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## Ultraviolet and infrared femtosecond laser induced periodic surface structures on thin polymer films

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This work demonstrates the formation of femtosecond laser induced periodic surface structures (LIPSS) by multipulse irradiation with the fundamental and 3rd harmonic of a linearly polarized Ti:sapphire laser (795 and 265 nm) on thin films of the polymers poly (ethylene terephthalate), poly (trimethylene terephthalate), and poly (carbonate bisphenol A) prepared by spin-coating. LIPSS, inspected by atomic force microscopy, are formed upon multiple pulse UV and IR irradiation with wavelength-sized period in a narrow range of fluences below the ablation threshold. Control and tunability of the size and morphology of the periodic structures become thus possible ensuring photochemical integrity of polymer films. © 2012 American Institute of Physics. [doi:10.1063/1.3679103]

The formation of laser induced periodic surface structures (LIPSS) at fluences,  $F$ , near the ablation threshold has been observed by many authors since the early investigations of the laser ablation phenomenon four decades ago.<sup>1</sup> Ripples were first reported in semiconductors<sup>1</sup> and subsequently studied in many homogeneous dielectrics<sup>2</sup> and metals<sup>3</sup> under nanosecond (ns) irradiation. In ns-LIPSS the periodicity is of the order of the laser wavelength,  $\lambda$ , and depends on the angle of incidence of the laser beam on the material surface. Their formation is explained on the basis of the interference between the incident laser light wave and surface-scattered waves created during irradiation.<sup>4</sup>

More recently, LIPSS induced by femtosecond (fs) pulses have been extensively studied in metals,<sup>5</sup> dielectrics,<sup>6</sup> and semiconductors.<sup>7,8</sup> Despite the great amount of studies on formation of LIPSS on polymers using pulses of few ns (Refs. 9–14) at fluences both below<sup>9–13</sup> and above<sup>14</sup> ablation threshold, few references report on fs-LIPSS on polymeric materials,<sup>15,16</sup> where ripples have been observed at the bottom of ablation craters, and detailed studies have yet to be performed. Polymers, as soft matter, have interest for nanoscience and nanotechnology and in particular, nanostructured polymers are applied in nano-electronics, in plastic solar cells, medical implants, biosensors, and biochips.

In the case of fs-LIPSS, together with the classical mechanism of interference between the incident light and the scattered waves,<sup>4,17</sup> self-organization from instabilities was stated to account for the formation of LIPSS.<sup>18,19</sup> In this mechanism, the high degree of surface instabilities induced by irradiation relax through two competing processes of surface roughening and smoothing. On one hand, surface roughening occurs as a result of ion emission while smoothing is caused by self-diffusion. Theoretical attempts to describe

this behavior are based on well-known hydrodynamical models<sup>20</sup> and on the Sipe-Drude model,<sup>21,22</sup> which considers the laser-induced changes in the complex refractive index due to the transient generation of quasi-free electrons in the conduction band of the solid. Notwithstanding these efforts, a comprehensive understanding of the mechanism for the formation of self-organized structures under fs irradiation has not been fully achieved to date.

In this work, we have investigated the formation of LIPSS with fs pulses at the wavelengths 795 and 265 nm on thin films of the polymers, poly (ethylene terephthalate) (PET) (Rhodia S80 from RhodiaSter), poly (trimethylene terephthalate) (PTT) (Ref. 23), and polycarbonate bisphenol A (PC) (Lexan ML3021A, SABIC I-P (Innovative Plastics)). Prior to irradiation, the linear absorption coefficients of the films were determined by UV-Vis absorption spectroscopy, resulting in values of around  $2 \times 10^4 \text{ cm}^{-1}$  at 265 nm and 20–50 times lower at 795 nm. LIPSS were created on the polymer films of ca. 150 nm thickness prepared by spin-coating, as previously described,<sup>13</sup> supported by silicon wafers (100).

