KAUNAS UNIVERSITY OF TECHNOLOGY

RAMŪNAS BAKANAS

HOLOGRAPHIC STRUCTURES FORMATION IN LIGHT SENSITIVE PHOTOPOLYMERIC MATERIALS USING PULSED LASER AND DIGITAL HOLOGRAPHY METHOD

Summary of Doctoral Dissertation
Technological Sciences, Materials Engineering (08T)

2017, Kaunas

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KAUNAS UNIVERSITY OF TECHNOLOGY

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HOLOGRAFINIŲ STRUKTŪRŲ FORMAVIMAS ŠVIESAI JAUTRIOSE POLIMERINĖSE MEDŽIAGOSE IMPULSINIU LAZERIU SKAITMENINIU METODU

Daktaro disertacijos santrauka
Technologijos mokslai, medžiagų inžinerija (08T)

2017, Kaunas

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INTRODUCTION

Due to their unique properties, lasers are an integral part of optical holography and optical lithography. Lasers also evolve various methods related to the diffractive structures formation, which defines their quality and usability. Diffraction structures formed by holographic methods are increasingly used in various fields, for example, in optical elements for military application, holographic data storage, in holographic topography, light guiding, advertisements, and holographic security elements.

Application of holographic elements formed in polymeric materials is quite widespread: from elementary signs for permits, invitations, mass events tickets (concerts, performances, sport events, etc.) up to use in products for packaging decoration, excise and metrology marks, government securities, banknotes, identity cards and passports, visas and other strictly accountable document protection. The structure of holographic security elements depends on the application field. Complex structures of the elements with optically variable protective effects (microtext, optically variable tags, hidden items, etc.), are mostly intended for use in governmental controlling services. Meanwhile, relatively simple holographic elements of first security level, for example, different depths or variable color, are intended for distinguishing product forgeries for ordinary people.

With free movement of goods, more and more goods are found with forged trademarks in the market. Improvement of security of holographic elements and equipment improves counterfeighting equipment; therefore, production companies experience huge losses. Consequently, development of unique forming methods of holographic diffraction structures suitable for security elements manufacturing is relevant to sustainable economic development. It is important to create an efficient, modern holographic diffraction structures for easy identification of counterfeits without additional equipment or means.

The aim of this doctoral dissertation is to create a high-speed surface relief diffractive structures formation method for restoring deep holographic images and to investigate the formation mode influence on the microrelief morphology and optical properties.

Tasks of the dissertation:
- to customize a digital holography method for the creation of deep image forming surface relief diffraction structures by pulsed laser;
- to investigate the positive photoresist based on thediazonaphthoquinone-novolac resin exposure regularities by single pulse of nanosecond laser and digital holography method;

- to determine exposure and developing mode influences on geometrical parameters and optical properties of diffraction structures shaped in positive photoresist;
- to compare diffraction structure optical parameters formed by single pulse at a digital method with the optical parameters obtained by other methods;
- to investigate the possibility to improve diazonaphthoquinone-novolac resin optical properties by modification of the composition with different nanoparticles;
- to evaluate the application possibilities of deep image diffraction structures obtained by single pulse laser and digital printer for high quality master hologram creation in polymeric films by embossing.

Scientific novelty and practical importance. In this work, digital holography method is adapted to create deep rainbow 3D holographic images, which fills the gap between the analogue holography and electronic lithography. The new digital holographic printer, which uses single wavelengths of solid-state pulse nanosecond laser, operating on interference principle, allows to obtain deep 3D holographic transmission holograms (color rainbow, achromatic – black and white, combined – rainbow-achromatic, only in laser light visible holograms) directly on the positive photoresist layer by one step. An image animation is also possible using this method.

Thus, the proposed method using the single wavelength pulse laser is suitable for security, protective packaging and other high-quality master hologram origination. According to the available data, this method is about ten-times faster than other currently existing deep hologram origination methods. Therefore, hologram replication processes via thermal imprinting (hologram recombination) is no longer needed, because the high-quality reproduction of the original can be performed directly by direct optical recombination method.

This method also can be used for diffraction structures thermal imprinting in plastics. It opens up new possibilities for the production of novel type master hologram origination. Combining the deep holographic master origination method with other existing hologram origination methods creates the way of new hybrid security and deep 3D holographic image hologram origination manufacturing.

Defensive statements

1. Deep holographic surface relief images can be created by digital holography method operating on the principle of single wavelength

interference in one step directly on positive photoresist layer using a single pulse of solid-state laser.

2. The optical properties and geometrical parameters of difraction structures formed on the surface of DNQ-novolac resin modified by nanoparticles of various nature depends on the exposure method and regime.

Approval of the research results. The research results are presented in 8 scientific publications: 2 of them are in journals from the list of Clarivate Analytics Web of Science, 6 of them in conference proceedings 2 – Lithuanian patents. The results of the research were presented at 8 international conferences and 1 national conference.

