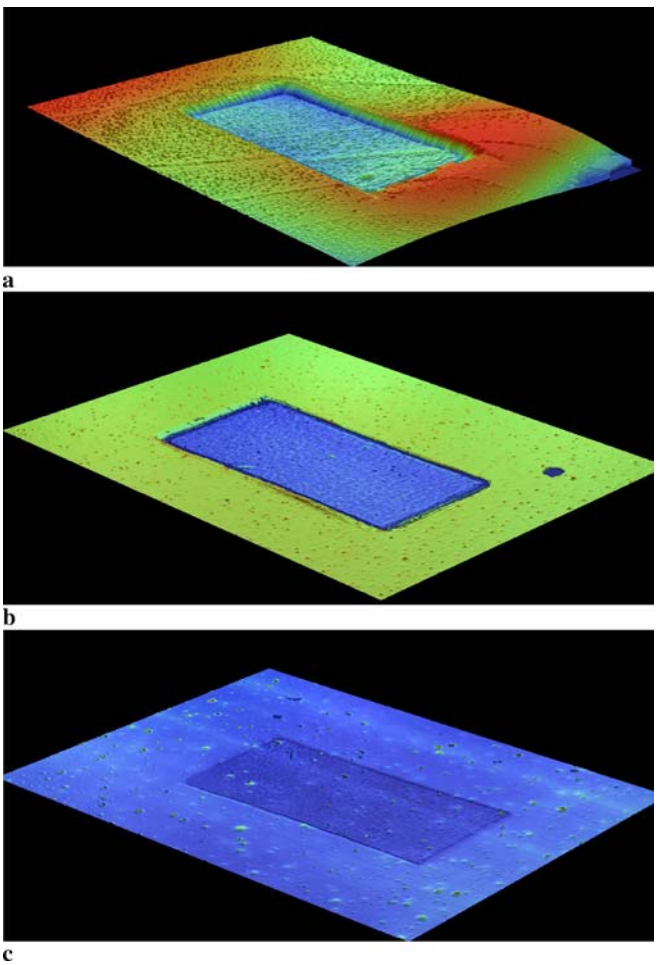


**FIGURE 2** Wyko white light interferometer profiles of ablation sites in $F_2$ laser ablated polymers: (**a**) GAP – 10 pulses at 1510 mJ cm$^{-2}$ (depth = 2300 nm), (**b**) TP6 – five pulses at 980 mJ cm$^{-2}$ (depth = 760 nm), (**c**) polyimide – single pulse at 1130 mJ cm$^{-2}$ (depth = 195 nm)

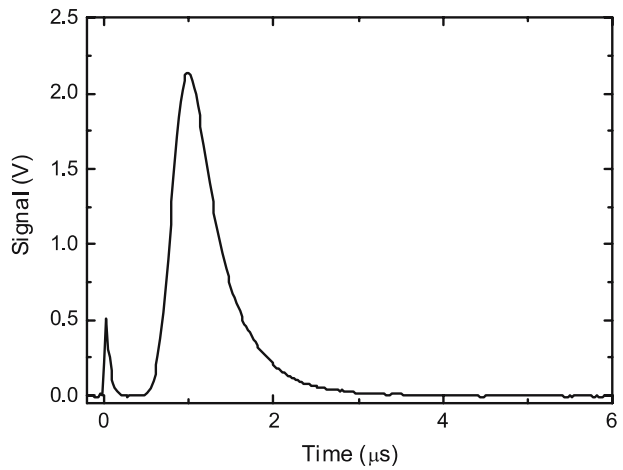


**FIGURE 3** Ion probe signal for polyimide (Kapton HN) ablated using the $F_2$ laser at 1100 mJ cm$^{-2}$ averaged over 10 pulses. The initial pulse at $t = 0$ is a photoelectric signal generated by scattered 157-nm laser radiation (probe–target spacing 12 mm)

