SURFACE STRUCTURING OF KAPTON POLYIMIDE WITH FEMTOSECOND AND PICOSECOND IR LASER PULSES

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Pulsed laser ablation is one of the most efficient and clean methods for high-precision processing and modification of polymers and biomaterials. Polymer ablation has been extensively investigated with ultraviolet lasers while little attention has been given to the infrared (IR) region, which becomes particularly interesting with the recent advances in ultrashort laser technologies. Here, we report the results of a comparative study on 1030-nm ultrashort laser structuring of Kapton polyimide, a polymer important in a variety of applications, with direct comparison of 247-fs and 7-ps laser pulses. The laser-induced damage thresholds for both pulse durations have been determined and the femtosecond laser threshold has been found to be considerably lower than that for picosecond pulses (by a factor of $\sim 3.5$). Both femtosecond and picosecond laser-produced craters have been thoroughly investigated as a function of pulse energy and focusing conditions. It has been demonstrated that femtosecond laser pulses enable accurate polyimide structuring while picosecond irradiation regimes result in a number of undesired effects such as re-deposition of the ablation debris, surface swelling, and the formation of high rims around the ablation craters. The mechanisms of polyimide ablation with femtosecond and picosecond IR laser pulses are discussed.

KEY WORDS: polymers, polyimide, ultrashort laser pulses, laser processing, laser ablation, damage threshold, crater profile, swelling, multiphoton absorption

1. INTRODUCTION

Since the first successful demonstration of laser ablation of polymers (Srinivasan and Mayne-Banton, 1982; Kawamura et al., 1982) laser polymer processing has become an important field of applied and fundamental research. Laser-processed polymers are presently found in a great variety of applications such as electronics, nonlinear optics, sensing and printing devices, microfluidics, biological and medical applications, and many others (Millon et al.,
Extensive studies of the mechanisms of polymer laser ablation have revealed the very complicated behavior of irradiated material, which involves chemical reactions and thermal, photophysical, and mechanical processes, both in the polymer bulk and on the surface. This has resulted in a variety of polymer ablation models based mainly on photothermal or photochemical mechanisms (Andrew et al., 1983; Luk’yanchuk et al., 1997; Arnold and Bityurin, 1999; Bityurin and Malyshnev, 2002; Urech and Lippert, 2010), although thermomechanics-based models have also been proposed (Malyshnev and Bityurin, 2005). However, there is still an ongoing discussion about which mechanism dominates under specific irradiation conditions.

A large part of the research on polymer laser processing has been carried out with polyimides, mainly with a film version of Kapton due to its importance in a variety of applications. Kapton possesses outstanding characteristics such as high thermal stability (up to 450°C), superior chemical resistance, high mechanical strength, low dielectric constants, biocompatibility, and strong adhesion to most superconductors (Sroog, 1976; Ortelli et al., 2000; Teo et al., 2016). The chemical structure of Kapton [poly(4,4′-oxydiphenylene-pyromellitimide)] is illustrated in Fig. 1. Laser processing of polyimide is a key process in a number of its applications such as organic electronics on flexible substrates (Gallias et al., 2014), microvia formation in microelectromechanical/nanoelectromechanical systems and metallization technologies (Zheng et al., 2001; Roeger, 2011), microfluidics (Gómez et al., 2005), reducing the triboelectric charging (Guo et al., 2015), ink-jet printers (Urech and Lippert, 2010), and producing cell scaffolds (Antanavičiūtė et al., 2018). It has been recently demonstrated that laser irradiation of polyimide is a promising method for efficient surface carbonization (Inada et al., 2015) and graphene production (Lin et al., 2014; Carvalho et al., 2018). Polyimide can be considered as a model system for biomaterials (Richardson et al., 1993), and thus it is used to study the biotissue response on laser irradiation in medical applications, e.g., in corneal sculpting (Haq et al., 2015).

Most experiments on polyimide laser processing have been performed with nanosecond excimer lasers at ultraviolet (UV) wavelengths, where the material shows strong linear absorption. At the same time, due to the relatively long pulse duration, the material often suffers from thermal damage around the irradiation zone, resulting in relatively poor edge quality (Kumagai et al., 1994; Urech and Lippert, 2010; Roeger, 2011). Ultrashort (femtosecond and picosecond) laser pulses offer unique advantages for polymer structuring, which include negligible heat-affected zones, low-threshold laser fluences, and the absence of plasma shielding effects. High-quality structures have been produced in polymers with femtosecond UV laser pulses (Adhi et al., 2004; Gómez et al., 2005). With advances in ultrashort laser technologies, great interest has been raised in relation to infrared (IR) laser processing of polymers, which would allow using conventional ultrashort titanium:sapphire and ytterbium:glass lasers without the need for upconversion of frequency from IR to UV wavelengths. Although most polymers (including polyimide) are transparent in the IR range, they exhibit remarkably efficient multiphoton absorption due to the high intensity of ultrashort pulses (Kumagai et al., 1994; Urech and Lippert, 2010). Recently, femtosecond IR laser pulses have been successfully applied to polyimide surface structuring (Haq et al., 2015; Antanavičiūtė et al., 2018). However, detailed analysis of the crater quality produced by IR ultrashort laser pulses in the polyimide surface is still lacking and no direct comparison has been performed between femtosecond and picosecond laser pulses.

