

Surface modification of organic polymer by dual action of extreme ultraviolet/visible-near infrared ultrashort pulses

T. Mocek,^{1,a)} J. Polan,¹ P. Homer,¹ K. Jakubczak,¹ B. Rus,¹ I. J. Kim,^{2,b)} C. M. Kim,^{2,b)} G. H. Lee,² C. H. Nam,² V. Hájková,³ J. Chalupský,³ and L. Juha³

¹Department of X-ray Lasers, Institute of Physics ASCR, Na Slovance 2, Prague 8-182 21, Czech Republic

²Coherent X-ray Research Center, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

³Department of Laser Plasmas, Institute of Physics ASCR, Na Slovance 2, Prague 8-182 21, Czech Republic

(Received 30 September 2008; accepted 10 December 2008; published online 30 January 2009)

We present the experimental evidence of structural surface modifications of poly(methyl methacrylate) (PMMA) caused by simultaneous action of extreme ultraviolet (XUV) (~ 21 nm) and visible-near infrared (visible-NIR) (820/410 nm) ultrashort pulses. Although the fluence of each individual beam was far below the surface modification threshold, very efficient and specific material expansion was observed after irradiation of PMMA by more than ~ 20 shots of mixed XUV/visible-NIR radiation. As the XUV photons generate free charge carriers, absorption of the optical radiation dramatically increases, which heats up the material and further enhances the XUV induced damage to the polymer chain. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3072628]

The investigation of irreversible surface responses of various organic and inorganic solids to extreme ultraviolet (XUV) and soft x-ray radiation is currently motivated mostly by nanotechnology interests; see, for example, Refs. 1–3 and references cited therein. The main task is to realize short-wavelength ($\lambda < 100$ nm), direct nanostructuring of materials resistant to optical radiation. Several research groups have investigated the behavior of poly(methyl methacrylate) (PMMA) at short wavelengths under irradiation conditions both above^{2–4} and below^{1,5–7} its single-shot ablation threshold. Erosion of the organic polymer induced by high-energy photons was generally reported.^{1–7}

Here we demonstrate a highly effective method for structural surface modification of PMMA achieved by dual action of XUV, obtained from high harmonic generation (HHG), and visible-near IR (visible-NIR) ultrashort laser pulses. While the separate use of the visible-NIR or XUV beam did not cause any change to the sample surface, the application of a mixed XUV/visible-NIR field resulted in clearly visible, irreversible modifications after irradiation by more than ~ 20 shots. The visible-NIR pulse interacts with the free charge carriers produced by the energetic XUV photons, such that its absorption dramatically increases. This results in heating of the PMMA surface while, simultaneously, XUV induced damage to the polymer chain is enhanced due to the temperature effect.

The experimental setup is shown in Fig. 1. For strong HHG, a two-color laser field, consisting of the fundamental and second harmonic (SH) of a femtosecond laser pulse, was applied to a gas jet of He.⁸ Femtosecond laser pulses at 820 nm with an energy of 2.8 mJ and pulse duration of 32 fs were

focused by a spherical mirror ($f=600$ mm) into a He gas jet. For SH generation, a 200 μm thick β -barium borate (BBO) crystal was placed between the focusing mirror and gas jet so that, after the BBO crystal, the laser field consisted of both the SH and the residual fundamental laser fields. For the optimum SH conversion, the BBO crystal was placed ~ 40 cm from the focusing mirror and the energy conversion efficiency was about 27%. A gas jet with a slit nozzle of 0.5 mm width and length of 6 mm was used for efficient HHG in the two-color laser field.⁹ The gas pressure in the interaction region was 150 Torr. Generated HHG were first characterized using a flat-field soft x-ray spectrometer. The strongest harmonic at the 38th order (21.6 nm) reached an energy of ~ 50 nJ.

