
Optical Nanocomposites Based on High Nanoparticles Concentration and Its Holographic Application

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1. Introduction

The main problem of current photolithography is diminishing of minimal feature sizes up to subwavelength value. The smallest feature size X_{\min} that can be projected by a coherent imaging system is $X_{\min}=\lambda/2NA$, where λ is the wavelength of the illumination and NA is the numerical aperture of the lens. The most ordinary way to attain smaller feature sizes is to reduce the wavelength up to 193 nm. The NA is typically 0,8, so the feature size is on the order of the exposure wavelength. State of the art semiconductor fabrication facilities in the year 2010 are forecasted to use a 32 nm process, in these conditions to achieve the required resolution and depth of field optical lithography techniques become increasingly difficult.

Now was developed new lithography technique - deep lithography that suitable for making elements with high aspect ratio. Here for vertical borders preparation it is need to use NA about 0,05 or less that limit resolution by value around 4 μm .

As the fundamental limits of optical lithography are approached, the nonlinear, self-focusing and self-writing properties of the photoresist become increasingly important.

Special UV-curable nanocomposite with strong non-linear and self-writing effects used as a photoresist to improve light distribution in the spot as well in volume of photoresist can be used. Same proposed technique is applicable for deep lithography based on 365 nm UV light with high scattering to improve shape of small feature in results violation of the laws of geometrical optics at use light self-focusing in materials. If to make nanocomposite system with self-writing effects and place it as a topcoat, we will obtain self-writing subwavelength artificial waveguide that will guide the light to small subwavelength spot. So to make it it's necessary to develop special material with self-writing effects.

Same material having self-writing effects will be applicable for holographic lithography, i.e. writing of 3D lattice by interference of two, three or four coherent laser beams. Self-writing effects will increase modulation of refractive index of material and therefore diffraction efficiency of ready element.

Current work describes development of nanocomposite material, investigation of its holographic properties and sub wavelength lithography application based on self-writing effects in material.

2. Nanocomposite based on nanoparticles in UV-curable monomers mixture

2.1. Materials and methods

Chemicals: Monomers 2-Carboxyethyl acrylate (2Carb, Aldrich № 552348), Bisphenol A glycerolate (BisA, Aldrich № 41,116-7), 2-Phenoxyethyl acrylate (PEA, Aldrich № 40,833-6). ZnO nanoparticles with a size of 20 nm (Russian local supplier); SiO₂ nanoparticles with a size of 14nm (Aldrich No. 066K0110) were used for structuring nanomodification. 2,2-Dimethoxy-2-phenylacetophenone (Aldrich No.19,611-8) and Bis (5-2,4-cyclopentadien-1-yl) bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium (Irgacure 784) were used as initiators of the photopolymerization.

Transmission spectra were measured on a spectrophotometer Perkin-Elmer 555 UV-Vis. For the IR spectra we used Fourier IR spectrometer FSM 1201 Manufacturer Company "Monitoring". Samples were prepared by pressing pellets with KBr. The index of refraction is determined by the Maxwell-Garnett effective medium theory [1] and by Abbe refractometer.

We study sorption of water vapor by gravimetric method. Hardness is measured by Brinell method with "Bulat-T1" device. Light scattering is measured by the photometric sphere method in accordance with the recommendations of the European standard ASTM D1003.

Investigation of the surface profile of samples was made with an atomic-force microscope Ntegra in contact mode.

2.2. Preparation of monomer solutions and films of the nanocomposites

We find some effects at mixing of nanoparticles with monomer mixture. At nanoparticles introduction in the composition of the monomer BisA/2Carb (30/70) above a concentration of 8 wt. % the viscosity of solutions increases greatly. At higher concentrations (14 wt. % ZnO and 10 wt. % SiO₂) the monomer mixture becomes very viscous transparent gel at room temperature.

Transparent nanocomposites were obtained up to 14 wt. % of ZnO and 12 wt.% SiO₂ nanoparticles with formation of transparent film after UV-curing. More than 14 wt. % of ZnO and 12 wt.% SiO₂ nanoparticles addition to the monomer mixture resulted in turbid films. The system becomes heterogeneous.

Polymer films (thickness from 12 to 100 microns) were obtained from the previously prepared solutions containing monomer, nanoparticles and initiator. The drop of solution is trapped between two polyester films to prevent inhibitory effects of oxygen. All experiments were accomplished at room temperature in air without special inert atmosphere. UV curing was made by a mercury lamp (100 W) used at the mercury line at 365 nm.

2.3. Results

The films are transparent in the visible and UV spectral region. A significant decrease in optical transmission is observed at high concentrations of ZnO (more than 14 wt. %) and concentrations of SiO₂ more than 8 wt. %.

The values of the refractive index nanocompositions shown on Figure 1.

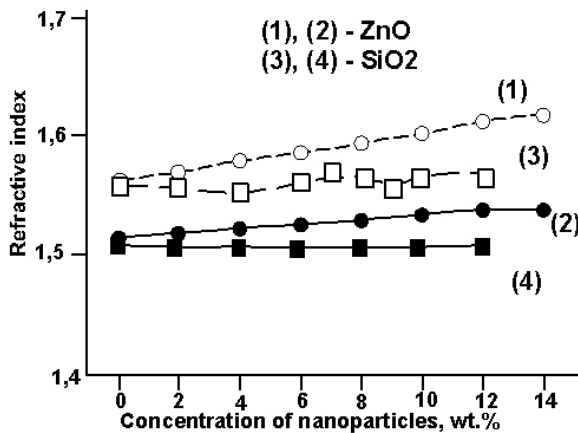


Figure 1. Refractive index is determined by the Maxwell-Garnett effective medium theory (3), (4) and by Abbe refractometer (1), (2)

For the refractive index were used effective medium model of Maxwell-Garnett:

$$\frac{\varepsilon_{eff} - \varepsilon_2}{\varepsilon_{eff} + 2\varepsilon_2} = f_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \quad (1)$$

ε_1 – permittivity of the medium;

ε_2 – permittivity of inclusions;

ε_{eff} – permittivity of the composite medium;

$$f_1 = \frac{1}{V} \sum_i V_i \quad (2)$$

volumetric filling factor; (V_i - volume of i -th particle, V - volume of the composite environment).