Laser irradiation was carried out in ambient air with the linearly polarized output of a system consisting of a Ti:sapphire oscillator (Tsunami, Spectra Physics) and a regenerative amplifier system (Spitfire, Spectra Physics) based on the chirped pulse amplification technique. The system produces 120 fs pulses at 795 nm with a repetition rate of 1 kHz. The pulse energy is finely controlled by a half-wave plate and a linear polarizer. Neutral density filters were used for further energy reduction. The average power of the beam was measured with a thermopile detector (407 A, Spectra Physics). The transversal mode is nearly a Gaussian TEM<sub>00</sub> with a 10 mm beam diameter (at  $1/e^2$ ). The second harmonic of the fundamental laser output (398 nm central  $\lambda$ ) was generated in a 1 mm thick beta barium borate (BBO) crystal (type-I,  $\theta = 29^\circ$ ), and the third harmonic (265 nm central  $\lambda$ ) was obtained in a second BBO

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crystal (1 mm thick, type-I,  $\theta = 44^\circ$ ) by sum-frequency mixing of the fundamental and second harmonic beams. An estimation of the temporal duration of the 265 nm pulses is 260 fs (taking into account the group-velocity mismatch of the interacting pulses within the crystal).

For irradiation of samples, the fs laser beam impinged perpendicularly onto the target surface which was placed on a motorized XYZ translation stage. The pulses were focused on the surface by a biconvex, achromatic spherical lens with a focal length of 100 mm, in the case of irradiation at 795 nm, and an uncoated fused silica plano-convex spherical lens with a focal length of 100 mm, for irradiation at 265 nm. The number of laser shots applied to the sample,  $N$ , was selected by an electromechanical shutter.

The topography of the polymer films was examined by atomic force microscopy (AFM, Nanoscope IIIA Multimode, Veeco) in tapping mode and images were analysed with the software NANOSCOPE ANALYSIS 1.10. The original spin coated samples present a flat surface, with mean roughness values  $\leq 1$  nm. The periods and heights of LIPSS were determined from AFM analysis by averaging the results of three different areas per sample. Values of the period were derived from fast Fourier transform (FFT) analysis.

The dependence of period and height of the ripples on  $F$  and  $N$  was determined. Figures 1(a)–1(c) show AFM topography images of the structures induced on PC upon irradiation with 5000 pulses of 265 nm, at  $F$  below the ablation threshold, in the range of 1.0–2.4 mJ/cm<sup>2</sup>. The onset of LIPSS formation takes place at about 1.0 mJ/cm<sup>2</sup> (Figure 1(a)). Good quality ripples, parallel to the polarization direction, were observed at increasingly higher  $F$  until the periodic structures start to distort at approximately 1.9 mJ/cm<sup>2</sup> (Figure 1(b)). Finally, disruption and ablation of the polymer film takes place at even higher  $F$ , as seen for 2.4 mJ/cm<sup>2</sup> in Figure 1(c). The period of the structures, as obtained from the FFT analysis of the images, and their height, are plotted in Figure 2(a). It is observed that both magnitudes increase with  $F$  until a plateau is reached at ca. 1.5 mJ/cm<sup>2</sup>. The final period is of the order of  $\lambda$ . Similar results were also obtained for PET and PTT in the same range of  $F$ . It has to be noticed

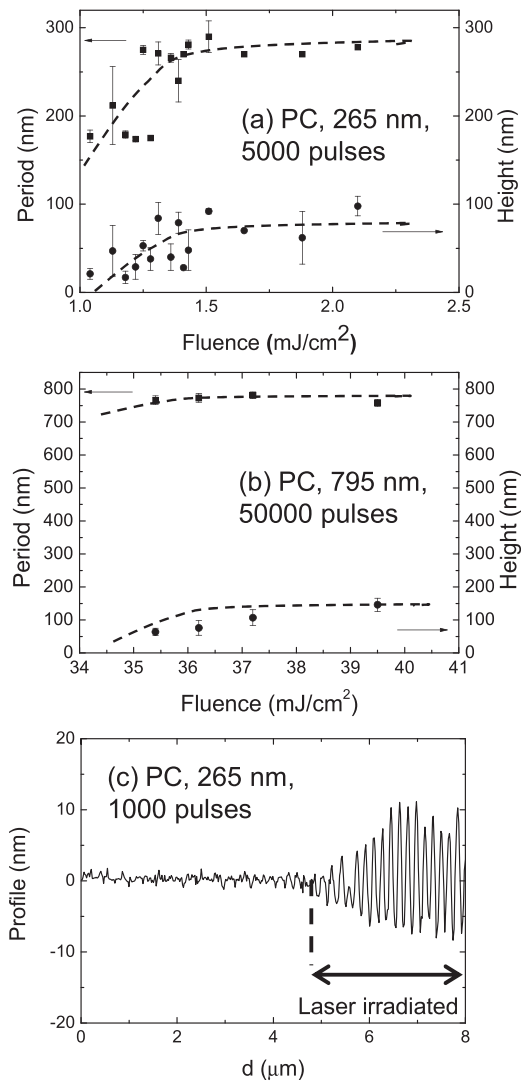


FIG. 2. Period and amplitude of LIPSS as a function of the laser fluence formed by irradiation with: (a) 5000 pulses of 265 nm and (b) 50 000 pulses of 795 nm; (c) AFM profile of the boundary between a non-irradiated and an irradiated area of PC using 1000 pulses of 265 nm at 1.2 mJ/cm<sup>2</sup>. Lines are visual guides.