Subsequently, the spectrometer was replaced with a 1 in. diameter off-axis parabolic mirror (OAP) ($f=125$ mm at 13°) with a Mo:Si multilayer coating ($R=30\%$ at 21 nm) placed 245 mm from the HHG source. The sample target (500 nm thin layer of PMMA spin coated on a 315 μm thick silicon substrate, Silson, U.K.) was positioned 125 mm from

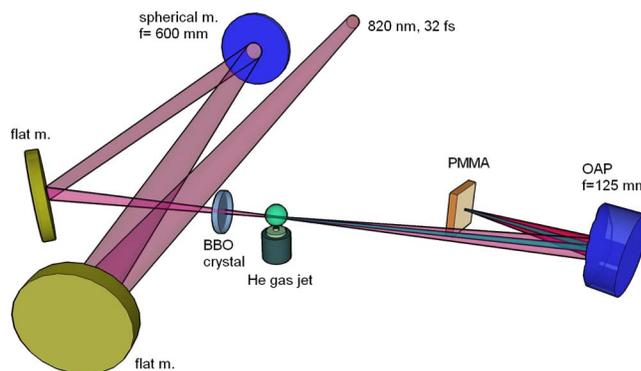


FIG. 1. (Color online) Schematic of the experimental setup for surface modification by dual action of XUV and visible-NIR ultrashort pulses.

^{a)}Electronic mail: mocek@fzu.cz.

^{b)}Present address: Femto Science Laboratory, Advanced Photonics Research Institute, GIST, Gwangju 500-712, Korea.