This model is applicable when the volume filling factor: $f_1 \leq \frac{1}{3}$, i.e. fraction of inclusions is small. The obtained values for the film samples by Abbe are greater than calculated by Maxwell-Garnett model. Model of Maxwell-Garnett is applicable in the case if nanoparticles are distributed inside any matrix without interaction between nanoparticles and polymer. According our recent results, there are interactions between nanoparticles and polymer matrix. Therefore, the use of this model is not entirely correct. In addition, the refractive index obtained by Abbe of the film samples are greater than calculated by Maxwell-Garnett model, as we assume due to the fact that the polymerization did not pass until the end and the residual monomer are contain in the matrix. With the introduction of the maximum possible concentration of SiO₂ (12 wt.%), the refractive index of the composition is reduced by 0.02 compared with the initial monomer mixture. Refractive index of composition with maximum ZnO concentration (14 wt. %) is increased by 0.045 compared with the polymer without nanoparticles.

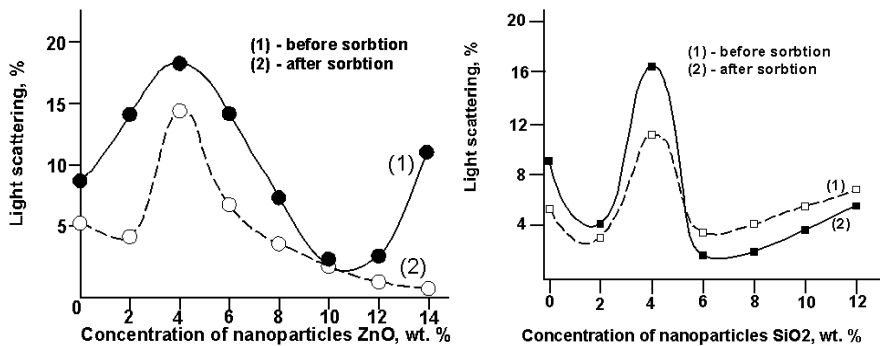


Figure 2. Scattering before and after water sorption of the composition BisA/2Carb (30/70) according to nanoparticles concentrations

The scattering before and after water sorption of the composition BisA/2Carb (30/70) according to nanoparticles concentrations shown on Figure 2. With increasing ZnO concentration scattering in nanocomposite is decreases, but near 4 wt. % there is a maximum of scattering. In our opinion a reorganization of polymer inner structure from polymeric structure with inclusion of nanoparticles to self-organized nanocomposite structure is occur near this concentration. When the concentration of ZnO is in the range from 8 to 14 wt%, scattering is almost independent on the concentration of nanoparticles. 8 - 14 wt% ZnO nanoparticles is sufficient for uniform distribution inside volume as a result homogeneous polymer nanocomposites are formed. In this nanocomposite structure, the scattering decreases compared to pure polymer, approximately twice. After the water sorption tests, the concentration dependence of the scattering of remains, but for all concentrations of the magnitude of sorption decreases.

Dependence of scattering of nanocomposites before and after the water sorption according to the SiO₂ nanoparticles concentration is shown in Figure 2.

Due to lack of nanoparticles concentration in the field up to 8 wt % the polymer is not homogeneous, resulting in a nonmonotonic variation of the scattering is observed. At concentrations higher than SiO₂ 8 wt%, nanoparticles are uniformly distributed throughout the volume and the quasi-homogeneous composite is formed. The scattering in the new structure is reduced compared to the polymer matrix approximately reduced by about half. After the water sorption tests the scattering dependence is conserved. For all compositions, except for pure composite and the composite with the addition of 12 wt.% SiO₂, the scattering is qualitatively does not change, but its value decrease. This phenomenon is explained by the possible water plasticizing effects, for example, see [2,3].

The water sorption experiments were conducted to study changing the internal structure as a result of the introduction of nanoparticles. As can be seen from the figure 3, the sorptions of nanocomposites have strong dependence from nanoparticles concentrations. There is a sorption maximum near 4 wt % ZnO (reorganization of polymer inner structure). At ZnO nanoparticles concentration above 12 wt. % water sorption increase, perhaps as a result of disordering of the nanocomposite. For pure polymer value, water sorption is 23 %. The introduction of 10 wt. % ZnO nanoparticles achieved reduction in water sorption by 5 times compared with the pure composition.

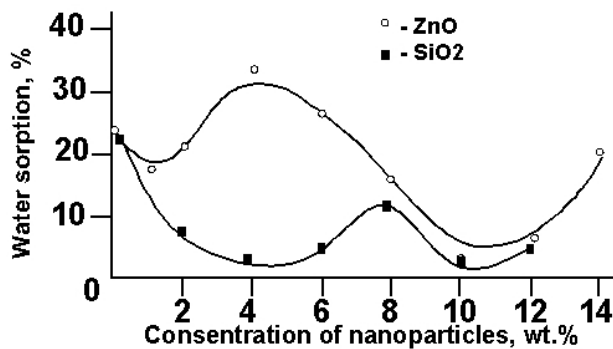


Figure 3. Water sorption BisA/2Carb(30-70) composites according to nanoparticles concentrations

With increasing SiO₂-concentrations higher than 12 wt.% the vapor sorption decreases steadily, reaching 2.5%. As compared to the unmodified polymer, the introduction of SiO₂ nanoparticles reduces the water absorption ten times. Formation of the extremum of adsorption at a concentration of 8 wt.% SiO₂ found no explanation.

The investigations of film hardness is an indirect way to study the effect of nanoparticles on the structural change of nanocomposites (Figure 4).

With the introduction of ZnO nanoparticles the film hardness decreases and remains almost unchanged until to 10%. Further, the hardness of the film increases and reaches the value of pure polymer. With the introduction of 2 wt.% SiO₂ film hardness increases sharply in comparison with the original. In the concentration range from 2 to 8 wt. % the composite film hardness is decreases sharply. Further, with increasing SiO₂ concentrations hardness

values start to increase and at the maximum concentration of SiO₂ (12 wt. %) it become comparable with the value of the pure polymer.

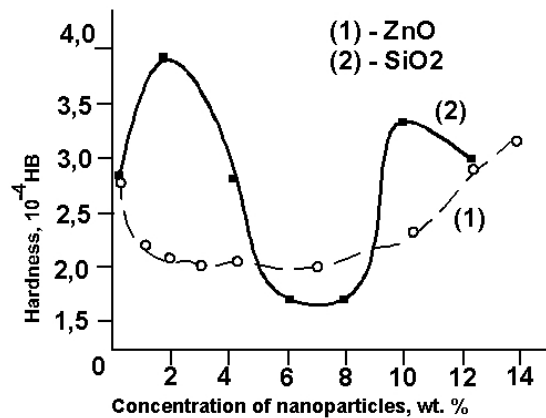


Figure 4. Hardness of BisA/2Carb(30-70) composites according to nanoparticles concentration

The above changes in the properties of polymer nanocomposites (water sorption, light scattering, hardness) can be explained by a modification of the supramolecular structure of the polymer as a result of possible interactions of nanoparticles with active groups of the monomers [4].

