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Modification of a new polymer photorecording material based on PMMA doped with 2,2-difluoro-4-(9-antracyl)-6-methyl-1,3,2-dioxaborine by ultrashort pulses

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Abstract. **Specific features of modification of a new photorecording material based on PMMA doped with 2,2-difluoro-4-(9-antracyl)-6-methyl-1,3,2-dioxaborine are studied. The recording of the filament distribution in the studied material occurs at the expense of two-photon photochemical processes. The three-dimensional modification of the material is achieved in the filamentation regime without supercontinuum generation. It is possible to order the volume structure by preliminary photo-modification of the near-surface layer of the material.**

Keywords: *filamentation, two-photon photoinduced modification, femtosecond pulses.*

1. Introduction

At present, it is rather urgent to study the formation of predetermined microstructured objects, needed for numerous applications, in particular, the fabrication of waveguide structures [1, 2], diffraction gratings [3], microresonators [4] and microinterferometers [5], photonic crystals [6], etc. In practice these microstructures are produced using different methods of electron [7] and ion beam [8] lithography that suffer from the essential drawbacks, namely, the multistep technology of making three-dimensional optical structures, as well as high cost and construction complexity of the used instrumentation.

Due to relatively high productivity, the use of different optical methods of preparing microscopically modified objects, in which the basic instrument is a laser source, provides an optimal alternative to electron and ion-beam lithography [9]. This approach allows the implementation of direct modification of a material in the course of interaction of laser radiation with matter, which may result in the change of its optical characteristics (such as refractive index and absorption coefficient), or in the manifestation of optical breakdown processes. In the laser-induced micromodification of a material it is promising to use high-intensity pulsed radiation of femtosecond duration, which, due to multiphoton phenomena, makes it possible to modify the material both in the subsurface layer and at a significant depth avoiding the danger of thermal destruction. The formation of filament structures with high spatio-temporal localisation of energy in the process of ultrashort pulse (USP) propagation through optically transparent media offers new possibilities for the formation of designated volume micro-modified objects.

The implementation of these potentialities requires photorecording materials meeting the criteria of mechanical strength, synthesis simplicity and relatively low cost. Earlier [10] we reported the development of a polymer material based on polymethylmethacrylate (PMMA) doped with a new anthracene derivative 2,2-difluoro-4-(9-antracyl)-6-methyl-1,3,2-dioxaborine ($AntBF_2$), in which the three-dimensional recording of laser-induced filament structures is possible using the mechanisms of nonlinear (two-photon) absorption of femtosecond laser radiation [11]. In the present paper this material is studied with the aim of determining the modification thresholds with subsequent recording of three-dimensional phase gratings in its structure in order to form an ordered pattern of separate filaments and further two-photon photoinduced modification of the material.

2. Experiment

To modify the material we used the experimental setup schematically presented in Fig. 1. The laser system (*1*), consisting of the femtosecond pulsed Tsunami oscillator and the Spitfire 40F-1k-5W amplifier (Spectra Physics) generated pulses with the duration 42–160 fs, the centre wavelength 800 nm and the spectral half-width $\Delta\lambda = 35$ nm. The beam diameter amounted to 6 mm. Depending on the experimental conditions, the pulse repetition rate could vary from 4 to 1000 Hz. The attenuator (*2*), consisting of a half-wave plate and a polarising cube, allowed continuous variation of the output radiation

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power. By means of the system of mirrors (*3*) the laser beam was entered into the microscope with the beam splitter (*4*) inside that sent the radiation onto the objective (*5*) with the magnification 50× and the numerical aperture 0.8. The focused radiation was then delivered to the sample (*6*), the spatial position of which was varied by the specially constructed automated system of Thorlabs MAX 302 positioners (*7*), controlled by the computer (*8*). The radiation intensity distribution over the beam cross section was recorded with the CCD camera (*9*). The background illumination was implemented using the incandescent lamp (*10*). To make the image of the obtained modifications more contrast we used the semiconductor laser (*11*) with the wavelength 650 nm, from which the radiation was also entered into the objective (*5*).