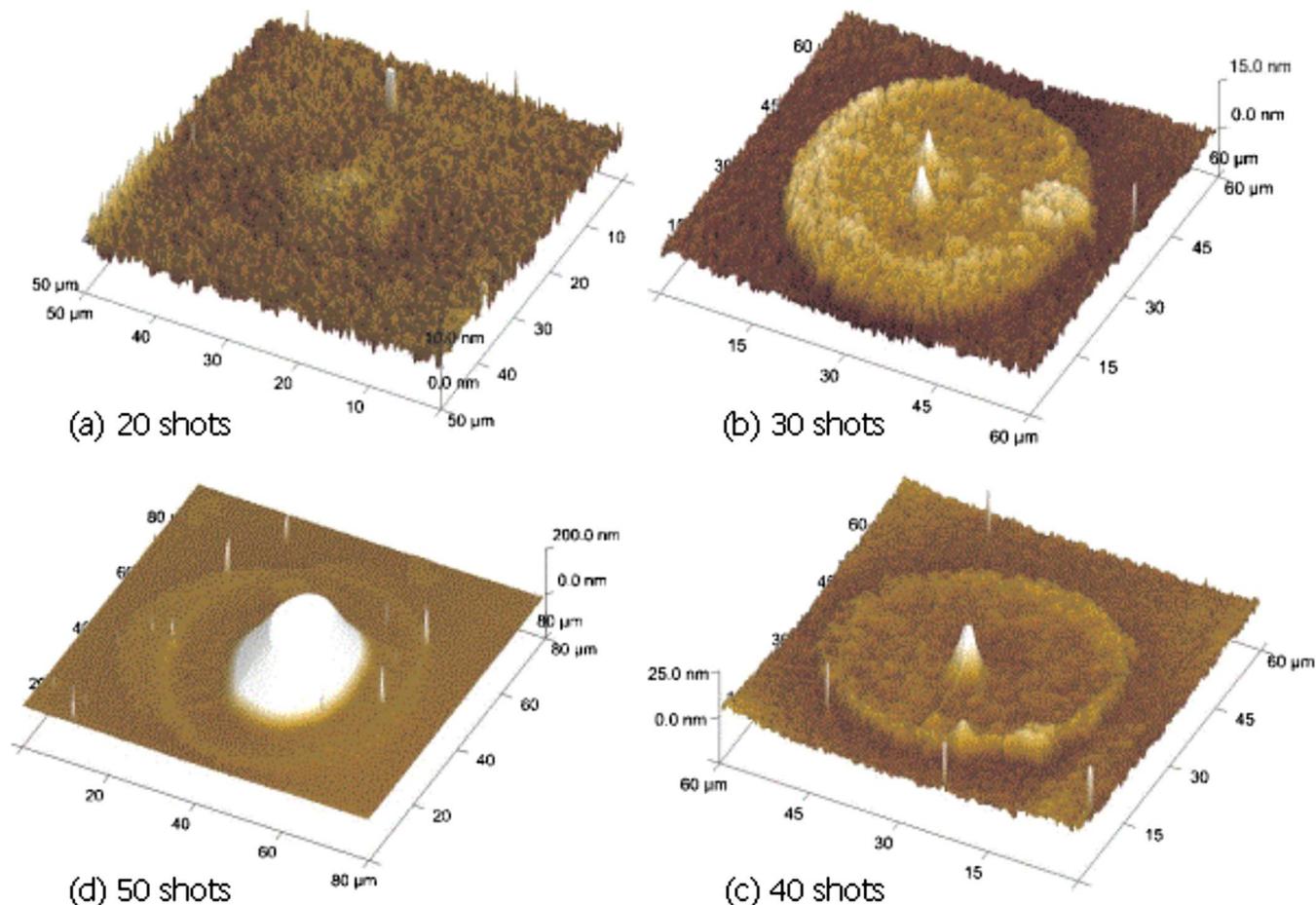


FIG. 2. (Color online) AFM images of the PMMA surface simultaneously irradiated with XUV and visible-NIR ultrashort pulses.

the OAP, perpendicularly to the incident beam. The measured reflectivity of the OAP in the optical region was 37%. The measured diameter (full width at half maximum) of the HHG beam incident on the OAP was $280\ \mu\text{m}$ while the diameter of the fundamental and SH laser beams was $\sim 4\ \text{mm}$. The morphology of irradiated target surface was first investigated by Nomarski differential interference contrast optical microscopy, and then with an atomic force microscope (AFM) (Dimension 3100 scanning probe microscope driven by a NanoScope IV controller; Veeco, USA) operated in the tapping mode to preserve high resolution.

To estimate the spot size for both XUV and visible-NIR beams at the target position, we have performed numerical simulations of the employed optical layout using the ZEMAX optical software.¹⁰ The modeling predicted an XUV spot size on PMMA of $140\ \mu\text{m}$, which is 17 times smaller than that of visible-NIR beams. The estimated single shot fluences on the surface of the PMMA were $97\ \mu\text{J}/\text{cm}^2$ at 21.6 nm, $14.7\ \text{mJ}/\text{cm}^2$ at 820 nm, and $6.3\ \text{mJ}/\text{cm}^2$ at 410 nm, respectively. As all these values lie far below the ablation threshold for PMMA by infrared ($2.6\ \text{J}/\text{cm}^2$ for single-shot and $0.6\ \text{J}/\text{cm}^2$ for 100 shots¹¹) as well as by XUV [$2\ \text{mJ}/\text{cm}^2$ (Ref. 12)] radiation, no damage of target surface is expected.

The PMMA target was irradiated under the following conditions: (a) visible-NIR beams only (no gas jet in operation), (b) XUV beam only ($0.4\ \mu\text{m}$ Al filter placed in front of the OAP), and (c) mixed XUV/visible-NIR field

(21.6 nm+820 nm+SH). In cases (a) and (b), we have not observed any signs of surface damage after irradiation by ~ 3000 shots despite the accumulated dose being significantly higher than in case (c). The target surface remained virtually unaffected, preserving its original quality and roughness. In striking contrast, the application of a mixed XUV/visible-NIR field resulted in clearly visible, irreversible surface modification after irradiation with only a few shots. Figure 2 shows AFM images of the PMMA exposed to the simultaneous action of XUV and visible-NIR ultrashort pulses. The damage is characteristic of material expansion, which is quite different from ablation craters observed in experiments with pure XUV pulses.^{2-4,12-14} A very interesting feature in Fig. 2 is the formation of nanoscale spike(s) in the center of a uniform flat pedestal. The size of pedestal increases with the number of shots applied to the target ($\sim 20\ \mu\text{m}$ for 10 shots and $\sim 60\ \mu\text{m}$ for 50 shots) while the spikes have a radius of the order of few microns down to a few tens of nanometers in length ($\sim 15\ \text{nm}$ for 30 shots and $\sim 25\ \text{nm}$ for 40 shots). The target was also analyzed by Fourier-transform infrared spectroscopy, which revealed that the expanded material is exclusively PMMA, not the silicon from substrate.