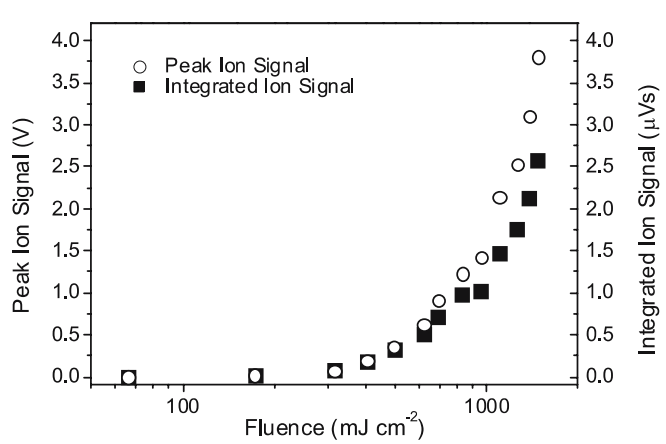


**FIGURE 4** Variation of the peak amplitude of the ion signal and the time-integrated ion signal as a function of fluence. Polyimide irradiated using the 157-nm $F_2$ laser

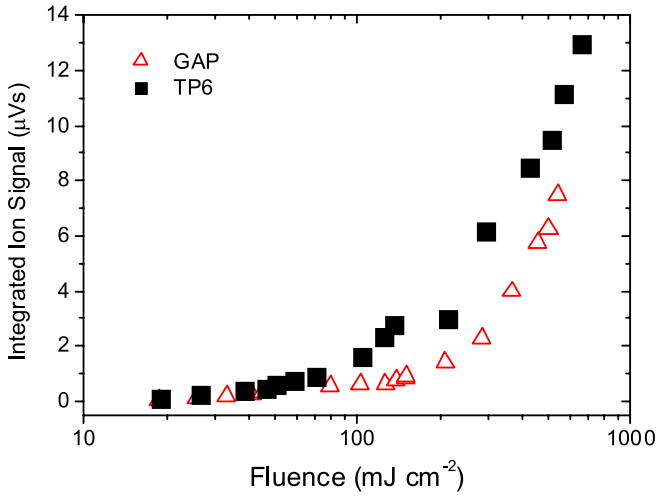


**FIGURE 5** Time integrated ion probe signals vs. $F_2$ laser fluence for GAP and TP6

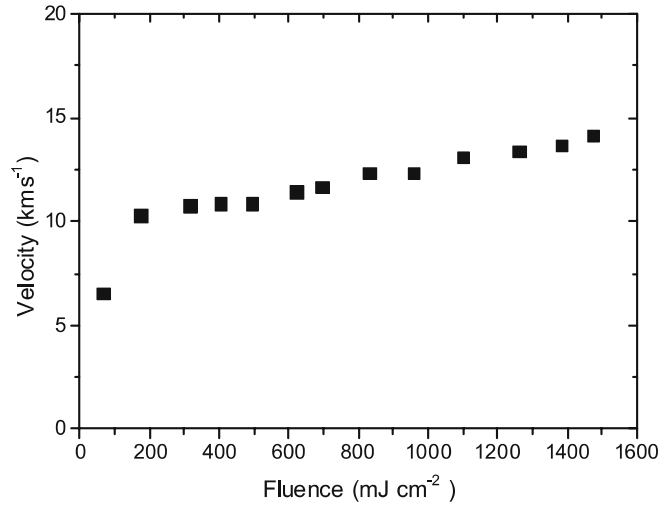


**FIGURE 7** Ion velocity based on peak of the ion signal vs. fluence. Polyimide ablated using the $F_2$ laser

spot size was used. In Fig. 5 the time-integrated ion signals vs. fluence for the photoreactive polymers GAP and TP6 are shown and are seen to have a similar form to that for polyimide in Fig. 4. By extrapolating low-fluence data for the integrated ion signals plotted on a logarithmic fluence axis, nominal ion thresholds of $\sim 14.5 \pm 2.0$, $18.5 \pm 1.0$ and $28 \pm 4.0\,\mathrm{mJ\,cm^{-2}}$ were obtained for TP6, GAP and polyimide, respectively. There is no evident correlation with the corresponding material removal thresholds, though it must be borne in mind that there is considerable uncertainty in deriving both sets of these 'thresholds'.

