Erosion of PMMA Induced by Multiple X-ray Laser Shots Below the Single-shot Ablation Threshold

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Abstract. We report results of investigation of damage to a thin layer of an organic polymer (PMMA) induced by irradiation with multiple laser shots below the single-shot ablation threshold. After exposure to a focused beam of a free-electron laser (LCLS, CA, USA) generating X-ray laser radiation at 835 eV the sample has been inspected with an atomic force microscopy (AFM) enabling analysis of the eroded craters. As expected, dependence of the maximum depth of the damaged area exhibits a nonlinear behaviour with respect to the accumulated dose of energy. A simple model describing this phenomenon in term of competition of two radiation driven processes, i.e. chain scission and cross-linking, has been developed and modified for X-ray laser sources. The first result of comparison of the experimental data and the simulations of the development of the maximum crater depth calculated with the model mentioned above is also reported in this contribution.

Introduction

Since the energetic X-ray photons carry enough energy to break many bonds inside macromolecules of organic polymers, surface of such materials can be easily damaged or modified with short-wavelength radiation at very low level of fluence of radiation impacting the sample surface. The irreversible changes induced by irradiation can be observed even in case the fluence of radiation is significantly lower than the single-shot ablation threshold, i.e., desorption-like damage of the material occurs. During such a process, the material removal is not as massive as in case of laser ablation, i.e. in case the fluence is well above the single-shot ablation threshold [1, 2]. Nevertheless, the knowledge of behaviour of material irradiated under these conditions is of the high importance in numerous branches of science and industry, e.g., optical elements development and protection, EUV (**E**xtreme **U**ltra**V**iolet) and soft X-ray nanopatterning, radiation chemistry, pulsed laser deposition, etc.

So far the method of ablative imprints into the surface of the organic polymers has been used also for characterization of transversal and longitudinal intensity distribution in focused short-wavelength laser beams [3, 4, 5]. However, the shorter wavelength of the radiation is used, the longer attenuation length of the material is observed. This implies the decrease in the local absorbed dose of energy and the desorption starts being more significant than the effect of ablation. Moreover to that, experimental results mentioned below show the etch rate is strongly dose-dependent in desorption mode as well as it decreases with the number of accumulated laser shots. This can be explained in terms of phase transitions and structural changes in the irradiated material.

In this contribution we report the results of comparison of the experimental data obtained from the organic polymer (**P**oly(**M**ethyl **M**eth**A**crylate) – PMMA) irradiated with the focused soft X-ray laser beam, with the numerical model of the desorption of the PMMA based on two main radiation-driven processes of chain-scission and cross-linking.

Experimental

The experiment was performed at the free-electron laser facility LCLS (**L**ight **C**oherent **L**ight **S**ource), CA, USA [6]. This system is designed to produce the radiation with the wavelength tunable from 1,5 nm (825 eV) to 0,15 nm (8,25 keV). For our experiment, the photon energy of 835 eV was

chosen. The PMMA sample was irradiated with laser pulses with time duration of 100 fs. Average energy of the unattenuated laser pulses fluctuated around 1 mJ. For varying the fluence impacting the sample surface a gas attenuator filled with krypton was used as well as a set of beryllium foils with various thicknesses.

The samples were mounted on a motorized X-Y-Z stage inside the vacuum chamber placed in an AMO experimental station [7] (**A**tomic, **M**olecular and **O**ptical Physics). Incoming laser beam was focused onto the sample surface by means of two Kirkpatrick-Baez mirrors. Energies of the laser pulses were measured by a photo-ionization detector GMD (**G**as **M**onitor **D**etector).

The single-shot ablation threshold for PMMA at photon energy of 835 eV was determined through analysis of the craters made on the surface of bulk of PMMA. The craters were inspected with the Nomarski DIC microscope (**D**ifferential **I**nterference **C**ontrast). The value of threshold fluence was found to be 93.4 ± 5.2 mJ/cm^2 [8]. Therefore, three sets of craters were made at different fluence levels (0,4 mJ/cm^2, 4 mJ/cm2 and 40 mJ/cm^2) and with a different number of accumulated pulses (30 to 300) on the surface of 5μm thick layer of PMMA deposited on the silicon slab. Morphology of these craters was investigated with an AFM (**A**tomic **F**orce **M**icroscope) working in tapping mode (Veeco D3100 NanoScope Dimension). Finally, a backscattering Raman spectrometer with a spatial resolution of around 4 μm (Renishaw Ramascope) was used to identify and investigate the chemical changes induced in PMMA irradiated by the soft X-ray laser radiation.