Nanoparticles influence on the polymer structure was confirmed by the investigation of the surface relief and rigidity of the surface nanocomposites films made atomic force microscopy (Figures 5 and 6).

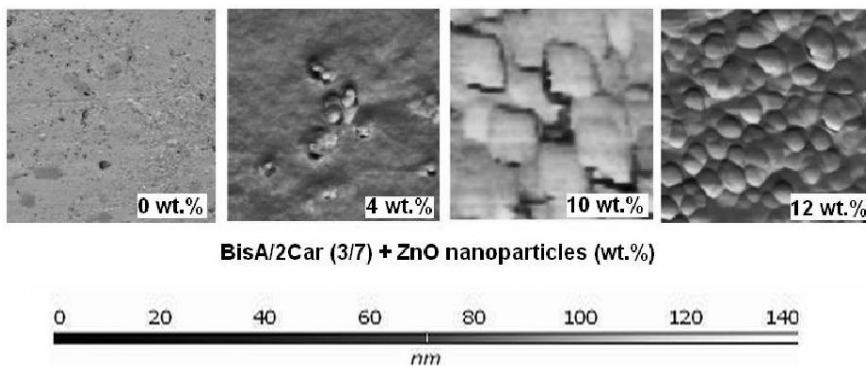
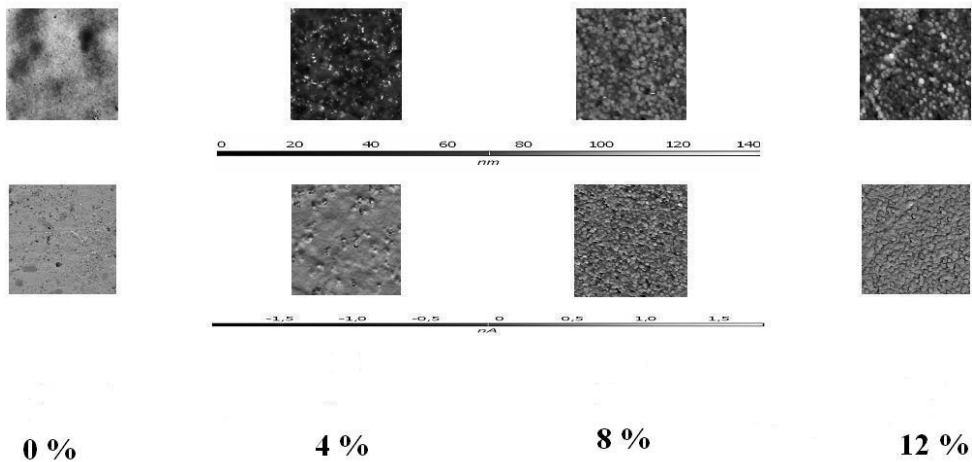


Figure 5. AFM. 5×5 mkm. Relief of surface ZnO polymer films

As can be seen from Fig.5, there are essential changes in the composition structure as compared with the original by introduction 4 wt. % ZnO nanoparticles. The formation of separate ZnO structured polymer regions were observed clearly. The graininess structure are observed throughout the volume of material when ZnO concentration are achieves 10 wt. %.



2 Car / Bis (70/30) + SiO₂ nanoparticles (wt %)

Figure 6. AFM. 5×5 mkm. Relief (top) and rigidity of surface SiO₂ polymer films (bottom)

As can be seen (Figure 6), already with the introduction of 4 wt.% of SiO₂ nanoparticles, significant changes in the nanocomposition structure are observed as compared to the pure polymer structure. The formations of separate domains are observed clearly. With the introduction of 12 wt.% SiO₂, structure of uniform graininess is formed throughout the material.

Apparently, formation of nanocomposition structure is due to the ability of nanoparticles to create on the surface bonds with the active groups of the monomer molecules and to act as centers of polymerization. When the ZnO concentration is more than 10 wt. % (SiO₂ concentrations of more than 8 wt.%) free polymer phase disappears and all the monomer is consumed for the formation of polymeric spheres on the surface of nanoparticles.

Thus, at low concentrations of nanoparticles, modified polymer areas are still small and composites are heterogeneous. Heterogeneous structures are reflected in their properties. Increasing nanoparticles concentration is lead to increasing hybrid field's amount and its size, so uniform nanocomposite structure begins to form. The result is the formation of submicron spheres around each nanoparticle and quasi-homogeneous material is formed. Indeed (Figures 5 and 6), submicron spheres formed around each nanoparticle possess almost identical diameters. This fact can be explained by identical growth rates of these spheres. As a result, a structure consisting of spherical particles forms a self-organized quasi-lattice. Eventually, above-named effects leads to a homogeneous distribution of nanoparticles and homogeneous composite environment are formed.

Possibility and mechanism of polymerization on surface of nanoparticles were investigated by FTIR (Figures 7, 8).

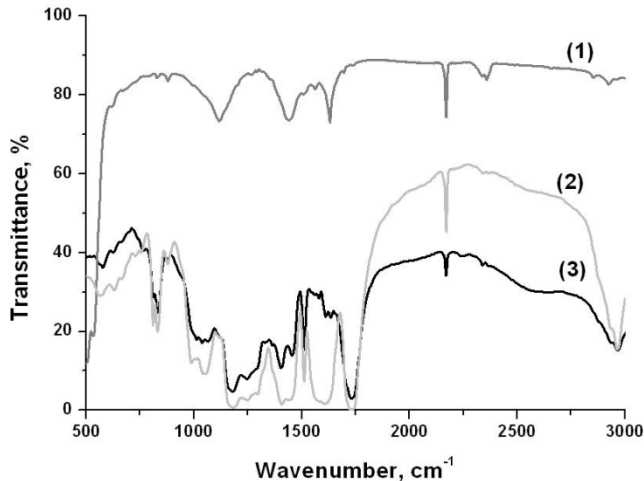


Figure 7. (1) - Nanoparticles ZnO; (2) - composition 2Carb/BisA (70/30) + 12 wt. % ZnO; (3) - 2Carb/BisA (70/30)

In the FTIR of BisA/2Carb (30/70) compositions the bands with maximum absorption at 1737 cm^{-1} , 1410 and 1188, 1050 cm^{-1} were observed. The first band is characteristic for the stretching vibrations of the carboxyl group, the next three due to a combination of plane deformation vibrations of the hydroxy group and the stretching vibrations of the C-O in carbonic acids [5].

Intense peak around 500 cm^{-1} belongs to the Zn-O vibrations in the ZnO crystal [6]. In the IR spectra of the nanocomposite the band at 1720 cm^{-1} (group C = O) is observed and the 1410-1450 cm^{-1} bands corresponding to symmetric stretching vibrations of the carboxylate anion are greatly enhanced.