Measurements of the angular distribution of ions were made for polyimide by varying the probe angle $\theta$ with respect to the target normal whilst maintaining a fixed distance from the target. The distribution was found to be sharply peaked with a full angular width of $\sim 40°$ assuming that this was symmetrical on either side of the normal (Fig. 6). This is qualitatively similar to results for the 157-nm laser reported in [4] and to that found for neutral species when polyimide is ablated

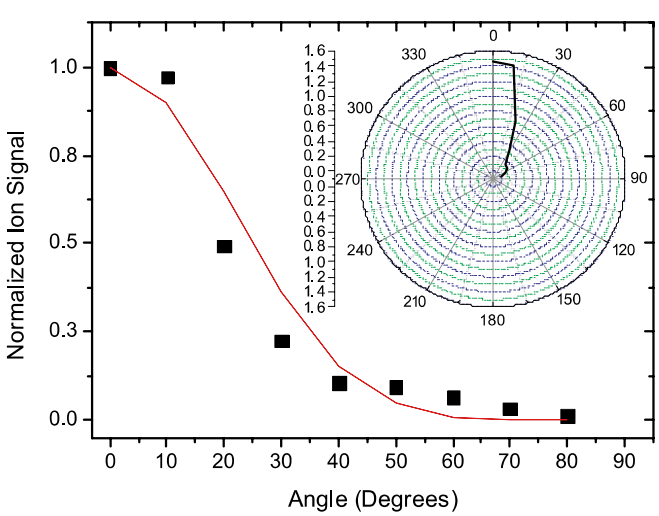


**FIGURE 6** Angular distribution of the ion signal for polyimide ablated using the $F_2$ laser at $600\,\mathrm{mJ\,cm^{-2}}$. The *solid line* is $\cos^7\theta$, where $\theta$ is the angle with respect to the target normal. *Inset*: polar plot of the ion signal

at 248 nm [12]. The total charge was found by fitting the distribution with the form $\cos^7\theta$ (Fig. 6) and integrating this over the forward hemisphere assuming emission to be axially symmetric about the target normal. In this way it was calculated that a total charge of $1 \times 10^{-7}$ C, equivalent to $6.3 \times 10^{11}\,e$, was generated at $\sim 1130\,\mathrm{mJ\,cm^{-2}}$. There is a degree of uncertainty in this value because the use of a rectangular rather than a circular irradiation site means that the plume expansion will not strictly be axially symmetric, as assumed. Further, no correction has been made for any secondary electrons that may be generated when excited neutrals fall on the probe [4, 7]. From the white light interferometer results the corresponding single pulse mass removal was $\sim 1.5 \times 10^{-11}$ kg, equivalent to $\sim 3.1 \times 10^{14}$ species assuming these to have an average mass of 30 amu for polyimide based on mass spectroscopic data (see Sect. 5 and [5]). This gives a fractional ionization of $\sim 0.2\%$.

The ion velocity deduced from the delay of the peak ion signal with respect to the laser pulse showed a weak fluence dependence, the velocity increasing from about $1 \times 10^4\,\mathrm{m\,s^{-1}}$ at $\sim 100\,\mathrm{mJ\,cm^{-2}}$ to $1.4 \times 10^4\,\mathrm{m\,s^{-1}}$ at $\sim 1500\,\mathrm{mJ\,cm^{-2}}$ (Fig. 7). This velocity is consistent with results in [4] and time-of-flight data obtained for the wide range of low-mass species identified by mass spectroscopy [14] when GAP, TP6 and Kapton are ablated at 157 nm. From the latter measurements ion energies have been found to be 5–20 eV for species such as $N_2{}^+$.