Results and discussion

The main goal of the experiment was to investigate the effects of chemical changes inside the irradiated material induced by the X-ray radiation to the efficiency of material erosion. Since the PMMA is well known to undergo the process of chain scission and cross-linking when exposed to the radiation of various wavelengths [7, 8], these effects were expected to occur even for the soft X-rays. Fig. 1 shows schematically these key processes taking place inside the irradiated PMMA.

It is obvious the effect of chain scission is essentially responsible for the producing of tiny volatile fragments, such as methyl or ester groups, etc., which easily escape the material surface and thus contribute to the crater development. On the other hand, when free end-links are present in the irradiated material, the effect of cross-linking can take place. This effect is indicated by means of a formation of double C=C bonds in the backbone chain of the PMMA which originally contains only single C–C bonds. Presence of both these effects was proven by the comparison of the Raman spectra taken from the irradiated and unirradiated part of the PMMA. Fig. 2 summarizes the difference in these spectra. A new peak at 1650 cm^{-1} appears in the spectrum corresponding to the irradiated area. This peak belongs to the double C=C bonds.

The number of double C=C bonds formed inside the irradiated material was supposed to increase with the deposited dose of energy. Fig. 3 illustrates the progress in probability of PMMA cross-linking with increasing dose of energy.

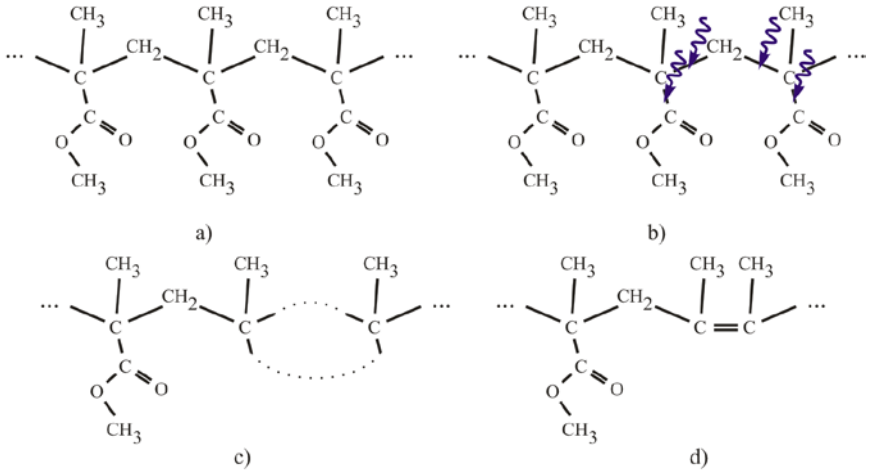

Figure 1. Formation of a PMMA molecule with a double bond C=C; (a) unaffected PMMA molecule, (b) chain scission caused by incident radiation, (c) and (d) cross-linking.

