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Increase in the resolution of the method of surface nanostructuring by femtosecond-laser impact through a layer of colloidal microparticles

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Abstract. **It is experimentally demonstrated that by converting a few percent of the fundamental frequency pulse energy into the second harmonic one can obtain surface structures using dielectric microspheres with the dimension of the order of the second harmonic wavelength. Structuring by means of the second harmonic solely requires a significantly greater energy density in the pulse than using bichromatic irradiation. It is impossible to obtain structures using only the fundamental frequency radiation pulses, because radiation at the fundamental frequency is not focused by the system of microspheres. Therefore, the use of bichromatic pulses allows an essential increase in the structure recording density. Theoretical calculations demonstrating the possibility of further improvement of the structure recording density by using nonspherical microlenses of a smaller size made of a material with a higher refractive index are presented.**

Keywords: *femtosecond pulses, second harmonic, bichromatic radiation, surface nanostructuring, colloid particle layers.*

1. Introduction

Fabrication of nanostructured surfaces attracts great interest because of their possible applications in photonics and biomedicine [1–3]. Optical methods of producing such array structures are inferior to the methods using electron beams in refining, but possess unquestionable advantages in fabricating single-type large-area structures with the use of arrays of ordered nanoscale elements playing the role of a focusing system [4–6]. Tight focusing of radiation by microspheres and low thresholds of laser-induced surface modification in combination with good localisation of the resulting structures allow the fabrication of ordered nanostructures with high recording density, in spite of radiation re-scattering effects in the arrays of particles [7–9].

In earlier papers [10–12] we presented the study of solid surface nanostructuring under the exposure to femtosecond laser pulses using dielectric microspheres deposited onto the surface. It was experimentally demonstrated that the conversion of a part of the initial femtosecond laser pulse energy into the second harmonic using a nonlinear crystal, i.e., the use of bichromatic pulses, leads to the reduction of the laser nanostructuring threshold nearly by two times, and to the decrease in the transverse dimension of the structural elements, e.g., the ablation craters in polymers. The radius of the craters umade by bichromatic pulses did not exceed 100 nm and was by 30% smaller than that in the case of irradiation at the fundamental frequency. As samples we used polymethylmethacrylate (PMMA) or glass plates with layers of polystyrene spheres 1 μm in diameter deposited on them.

The modification of surface (ablation, swelling) at the intensities higher than 10^{12} W cm^{-2} occurs via ionisation. We have shown that the second harmonic radiation is more efficient for multiphoton ionisation, i.e., for creating seed electrons in the conduction band, whereas the fundamental frequency radiation multiplies the seed electrons via impact ionisation. Thus, the second harmonic creates the seed for the formation of structures, while the fundamental frequency radiation provides the power effect.

At the present stage of the work we continued the study of surface nanostructuring using bichromatic femtosecond laser pulses with the aim to achieve a significant increase in the recording density of the structures per unit area and to optimise the structure parameters with respect to the earlier achieved ones. The created microstructures are localised within the areas where the second harmonic has an effect; therefore, the spheres used as microlenses were chosen small enough to provide the focusing on the surface of the modified sample for the second harmonic only, without increasing the radiation intensity at the fundamental laser frequency. We managed to obtain nanostructures using the spheres 0.45 μm in diameter, which allowed an increase in the recording density in the resulting structures by nearly five times.

2. Deposition of a layer of colloid particles onto the surface of a solid

In order to obtain a large ordered structure array on a dielectric surface we used dielectric transparent spherical microparticles (microspheres), which played the role of microlenses focusing the laser radiation (Fig. 1). The layers of microparticles were deposited directly on the substrate.