It is important to note the following. The band 500 cm^{-1} , relating to the Zn-O vibrations in the crystal ZnO, is preserved. The absorption band 1620-1550 cm^{-1} appear in the composite. This region is characteristic of asymmetric stretching vibrations of the carboxylate anion. As reported in [7 - 9], the interaction of inorganic nanoparticles (ZnO) and carbonyl groups can cause changes in the IR, because the metal atoms can be taken electron pair of the carbonyl oxygen.

The increase in the absorption band of 1600 cm^{-1} may be due to the complexation between the polymer and nanoparticle.

In addition, the band 1640-1650 cm^{-1} is characteristic of the C = C stretching vibrations in the $\text{CH}_2 = \text{CHR}$, and the band 990 cm^{-1} is characteristic for C-H bending vibrations in the $\text{CH}_2 = \text{CHR}$ [10]. The appearance in the spectra of the composites above the bands confirmed that the group $\text{CH}_2 = \text{CHR}$ formed. These bands may be formed during the polymerization of the composite only on the surface of nanoparticles of zinc oxide when the latter acts as a photocatalyst.

Principal scheme of described photopolymerize process is shown in Figure 8.

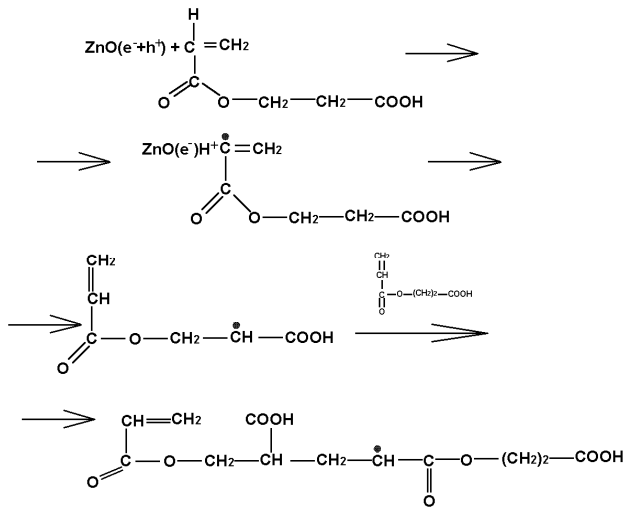


Figure 8. Scheme of photopolymerize process

The SiO_2 nanoparticles can form bonds with the monomers and act as centers of polymerization the same way. It was confirmed by FTIR spectroscopy (Figure 9). The peaks 500 cm^{-1} and 1109 cm^{-1} were attributed as the stretching vibrations of Si-O-Si bounds on SiO_2 surfaces [10]. The 1061 cm^{-1} band is attributed as the C-O stretching vibrations in the C-O-H [10]. The degradation of strong bands 471 cm^{-1} and 1107 cm^{-1} and the emergence of new band 1061 cm^{-1} in the nanocomposites may be indicative of polymerization on the surface of nanoparticles due to the interaction of COOH-groups of the monomer with nanoparticles SiO_2 .

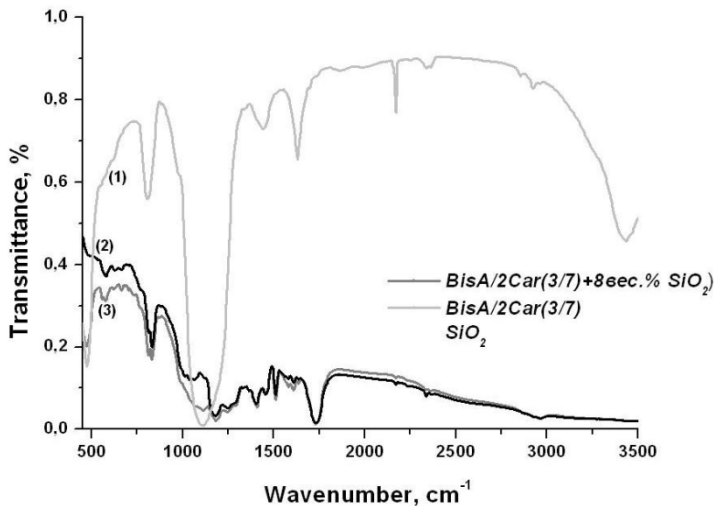


Figure 9. FTIR spectra: (1) - SiO_2 ; (2) - $\text{BisA/2Car (30/70) + 8 sec. \% SiO}_2$; (3) - pure polymer BisA/2Car (30/70)

2.4. Discussion results

According to the previously mentioned nanoparticles can be involved in UV polymerization process by formation of bonds between nanoparticle surfaces and carbonyl polymer group. Thus, the nanoparticles act as formation centers of a new polymer phase - the nanocomposite possessing different properties in comparison with the unfilled polymer. According to FTIR spectra of nanocomposites we assume that nanoparticles are participated in polymerization processes and act as a photocatalysts. Our hypotheses is supported by the formation of micron size spheres in nanocomposite around each nanoparticle (Figure 5, 6).

Nanosized semiconductor clusters have the potential to photooxidation. Photocatalysis take place through the combined effects of photoelectrons production at UV light absorption and high surface area in that electron transfer induced polymerization.

Nanosized semiconductor clusters may participate in catalysis of redox - processes on surfaces exposed to light, that is, they can be photocatalyst [11,12]. This is due to a combination of effects: formation of photoelectrons by absorption of UV light and, in addition, a large specific surface of nanoparticles contributes to their high catalytic activity. Thus, when the semiconductor catalyst absorbs the photon with energy equal to or greater than the value of the band gap, an electron from the valence band can move into the conduction band to form electron-hole pairs. In the future, such a pair can take part in the reactions of donor-acceptor mechanism on the catalyst surface, that is, can begin the process of polymerization. According to the work [13], the UV illumination of a semiconductor photocatalyst activates the catalysis and accelerates establishing a redox environment in the aqueous solution. Semiconductors act as sensitizers for light induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band [14]. So, the photocatalytic process of photopolymerization was induced as a result of light absorption on the surface semiconductor nanoparticles. The work [12] describes the process of polymerization of methylmethacrylate initiated by TiO₂ nanoparticles.

In our experiments we observed a similar process that proves by AFM and FTIR (the formation of equal spheres around the each nanoparticle, which are the center of polymerization and creation of chemical bonding between nanoparticle surface and polymer). Formation of spheres around each nanoparticle during photopolymerization on its surface appears to change a transformation of polymer structure. All nanocomposite properties exhibit extrema in the same areas of concentration of nanoparticles. Characteristic ranges of concentrations are 4 and 10 wt % for ZnO and 4 and 8 wt % for SiO₂. According AFM photos in this concentration range, new phase - nanocomposite are generated on nanoparticles surface with increasing amount nanocomposite in volume. This patterning affects the changes in material properties, light scattering and a water sorption are decreasing significantly.