In this paper, we report the results of a comparative study on IR ablation of Kapton using femtosecond and picosecond laser pulses under single-shot irradiation conditions. The laser-induced damage thresholds for both cases are measured and the produced crater profiles are investigated. It is demonstrated that the femtosecond threshold is considerably lower than the picosecond threshold (by a factor of ~3.5), and the crater shapes produced with femtosecond and picosecond pulses differ dramatically. The results indicate that different ablation mechanisms are involved in these two irradiation regimes.

![Chemical structure of polyimide (Kapton HN)](image)
2. EXPERIMENTAL DETAILS

The material used in the ablation experiments was the polyimide DuPont Kapton HN (125-µm-thick films supplied by Goodfellow). The irradiation was performed by a PHAROS laser (Light Conversion, Vilnius, Lithuania) providing Gaussian pulses at a wavelength of $\lambda = 1030$ nm with maximum pulse energy of 1 mJ at a 3-kHz repetition rate. The laser was operated in femtosecond and picosecond modes with pulse durations, $\tau$, of 247 fs and 7 ps, respectively. The laser beam was focused on the sample surface by a focal lens at normal incidence, as shown schematically in Fig. 2. The pulse energy was varied in the range of 20–750 µJ using a beam attenuator consisting of a $\lambda/2$ plate and a polarizing cube beam splitter. The pulse energy was monitored with a thermal power sensor Ophir-12A-P placed after the lens. In order to investigate the effect of the irradiation spot size on polyimide ablation, three lenses with different focal lengths, $f$, of 150, 300, and 500 mm were used in the experiments. For every lens, the sample was located in the corresponding focus, and thus the theoretical spot radius, $w_{0,th}$ (the beam waist defined by the $1/e^2$ criterion), can be estimated according to Gaussian beam optics (Saleh and Teich, 1991) as

$$w_{0,th} = \frac{2\lambda}{\pi D} M^2$$

where $D$ is the beam diameter at the laser output, and $M^2$ is the beam quality factor. For our conditions ($D \sim 5$ mm, $M^2 = 1.1$), we have $w_{0,th}$ of $\sim 22$, 43, and 73 µm for the 150-, 300-, and 500-mm lenses, respectively. All experiments were performed under single-shot irradiation conditions in order to separate the basic ablation mechanisms from accumulation effects due to multiple pulse irradiations. The laser-produced spots on the Kapton surface (damaged area and ablation crater profile) were analyzed using an optical microscope (Olympus-BX43) and a laser confocal microscope (LEXT OLS4000).

3. RESULTS AND DISCUSSION

The determination of the laser-induced damage threshold was based on measurements of the damaged spot area, $S$, as a function of the laser pulse energy, $E_0$, using the $D^2$ method (Liu, 1982; Starinskiy et al., 2017). The method uses the following relationship between $S$ and $E_0$ for Gaussian beams:

$$\frac{S}{S_{\text{eff}}} = \ln \left( \frac{E_0}{E_{\text{th}}} \right)/2$$

where $S_{\text{eff}} = \pi w_0^2$ is the actual effective cross-sectional area of the beam on the surface (the $1/e^2$ criterion), and $E_{\text{th}}$ is threshold energy (the minimal pulse energy needed to produce visible modification on the sample surface). Therefore, by plotting the measured $S$ values versus the logarithm of the pulse energy, one can obtain a linear dependence that gives the possibility of determining both the effective spot area and the threshold energy. Correspondingly, the peak threshold fluence, $F_{\text{th}}$, can be calculated as $F_{\text{th}} = 2E_{\text{th}}/S_{\text{eff}}$.