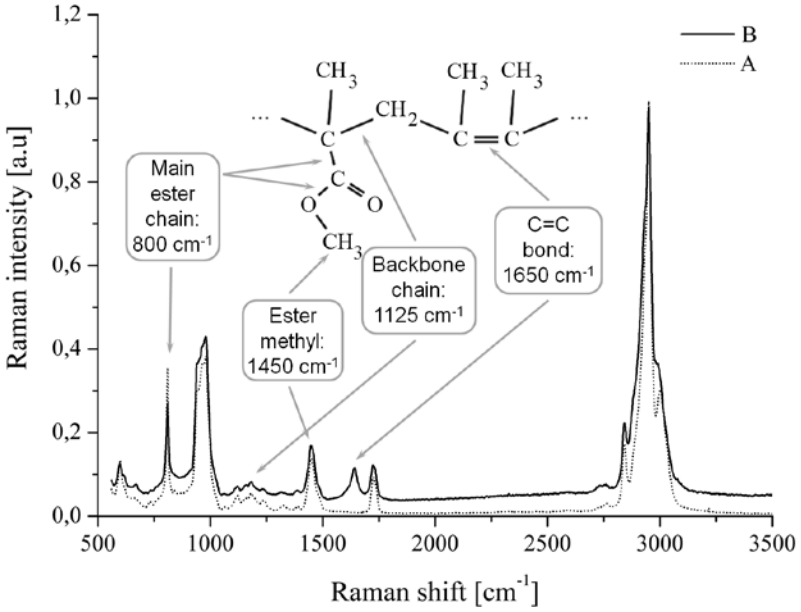

Figure 2. Raman spectra of PMMA irradiated by 300 X-ray laser shots at a fluence level of 40 mJ/cm^2. The difference between the irradiated (solid line) and the unirradiated (dotted line) area is characterized by a new peak at 1650 cm^{-1} representing the presence of C=C bonds formed due to the effect of cross-linking.

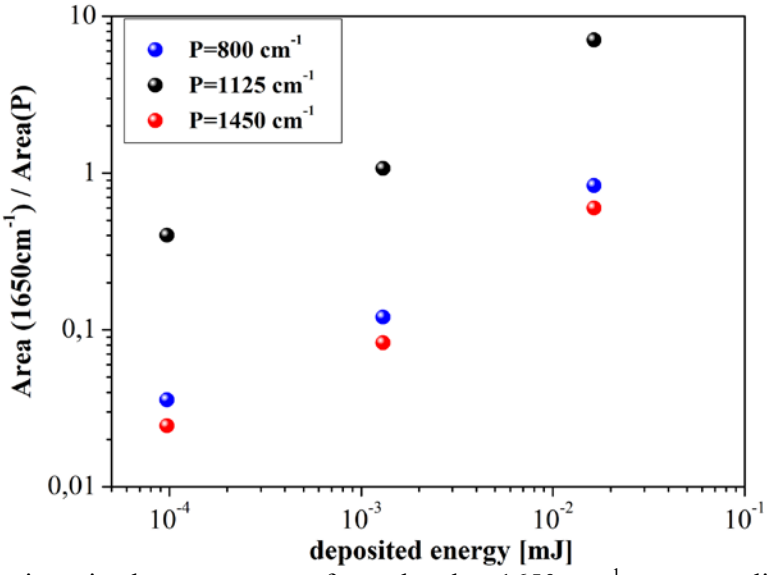

Figure 3. Progress in ratios between areas of new band at 1650 cm^{-1} corresponding to formed C=C double bonds and bands representing the density of backbone chains (1125 cm^{-1}) and ester (800 cm^{-1}) and methyl (1450 cm^{-1}) groups in dependence on accumulated dose of energy.

It is clearly visible the ratios between areas of the new peak at 1650 cm^{-1} and the peaks corresponding to another bonds in the PMMA molecule grows with the dose, even steeper than in the linear way. Actually, such a growth is caused both by the increase in number of formed double C=C bonds and by the decrease in density of ester and methyl groups which desorb out of the material due to the chain scission effect. The data was taken from craters made at fluence level of 4 mJ/cm^2.

Since the binding energy of double C=C bond is higher than of the single C–C one, the efficiency of radiation-induced desorption is supposed to decrease with the increasing number of accumulated pulses. This presumption was proven by the analysis of dependence of maximum crater depth on the number of accumulated pulses. The results of this analysis are summarized in Fig. 4.