At nanoparticles concentration more than 8 wt % for SiO₂ and 10 wt % for ZnO all monomer mixture will involved in formation of nanocomposite phase, perhaps next increasing of

nanoparticles concentration will result on competition between nanoparticles as the center of polymerization. At 8 wt % for SiO₂ and 10 wt % ZnO AFM photo show structures consisting from micro - spheres occupying all volume. In this concentration range light scattering as well as water sorption increasing. The above considerations explain the extrema of properties with increasing concentration of nanoparticles.

3. Holographic writing of periodic lattice in nanocomposite material

Holographic writing was conducted when recording the periodic structures in an interference field created by the interaction of two plane waves with wavelengths of 325 nm and 442 nm. The structures period was 2 microns. The diffraction efficiency was determined at a wavelength of 633 nm as a ratio of the first-order diffraction intensity to the incident radiation intensity. The layers were formed on a glass substrate in the gap between the glass and a polyester film. The thickness of the layer depended on the size of the filling and was 20 microns.

Abbreviation of used chemicals: 2-carboxyethyl acrylate (2Carb); Bisphenol A glycerolate (BisA); 2-Phenoxyethyl acrylate (PEA).

Three methods of post exposition processing were used:

1. After exposure by interference field any additional processing was not made.
2. After exposure by interference field nanocomposite film were developed by isopropyl alcohol ablation.
3. After exposure by interference field were made uniform UV-radiation exposure.

Holographic writing on nanocomposites is due on light induced nanoparticles redistribution. Effects of light induced nanoparticles redistribution in nanocomposite is a new effect discovered recently. It takes place at photopolymeric nanocomposite irradiation by periodic light distribution, for example by lattice made by interference of two laser beams.

The first time these processes were found by Tomita and co-workers in 2005 on organic-inorganic nanocomposite photopolymer system in which inorganic nanoparticles with a larger refractive index differs from photopolymerized monomers are dispersed in uncured monomers [15]. Inorganic materials possess a wide variety of refractive indices that give us the opportunity to obtain much higher refractive index changes Δn than conventional photopolymers, while maintaining low scattering losses [16].

Explanation of effects was made in the work Y. Tomita at all [17]. For monomers with radical photopolymerization spatially nonuniform light illumination will produce free radicals by dissociation of initiators, and subsequent reaction of free radicals with monomers, which leads to chain polymerization of individual monomers in the bright regions.

This polymerization process lowers the chemical potential of monomers in the bright regions, leading to diffusion (short distance transportation) of monomers from the dark to the bright regions. On the other hand, photosensitive inorganic nanoparticles have

diffusion from the bright to the dark regions, as illustrated in Figure 10 left, since the particles are not consumed and their chemical potential increases in the bright regions as a result of the monomer consumption. Such a mutual diffusion process essentially continues until the monomers are consumed completely by the monomolecular and bimolecular termination processes and until the high viscosity of a surrounding medium consisting of polymerized monomers makes monomers and nanoparticles immobile. As a result the spatial distribution of nanoparticles is also fixed and a refractive-index grating is created as a result of compositional and density differences between the bright and the dark regions [17].

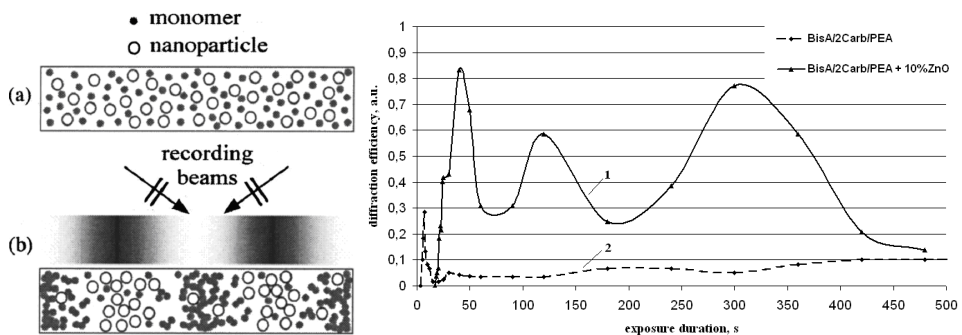


Figure 10. In the left - nanoparticles transportation in photopolymer according to work [18], in the right - our experimental diffraction efficiency dependence on exposition with and without nanoparticles.

Figure 10 shows diffraction efficiency dependence of photopolymerizable nanocomposite material from exposition time and nanoparticles concentration. Unlike of classic holographic photopolymer in our material unpolymerized materials were dissolved by alcohol and removed after exposition (method 2). According to schema (Figure 10 left) unpolymerized monomer in dark areas was removed by dissolution. High augmentation of diffraction efficiency at 12% nanoparticles concentration is a result of nanoparticles redistribution.

Detailed investigation of temporal traces of the first order diffraction efficiencies DE for the nanocomposites samples give oscillation of DE at increasing of exposition time and its dependence from processing of the samples. Figure 10 left shows the diffraction efficiency dependence from exposition for the nanocomposite BisA/2Carb/PEA 25/55/20, ZnO 10% in comparison with the monomer composition based of the same components without nanoparticles (Energy density: $2 \cdot 10^{-2}$ J/cm², a period of structures: 2 microns). We see a significant increase in the diffraction efficiency for the nanocomposite.

Figure 11 shows diffraction efficiency dependence from exposure and its change during one day storage and after uniform UV-radiation exposure (365 nm, $3 \cdot 10^{-1}$ J/cm²) (method 3).

The periodic nature of the kinetic curves can be seen. The first maximum of diffraction efficiency just after exposure (Figure 11, curve 1) at low exposures can be connected to

increasing of refractive index of composition after polymerization. Refractive index are increasing on 0,04 in result of photopolymerization In bright areas. In dark areas photopolymer will keep in liquid state. Difference of RI between liquid and solid (polymerized) composition will result in increasing of DE. After entire polymerization either by long exposition or by UV light 365 nm, whole composition will be polymerize and DE will decrease (curve 2, Figure 11).

At the same time nanoparticle diffusion process take place. It is seen that DE builds up after a relatively long induction time period that usually corresponds to the time duration to consume contaminated oxygen [18]. In fact nanoparticles displacement will begin after at last 50% photopolymer conversion that result on induction period. If uniform exposition of nanocomposite after laser lattice writing take place, whole composition will be polymerized and refractive index modulation of cured material will be connected to displacement of components only.