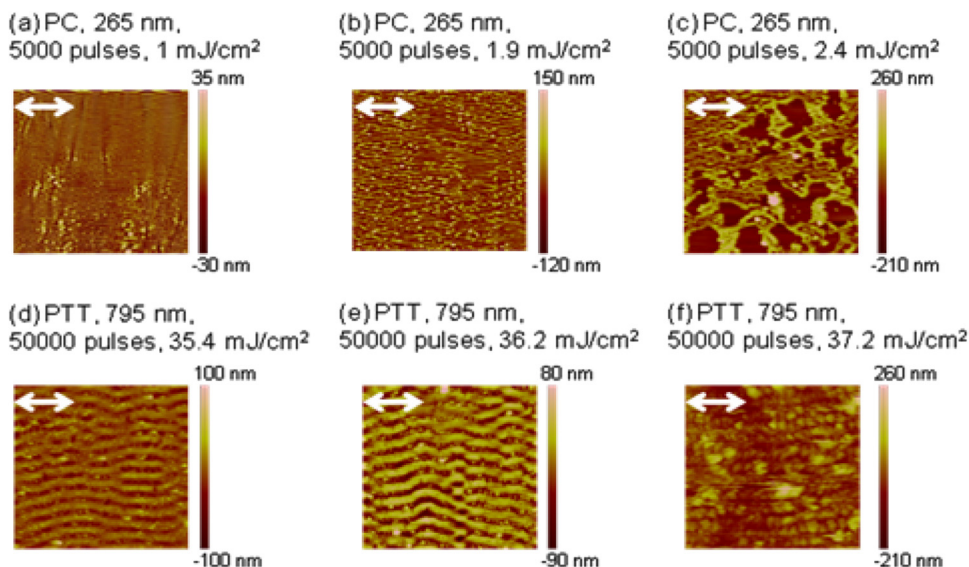


FIG. 1. (Color online) AFM topography images of PC irradiated at 265 nm and PTT irradiated at 795 nm at the indicated fluences and number of pulses. The arrows indicate the polarization direction.

that irradiation of the polymer films with pulses of 6 ns at 266 nm also yielded LIPSS with wavelength-sized period.<sup>13</sup>

The dependence of LIPSS dimensions on  $N$  for a constant  $F$  was also evaluated. It was observed that in the range of  $F$  studied (1.0–2.4 mJ/cm<sup>2</sup>)  $N$  needed for LIPSS formation is higher for lower  $F$ , which reveals that a feedback mechanism must be involved in LIPSS formation, as it is also accepted for irradiation with ns pulses.<sup>13</sup> Again, both the period and the amplitude of the structures increase with  $N$  until a plateau is reached after a few thousand pulses.

LIPSS were also observed upon irradiation at 795 nm in a narrow range of  $F$ . Figure 1(d)–1(f) show AFM images of PTT irradiated with 50 000 pulses of 795 nm at different  $F$  values. LIPSS parallel to the polarization direction are clearly observed at 35.4 and 36.2 mJ/cm<sup>2</sup>, but irradiation at 37.2 mJ/cm<sup>2</sup> causes distortion of the polymer thin film structure and higher  $F$  induce polymer ablation. The period and height of ripples as a function of  $F$  are shown in Figure 2(b). The period is again of the order of  $\lambda$ , and their amplitude is systematically larger than in the case of UV irradiation. The dependence of ripple parameters with  $N$  was also studied when the films were irradiated in the IR and the main difference with the results obtained upon UV irradiation concerns the larger  $N$  needed to induce the periodic structures, which in this case is some tens of thousands.