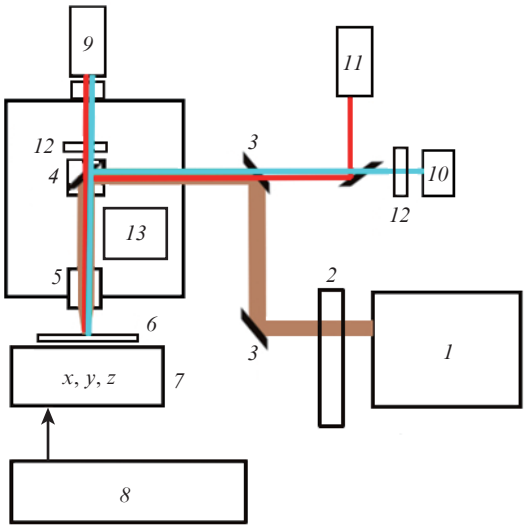

Figure 1. Schematic diagram of the experimental setup for microstructure formation:
(*1*) Spitfire 40-1k-5W+Tsunami laser system; (*2*) attenuator; (*3*) mirrors; (*4*) beam splitter; (*5*) objective; (*6*) sample; (*7*) Thorlabs MAX 302 positioner; (*8*) computer; (*9*) CCD camera; (*10*) incandescent lamp; (*11*) semiconductor laser (λ = 650 nm); (*12*) filters; (*13*) microscope.

Figure 2 presents the experimentally obtained threshold energies of the optical breakdown for the studied material (PMMA + $AntBF_2$ and pure PMMA), depending on the depth of laser radiation focusing inside the samples. Near the surface a higher threshold of optical breakdown is observed in the pure PMMA sample. In the doped PMMA the increase in the focusing depth leads to the growth of the incident radiation energy, necessary for the initiation of optical breakdown processes, as compared to the samples of pure PMMA. On average, at the focusing depths exceeding 70 μm the optical breakdown threshold in doped PMMA was by 1.15 times greater than the analogous parameter in pure PMMA. This is due to the increase in the linear absorption coefficient in doped PMMA in the region of 800 nm [11]. In turn, an additional factor affecting the optical breakdown thresholds can be related to the change in nonlinear optical characteristics due to the penetration of the $AntBF_2$ compounds into the PMMA matrix. To determine the effect of the doping component, the automated experimental setup based on the *z*-scanning method was constructed (Fig. 3) [12].

The radiation source was the same laser system, as in Fig. 1. The duration of the input pulse was controlled with the

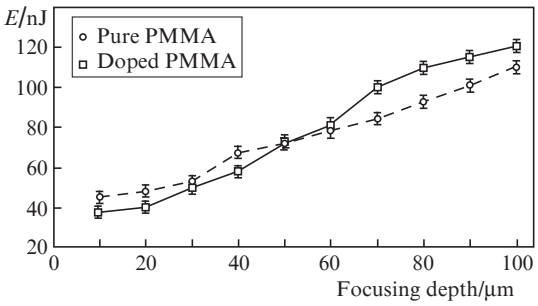

Figure 2. Optical breakdown threshold energies for PMMA and PMMA + $AntBF_2$ as functions of the laser radiation focusing depth inside the samples for the radiation at the wavelength 800 nm and the pulse duration 42 fs.

