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Microstructuring of polymer films by femtosecond pulses through optically trapped polystyrene microspheres

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Abstract. **We report the laser ablation of polymers by femtosecond (18 and 54 fs) pulses focused by 1 and 3.8 μm diameter spherical microlenses, which are held by optical traps. It is shown that this technique allows one to produce surface structures with lateral dimensions up to $\lambda/6$ (125 nm). It is found that the size of the structures depends on the diameter of the microlens; the highest spatial resolution is achieved by using 1 μm diameter microlenses.**

Keywords: *surface microstructuring, femtosecond pulses, laser ablation, spherical microlenses.*

1. Introduction

A number of works have been published on micro- and nanostructuring of the surface of various materials by laser ablation [1–6], in which the research was carried out using nanosecond, picosecond and femtosecond pulses. The disadvantage of this method is the production of sprays, remelted layers and microcracks due to thermal effects in surface micromachining by nanosecond pulses [7, 8]. Because femtosecond pulses lead to insignificant heating [5], they are increasingly used for surface micromachining [1, 8, 9]. Femtosecond lasers in combination with multiphoton absorption processes allow for structuring the surface of various materials with a spatial resolution down to the nanometre. [1].

In nanostructuring materials, the question arises about how to improve the spatial resolution. As is known, due to the wave nature of light, the spatial resolution is limited by the diffraction limit $d = 1.22\lambda/\mathrm{NA}$, where d is the minimum possible size of the region into which the laser beam with a wavelength of λ can be focused through a lens with a numerical aperture NA. Thus, for radiation with a wavelength of 800 nm and NA = 1.4, the resolution of ~700 nm is obtained. The use of multiphoton absorption processes can increase the resolution as compared to the diffraction limit by $\sqrt{n}$ times, where n is the multiphoton order of the process. Therefore, the main technique for increasing spatial resolution under normal ablation of polymer films is to reduce the wavelength of the laser radiation (up to hard ultraviolet), but along this way there are some difficulties associated with focusing and generation of such radiation. An alternative method is to use the near-field arising due to focusing of light by dielectric microspheres. This field is rapidly attenuated and localised in regions smaller than $\lambda/2$. The microspheres, if their diameters are larger than the wavelength, can be regarded as spherical microlenses [10]. Their characteristics are well reproduced, and the small scatter in diameter and sphericity has little effect on focusing. The problem of positioning the microsphere is solved by optical trapping, which is controlled by a video camera. To this end, methods of field enhancement using dielectric spheres are an attractive, simple and cheap way to increase the spatial resolution. The results of experiments were published in which ablation was carried out through dielectric microspheres. In some cases, for producing structures with a typical resolution much higher than the diffraction limit, use was made of a monolayer of spheres on the surfaces of different materials [10–13]. In other works, positioning of microspheres on the surface of samples relies on the method of optical trapping using cw lasers. This opens up the possibility of writing user-defined patterns due to ablation when pulsed laser radiation is focused through the microspheres [14–17]. In this case, use is made of lasers generating radiation at different wavelengths and pulse durations. However, ablation with Ti:sapphire laser pulses of duration of tens of femtoseconds with a repetition rate of about 100 MHz, propagating through optically trapped microspheres, has not yet been studied.

2. Experiment

The experiments were conducted using two setups. The first setup employed an Avesta TiF-20 Ti:sapphire laser, which generates pulses at a wavelength of 790 nm with a repetition rate of 75 MHz and a duration of 18 fs. The microspheres were trapped by 532 nm cw laser (Coherent Verdi V8). Radiation of cw and pulsed lasers was coupled into the microscope, where it was coaxially incident onto the Olympus 40× 0.55NA lens. The pulse duration was measured with an Avesta AA-M autocorrelator in the focal plane of the lens, the dispersion was compensated for by a quartz prism compressor, and a Thorlabs video camera was used to observe the sample.

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In the second setup, use was made of a Tsunami Ti : sapphire laser (Spectra-Physics), which generates pulses at wavelengths of 780 and 390 nm (second harmonic) with a pulse repetition rate of 80 MHz. The minimum duration of pulses was 54 fs and could vary due to their chirping in a CRI SLM-128 spatial light modulator. In our experiments we used Olympus 100× 1.4NA and Olympus 60× 0.7NA objective lenses, which were installed in an Olympus IX71 inverted research microscope. The microscope also utilised an NT MDT scanning piezodriver and a scanning atomic force head. Both optical trapping and ablation through microspheres were performed using pulsed radiation. The patterns on the surface of the polymer were written by moving the sample relative to the focus of the lens with trapped microspheres. The surface profile of the polymer subjected to ablation was measured by the atomic force scanning head.