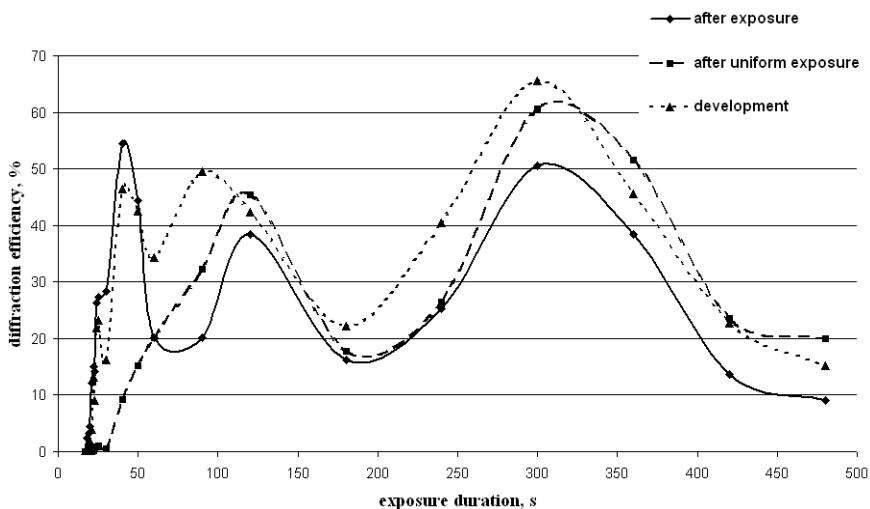


Figure 11. The dependence of the diffraction efficiency from exposure duration for the nanocomposite BisA/2Carb/PEA 25/55/20, ZnO 10%. Just after exposure (1), after uniform exposure (2) and one day after exposure (3). Energy density: 10^{-2} J/cm², a period of structures: 2 microns

According to the work [19] DE builds up after a induction time period, going to the maximum and finally decays almost to zero, which is a typical behavior of one component photopolymers without any binder materials. Our nanocomposite have no conventional binder, so its exposition curves should have the maximum, but unlike of conventional photopolymer, nanocomposite having two diffusing comments, i.e. monomer and nanoparticles form two maximums. Mutual location of the maximums depend on diffusion coefficients of monomer and nanoparticle.

Stability of obtained DE at last during one day proves components diffusion nature of the maximums at 120 and 300 s (Figure 11). After uniform exposition by 365 nm UV,

nanocomposite become solid, diffusion processes will stop and will keep existing distribution of nanoparticles in composition. Some increasing of DE after exposure can be due to compression of nanoparticles in dark areas in solid nanocomposite.

Application of more viscous composition will result of diffusion braking and can be expect to braking of back diffusion at overexposure resulting of DE fall after maximum (Figure 11).

For that reason we use SiO₂ based nanocomposite very viscous and receive absence of DE fall after maximum (Figure 12).

Instead of lattice writing in ZnO based nanocomposite (Figure 12), DE increase here up to maximum value and keep stable after exposition. Lattice made in nanocomposite is stable and survive heating up to 150C during one hour without fall of DE.

DE of material is result of nanoparticles displacement, so nanoparticles moved to the dark areas can be made visible by different microscopy methods.

Transmission optical microscopy photo on micro- cut and confocal microscopy photo of micro lattice are shown in Figure 13. According Figure 13 (right) there takes place short distance nanoparticles transportation to the bright regions with change of solubility of material and reinforcement of polymerized 3D lattice formation.

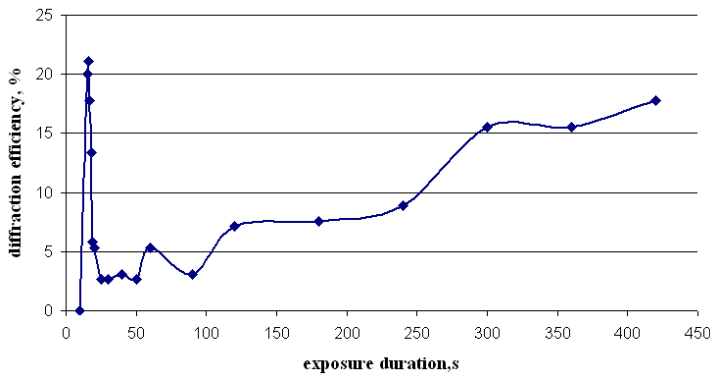


Figure 12. The dependence of the diffraction efficiency from exposure duration for the nanocomposite BisA/2Carb 30/70, SiO₂ 6%. Energy density: 10⁻² J/cm², a period of structures: 2 microns

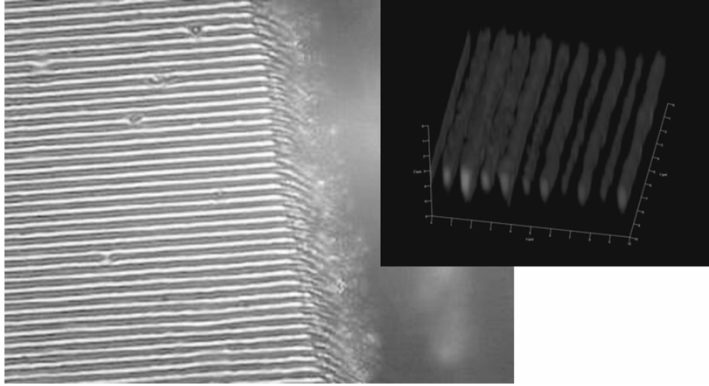


Figure 13. Micro- photo of cut of 3D structure (objective 160x, aperture 1,4) and confocal microscope plot of same structure (insert)

Next show the first experiments on making visible nanoparticles redistribution by removing of polymer without nanoparticles by ion etching. Result of ion etching of previously made holographic micropatterns in nanocomposite is shown on Figure 14.

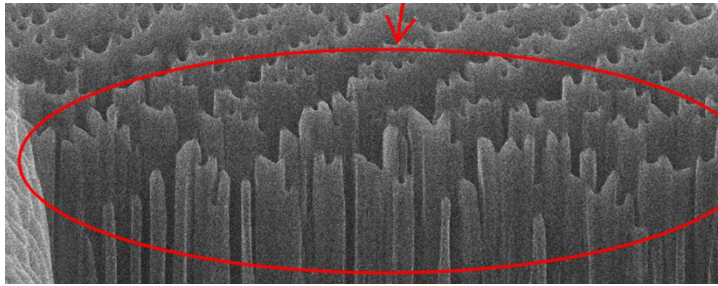


Figure 14. Ion beam etching of micropatterns will result on evaporation of polymer and keeping of nanocomposite areas with formation of vertical elements 100 nm width and 10 nm height

We think that ion beam etch free polymer and to not touch nanoparticles enriched areas. In result after that nanoparticles redistribution becomes visible, it is forms subwavelength nano- sized columns with high aspect ratio.