Structure of doctorial thesis. The thesis consists of an introduction, 3 chapters, conclusions, list of references (169 entries) and a list of scientific publications. The thesis is submited in 114 pages, including 80 figures and 14 tables.

CONTENT OF DOCTORAL DISSERTATION

Introduction presents problem and the relevance of the presented investigations, definition of the research aim and objectives, survey of the scientific novelty and practical value of the dissertation.

Chapter 1 presents scientific literature review related to the topic of the dissertation thesis.

Chapter 2 presents materials characterization, sample preparation and their testing procedures.

Materials. In this study, positive photoresist composition comprising phenol formaldehyde resins known as novolac resin and diazonaphthoquinone (DNQ) is used (C ≈ 70 %.)

DNQ-novolac resin nanocomposites were formed by addind different amounts of various nanoparticles (Ag, Cu, SiO_2, TiO_2) and stirring mechanically with a glass stick until a homogeneous composition was formed at room temperature. The number of nanoparticles in the composition ranged from 0.005-0.3 %.

Experimental methodology. Positive photoresist coatings were formed on 2 mm thick polished quartz glass plate by centrifuge method at 2000 min^{-1} speed. Coating thickness depends on the spin rotation speed, photoresist viscosity and formation time. For structures developing concentrated alkaline aqueous solution of NaOH was used. In order to control the developing rate and linearity, developer was diluted with deionized water at ratio 1:9 ($NaOH:H_2O$). The developments were performed at room temperature (20 ± 2 °C) for $5 - 30$ s. After developing, the samples were washed with deionized water and dried in compressed nitrogen gas stream.

Holographic grating formation method. In the layer of positive photoresist holographic gratings formed using two exposure methods: **analogue** and **digital**. Analogue method of diffraction grating formation layout shown in Fig.1

Diffraction efficiency evaluation methodology (analogue method). Diffraction efficiency evaluation method was used for optical property evaluation of microrelief formed on positive photoresist by exposure using laser light. Specimens exposed by analogue method have been evaluated using collimated He-Ne laser ($\lambda = 632.8$ nm, GN-70) beam, which has equal polarization ratio at the output $S{:}P - 1{:}1$ (Fig. 1, b1-b2).

a

b1

b2
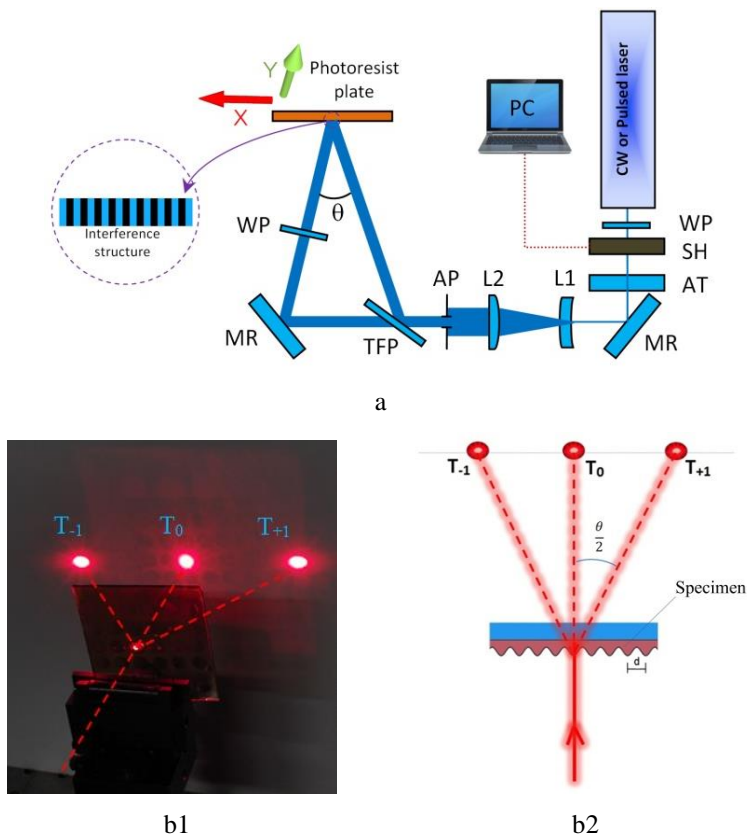
Fig. 1. a) Diffraction grating formation layout by analogue method (*WP* – wave plate, *MR* – dielectric mirror, *TFP* – thin film polarizer, *AT* – optical attenuator, *L1, L2* – lenses, *AP* – mechanical aperture, *SH* – electro-mechanical shutter).
b) Layout used for analogue holographic gratings diffractive efficiency evaluation (b1 – layout general view; b2 – layout scheme)

The relative diffraction efficiency was calculated according to the formula

$$DE = \left[\frac{I_D}{I_D + I_{T_0}}\right] \cdot 100\%, \tag{1}$$

where I_{T_0} is the intensity of non-diffracted T_0 beam, I_D is the averaged intensity of the two transmitted diffraction orders $I_{(T_{-1})}$ and $I_{(T_{+1})}$.