The formation of colloid crystals was a subject of considerable attention starting from the work by Langmuir [13], in which the effect of interaction between colloid particles in solutions and in a sediment state on the formation of high-

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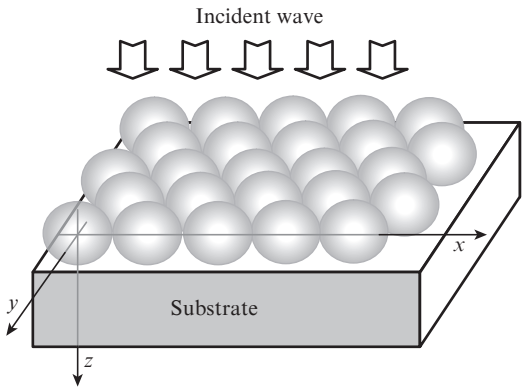

Figure 1. Closely packed structure of microspheres on the substrate surface. The shown Cartesian coordinate system is used in the explanations below.

quality colloid crystals was considered. At present, tens of methods are developed for surface deposition of particle layers from solutions, many of them being based on the Langmuir–Blodgett method. The resulting ordered arrays of particles [14, 15] are then used as microscopic focusing elements. Under laser irradiation, this leads to the formation of ordered surface structures with the scale beyond the diffraction limit. Transparent dielectric microspheres deposited on dielectric substrates, including polymers, are traditionally chosen for this purpose. The particles and substrates, similar to those presented in this paper, were used in Ref. [16], where polystyrene and glass microspheres could be deposited onto the polymer substrates with the densities at the level of up to $\sim 10^5$ cm^{-2}, which is insufficient for creating structures with submicron period.

Reducing the diameter of microspheres deposited on the substrate surface by more than two times (in the previous work we used spheres with a diameter ~1 μm) essentially increases the complexity of creating high-quality structures on the surface.

In the present experiment polystyrene (PS) spheres with a diameter ~0.45 μm and a mean deviation of the diameter not exceeding 0.06 μm were deposited on PMMA (1.5-mm-thick AKRIMA 72 organic glass plate). The suspension with the chosen concentration of microspheres was prepared so that after drying of a drop on the horizontal substrate a monolayer was obtained. As a result of this operation, the closely packed layers with hexagonal symmetry were obtained. The structure defects in such layers and the domain dimensions are determined by the dispersion of the sphere sizes. Each of the closely packed domains consisted of hundreds of microparticles (Fig. 2).

The difficulty of creating structures on the surface is due to the fact that in colloid solutions the solvent is often (e. g., in our case) water (its advantage is the large dielectric constant), while the polymers are typically hydrophobic. The process becomes more difficult with decreasing microsphere size. In the present paper, in order to obtain layers of microparticles on the PMMA surface we have chosen the way of preparing the suspension of particles in a complex solvent [lyophilic solvent (ethanol) – water] directly on the polymer surface. On the one hand, this reduced the dielectric constant of the solvent, making the parasitic particle coagulation more probable, but, on the other hand, this enhanced the substrate surface wettability. The simultaneity of these processes and the

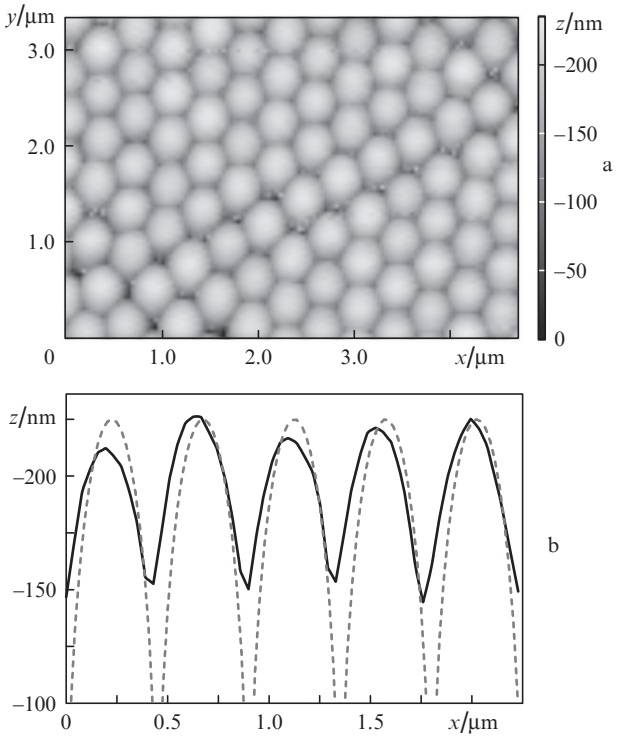

Figure 2. (a) Image of a closely packed structure of PS microspheres with the diameter 0.45 μm on the PMMA surface, obtained using the scanning probe microscope, and (b) the structure profile of the spheres (solid line) and the ideal contacting spheres with the diameter of 0.45 μm (dashed line).