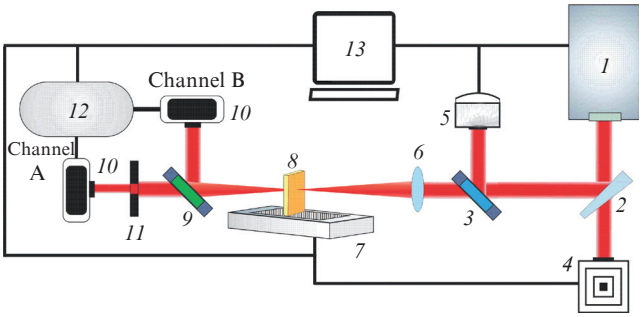

Figure 3. Experimental system for measuring nonlinear optical coefficients using the *z*-scanning method:
(*1*) Spitfire 40F-1k-5W+Tsunami laser system; (*2*) wedge-shaped plate; (*3*) flap mirror; (*4*) autocorrelator; (*5*) power meter; (*6*) lens with the focal length 200 mm; (*7*) positioner; (*8*) sample; (*9*) beam splitter; (*10*) photodiodes; (*11*) iris aperture; (*12*) TDS 2024B Tektronix oscilloscope; (*13*) computer.

autocorrelator (*2*). The ultrashort pulses were focused on the sample by the lens with the focal length F = 200 mm, and the intensity of radiation in the focus was varied by changing the laser pump current. After passing through the sample the laser beam was split unto two beams by means of the beam splitter (*9*). The intensity of radiation transmitted through the sample under study was measured in channel A, while channel B was used for recording the reference radiation intensity. The *z*-scanning method is based on the analysis of the intensity distribution change in the far-field zone of the laser beam, restricted by the aperture diaphragm (*11*). The intensity change is caused by the appearance of nonlinear refraction in the sample when it is moved in the focus region along the direction of light propagation. In the experiment we obtain characteristic dependences of normalised transmission of light by the sample on the sample position z in the waist region. The magnitude of the normalised transmission drop linearly depends on the nonlinear phase increment at the sample output, and the nonlinear refractive index is expressed as [12]

$$n_2 = \frac{\Delta T \lambda}{0.406(1-S)^{0.25} 2\pi I_0 L},$$

where ΔT is the magnitude of the normalised drop of the transmission curve; λ is the radiation wavelength (m); I_0 is the intensity of incident radiation (W cm^{-2}); L is the sample thick-

ness (m); and S is the transmission coefficient of the aperture diaphragm. The distribution of normalised transmission for the doped PMMA obtained in the experiment is presented in Fig. 4. For pure PMMA we obtained $n_2 = 3.2 \times 10^{-16}$ cm^2 W^{-1}. After doping PMMA with $AntBF_2$, the nonlinear refractive index decreases to 2.8×10^{-16} cm^2 W^{-1}; this is negligible within the error limits of 10% and does not affect the self-focusing process. The two-photon absorption coefficient for these samples amounted to 7.9×10^{-12} and 5.4×10^{-11} cm^2 W^{-1}, respectively.

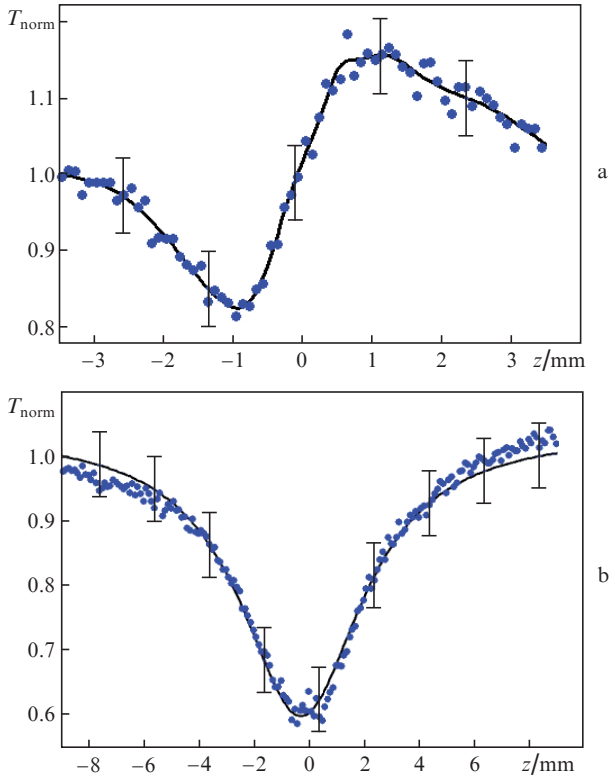

Figure 4. Experimental data and approximating curves for the normalised transmission of radiation by the PMMA + $AntBF_2$ sample: (a) the beam is aperture restricted; (b) the aperture is absent.