## 4 Modelling

For the 157-nm laser we suppose that photoionization of fragments that form the plume of the ablated polymer is the dominant mechanism for ion generation. Estimates of the inverse Bremsstrahlung absorption coefficient [15] show that this is sufficiently small at this wavelength to rule out significant free-electron heating. Hence, the electron avalanche breakdown threshold will be much higher than the relatively modest peak irradiance levels of $< 10^8\,\mathrm{W\,cm^{-2}}$ used in these experiments and it appears reasonable to neglect this as a significant contributor to ion formation. As the $F_2$ laser photon

energy of $h\nu = 7.9$ eV will be greater than the ionization potential $I_p$ of certain of the species in the plume, and two photons (= 15.8 eV) will exceed $I_p$ for nearly all species present, we limit consideration to two cases:

1. Single-step ionization where $h\nu \geq I_p$.
2. Two-photon ionization where $h\nu \leq I_p < 2h\nu$. Here ionization is assumed to occur from an excited state of a species produced by quasi-resonant single-photon absorption.

The production rate $R$ of positive ions (and the sum of free electrons and negative ions formed by attachment) is then taken to scale as

$$R = \left(\frac{I}{h\nu}\right)\sigma_{i1}N \quad \text{one-photon absorption}\,, \tag{1a}$$

$$R = \left(\frac{I}{h\nu}\right)^2\sigma_{i2}\sigma_o\tau N \quad \text{two-photon absorption}\,. \tag{1b}$$

Here $I$ is the $F_2$ laser irradiance, $N$ the number density of species that participate in ionization, $\sigma_{i1}$ and $\sigma_{i2}$ ionization cross sections for the one- and two-photon cases, respectively, and $\sigma_o$ the cross section for absorption by the neutral species. In obtaining (1b) it is assumed that intramolecular excitation energy is rapidly thermalized so that the lifetime $\tau$ of the excited state from which ionization occurs is short compared with the laser pulse duration. For a layer-by-layer ablation process obeying a Beer's law form for removal from the surface with a threshold fluence $F_T$, the time-dependent mass of material ablated per unit area $m(t)$ can be expressed as

$$m(t) = 0 \quad \text{for} \quad \int_0^\infty I\,\mathrm{d}t \leq F_T\,,$$

$$m(t) = \frac{\varrho}{\alpha}\ln\left[\frac{\int_0^t I\,\mathrm{d}t}{F_T}\right] \quad \text{for} \quad \int_0^\infty I\,\mathrm{d}t > F_T\,. \tag{2}$$

Here $\varrho$ is the solid density and $\alpha$ is the effective absorption coefficient of the solid, and in this Beer's law form it is assumed that the plume continues to absorb with the same mass absorption coefficient $(\alpha/\varrho)$ as the solid [16]. Taking $N$ to be proportional to $m(t)$, we obtain from (1) and (2) production rates of

(one-photon) :

$$R \sim \frac{I\sigma_i}{h\nu}\frac{\varrho}{\alpha}\ln\left[\frac{\int_0^t I\,\mathrm{d}t}{F_T}\right] \quad \text{for} \quad \int_0^\infty I\,\mathrm{d}t > F_T \tag{3}$$

and

(two-photon) :

$$R \sim \left(\frac{I}{h\nu}\right)^2\frac{\sigma_i\sigma_o\varrho\tau}{\alpha}\ln\left[\frac{\int_0^t I\,\mathrm{d}t}{F_T}\right] \quad \text{for} \quad \int_0^\infty I\,\mathrm{d}t > F_T \tag{4}$$