small time of the drop drying reduce the negative effect of the PMMA hydrophobic property. By optimising the solvent composition, one can obtain microparticle layers on the polymer surface with the quality sufficient for performing laser irradiation experiments. For this aim, a drop of ethanol is first applied to the substrate. Due to its high wettability ethanol easily spreads over the surface. Then, on the layer of ethanol a drop of aqueous suspension of PS spheres with the necessary concentration (~0.1 mass %) is deposited. The drop of aqueous suspension spreads over the surface of the ethanol drop and after drying under laboratory conditions forms the colloid coating consisting of PS spheres on the substrate.

To visualise the structure consisting of microspheres and to control its quality we used an NT MDT Solver Pro scanning probe microscope, operating in the semi-contact regime.

Under laser irradiation each of the microparticles in the layer produces a region of local magnification of the laser field in the substrate directly beneath it. As a result, the formation of periodic structures on the substrate is possible. However, in a closely packed array the microspheres are not separate independent microlenses. The effects of radiation rescattering between adjacent microparticles can have an essential influence, and different collective effects can also manifest themselves [12]. The detection and investigation of such effects is necessary for efficient use of arrayed microspheres as near-field focusing devices in solving the nanostructuring problems.

To optimise the characteristics of microstructures obtained on the surface, the calculations have been carried out for the distribution of the electric field amplitude absolute squared value $|E|^2$ near the configurations of PS spheres with

the diameter ~0.5 μm on the substrate. The calculations were performed for the cases of irradiating the sample with a plane monochromatic wave having the wavelength 800 nm (the fundamental frequency of the Ti : sapphire laser) and 400 nm (the second harmonic). The results of calculations [11] show that for the second harmonic there is a region near the surface of the substrate where the squared absolute value of the electric field strength essentially increases (has maxima), whereas the radiation at the fundamental frequency has no such maxima. The radiation at the wavelength 800 nm passes through the layer of microspheres so that the effect on the dielectric to be modified is relatively uniform.

For the calculation we used the finite-difference time-domain (FDTD) method with the step of numerical scheme 2 nm. For modelling an infinite monolayer of microspheres the periodic boundary conditions along the directions x and y were applied.

3. Effect of femtosecond laser pulses

The experimental scheme of irradiation of the prepared samples by femtosecond laser pulses was similar to that presented in Refs [10, 11], in which the principle of the elements's functioning and the specific features of constructing the optical scheme were described in application to short femtosecond pulses.

A Spitfire Pro femtosecond laser system generated radiation pulses at the fundamental frequency (FF) with the wavelength 800 nm. The autocorrelation function width measured using a single-shot autocorrelator (SSA) amounted to 72 fs, which corresponds to the pulse duration of 50 fs, provided that the envelope function shape is Gaussian. In the converging beam after the lens with the focal length 15 cm the second harmonic (SH) generation occurred in the thin (100-μm-thick) BBO crystal. The substantiation of choosing this scheme is presented in Ref. [17]. With such an arrangement of the crystal with respect to the lens the minimal delay between the pulses of the first and the second harmonics is achieved; according to the estimates, it does not exceed a few femtoseconds, which is significantly smaller than the pulse duration. For the irradiation we used single bichromatic (FF + SH) laser pulses. The efficiency of the second harmonic generation was 7% (estimated by the pulse energy ratio at two wavelengths). The microspheres with the diameter 0.45 μm came off from the PMMA surface leaving smooth areas (free of sphere remainders) only in the case of combined effect of the second and the first harmonics in the intensity range 5–12 TW cm^{-2} (the second harmonic intensity being 0.7–1.7 TW cm^{-2}), which significantly exceeds the elimination threshold for micron-size spheres, the laser beams being the same. Only at the intensity of the bichromatic pulse of 8–10 TW cm^{-2} this irradiation made it possible to detect surface structures, corresponding to the preceding arrangement of spheres and being not their remainders, using the scanning probe microscope.