If the duration of the incident radiation pulse is increased from 42 to 160 fs, then near the surface of PMMA + $AntBF_2$ the threshold increases up to 60 nJ. At the depth of 100 μm the threshold increases to 230 nJ. The dependence of the optical breakdown threshold energy on the focusing depth for the first and second harmonic of the Ti:sapphire laser radiation is presented in Fig. 5. The essential increase in the optical breakdown threshold at the wavelength 400 nm is due to the attenuation of radiation in the samples as a result of its absorption by the photorecording additive $AntBF_2$ [11].

Under the action of singe pulses with the energy close to the optical breakdown threshold the modifications are formed with the following spatial characteristic: for the wavelength 800 nm the mean crater diameter is 1–1.2 μm, the modified region depth is 8–12 μm (Fig. 6); for the wavelength 400 nm the diameter is 0.8–1 μm, and the depth is 6.5–8.5 μm. In the case of moving the sample with respect to the laser beam by means of positioners (*7*) (see Fig. 1) the depth of the modified region produced by the action of pulses with the repetition rate 1 kHz was reduced to 2–3 μm (Fig. 7).

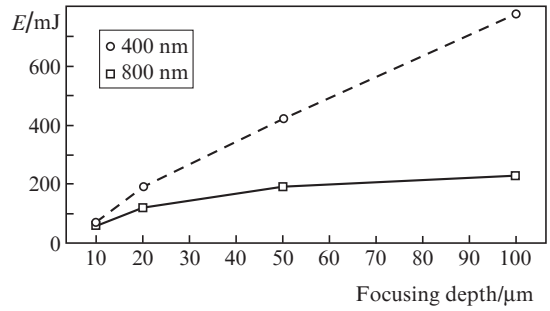

Figure 5. Threshold energies of the optical breakdown for PMMA + $AntBF_2$ vs. the depth of laser radiation focusing in the samples. The pulse duration is 160 fs.

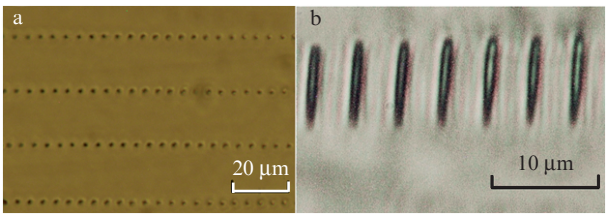

Figure 6. Modifications of PMMA + $AntBF_2$ samples, produced by single pulses of radiation at the wavelength of 800 nm with the energy, close to the optical breakdown threshold; top view (a) and side view (b).

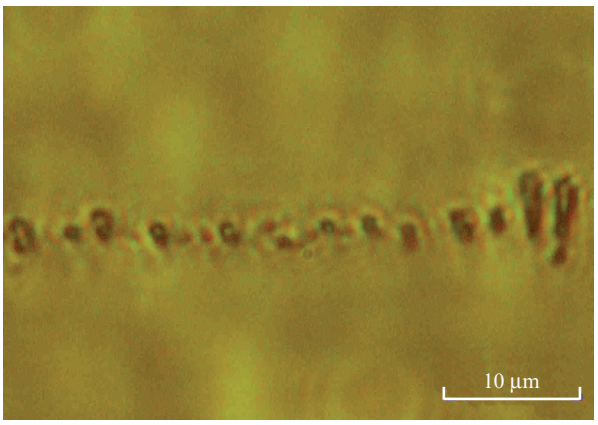

Figure 7. Modification of the PMMA + $AntBF_2$ samples produced by a moving beam of pulsed radiation with the pulse repetition rate 1 kHz at the wavelength 800 nm; the pulse energy is slightly above the optical breakdown threshold (side view).