Direct observations of nanoparticles displacement were made by dissolution of liquid uncured composition and surface investigation by AFM method.

Figure 15, c show AFM surface of nanocomposite cured by uniform UV exposition. It is seem as nanoparticles distributed on whole surface.

After lattice writing and dissolution of uncured composite we obtain AFM photo (Figure 15 a, b). Clear visible concentration of nanoparticles in dark areas. Nanoparticles arrange maximal densely and have no in light areas.

So we find direct confirmation of light assistant nanoparticles displacement in nanocomposite.

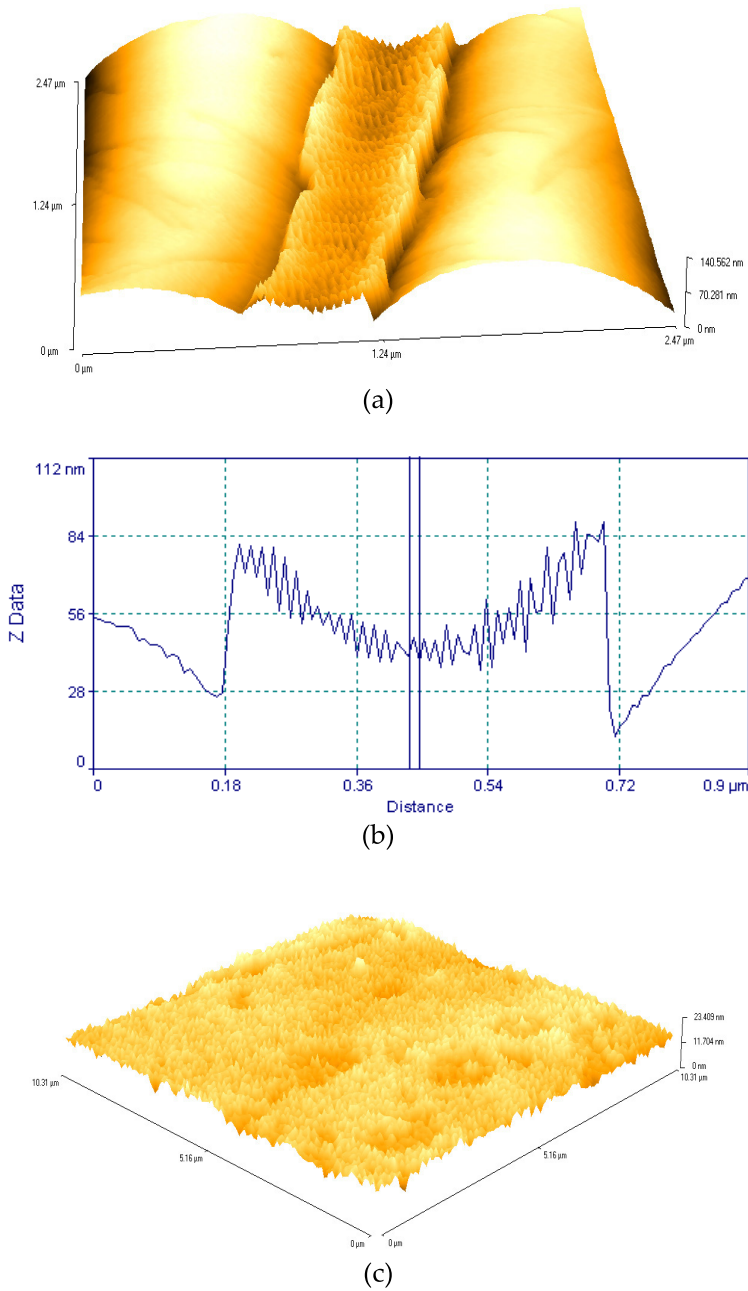


Figure 15. 3D image (a) and plot (b) of a fragment of a polymer structure recorded on the nanocomposite BisA/2Carb/PEA 25/55/20, ZnO 10% and the structure of films of the nanocomposite (c). Period of structures: 2 microns

4. Self-organization processes in photopolymerizable nanocomposite

The main problem of current photolithography is diminishing of minimal feature sizes up to subwavelength value. The smallest feature size X_{\min} that can be projected by a coherent imaging system is $X_{\min}=\lambda/2NA$, and the depth of focus DOF is $DOF=\lambda/[2NA^2]$, where λ is the wavelength of the illumination and NA is the numerical aperture. The most ordinary way to attain smaller feature sizes is to reduce the wavelength up to excimer laser wavelengths (248 or 193 nm). The NA is typically between 0,5 and 0,8, so the feature size is on the order of the exposure wavelength.

A unique way to overcome diffraction limit of resolution is to use non-linear light transformation in special photoresist. For the same reason special UV-curable nanocomposite with strong non-linear and self-writing effects overcoated on photoresist to improve light distribution in the spot can be used.

Same proposed technique is applicable for deep lithography based on 365 nm UV light with high scattering to improve shape of small feature in results of geometrical optical laws perturbation at use light self-focusing in materials. If to make nanocomposite system with self-writing effects and place it as a topcoat, we will obtain self-writing subwavelength artificial waveguide that will guide the light to small subwavelength spot on photoresist surface. So to make it it's necessary to develop special material with self-writing effects.

Light self-focusing and self-organization effects at UV curing of acrylate based nanocomposites were investigated previously [20].

There are a few effects:

1. *Self-focusing of the light in material with positive refractive index change at photopolymerization*

Effect of light self-focusing in optical material having properties of positive change of refractive index (RI) at light action is widely investigated recently. For example, in cited work the results of light self-focusing and self-written waveguide preparation process obtained on glass light sensitive materials are summarized [21].

Our experiments show important influence of well known oxygen inhibition action on reinforcement of self-focusing light in photopolymer. Oxygen inhibition action to acrylate photopolymerization described previously [18].

2. *Short distance nanoparticles transportation*

Effect of light induced nanoparticles redistribution in nanocomposite is a new effect discovered recently. It takes place at photopolymeric nanocomposite irradiation by periodic light distribution, for example by lattice made by interference of two laser beams.

The first time these processes were found by Tomita and co-workers in 2005 on organic-inorganic nanocomposite photopolymer system in which inorganic nanoparticles with a larger refractive index differs from photopolymerized monomers are dispersed in uncured monomers [15].

Explanation of effects was made in the work [17]. We use these effects to improve distribution of photopolymer at its curing in light spot. Next show results obtained at microstructure writing by projection lithography.