The result of the femtosecond laser pulse impact on PMMA is presented in Fig. 3. Under the sole irradiation by SH or FF pulses it was impossible to detect structures, because either the spheres did not come off, i.e., no smooth areas free of spheres appeared (in the entire operating range of the SH intensity or small FF intensity), or after the sole FF laser pulse action at large intensities (greater than 12 TW cm^{-2}) the probing of the surface with the atomic-force microscope

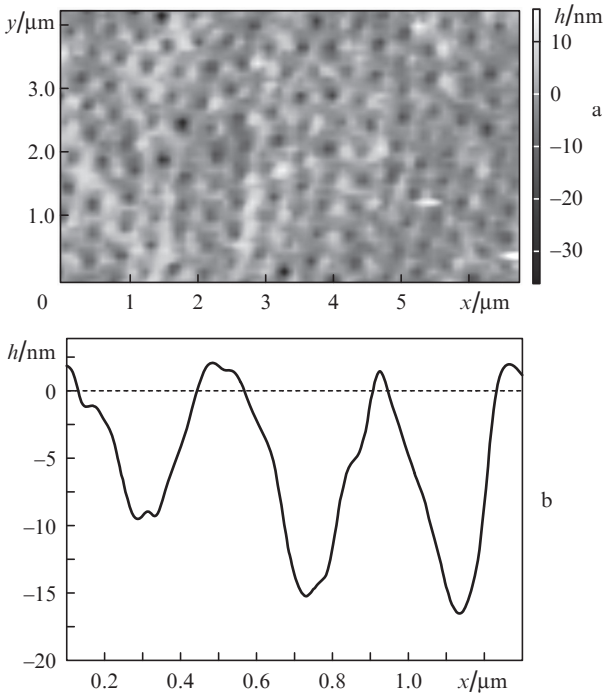

Figure 3. (a) Ablation structures, formed on the surface of PMMA under the effect of a single bichromatic femtosecond pulse using the layer of microspheres with the diameter 0.45 μm, and (b) the cross section of the sample surface with the xz plane, i.e., the distribution of heights h above the substrate plane. The dashed line shows the mean level of the substrate height.

(AFM) detected a jelly-like coating due to the destruction of spheres.

One more difficulty was that under the sequential irradiation of closely spaced (with the separation of 0.5–1 mm) areas of the sample it appeared that at the next point the field of coating with spheres is already destructed and perturbed in height by the previous laser pulse. In this perturbed area the spheres came off at an essentially (by 2–3 times) smaller threshold power, but in this case no surface structures appeared. The perturbed and unperturbed surfaces coated with a monolayer of spheres visually differed in colour hues. Only when irradiating the areas separated by more than 5 mm it was possible to obtain high-quality surface structures.

The best and high-quality image of the surface structures was obtained using AFM in the contact scanning regime. It was found that at the positions corresponding to the initial position of spheres with the diameter 0.45 μm at the surface the ablation craters were formed (Fig. 3).

As a result of processing 50 different surface profiles after the effect of bichromatic laser pulses with peak intensity ~8 TW cm^{-2} the following statistical parameters of the obtained structures were found: the depth 11.5 ± 2.8 nm, the half-depth diameter of the structures 169 ± 20 nm. The results of the statistical processing are presented in Fig. 4.

Thus, using bichromatic femtosecond laser pulses it is possible to obtain surface structures using spheres with the dimension of the order of the second harmonic wavelength, when the second harmonic creates a seed of the structure, and the fundamental frequency is used for the energy effect. The focusing of the radiation at the fundamental frequency is not required.