For the radiation pulses at the wavelength 800 nm with the duration 160 fs and repetition rate 1 kHz the thresholds were determined as functions of the pulse energy, the sample motion velocity and the depth of the objective focus localisation. This allowed the material modification without optical breakdown up to the depth exceeding 100 μm, the region width being 2 μm (Fig. 8). When this modification was observed at a right angle with the beam axis of the modifying radiation beam, no apparent changes were found. The modification is a phase structure oriented along the beam axis direction, like the modification in the case of optical breakdown (Fig. 6b). At the depth 50 μm and the velocity of sample motion 50 μm s^{-1} the pulse energy required for modification is 170 nJ, which is 90% of the optical breakdown threshold.

Under these conditions in the automated regime a 3D grating with the dimensions 1 × 1 mm and the spacing 10 μm was formed (Fig. 9). When using shorter pulses the modification obtained without optical breakdown was rather unstable and, as a result of optical breakdown, turned into the point modification, similar to that shown in Fig. 7.

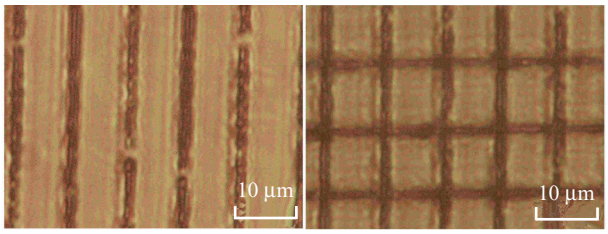

Figure 8. Modifications of the PMMA + $AntBF_2$ samples produced by a moving beam of pulsed radiation with the pulse repetition rate 1 kHz at the wavelength 800 nm; the pulse energy is slightly below the optical breakdown threshold (top view).

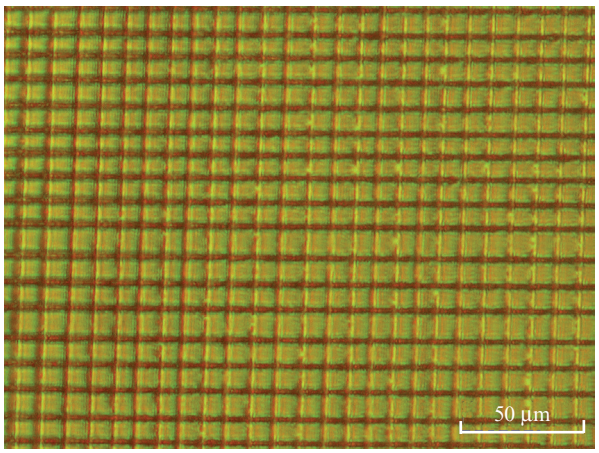

Figure 9. Matrix structure with the grid step 10 μm obtained in the PMMA + $AntBF_2$ sample by the modification of the material without optical breakdown.

In the process of propagation of high-intensity femtosecond laser pulses with the energy exceeding the critical energy of self-focusing, it is possible to observe the decay of the initial pulse due to the Bespalov–Talanov instability [13] and the formation of thin luminous filaments with high localisation of energy. One of the ways to arrange the filaments regularly in space is to provide the periodic spatial modulation of the light field phase in the transverse section of the beam [14]. The matrix structure (Fig. 9) formed in the PMMA + $AntBF_2$ sample was used as such a phase modulator for spatial ordering of the filamentation process. In Ref. [11] the presence of filamentation in the PMMA + $AntBF_2$ sample without supercontinuum generation is demonstrated. When the energy of the incident radiation exceeds the threshold of supercontinuum generation, its glow continues during a few minutes, after which the supercontinuum disappears due to the material destruction.

