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Peculiarities of photonic crystal recording in functional polymer nanocomposites by multibeam interference holography

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ABSTRACT

Two-dimensional photonic crystal structures (PCS) were fabricated using a one-step recording process, multi-beam interference in smart polymer nanocomposites incorporating SiO_2 and Au nanoparticles sensitized to 532 nm laser radiation. It was shown, that PCS with different geometry can be recorded in thick nanocomposite layers. The typical two dimensional (2D) PCS have square structure with 2–8 μm period, being in good agreement with theoretical structures obtained by mathematical modeling of the recorded PCS. The peculiarities of the photo-polymerization of nanocomposites with plasmonic Au nanoparticles were analyzed on the basis of Surface Plasmon Resonance Imaging (SPRi) and Raman spectroscopy investigations and used for the interpretation of the recording process and periodic structure formation.

1. Introduction

During the last decades photonic crystals attract essential basic scientific and increasing application oriented interests for the development of integrated optics, sensors, info-communication technologies [1–3]. A wide number of materials and proper fabrication methods and processes were developed: lithography, e-beam or laser-beam recording, holography [4–7]. Lithography can be used for photonic crystals' (PC) fabrication in basic semiconductor materials like silicon [4]. Such structures contain elements with dimensions in the micrometer range. Nanoimprint method was proposed [7] for the fabrication of one and two dimensional PCS in polymethyl-methacrylate, structures with 800 nm period were obtained this way. Using special multi-faced prism, which splits the laser beam into four beams and converges them afterwards on a light-sensitive material, authors of [8] recorded PC with forbidden gap at 1400 nm. In Ref. [8] 3D PC was fabricated by the multi-beam holographic lithography in SU-8 photoresist using single optical element, which formed beams' convergence at selected necessary angles.

The most of the well-known fabrication methods have a number of technological shortcomings. For example, the application of the multi-face prism or optical element, which converges light beams do not allow an *in situ* variation of interference patterns. Application of holographic lithography for PCS fabrication makes the additional step of selective etching necessary, with all possible shortcomings of this process. This method makes it possible to fabricate a large photonic element by continuous, step by step incorporation of separate elements. Lithography method, together with copying and multiplexing allows us to obtain PCS down to sub-micrometer dimensions in semiconductors and polymers. Electron-beam lithography makes it possible to produce elements with much higher resolution, but the low throughput restricts its application in a large scale production. Application of lithography with copying, imprint technology provides possibility for serial production of simple surface structures. Here problems can appear with selective etching of prototype elements.

The range of known materials for PCS is rather wide: thin films of noble metals, silicon, different semiconductors and polymers. Hybrid materials for PCS are perspective, especially with combination of photonic and plasmonic properties; they are so called hybrid photonic-plasmonic heterocrystals [9].

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In the present paper periodical structures in acrylate-SiO_2 nanocomposites are formed by holographic method of multi-beam interference of coherent light in a system of four beams. In this method the formation of the recording beams provides a possibility of creation of periodical structures with different forms and dimensions without changes of optical elements. Photonic structures are formed in special acrylate-urethane nanocomposites, which contain silica nanoparticles (SiO_2NP) and were developed and used in our laboratories. Some of them contain gold nanoparticles (AuNP) besides the SiO_2NP, which can essentially influence on the polymerization process and on the formation of periodical structures [10]. It is essential, that no additional treatments of the material after the recording are necessary.

The goal of the present work was the development and application of the above mentioned multi-beam interference method for one step formation of photonic structures in functional acrylate nanocomposites, which are sensitized to green laser illumination and possess plasmonic effects due to the presence of gold nanoparticles.

2. Experimental

2.1. Sample preparation

Monomer compositions were used for holographic recording of periodical structures. These materials are mixtures of urethane – acrylate monomers with SiO_2NP and photo-initiator, which is sensitive in the green region of optical spectrum. This spectral region was selected specially, since in our experiments we use monomer compositions with AuNP, which possess plasmon resonance and absorption just in the green spectral region.