The sample was a polymer synthesised from a mixture of monomer ethoxylated bisphenol-A diacrylate (CAS No. 64401-02-1) and 5% Darocour 4265 photoinitiator, a low pressure mercury lamp being used for photopolymerisation. The absorption spectrum of the polymer was measured with a Shimadzu UV-3600 spectrophotometer. Strong absorption was observed at wavelengths less than 300 nm. This means that the main process of laser radiation absorption at a wavelength of 800 nm was three-photon absorption. To trap and manipulate the microspheres, we used a suspension of 3.8 or 1 μm diameter polystyrene spheres in water, which was added to the cell with the polymer film.

3. Results

Using the first setup, we performed a comparative experiment on ablation of polymers using the microspheres and without them. The goal of the experiment was to find the dependence of the depth of the produced patterns on the radiation power at a fixed exposure and to compare the transverse dimensions of the patterns written in these two cases. The experimental conditions were as follows: exposure, 20 s; wavelength, 790 nm; pulse repetition rate, 75 MHz; pulse duration, 18 fs; objective lens, 40× 0.55NA; and polystyrene microspheres, 3.8 μm in diameter. In agreement with the results of [18–21], when the laser power exceeded the threshold, at a fixed exposure time craters were formed, and when the power was below the threshold, convex structures emerged. Figure 1 shows images of the craters on the surface of the polymer under radiation focusing in the absence of a microsphere and under focusing through a microsphere. One can see that the transverse dimensions of the craters in the presence of a microsphere are two times less than without it, but their depth is almost the same. Figure 2 shows the depth of the craters as a function of the laser power. One can see that the formation of craters of the same depth during ablation without a microsphere requires a five times higher average radiation power than that during ablation with a microsphere.

Using the second setup, we also carried out experiments on ablation with microspheres/microlenses when the femtosecond laser served to trap the microspheres and to irradiate the sample through them. When use was made of a 60× 0.7NA lens, the piezodriver ensured the circular trajectory of the microsphere in a circle of radius ~10 μm at 2.4 μm s^{-1}, the average output power was 75 mW, and 3.8 μm diameter microsphere made 20 rounds. Thus, we obtained a circular groove with a width at half maximum of 300 nm and a depth

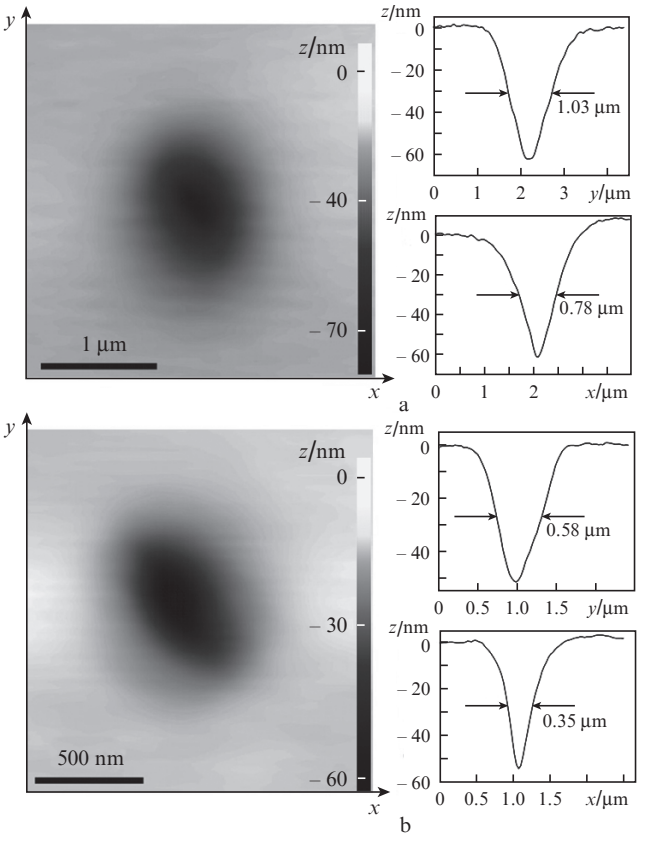

Figure 1. AFM images of the polymer surface after exposure to the laser pulse, focused (a) without microspheres and (b) through 3.8 μm diameter microspheres; z is the height of the surface.