In the beginning of the experiment the parameters were chosen such that the intensity of the incident pulses corresponded to the pre-threshold conditions of supercontinuum generation. The modified region was subjected to the action of ultrashort pulses with the duration 42 fs and the repetition rate 100 Hz. To match the beam diameter with the formed matrix structure, the long-focal-length lens (F = 1 m) was used. The distance from the focal plane to the input face of the sample was equal to 875 mm, the exposure time was 3 h. As a result, under the action of individual filaments without optical breakdown a three-dimensional ordered two-photon modification of the material was obtained (Fig. 10). Its period corresponded to the period of the matrix structure (phase modulator). The modified region is located at the depth up to 4 mm from the matrix; the optimal contrast is preserved up to the depth of 1.5 mm. Then the energy of the pulses was increased till the appearance of stable supercontinuum (a little higher than the supercontinuum generation threshold). The exposure time was 1 h. Under the action of the optical breakdown a three-dimensional ordered modification structure was obtained in the material, spatially localised at the depth of 80–110 μm from the matrix structure (Fig. 11).

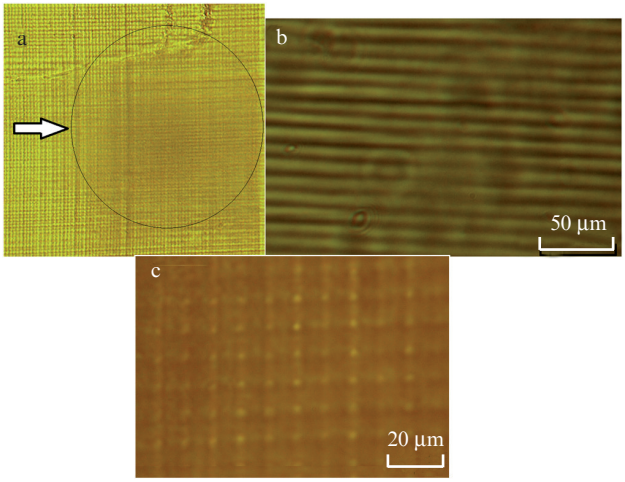

Figure 10. Three-dimensional structured modification of PMMA + $AntBF_2$ sample in the absence of optical breakdown:
(a) photograph of the sample after the radiation impact; (b) three-dimensional ordered modification (side view), (c) three-dimensional ordered modification (top view).

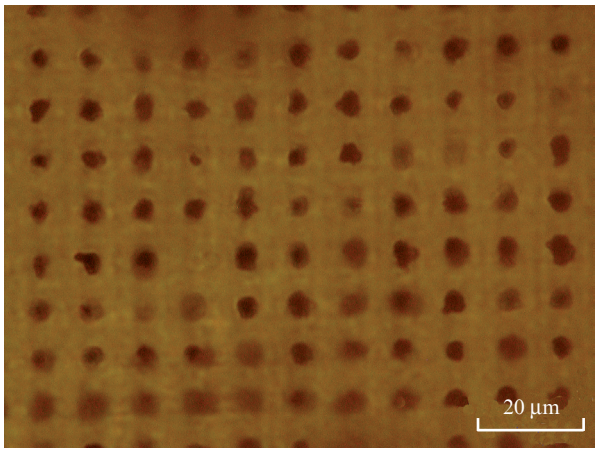

Figure 11. Three-dimensional structured modification of the sample obtained under the optical breakdown.

3. Conclusions

The incident radiation energies that determine the optical breakdown thresholds in the sample of PMMA + $AntBF_2$ for the fundamental frequency and second harmonic of the Ti:sapphire laser femtosecond radiation are found as functions of the focusing depth. Under the action of focused laser radiation at the wavelength 800 nm the stable modification without optical breakdown is obtained in the near-surface layer of the material, using which at the depth of 50 μm the matrix with the step 10 μm was formed. Under the irradiation of the sample with weakly focused (smaller than 0.5°) laser pulses having the intensity near (or lower than) the supercontinuum generation threshold through the fabricated matrix we obtained the ordered three-dimensional photoinduced modification of the material, consisting of separate filaments. It is found that when the supercontinuum generation threshold is exceeded, the ordered modifications caused by optical breakdown appear, spatially localised at the depth of 80–110 μm from the matrix structure.

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