and an ion yield

$$Y = \int_0^\infty R\,\mathrm{d}t\,. \tag{5}$$

In Fig. 8, $m(t)$ and $R$ for the one-photon and the two-photon processes are shown for a pulse irradiance varying as $I(t) = I_0(1-\exp(-t/\tau_1))\exp(-t/\tau_2)$. The time constants $\tau_1$ and $\tau_2$ here were set to $\tau_1 = 10$ ns and $\tau_2 = 5$ ns (pulse width 10.2 ns FWHM) to give an approximate description of the $F_2$ laser pulse shape, and the fluence was assumed to be $2F_T$, i.e. twice threshold. For these parameters ablative mass removal and ion generation commence at about 7 ns into the pulse. On increasing the fluence to $4F_T$, the modelling showed that ablation and ion generation commenced at the earlier time of 3.9 ns and led to a somewhat longer duration ion pulse for the two-photon case (6.58 ns FWHM, cf. 6.06 ns FWHM for $F/F_T = 2$). Figure 9 shows the predicted ion yield, $Y$, for one-photon ((3) and (5)) and for two-photon ionization ((4) and (5)), and as would be expected there is a stronger fluence scaling for the two-photon case. A comparison of the modelling with the experimental data for polyimide in Fig. 9 shows that two-photon photoionization provides an excellent description of the fluence dependence observed. It was also found that essentially the same fluence scaling was obtained when either the time-integrated yield (5) or the peak ion generation rate (from (3) or (4)) were used because of the near constancy of the ion pulse shape. Similar results for the yield–fluence scaling were obtained for a Gaussian temporal irradiance distribution, indicating that the scaling is insensitive to the precise form of the laser pulse shape.

Calculations were also made using a model for thermal ionization based on the average plume temperature, $T$, produced by laser heating and the Saha equation [17] in the limit of low fractional ionization ($I_p \gg kT$). The ion yield–fluence scaling with this model for a range of $I_p$ values always led to a very sudden sharp increase in yield that could not be reconciled with the experiments. It thus appears unlikely that thermal ionization is significant [4].

The ion signals were fitted assuming a Maxwell–Boltzmann thermal distribution at temperature $T$ superimposed on

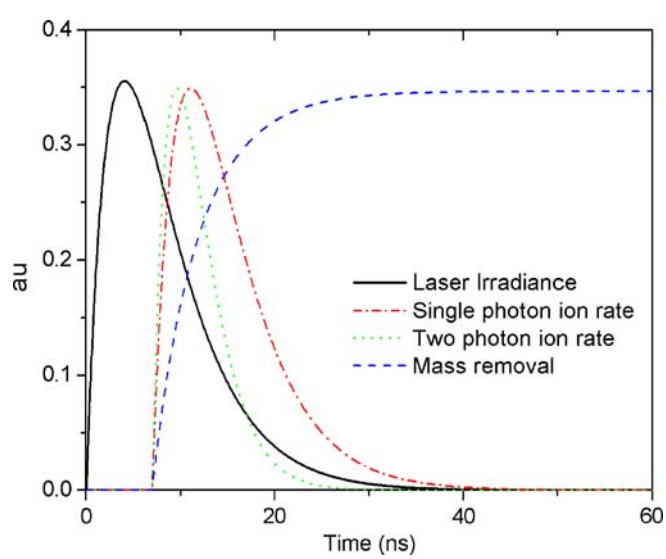


**FIGURE 8** Laser pulse irradiance, ionization rate for a one- and a two-photon ionization mechanism and mass removal vs. time. Irradiance distribution $I(t) = I_0(1-\exp(-t/\tau_1))\exp(-t/\tau_2)$ with pulse parameters $\tau_1 = 10$ ns and $\tau_2 = 5$ ns. Normalized laser fluence $F/F_T = 2$, where $F_T$ is the threshold fluence