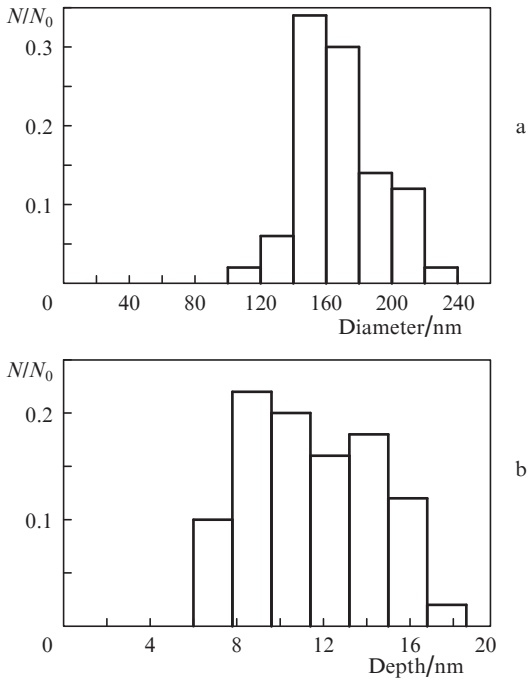

Figure 4. Results of statistical processing of the data on (a) the diameter and (b) the maximal depth of ablation craters in PMMA from the analysis of 50 spatial profiles.

4. Discussion of the mechanisms of generating seed electrons

Earlier we supposed that in the process of ionisation of the substrate material at the stage of creating the seed electrons, the main role is played by the second harmonic radiation. Indeed, the two-photon absorption at the wavelength of the second harmonic leads to the transition of an electron into the conduction band. However, the used PMMA substrates contain methyl methacrylate that has the absorption band near the wavelength 266 nm, which corresponds to the energy of three quanta of radiation at the fundamental frequency. Therefore, both the two-photon absorption of two SH quanta and the two-photon absorption of SH + FF quanta can lead to the generation of seed electrons. These two mechanisms determined the spatial localisation of the structure to be created, determined by the minimal dimensions of the focal spots of the interacting harmonics, i.e., actually by the dimensions of the SH focal spot, as it was shown above by theoretical calculations. Then the fundamental frequency radiation increases the number of free electrons by impact ionisation. To separate the mechanisms of seed electrons creation we propose to use the optical scheme that introduces a time delay between the first and the second harmonic pulses. It is expected that in the case of spatial coincidence of both pulses both mechanisms will act, while in the case when only the SH pulse is first acting (the FF pulse being delayed) the mechanism of generating the electrons at the expense of SH + FF two-photon absorption will be considerably weakened. Such experiments will allow better understanding of the nature of processes that underlie the nanostructuring. The construction of an appropriate optical setup is planned by us in the nearest future.

5. Theoretical development of methods for increasing the recording density of nanostructures

The possibility of a further increase in the recording density of nanostructures at the substrate surface using the method of near-field nanoparticle-assisted lithography was studied theoretically. It was shown that a decrease in the sphere size with