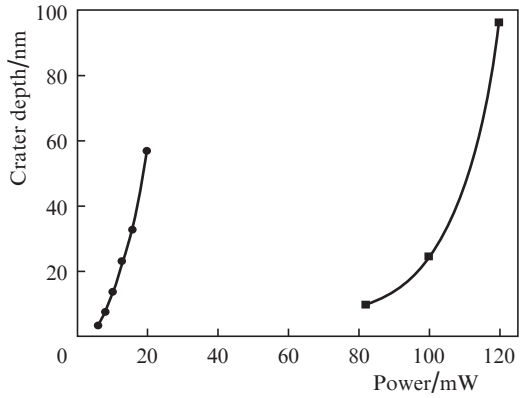

Figure 2. Dependence of the crater depth on the laser power under focusing of laser radiation without spheres (■) and through 3.8 μm diameter spheres (●).

of ~200 nm. In the experiment without the microsphere the groove was not formed, and the ring pattern had a convex shape of width 1.4 μm, which is significantly larger than the characteristic size of the groove in the previous experiment. A similar experiment was conducted using microspheres with a diameter of 1 μm. We found them to exhibit less stable trapping than 3.8 μm diameter microspheres. Therefore, with other parameters of the experiment being equal, the average power of the radiation incident on the lens was increased to 100 mW, and the trajectory of the microsphere was given as a straight line. The groove profile after one pass along the line

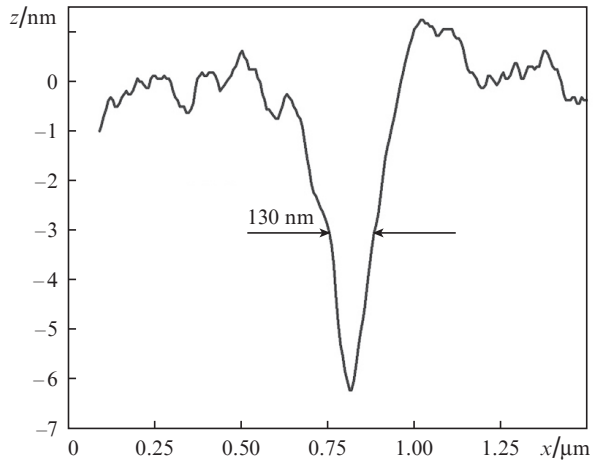

Figure 3. AFM profile of the groove after irradiation of the polymer through a 1 μm diameter sphere.

is shown in Fig. 3. The groove width was 130 nm at a laser wavelength of 780 nm.

To demonstrate the increase in resolution, we performed a comparative experiment for two cases – ablation through the 100× 1.4NA lens without microspheres and ablation through a weaker 60× 0.7NA lens using micron diameter microspheres. Ablation was carried out at a point, resulting in a crater. Figure 4a shows the profile of the crater produced by focusing radiation with a power of 7 mW at a wavelength of $\lambda = 780$ nm through the 100× 1.4NA lens. One can see that the crater width at half maximum in two orthogonal planes were 220 and 210 nm, i.e., 0.28λ.

A similar experiment was conducted using the 60× 0.7NA lens and 1 μm diameter microsphere at a wavelength of 780 nm and power of ~100 mW. Figure 4b shows the profile of the crater surface. As in the experiment with the formation of a groove, high spatial resolution is achieved. The crater has an elliptical shape: on the minor axis its size reaches 125 nm at FWHM, and on the major axis – 180 nm. These are 0.16λ and 0.23λ, respectively, at a wavelength of 780 nm, which is less than the characteristic dimensions of the crater produced by ablation through the 100× 1.4NA lens. Thus, the use of microspheres enables a higher spatial resolution than in the case of high-aperture lenses with a numerical aperture close to the limit.

4. Discussion of results

When the surface is irradiated by 18-fs pulses during 20 s, ablation without microspheres took place only in a small range of output powers. The transitional power, at which the crater was formed, was ~70 mW, and pronounced convex patterns were observed at a power of 25–30 mW.

In the experiment with 3.8 μm diameter microspheres the ablation threshold through them was only ~11 mW at the same exposure (20 s). Lowering the ablation threshold with the introduction of the microsphere is due to the additional focusing of the radiation by the microsphere/microlens that at an equal power of the radiation incident on the lens leads to