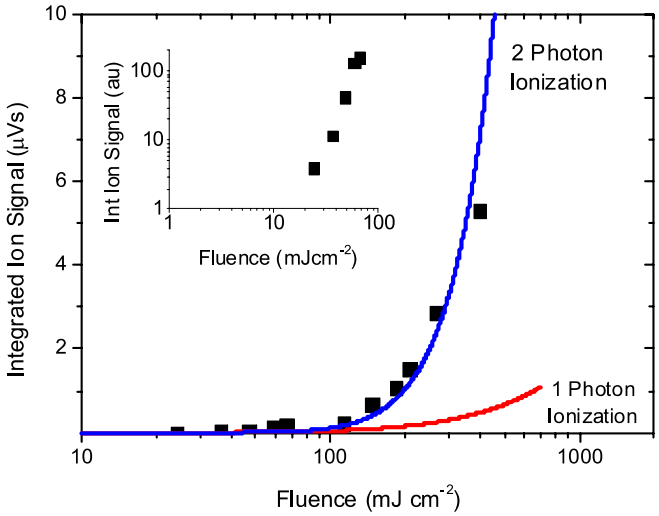


**FIGURE 9** Integrated ion signal as a function of fluence for polyimide ablated using the $F_2$ laser. *Inset*: expansion of low-fluence experimental data on a log–log plot. (■) Experimental data; (–) modelled ion signal (arbitrary units) with ablation threshold taken as 20 mJ cm$^{-2}$. A two-photon ionization mechanism provides a good description of the observed scaling

a centre-of-mass velocity $u$. The temporal form of the ion current density $J(t)$ is then [18]

$$J(t) = A\left(\frac{M}{kT}\right)^{3/2}\frac{x}{t^4}\exp\left[-\frac{M\left(\frac{x}{t}-u\right)^2}{2k_BT}\right], \tag{6}$$

where $x$ is the probe–target spacing, $M$ is the species mass, $k_B$ is Boltzmann's constant and $A$ is a constant. Figure 10 shows data taken from the ion probe signal for polyimide ablated at 1100 mJ cm$^{-2}$ in Fig. 3, together with a fit made using (6) with mass/temperature ratio of $M/T = 7.69 \times 10^{-4}$ amu K$^{-1}$ and $u = 0.86 \times 10^4$ m s$^{-1}$. The agreement is remarkably good, suggesting that a thermal distribution suitably describes the ions. Similarly good fits were also obtained using a weighted range of $M/T$ values. Deduction of the effective ion temperature from these fits is hampered, however, because mass spectroscopic studies show [5] that a wide range of low-mass products are ablated by the 157-nm laser, but the (dominant) ion masses collected by the ion probe are not known. If the ions were formed from the predominant fragment of CO (28 amu) in Kapton ablation at 157 nm [5], then a value of $T = 36.400$ K (3.1 eV) would follow, with $u$ corresponding to 10.8 eV. For comparison, a fit to ion signals made at a lower fluence of 693 mJ cm$^{-2}$ gave a slightly increased value of $M/T = 8.57 \times 10^{-4}$ amu K$^{-1}$ and a flow speed of $0.76 \times 10^4$ m s$^{-1}$, indicating that these parameters have a weak fluence dependence. These relatively high ion energies are not inconsistent with previous reports for neutral [12] and ionic species [19] produced in polyimide ablation with longer UV wavelength lasers at modest fluence.

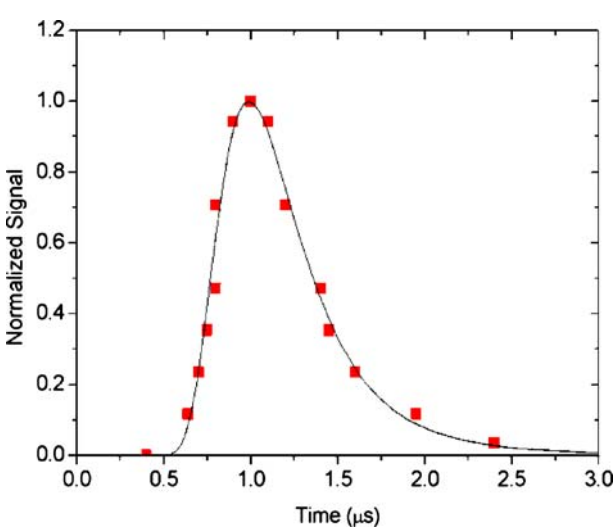


**FIGURE 10** (■) Ion current from experimental result for polyimide in Fig. 3. (–) Fit made using a Maxwell–Boltzmann distribution with mass/temperature ratio of $M/T = 7.69 \times 10^{-4}$ amu K$^{-1}$ and centre-of-mass velocity $u = 0.86 \times 10^4$ m s$^{-1}$