Since the separate application of visible-NIR or XUV beams did not lead to any observable change on the irradiated surface, the expansion in Fig. 2 must be attributed to the

dual action of 21.6 nm high-order harmonic and 820 nm laser radiation, contaminated with SH in the visible spectral region. The mechanism of dual action can be described in terms of a simplified physical picture. It is well known that PMMA exhibits a very weak linear absorption at 820 nm. Therefore, the single-shot ablation threshold lies for the near-infrared beam at a level of 2.6 J/cm^2 even for femtosecond laser pulses.¹¹ However, if the beam contains both 820 and 21.6 nm radiation, the high-energy XUV photons do indeed generate free charge carriers in the nearly transparent polymer dielectrics. The visible-NIR radiation can then interact strongly with the charge carriers formed through simultaneous irradiation by XUV so that its absorption dramatically increases in PMMA. The effect of a significant, transient decrease of UV transmittance induced in inorganic dielectrics by laser plasma soft x-ray pulses has been reported by Makimura *et al.*¹⁵ In addition to the transient phenomena, the XUV radiation can also create irreversible rise of visible-NIR absorption in the material, which is a well known effect of radiation coloration of transparent dielectrics. This effect is generally dose dependent, i.e., the ability of material to absorb visible-NIR radiation increases with number of accumulated shots. In contrast, the XUV induced transient absorption is likely to be independent of permanent changes initiated in the material by previous shots. Thus the irreversible coloration might be responsible for the observed nonlinear dependence of growth rate of expanded structure on the number of accumulated shots.

The laser pulse energy deposited in the system due to radiation-enhanced absorption also heats the material. It has been shown with synchrotron radiation, as well as using the laser-plasma emission, that the efficiency of soft x-ray radiation-induced etching processes strongly depend on temperature.^{1,16} In this way, the 820 nm radiation enhances the molecular fragmentation and rearrangement processes following the initial ultrafast action of energetic XUV photons on nanosecond-microsecond time scales. The influence of a temperature jump on the photoetching of PMMA has been suggested to explain the dual action of nanosecond pulses of focused x-rays and UV-to-optical radiation emitted by a laser-produced plasma.⁷ The photothermal heating enhances material removal processes, i.e., etch rate increases in dual fields,⁷ as it has been proven earlier by external heating of irradiated material.¹⁶ The nanosecond pulses cause predominantly the material erosion while the expansion behavior reported here with the ultrashort pulses is not observed.

The combination of these two processes (generation of charge carriers by XUV and temperature effect) causes fragmentation of PMMA and forms a liquid, oligomeric phase.¹⁷ The viscous liquid subsequently solidifies, forming the central spike(s) clearly visible in Figs. 2(b)–2(d) through extrusion of the fluid core pressurized by surrounding, already solidified, material.^{18,19}

To summarize, we have experimentally demonstrated that the dual action of XUV/visible-NIR ultrashort pulses is capable of producing highly efficient structural surface modifications of PMMA. The visible-NIR radiation strongly interacts with XUV-induced charge carriers so that its absorption

dramatically increases. This heats up the PMMA and alters it thermally, while the simultaneous temperature jump further enhances XUV induced damage to the polymer chains. The observed phenomena can be utilized in applications such as surface nanopatterning with widely available, inexpensive table-top radiation sources.

This research was supported by the Czech Science Foundation (Grant No. 202/07/J008), the Czech Ministry of Education (Grant Nos. LC510, LC528, and LA08024), the Academy of Sciences of the Czech Republic (Grant Nos. KAN300100702 and Z10100523), the Korea Science and Engineering Foundation through the Creative Research Initiative Program, and the Korea Research Foundation.

¹Y. Zhang, *Adv. Polym. Sci.* **168**, 291 (2004).

²L. Juha, M. Bittner, D. Chvostova, J. Krasa, M. Kozlova, M. Pfeifer, J. Polan, A. R. Präg, B. Rus, M. Stupka, J. Feldhaus, V. Letal, Z. Otcenasek, J. Krzywinski, R. Nietubyc, J. B. Pelka, A. Andrejczuk, R. Sobierajski, L. Ryc, F. P. Boody, H. Fiedorowicz, A. Bartnik, J. Mikolajczyk, R. Rakowski, P. Kubat, L. Pina, M. Horvath, M. E. Grisham, G. O. Vaschenko, C. S. Menoni, and J. J. Rocca, *J. Microlithogr., Microfabr., Microsyst.* **4**, 033007 (2005).

³G. Vaschenko, A. G. Etxarri, C. S. Menoni, J. J. Rocca, O. Hemberg, S. Bloom, W. Chao, E. H. Anderson, D. T. Attwood, Y. Lu, and B. Parkinson, *Opt. Lett.* **31**, 3615 (2006).