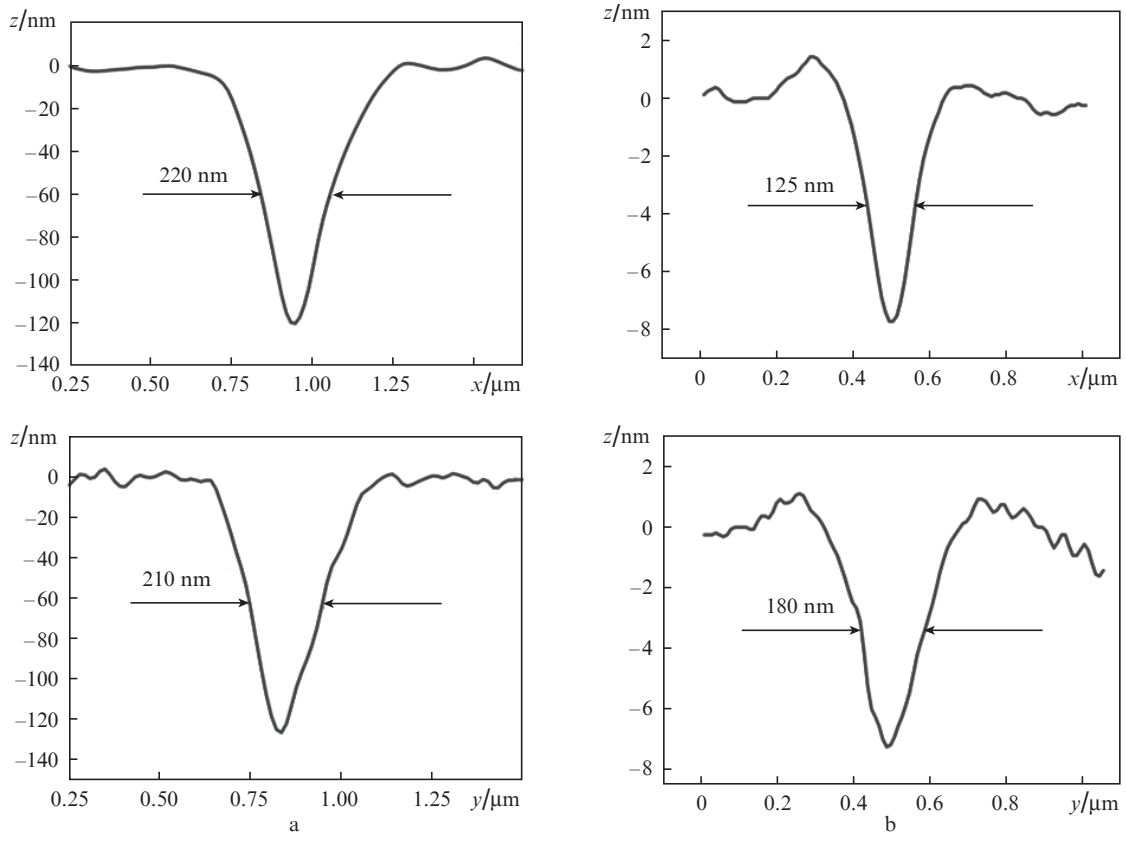

Figure 4. AFM profiles of the craters after irradiation through (a) the 100× 1.4NA objective lens and (b) the 60× 0.7 NA objective lens and a 1 μm diameter sphere.

higher intensities near the polymer surface in comparison with the case of focusing of the radiation by the lens only. Thus, to achieve the threshold intensity requires a smaller average power. When use is made of 1 μm diameter microspheres, smaller transverse dimensions of the patterns and higher spatial resolution are achieved than in the case of 3.8 μm diameter microspheres. The differences in the transverse dimensions of the patterns formed during ablation using microlenses of different diameters are a non-trivial result, because the known calculations of the electromagnetic field distribution near the dielectric spheres show that the width of the distribution is almost independent of the diameter of the sphere [22]. However, it follows from geometrical optics that the focus of the lens/sphere is at a distance from the surface, and the greater the distance, the larger the diameter of the sphere. Consequently, for a small-diameter sphere on the surface of the polymer film, the radiation is focused in the near-surface layer, whereas for a sphere with a diameter of a few microns the focus is located deep in the material. Apparently, the difference in the focusing can cause differences in the surface patterns. Perhaps, accumulation of ablation products in the thickness of the material leads to the formation of microcavities, causing local surface swelling and the formation of convex patterns. These assumptions may explain the fact that the type of a pattern obtained by ablation depends on the size of the spheres. Indeed, when moving the 1 μm diameter spheres along the sample surface, cavities were formed, and in the case of 3.8 μm diameter spheres – convexities. It was found that in the case of the cyclical movement of the spheres, the height of the convexities decreased with increasing number of cycles and they gradually transformed into the grooves, which is explained by the ablation of the surface layer and the appearance of microcavities on the surface.

The difference in spatial resolutions when use is made of spheres of different diameters can also be due to the difference in the depth of focusing. In the case of large diameter spheres radiation is focused in the depth of the material. In this case, the transverse dimensions of the patterns formed during the ablation, which are determined by the intensity distribution on the surface of the material, are higher than for micron-diameter spheres. In addition, it can be assumed that the processes of surface swelling may cause displacement of the sphere from the equilibrium, which may further degrade the resolution. Together, these phenomena may explain the differences in the nature of the ablation and lateral size of the patterns observed in the experiment.

5. Conclusions

We demonstrate the possibility of producing patterns with sub-diffraction resolution during ablation of the surface by femtosecond laser radiation focused though optically trapped micron spheres. Spatial resolution of microstructuring, which is achieved when using a lens with a high (1.4) numerical aperture, is lower than that when using a microsphere and a lens with a much smaller aperture (0.7).

Resolution enhancement in nanostructuring can be achieved by improving the stability of optical trapping. An increase in the resolution can also provide a decrease in the laser pulse duration, i.e., use of 12–15 fs pulses.

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