It is important to stress the fact that the observed LIPSS were not created at the bottom of ablation craters. In fact, the AFM analysis of the boundary between a non-irradiated and an irradiated area, Figure 2(c), shows that the peaks and valleys of the ripples lie, respectively, above and below the initial surface. The figure also shows that the height of the untreated surface is equivalent to the average height of the nanostructured region of the polymer film. This confirms that the amount of material removed during laser irradiation is negligible and that the structures originate from a self-organization process and not caused by ablation.

Previous studies by some of us in the ns regime<sup>13</sup> have shown that efficient absorption of laser light by the polymer film is essential to induce LIPSS formation. In fact, it was not possible to generate LIPSS on the polymer films studied herein by irradiation with ns pulses of 532 nm in a wide range of  $F$  (up to 120 mJ/cm<sup>2</sup>). As mentioned above, 265 nm radiation is efficiently absorbed by the films, while at 795 nm the absorption is negligible. However, upon irradiation with fs pulses, due to the large laser intensities involved, multiphoton absorption and ionization processes mediate the coupling of laser light with the outer layer of the films at the long irradiation  $\lambda$ . In fact, the contribution of multiphoton (MP) processes can be assessed by calculating the adiabaticity parameter,  $\gamma$ , introduced by Keldysh<sup>24</sup>

$$\gamma = \left( \frac{E_i}{1.87 \cdot 10^{-13} I \lambda^2} \right)^{1/2}$$

where  $E_i$  is the molecular ionization potential (in eV),  $I$  the peak laser intensity (in W cm<sup>-2</sup>), and  $\lambda$  is given in  $\mu$ m. Assuming a ionization potential of around 7 eV,<sup>25,26</sup>  $\gamma$  is around 15 at 795 nm and 400 at 265 nm for the fluences used for LIPSS formation. These values, well above 1, are indicative of a MP ionization mechanism governing the initial light

absorption step and accounting for LIPSS formation on the outer layer of the films. The somehow smaller height of the structures upon irradiation at 265 nm can be explained by the more effective absorption at this  $\lambda$ , suggesting that absorption is confined onto the outer layer of the material.

Regarding the ensuing thermal effects induced by laser irradiation, it has been previously shown in the case of polymer films irradiated with ns pulses, that the temperature increase needed for LIPSS formation should be above the glass transition temperature and below the melting temperature of the material, as the formation of this kind of structures is ruled by a surface instead of a bulk process.<sup>13</sup> In the fs regime, the temperature increase reached in the sample after irradiation with a single laser pulse can be calculated by (Ref. 27)  $\Delta T = \varepsilon / (\rho_0 C_p)$ , where  $\varepsilon$  is the plasma energy density at the end of the laser pulse and  $\rho_0$  and  $C_p$  are, respectively, the density and the heat capacity of the material. The plasma density is given by  $\varepsilon = \rho_{cr} (9/4) E_i$ ,  $\rho_{cr}$  being the critical free electron density needed to generate both a strongly reflective and absorbing plasma. Following (Ref. 28)  $\rho_{cr} = (2\pi/\lambda)^2 m_e \varepsilon_0 / e^2$ , with  $\varepsilon_0$  the vacuum dielectric permittivity,  $m_e$  the mass of the quasi-free electron in the conduction band and  $e$  the electron charge.

For a given polymer,  $\Delta T$  should be an order of magnitude higher in the case of irradiation at 265 nm. This can explain why a larger  $N$  and higher  $F$  are needed for LIPSS formation upon fs irradiation at 795 nm. The fact that multiple pulses are needed for LIPSS formation indicates the important role of a feedback mechanism in the ripple formation process. Differences among the LIPSS formed in the three polymers are not significant since no large differences in values of  $C_p$ ,  $\rho_0$  and  $E_i$  exist.<sup>13,25,26</sup> It is also important to note that irradiation at higher  $F$  or  $N$  induces modifications not only within the outer, superficial layer of the films but also in the bulk. In this case, heating above melting temperature can be the factor responsible for polymer dewetting as it is evident in Figure 1(c).

In summary, the results presented show the possibility of tuning and controlling the morphology and size of the periodic structures in the fs regime by changing  $\lambda$  and the irradiation parameters. Full characterization of the chemical modifications induced upon fs irradiation, expected to be reduced in comparison to the ns case, is in progress in order to develop the applications of periodically nanostructured synthetic and natural polymers.

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<sup>1</sup>M. Birnbaum, *J. Appl. Phys.* **36**, 3688 (1965).

<sup>2</sup>J. F. Young, J. E. Sipe, J. S. Preston, and H. M. Van Driel, *Appl. Phys. Lett.* **41**, 261 (1982).