Figure 3 shows optical images of typical spots produced on the Kapton surface by femtosecond and picosecond laser pulses at several identical energies with the 300-mm focal lens. Similar data were obtained for the other lenses. The spot edges are quite sharp, enabling unequivocal determination of the spot area. A remarkable feature of the spot shape evolution with increasing $E_0$ values is observed for the femtosecond-produced spots. At sufficiently high pulse energies, the originally circular spots become elliptical with the major axis oriented along the polarization vector of our linear-polarized laser light. Similar polarization-dependent crater elongation was observed previously

![FIG. 2: Experimental setup: the Kapton target was placed on a xyz-stage (HW, PBS, and BD denote the half-wave plate, polarizing-cube beam splitter, and beam damper, respectively)](image-url)
in femtosecond single-shot laser ablation of poly(methyl methacrylate) in the fluence range of 4–20 J/cm$^2$ that was explained by the interaction of the laser pulse with the solid-state plasma produced by the leading edge of the pulse (Guay et al., 2012). This light–plasma interaction leads to local field enhancement parallel to the laser polarization if the plasma density is above a critical value. Violation of the laser beam symmetry was also obtained in simulations of the propagation of a linear-polarized femtosecond pulse in transparent dielectrics (Bulgakova et al., 2014). We believe that the elongation observed here for femtosecond-produced spots on the Kapton surface is also due to the interaction of the laser light with the transient plasma produced by the leading edge of our 247-fs pulse. The threshold fluence for the spot elongation was found to be around 2 J/cm$^2$, which corresponds to a peak intensity of $8 \times 10^{12}$ W/cm$^2$. However, the spots produced with picosecond pulses were round in shape in the entire studied range of the pulse energy (Fig. 3). This indicates that the elongation effect is rather intensity dependent, not fluence dependent.

Figure 4 shows the measured damaged area as a function of pulse energy for femtosecond and picosecond laser irradiation of Kapton using the 300-mm focal lens. The experimental points yielded good straight line fits in the semilog plots, thus confirming the Gaussian profile of the laser pulses. The slopes of the linear fits provided the effective spot radii, which were nearly identical for the femtosecond and picosecond pulses (48.7 and 44 µm, respectively) and corresponded well to the theoretical beam waist value of $w_{0,th} \approx 43$ µm for the 300-mm lens. Similar
results were obtained with the other lenses. However, the threshold pulse energies (determined from the intercepts of the linear fits with the horizontal axis) differed dramatically for the femtosecond and picosecond pulses. In the latter case, the \( E_{th} \) value was larger by a factor of \( \sim 3.5 \) (Fig. 4). When averaging over measurements with the three lenses, the corresponding threshold fluences were found to be \( F_{th} = (0.66 \pm 0.04) \text{ J/cm}^2 \) for the femtosecond pulses and \( F_{th} = (2.35 \pm 0.1) \text{ J/cm}^2 \) for the picosecond pulses. Assuming a power-law scaling of the threshold fluence with the pulse duration, \( F_{th} \propto \tau^\alpha \) (Wood, 1986), we obtain \( \alpha = 0.38 \). This indicates that the Kapton damage mechanism under the considered conditions is different from conventional melting when the diffusion-dominated \( \tau^{1/2} \) scaling is expected (Wood, 1986). Note that a similar deviation from the \( \tau^{1/2} \) scaling was observed in the dielectrics irradiated by ultrashort laser pulses at \( \tau \leq 10 \text{ ps} \) (Stuart et al., 1995).

To obtain further insight into the Kapton ablation mechanisms with ultrashort laser pulses, we performed a thorough investigation of the final crater profiles. The results are summarized in Figs. 5 and 6. In Fig. 5 (left-hand side), a comparison of the crater profiles for the femtosecond and picosecond pulses is presented for the three lenses at the fixed pulse energy of 270 \( \mu \text{J} \). Figure 6 demonstrates the evolution of the crater profiles with the pulse energy for the 150-mm focal lens. On the right-hand side in Fig. 6, the corresponding three-dimensional (3D) and two-dimensional (2D) images are shown. From Figs. 5 and 6 it can be concluded that the femtosecond laser pulses are much more suitable for high-precision Kapton processing. The craters produced by the femtosecond pulses have accurate, almost rimless profiles, and a negligible amount of ablated material is redeposited around the craters. On the contrary, the picosecond laser pulses produce high rims around the ablated area. The height of the rims is comparable with the

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**FIG. 5:** Crater profiles (left) and corresponding 3D and 2D images of the damaged areas (right) resulting from femtosecond and picosecond irradiation of Kapton with 500-, 300-, and 150-mm lenses at a fixed laser pulse energy of 270 \( \mu \text{J} \) (the corresponding peak fluences are 3.2, 8.5, and 27 J/cm\(^2\))

**FIG. 6:** Crater profiles (left) and corresponding 3D and 2D images of the damaged areas (right) resulting from femtosecond and picosecond irradiation of Kapton with a 150-mm focal lens at different pulse energies

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depth of the craters. It is also seen that in the picosecond irradiation regime with the 500-nm lens at this particular laser energy ($F = 3.2$ J/cm$^2$), surface swelling is observed instead of a crater. Additionally, redeposited material fragments are abundant on the irradiated surface inside and beyond the ablated area and the crater bottoms are rough.