The technology of nanocomposite preparation consists of following steps:

- SiO_2NP (7 nm in diameter) are added by small portions into the mixture of diurethane dimethacrylate (436909 Aldrich, UDMA) and isodecilacrylate (408956 ALDRICH, IDA),
- Adding toluene to the mixture to decrease the viscosity of it.
- After mixing the composition, the necessary amount of AuNP in toluene is added.
- Further the initiator of photo-polymerization is added (Irgacure 784, bis-(5-2,4-ciklopentadien-1-il) bis-[2,6-difluor-3-(1H-pirolle-1-il) phenyl] titanium.
- Afterwards the toluene is evaporated at 35 °C till the constant weight. The composition is stored at 25 °C.

The composition of the prepared nanocomposites is shown in Table 1.

2.2. Experimental setup for recording of PCS

The general scheme of the experimental setup is presented in Fig. 1.

The beam of light with 532 nm wavelength and 100 mW power from single-mode DPSS laser is widened by telescope system with lenses (3 and on Fig. 1) to the diameter, which is enough for uniform illumination of the four-mirror system (5 on Fig. 1). The diameter of the illuminated field in this system of mirrors was near 80 mm.

Table 1
Composition of the prepared nanocomposites.

№	Monomers	SiO_2 NPs wt%	Au NPs wt%	Irgacure 784 wt%
64a	UDMA/IDA = 1/2	10	–	0,5
64Au1	UDMA/IDA = 1/2	10	0.08	0,5
64Au2	UDMA/IDA = 1/2	10	0.15	0,5

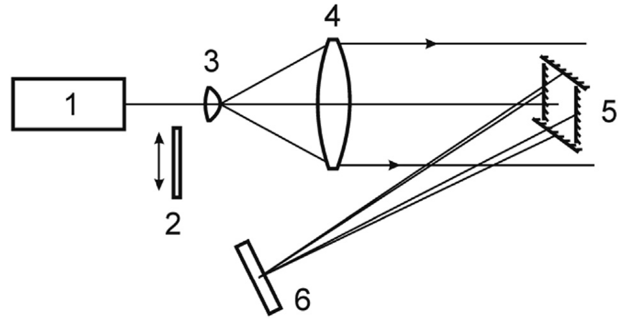

Fig. 1. Scheme of PC recording.1 - DPSS laser (λ = 532 nм); 2 - optical filter; 3,4 - telescope with wide aperture, 5 - four-mirror system, 6 - the sample with monomer nanocomposite layer.

Each of four mirrors is attached to the separate micrometer stage, which in turn are attached to the separate common stage with micro-positioners in two directions. This way four independently operated beams are available in the given optical system, and their diameters are determined by the dimensions of mirrors, i.e. the mirrors serve as limiting diaphragms at the same time. Further, the beams are settled to the position 6, where the nanocomposite sample is placed. The intensity of beams can be regulated by light filters (2 on Fig. 1). The adjustment of four beams for obtaining interference picture was done by the method of continuous approximations with aim to select the minimum difference between optical paths of beams from the given laser. At each step of approximation the interference picture was monitored through an optical microscope, located at the sample place (6 on Fig. 1). The adjustment process was finished if a good quality periodical structure was observed.

The recording zone, where the four beams intercept, was usually about 10 × 10 mm, although the size could be increased or decreased as well. It is necessary to notice that this system of mirrors allows high accuracy regulation of beam convergence and overlap different illuminated zones. Different periodical structures can be produced this way.

The following PCS were created:

PCS 1 – monomer of 64a, 3 min recording.

PCS 2 – monomer of 64a, 3 min recording, and one beam was shifted for 2 mm in vertical direction relative to other three beams in comparison to PCS 1.

PCS 3 – monomer of 64Au1, 3 min recording, the same as for PCS 1.

2.3. Theory of interference holography through multi-beam interference

The electric field for each $p = 1,2,3,4$ beam can be determined by the following equation of a plane wave with wavelength λ, unit vector along the wave vector $\boldsymbol{\varepsilon}^{(p)} = (\sin(\alpha_p)\cos(\phi_p), \sin(\alpha_p)\sin(\phi_p), \cos(\phi_p))$, with azimuth angles α_p and polar angles ϕ_p :

$$\boldsymbol{E}^{(p)}(\boldsymbol{r}, t) = \boldsymbol{A}^{(p)} \cdot \exp\left(i\frac{2\pi}{\lambda}\left(ct - \left(\boldsymbol{\varepsilon}^{(p)}, \boldsymbol{r}\right)\right)\right). \quad (1)$$

Angles are determined relative to the vector perpendicular to the surface of layer (sample 6 in Fig. 1). The z axis is perpendicular