<sup>3</sup>J. F. Young, J. S. Preston, H. M. van Driel, and J. E. Sipe, *Phys. Rev. B* **27**, 1155 (1983).

<sup>4</sup>J. E. Sipe, J. F. Young, J. S. Preston, and H. M. van Driel, *Phys. Rev. B* **27**, 1141 (1983).

<sup>5</sup>A. Y. Vorobyev and C. Guo, *Appl. Phys. A* **86**, 321 (2007).

<sup>6</sup>T. Z. Kosci, A. A. Kozlov, and A. W. Schmid, *Opt. Express* **14**, 10921 (2006).

- <sup>7</sup>O. Varlamova, F. Costache, M. Ratzke, and J. Reif, *Appl. Surf. Sci.* **253**, 7932 (2007).
- <sup>8</sup>J. Reif, M. Ratzke, O. Varlamova, and F. Costache, *Mater. Sci. Eng. B* **134**, 114 (2006).
- <sup>9</sup>M. Bolle, S. Lazare, M. Le Blanc, and A. Wilmes, *Appl. Phys. Lett.* **60**, 674 (1992).
- <sup>10</sup>M. Csete and Z. Bor, *Appl. Surf. Sci.* **133**, 5 (1998).
- <sup>11</sup>P. Slepíčka, E. Rebolgar, J. Heitz, and J. Švorčík, *Appl. Surf. Sci.* **254**, 3585 (2008).
- <sup>12</sup>E. Rebolgar, I. Frischauf, M. Olbrich, T. Peterbauer, S. Hering, J. Preiner, P. Hinterdorfer, C. Romanin, and J. Heitz, *Biomaterials* **29**, 1796 (2008).
- <sup>13</sup>E. Rebolgar, S. Pérez, J. J. Hernández, I. Martín-Fabiani, D. R. Rueda, T. A. Ezquerro, and M. Castillejo, *Langmuir* **27**, 5596 (2011).
- <sup>14</sup>P. E. Dyer and R. J. Farley, *Appl. Phys. Lett.* **87**, 765 (1990).
- <sup>15</sup>M. Forster, W. Kautek, N. Faure, E. Audouard, and R. Stoian, *Phys. Chem. Chem. Phys.* **13**, 4155 (2011).
- <sup>16</sup>S. Baudach, J. Bonse, and W. Kautek, *Appl. Phys. A* **69**, S395 (1999).
- <sup>17</sup>H. M. van Driel, J. E. Sipe, and J. F. Young, *Phys. Rev. Lett.* **49**, 1955 (1982).
- <sup>18</sup>J. Reif, O. Varlamova, M. Ratzke, M. Schade, and H. S. Leipner, *Appl. Phys. A* **101**, 361 (2010).
- <sup>19</sup>M. Schade, O. Varlamova, J. Reif, H. Blumtritt, and W. Erfurth, *Anal. Bioanal. Chem.* **396**, 1905 (2010).
- <sup>20</sup>M. Bestehorn and K. Neuffer, *Phys. Rev. Lett.* **87**, 046101 (2001).
- <sup>21</sup>J. Bonse and J. Krüger, *J. Appl. Phys.* **108**, 034903 (2010).
- <sup>22</sup>D. Dufft, A. Rosenfeld, S. K. Das, R. Grunwald, and J. Bonse, *J. Appl. Phys.* **105**, 034908 (2009).
- <sup>23</sup>A. Szymczyk, *Eur. Polym. J.* **45**, 2653 (2009).
- <sup>24</sup>L. V. Keldysh, *Sov. Phys. JETP* **20**, 1307 (1965).
- <sup>25</sup>N. R. Rajopadhye and S. V. Bhoraskar, *J. Mater. Sci. Lett.* **5**, 603 (1986).
- <sup>26</sup>D. Virgili, M. Cocchi, V. Fattori, C. Sabatini, J. Kalinowski and J. A. G. Williams, *Chem. Phys. Lett.* **433**, 145 (2006).
- <sup>27</sup>S. Gaspard, M. Oujja, R. de Nalada, C. Abrusci, F. Catalina, L. Bañares, S. Lazare, and M. Castillejo, *Appl. Surf. Sci.* **254**, 1179 (2007).
- <sup>28</sup>A. Vogel, J. Noack, G. Huttman, and G. Paltauf, *Appl. Phys. B* **81**, 1015 (2005).