Analysis of the obtained crater profiles revealed several remarkable features that provided valuable information, both direct and indirect, about the ablation mechanisms involved. First, the ablation depths for femtosecond and picosecond laser pulses at fairly high pulse energy, well above the threshold energies, were nearly identical ($\sim 0.25\ \mu$m in both cases at 135 $\mu$J, i.e., at $\sim 17$ J/cm$^2$, see Fig. 6) despite the strong difference in the damage thresholds. This suggests different mechanisms of material removal with femtosecond and picosecond pulses. Second, the laser-induced swelling observed for picosecond pulses is a known phenomenon in polymer ablation, which is attributed to heating of an extended surface layer (Masubuchi et al., 2002; Malyshev and Bityurin, 2005); this is a clear indication of a thermal ablation mechanism (Hauer et al., 2004). In contrast, the absence of swelling in the femtosecond laser irradiation regimes indicates the rather non-thermal nature of light absorption, plausibly with the dominance of multiphoton excitation of the material. Finally, analysis of the femtosecond-produced craters demonstrated a very weak fluence dependence of the crater depth. Thus, increasing the pulse energy from 70 to 270 $\mu$J under fixed focusing conditions leads to a less than twofold increase in the crater depth (Fig. 6). For ultrashort pulses, when the beam attenuation by the ablation plasma is negligible, such a weak dependence indicates the presence of nonlinear effects such as chromophore saturation and multiphoton absorption (Pettit and Sauerbrey, 1993; Kumagai et al., 1994). For our 1030-nm photons, we can expect a 4–5 photon absorption process since the linear absorption coefficient of polyimide shows a strong decrease in the wavelength range of 200–250 nm (Urech and Lippert, 2010).

Based on the aforementioned considerations, processes occurring during ultrashort laser ablation of polyimide can be generally described as follows (Fig. 7). At picosecond laser pulses [Fig. 7(a)], due to relatively low peak intensities, absorption of the laser energy takes place in an extended surface layer. Polymer expands in the heated region and is extruded above the initial surface level by the laser-induced stress already at the laser fluences when the ablation threshold is not yet reached (Malyshev and Bityurin, 2005), resulting in swelling of the irradiated surface instead of a crater [picture 2 in Fig. 7(a)]. At higher laser fluences, ablation of superficial surface layers starts and the recoil pressure of the ablation plume squeezes the extended softened/molten material to the periphery with the formation of a high rim around the crater [picture 3 in Fig. 7(a)]. Due to hydrodynamic instabilities typical for viscous liquid relocation under recoil pressures, the bottom of the resulting crater is not smooth (Fig. 5, picosecond pulses). At femtosecond laser pulses due to high laser intensity, nonlinear absorption of laser light leads to the formation of a thin skin layer, where the material is substantially heated and ablated [Fig. 7(b)]. Since the hot layer is very thin, only a small amount of softened material can be squeezed to the periphery by the recoil pressure of the ablation plume and hydrodynamic instabilities do not develop, thus leading to the high quality of the ablation craters (Fig. 5, femtosecond pulses).

FIG. 7: Schematics of the laser damage and ablation of Kapton by picosecond (a) and femtosecond (b) laser pulses (pictures 1 and 4 show laser absorption events; pictures 2, 3, and 5 illustrate processes after the pulse termination; the picosecond laser fluence in picture 2 is lower than that in picture 3; see the text for details)
4. CONCLUSIONS

Ultrashort IR laser irradiation of polyimide films (Kapton) was performed to gain insight into the laser modification of the surfaces of this material for future studies of its possible applications. At fairly high laser intensity, above a threshold value of about $8 \times 10^{12}$ W/cm$^2$, elongation of the originally circular laser spots at the surface along the pulse polarization is observed, presumably due to the interaction of the laser light with the transient solid-state plasma. The laser-induced damage thresholds of Kapton have been determined for picosecond and femtosecond laser pulses, and the latter is found to be considerably larger, by a factor of $\sim 3.5$. Inspection of the crater profiles obtained in the picosecond and femtosecond irradiation regimes has shown that femtosecond laser pulses are advantageous for precision processing of the material surface. Femtosecond laser processing of Kapton produces much more accurate crater shapes compared to picosecond laser irradiation, while the depth of the craters is approximately the same for both the femtosecond and picosecond modes. The obtained data are of general importance in understanding the polymer response to laser irradiation with different pulse durations, representing interest from the viewpoint of polymer nanoparticle fabrication (Bulgakova et al., 2009), and will be used as a model example for our future works devoted to investigating laser modification of biopolymers and tissues.

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