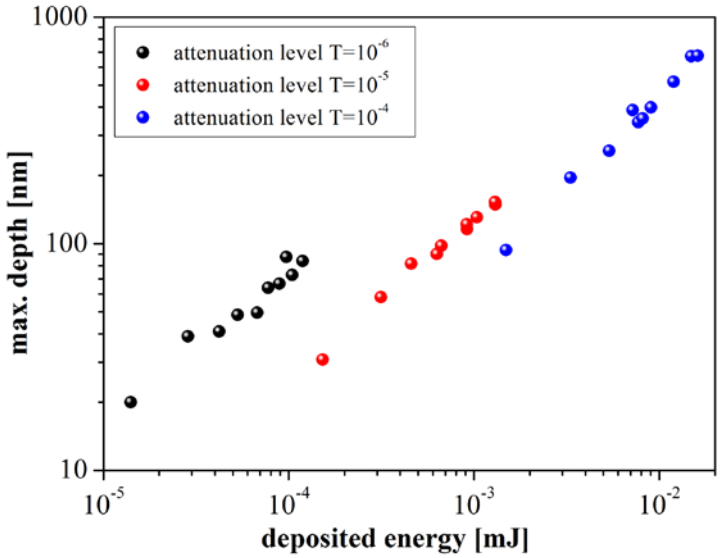

Figure 4. Dependence of maximum crater depth on the deposited dose of energy at three different fluences: (black) 0.4 mJ/cm^2, (red) 4.0 mJ/cm^2, and (blue) 40 mJ/cm^2. Deposited energy was determined considering an energy content of each particular laser pulse measured by photo-ionization detector.

The nonlinearity of at least two kinds can be observed in the dependences in Fig. 4. The first one corresponds to the decrease in the etch rate with the increasing dose of energy and it is the result of the higher number of more strongly coupled double C=C bonds. The second kind of nonlinearity can be observed in discontinuities in maximum depths corresponding to the same dose of energy but to the different level of fluence of the incident radiation. This phenomenon can be explained in term of the producing of the volatile fragments in the deeper layers of the PMMA where they cannot escape out into the free space. These fragments remain inside the material, cause the additional losses and thus lower the effective yield of the erosion. It means part of the incident radiation is absorbed by these trapped fragments; however, it does not contribute to the yield of chain scission effect.

For the simulation of the crater development under irradiation of PMMA, a simple model [9] based on evaluation of the density of single C–C bonds (n_{SB}), double C=C bonds (n_{DB}) and the free fragments (n_{FRAG}) was used. Originally, this model was used for simulation of an interaction of PMMA with high order harmonics radiation. Nevertheless, it was modified for the soft X-rays and thus could be used even for the experiment with LCLS radiation.

This model deals with a sequence of laser pulses with time duration well separated in time. Variations in densities n_{SB}, n_{DB} and n_{FRAG} are to be described by kinetics equations.

The fluence F [mJ/cm^2] decreases inside the material with a depth z*[nm]* in accordance with the Lambert-Beer law:

$$\frac{dF(z)}{dz} = -\xi(z)F(z)n_{SB}(z) - \xi_{FRAG}F(z)n_{FRAG}(z) \qquad (1)$$

where ξ [cm^2], ξ_{FRAG} [cm^2], n_{SB} [cm^{-3}] and n_{FRAG} [cm^{-3}] denotes a cross-section for the effect of main chain scission, cross-section of absorption in non-desorbed fragments, density of intact molecules (without a double bond in the backbone chain) and density of non-desorbed fragments, respectively.

Since LCLS pulses are very short (100 fs), cross sections ξ and ξ_{FRAG} are assumed to be constant over the pulse duration period. Effects of cross-linking and other relaxations are neglected as well. On the other hand, a pause between each two pulses (more than 30 ms) is many orders of magnitude longer in comparison with characteristic time of relaxation and cross-linking effect. Thence, changes in densities n_{SB}, n_{DB} and n_{FRAG} can be evaluated separately for each single pulse of the irradiation sequence and they are described by the set of sequential equations and initial conditions as follows:

$$\begin{aligned} n_{DB}^{(n)} &= n_{DB}^{(n-1)} + n_{FRAG}^{(n)} = n_{DB}^{(n-1)} + \alpha\xi^{(n-1)}F^{(n)}n_{SB}^{(n-1)} \\ n_{SB}^{(n)} &= n_{SB}^{(n-1)} - \frac{1}{2}\alpha\xi^{(n-1)}F^{(n)}n_{SB}^{(n-1)} \\ n_{FRAG}^{(n)} &= n_{FRAG}^{(n-1)} + 2\alpha\xi^{(n-1)}F^{(n)}n_{SB}^{(n-1)} \end{aligned} \qquad \begin{aligned} n_{SB}^{(0)} &= n_0 \\ n_{FRAG}^{(0)} &= 0 \\ n_{DB}^{(0)} &= 0 \end{aligned} \tag{2}$$

where the integer in superscript denotes the number of accumulated pulse and α expresses the number of bonds broken by the one X-ray photon.