Self-writing and self-focusing effects discussed above are applicable for diminishing polymerized area initially corresponding to light distribution in objective spot as well as to overcome geometric distribution of the light in focus. The main effect is light self-focusing that can be reinforced by oxygen inhibition [22, 23] and nanoparticles redistribution at photopolymerization. Figure 16 shows proposed application of self-writing processes in projection photolithography: using nanocomposite with self-writing effects overcoated on photoresist to improve light distribution in the spot on the photoresist surface.

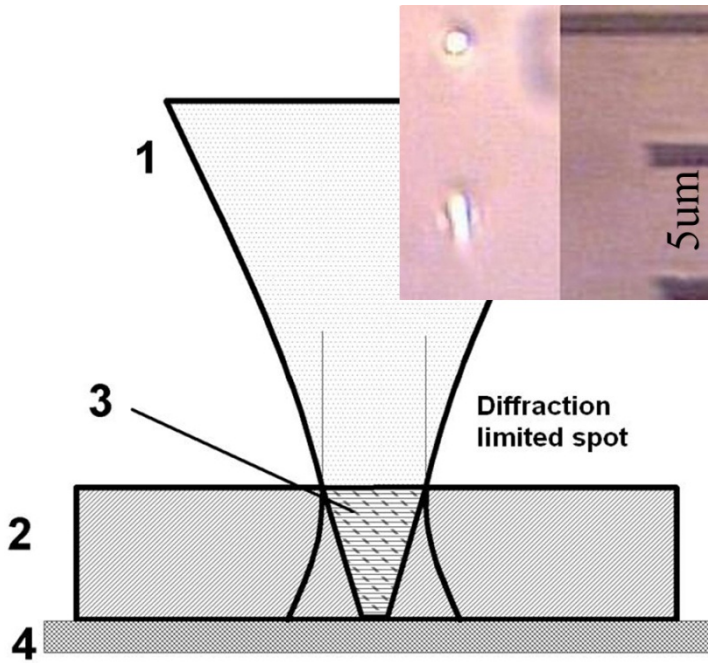


Figure 16. Model of light redistribution behind of lens spot in result of self-writing processes. 1 - UV light beam, 2- nanocomposite, 3- Tip self-writing, 4- photoresist. Polymerized small one micron sized cylinder with vertical borders made by this process (insert).

Two monomer compositions (with and without nanoparticles) were used. In Figure 17 are represented polymer microstructures obtained in case of 2-carboxyethyl acrylate and bisphenol A glycerolate composition (without nanoparticles). Relation between dimensions/structure shape and exposition is observed. In this experiment was used projection of spot expected diameter 1, 2, 4, 6 μm . Composition without nanoparticles doesn't allow to obtain structures with all expected diameters. All cylinders based on this composition were at least 3-4 μm diameter; in case of 1 μm expected spot size formation of elements didn't take place.

Elements form tends to the cone that corresponds to energy distribution in spot.

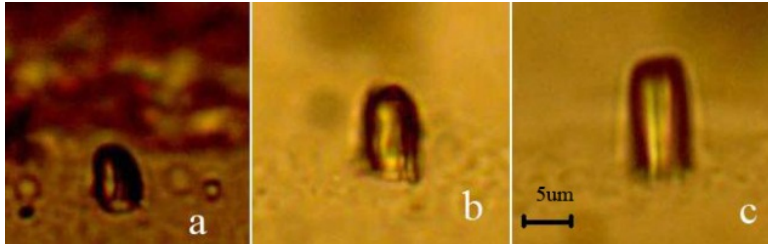


Figure 17. Structures obtained from photopolymer without nanoparticles: a – diameter 3 μm (spot size 2 μm); b – diameter 4 μm (spot size 4 μm); c – diameter 6.5 μm (spot size 6 μm)

In contrast with this series, experiments with nanocomposite gave different results – we made structures with expected diameters 1 μm and obtained diameter less than 1 μm with form near to cylinder Figure 18.

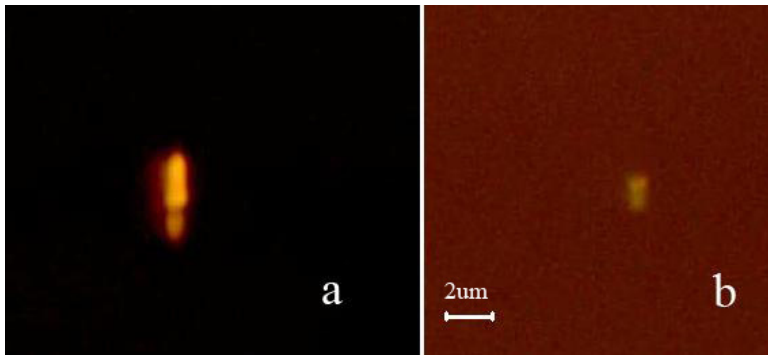


Figure 18. 2 μm -height structures obtained from nanocomposite: a – diameter 0.7 μm (spot size 1,5 μm), b – diameter 0.6 μm (spot size 1,5 μm)

Figure 18 shows that use of nanocomposite give formation of subwavelength elements formed with geometric optics law violation (formation of self-writing cylinder smaller in comparison to spot size two times). In fact used lens should form cone 20 degrees, but in result of nanocomposite self-organization it is form cylinders with vertical borders and size two time less than calculated one, that confirm our guess-work on self-organization effects in nanocomposite.

5. Conclusion

Nanocomposite UV-curable material having set of self-writing proprieties such as: light self-focusing and light induced nanoparticles redistribution were development. The sorption of water vapor, Brinell hardness, optical transmission, refractive index and light scattering of film polymer ZnO -nanocomposites were studied. Composites are transparent in the visible area at high concentrations of ZnO nanoparticles (14 wt. %). With the introduction of 14 wt % ZnO refractive index increases by 0.045. With the introduction of 10 wt. % ZnO the sorption decreases by five times. Hardness, until a maximum concentration of nanoparticles 12 wt. % ZnO does not exceed the hardness of the pure polymer, while light scattering is not increased. Nonmonotonic changes in the properties, the AFM data and the IR spectra were explained the ability of nanoparticles to act as centers of polymerization and to form a granular structure in the nanocomposite

Nanocomposite material is applicable for subwavelength optical projection lithography and holography. Experiment on optical projection writing made at use of 0,2 aperture lens shows diminution of polymerized element smaller in comparison to spot size two times and transformation of initial conical light distribution to cylindrical one in result of self-organization processes in nanocomposite material. Holographic proprieties of material show high diffraction efficiency. Light induced nanoparticles distributions were investigated by different methods. AFM show redistribution of nanoparticles in dark areas.

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