## 5 Discussion

Early work on UV laser polymer ablation mainly concentrated on physical characterization of the interaction for 308-, 248- and 193-nm laser exposure. This was subsequently complemented by more detailed mass spectroscopic and other chemically oriented analyses that shed further insight into the processes involved, notably for polyimide [1, 20] but also for TP6 at 248 nm and 308 nm [21] and for GAP at longer wavelengths [22]. The decomposition of these polymers was also studied by mass spectrometry at an irradiation wavelength of 157 nm [5], revealing that all three decompose into neutral and ionic species with mass < 50 amu. GAP and the triazene polymer TP6 have in common that one of the main fragments is $N_2$ in neutral and ionic form, where the latter is not observed for longer irradiation wavelengths. For Kapton HN a fragment with mass 28 is also among the strongest products, but it can be assigned in this case to CO.

It is generally accepted that for UV laser ablation of inorganic and organic substrates ionization plays only a modest role at least for fluences below typically the few-J cm$^{-2}$ level [6, 8, 23]. In the present work, ablating polyimide, GAP and TP6 using the 157-nm $F_2$ laser, ion signals were detected at fluences down to at least as low as that for significant ablative material removal from the surface (ablation threshold $\sim$ 20–30 mJ cm$^{-2}$). Here the term 'significant' is used because for polymers like polyimide there may not be a true threshold for removal, although at shorter wavelengths this does become more sharply defined [24]. The 'threshold' is then set by the accuracy with which the experiment is able to resolve mass removal. Likewise, although extrapolation of ion data at low fluence gives indicative 'thresholds' of $\sim 14.5 \pm 2.0$, $18.5 \pm 1.0$ and $28 \pm 4.0$ mJ cm$^{-2}$ for TP6, GAP and polyimide, respectively, more sensitive detection would likely reveal ions to be present at lower fluences.

It has been found that the experimental ion yield scaling can be described quite well by an elementary model in which ablated species are produced by a threshold Beer's law type mechanism and ionized by two-photon absorption. This scaling applies equally well to all three polymers studied even though these have very different properties. This appears reasonable, however, given that two $F_2$ laser photons, with $2h\nu = 15.8$ eV, should provide sufficient energy to ion-

ize the small mass fragments that appear in the plume. The species observed, e.g. $N_2$, CO, CHN, CN, $C_2H_2$, $C_2H$, $CH_2$ and $CH_3$ among others, have $I_p < 15.8$ eV [25, 26] and at least from an energetic standpoint can be ionized by two photons. The agreement provided by this simple model suggests that two-step ionization is dominant in the $F_2$ laser surface/plume interaction. This likely occurs via sequential steps in the species generated by the VUV laser ablation and is consistent with the predominant species having ionization potential $I_p > h\nu = 7.9$ eV but $I_p < 2h\nu = 15.8$ eV. For polyimide the results show that the ions have a strongly forward peaked distribution and that, at a modest fluence of $\sim 1100$ mJ cm$^{-2}$, the ratio of total number of ions to neutral species has a value of $\sim 0.2\%$ assuming 30 amu for the average mass of products. The temporal variation of ion current was found to be closely described by a Maxwell–Boltzmann distribution superimposed on a centre-of-mass velocity.

The results obtained when ablating these polymers with the 157-nm laser differ from those for longer UV wavelengths of 248 and 308 nm, where a substantial fraction of ions is only detected at fluences in the several-J cm$^{-2}$ range. The propensity for more extensive polymer fragmentation and the photogeneration of ions at low fluence make the $F_2$ laser interaction of considerable interest for further basic studies.

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