The nonlinearity of the process caused by the increasing density of double C=C bonds can be include into the dependence of ξ on this density:

$$\xi(n_{DB}) = \xi_{SB}\frac{n_{SB}}{n_{SB}+n_{DB}} + \xi_{DB}\frac{n_{DB}}{n_{SB}+n_{DB}} = \xi(0)\frac{\tilde{n}_{DB} - n_{DB}}{\tilde{n}_{DB}} \tag{3}$$

where $\tilde{n}_{DB}$ is a wavelength-dependent parameter of the model.

The set of equations (2) can be solved with the finite step in the depth. Since the maximum crater depth is supposed to follow some isodensity of single C–C bonds [9], the experimental data were iteratively fitted with the simulated curves. Fig. 5 shows the result of this procedure. It was found out the experimental data can be fitted with the isodensity of 0.985 of the initial density of single C–C bonds.

Although the experimental data can be fitted with the mathematical model described above and crater depth can be predicted, some limitations for this model were determined. First of all, for short sequences of laser pulses a linear dependence of the depth of the eroded crater on the number of accumulated pulse is presumed. Contrary to that, none of isodensities in the model can match such a presumption. Other limitation is joined with the parameter ξ_{FRAG}. When it is set to zero, it means all fragments desorb out of the material. On the other hand, when this parameter is non-zero and constant, it implies all fragments remains inside the material or very close to the surface, and all of them contribute to the losses in fluence. In our case, the fragments produced in layers very close to the surface of the sample mostly desorb out, whilst the fragments in deeper layers remain inside the material. Here they can absorb incoming radiation or recombine with the end-links and thus lower the yield of forming double bonds.

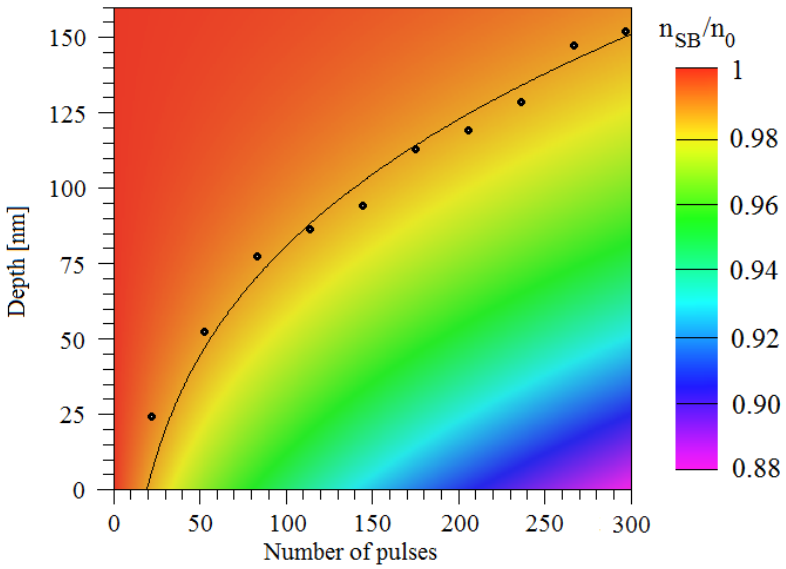

Figure 5. Maximum depths of craters eroded with accumulated LCLS laser pulses at fluence level of 4mJ/cm^2 fitted with iteratively computed isodensity of $n_{SB}/n_0 = 0.985$.

Conclusion

Efficient erosion of organic polymer – PMMA – has been observed even for the fluence level many times lower than that of the single-shot ablation threshold. This sub-threshold, desorption-like damage to the material is initiated by the single-photon radiolytical effect known as chain scission.

Dependence of the efficiency of the material removal on the total dose of energy exhibits nonlinear behaviour of at least two types. First of them is related to the decrease in etch rate with the increasing number of accumulated shots. The second one corresponds to the lower efficiency of erosion when material is exposed to the radiation at higher fluence. Both of these types of nonlinearity can be described in term of chemical changes inside the irradiated material induced by the incident radiation, especially the effect of formation of double C=C bonds (known as cross-linking) and creation of free fragments which remain in the material.

The progress in maximum depth of the eroded area can be simulated numerically as a function of number of accumulated shots. Although the experimental data can be fitted with the numerical model described above, some phenomena, such as ability of simulation of short irradiation sequences with almost linear increase in depth, are to be implemented into the model in future.

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