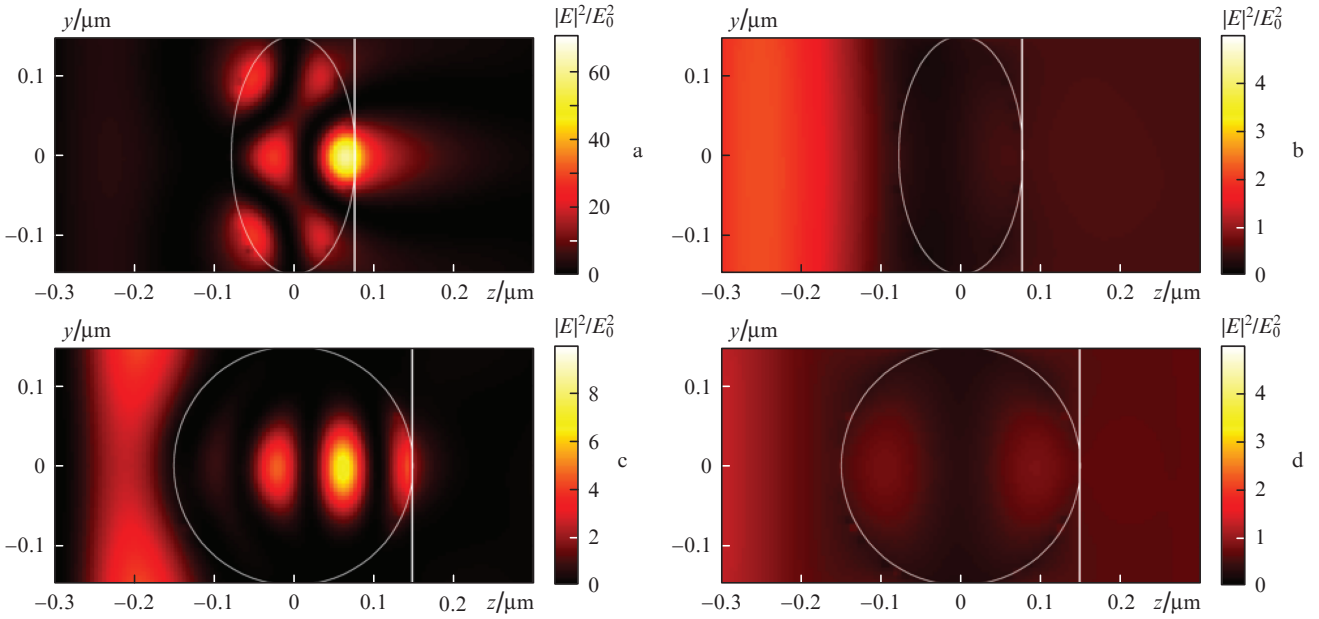

Figure 5. Distributions of the squared absolute value of the electric field strength, formed near the closely packed arrays of (a, b) spheroids and (c, d) spheres made of TiO_2 on the PMMA substrates under the effect of the radiation at the wavelengths (a, c) 400 and (b, d) 800 nm, incident normally to the substrate surface.

the refractive index 1.4–1.6 (silica, polystyrene, etc.) to the diameter smaller than the wavelength practically leads to the elimination of the field focusing behind the spheres. The attempt to decrease the sphere size with a simultaneous increase in the refractive index leads to a shift of the main maximum of the field into the sphere, which also makes it difficult to use the systems of such microparticles for surface nanostructuring. It is shown that this problem can be solved by using arrays of spheroidal particles rather than spherical ones. The oblate shape of the spheroidal microlens reduces the negative effect of aberrations and makes it possible to obtain a pronounced maximum of the field at the boundary between the particle and the substrate even using microlenses with a large reflective index (e. g., spheroids made of titanium dioxide) and the diameter, smaller than the wavelength. As a result, it is possible to achieve a further increase in the nanostructure recording density.

Figure 5 presents the distributions of a squared absolute value of the electric field amplitude near the closely packed arrays of spheroids and spheres made of TiO_2 on PMMA substrates under irradiation at the wavelengths 400 and 800 nm, calculated using the FDTD method. The diameter of spheres and spheroids is 300 nm; the height of spheroids is 155 nm. The incident wave is linearly polarised along the x axis. The refractive indices amount to 3.0 (λ = 400 nm) and 2.6 (λ = 800 nm) for TiO_2 and 1.5 (λ = 400 nm) and 1.49 (λ = 800 nm) for PMMA.

As seen from Fig. 5, the spheroids focus well the second harmonic radiation near the surface of the substrate, whereas the radiation at the fundamental frequency is not focused by this system of particles. Note also that the use of titanium dioxide spheres is not efficient, since the radiation is focused inside the spheres. The spheres of this size made of polystyrene do not focus the second harmonic radiation.

6. Conclusions

The method of depositing the microspheres with the diameter smaller than 0.5 μm onto hydrophobic polymer substrates is developed and implemented.

Using the method of surface structuring under the combined effect of the fundamental frequency and the second harmonic of a femtosecond laser through the ordered array of microlenses allowed an increase in the recording density (by nearly five times) using microlenses with the diameter of 0.45 μm that do not focus the laser radiation at the fundamental frequency.

The theoretical calculations are carried out that demonstrate the possibility of further improvement of the characteristics of a separately taken structure and the resolution increase using non-spherical microlenses with a high refractive index.

The mechanisms of the surface nanostructure formation under the laser impact are proposed, as well as the methods experimentally revealing the contributions from different mechanisms.

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