⁴J. Krzywinski, R. Sobierajski, M. Jurek, R. Nietubyc, J. B. Pelka, L. Juha, M. Bittner, V. Letal, V. Vorliceck, A. Andrejczuk, J. Feldhaus, B. Keitel, E. Saldin, E. Schneidmiller, R. Treusch, and M. Yurkov, *J. Appl. Phys.* **101**, 043107 (2007).

⁵A. Bartnik, H. Fiedorowicz, R. Jarocki, L. Juha, J. Kostecki, R. Rakowski, and M. Szczurek, *Microelectron. Eng.* **78–79**, 452 (2005).

⁶M. De Grazia, H. Merdji, B. Carré, J. Gaudin, G. Geoffroy, S. Guizard, N. Fedorov, A. Belsky, P. Martin, M. Kirm, V. Babin, E. Feldbach, S. Vielhauer, V. Nagirnyi, A. Vassil'ev, F. Krejci, J. Kuba, J. Chalupsky, J. Cihelka, V. Hajkova, M. Ledinsky, and L. Juha, *Proc. SPIE* **6586**, 65860I (2007).

⁷F. Barkusky, C. Peth, A. Bayer, and K. Mann, *J. Appl. Phys.* **101**, 124908 (2007).

⁸I. J. Kim, C. M. Kim, H. T. Kim, G. H. Lee, Y. S. Lee, J. Y. Park, D. J. Cho, and C. H. Nam, *Phys. Rev. Lett.* **94**, 243901 (2005).

⁹I. J. Kim, G. H. Lee, S. B. Park, Y. S. Lee, T. K. Kim, C. H. Nam, T. Mocek, and K. Jakubczak, *Appl. Phys. Lett.* **92**, 021125 (2008).

¹⁰ZEMAX Development Corporation, www.zemax.com.

¹¹S. Baudach, J. Bonse, J. Krüger, and W. Kautek, *Appl. Surf. Sci.* **154–155**, 555 (2000).

¹²J. Chalupský, L. Juha, J. Kuba, J. Cihelka, V. Háková, S. Koptyaev, J. Krása, A. Velyhan, M. Bergh, C. Coleman, J. Hajdu, R. M. Bionta, H. Chapman, S. P. Hau-Riege, R. A. London, M. Jurek, J. Krzywinski, R. Nietubyc, J. B. Pelka, R. Sobierajski, J. Meyer-ter-Vehn, A. Krenz-Tronnier, K. Sokolowski-Tinten, N. Stojanovic, K. Tiedtke, S. Toleikis, T. Tschentscher, H. Wabnitz, and U. Zastra, *Opt. Express* **15**, 6036 (2007).

¹³L. Juha, M. Bittner, D. Chvostova, J. Krasa, Z. Otcenasek, A. R. Präg, J. Ullschmied, Z. Pientka, J. Krzywinski, J. B. Pelka, A. Wawro, M. E. Grisham, G. Vaschenko, C. S. Menoni, and J. J. Rocca, *Appl. Phys. Lett.* **86**, 034109 (2005).

¹⁴T. Mocek, B. Rus, M. Kozlová, M. Stupka, A. R. Präg, J. Polan, M. Bittner, R. Sobierajski, and L. Juha, *Appl. Phys. Lett.* **89**, 051501 (2006).

¹⁵T. Makimura, S. Mitani, Y. Kenmotsu, K. Murakami, M. Mori, and K. Kondo, *Appl. Phys. Lett.* **85**, 1274 (2004).

¹⁶A. Bartnik, H. Fiedorowicz, R. Jarocki, L. Juha, J. Kostecki, R. Rakowski, and M. Szczurek, *Appl. Phys. B: Lasers Opt.* **82**, 529 (2006).

¹⁷L. Juha, J. Krása, A. Präg, A. Cejnarová, D. Chvostová, K. Rohlena, K. Jungwirth, J. Kravárik, P. Kubeš, Yu. L. Bakshaev, A. S. Chernenko, V. D. Korolev, V. I. Tumanov, M. I. Ivanov, A. Bernardinello, J. Ullschmied, and F. P. Boody, *Surf. Rev. Lett.* **9**, 347 (2002).

¹⁸K. G. Libbrecht and K. Liu, *J. Glaciol.* **50**, 371 (2004).

¹⁹D. Mills and K. W. Kolasinski, *Nanotechnology* **17**, 2741 (2006).