Continuous wave laser power was measured using a photodiode PD300-3W-V1 and display NOVAII. Pulse laser output energy was measured using a pyroelectric sensor PE25-C and display NOVAII.

Characterization. Diffractive microrelief structures formed by holographic methods were characterized by following techniques: atomic force microscopy (AFM), ultraviolet–visible light spectroscopy (UV-VIS), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR).

Chapter 3 presents the results of experimental investigations.

Pulse laser use for holographis structures formation by digital method. Optical scheme of diffraction grating formation by digital holography method is shown in Fig. 2. In this case the microrelief is formed by two spatially coherent beams of pulsed laser, where one beam is modulated by means of spatial light modulator (SLM) and computer (PC), while another beam is used as reference for light interference. Object information appearance on diffraction grating surface is created by object beam modulation, which is performed by optical light modulator *SLM* LCX017 (Sony), which have an interface with the computer. Prior to printer object beam modulation by *SLM* modulator, the object data information has been prepared in advance.

Diffraction efficiency evaluation methodology (digital method). Using digital holography method on surface of positive photoresist, asymmetric microrelief structures forming a white square (Fig. 2, b1-b2) were recorded. The relative diffraction efficiency for digital holography was calculated by the formula

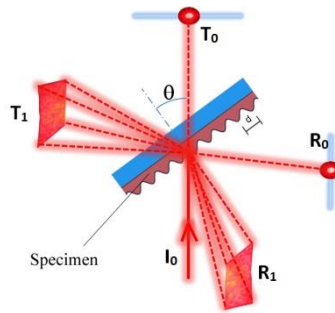$$DE = \left[\frac{I_{T1}}{I_0}\right] \cdot 100\%, \tag{2}$$

where I_{T1} is intensity of diffracted beam, and I_0 is intensity from He-Ne laser.
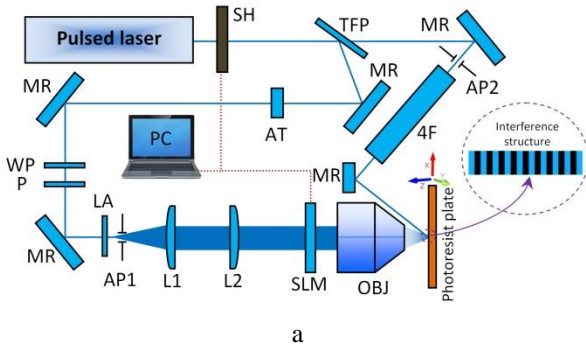
a
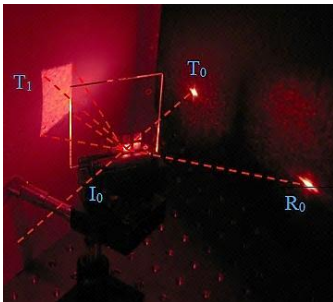
b1

b2

Fig. 2. a) Experimental digital holographic printer layout (*WP* – waveplate, *MR* – dialectric mirror, *TFP* – thin film polarizer, *AT* – optical attenuator, *P* – polarizer, *LA* – optical diffusor, L1*, L2* – lenses, *AP* – mechanical aperture, *SH* – electro-mechanical shutter, *SLM* – spatial light modulator, *4F* – reference beam formation system, *OBJ* – objective)
b) Layout used for digital holographic gratings diffractive efficiency evaluation (b1 – layout general view; b2 – layout scheme)

Looking at a classic analog hologram, at least two parallax-related images can always be seen, i. e. taking picture of any two of classical holographic images with cameras situated by binocular distance from one another, come to linked pair stereo image. Two images of such stereo pairs form a visible image in space as a three-dimensional (Reichelt, 2010). In classical hologram, innumerable parallax related object images were recorded, in the case of digital hologram – recorded finite quantities, from a few hundred to several thousand images.

These images are transferred to the material so that at the different material visualization angles are visible different parallax related images (Fig. 3). Parallax related pixels are combined into sequences of holographic

dots, called hogels. Hogel is used for photoresist material spot exposure, the image of which is displayed on the SLM. Therefore, for one hogel formation used all pixels having the same coordinates from associated parallax related images. Pixel quantity of two-dimensional images and a number of active pixels of the SLM modulator determine how many different images will be recorded in the digital hologram.
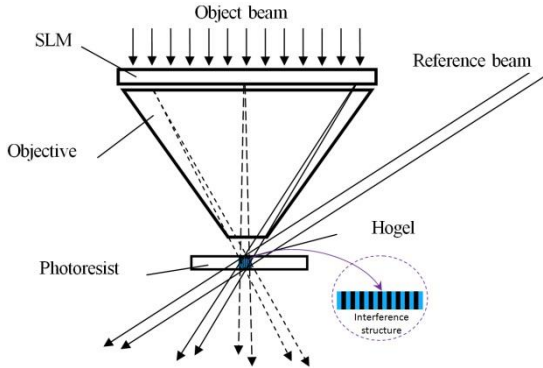

Fig. 3. Object beam formation layout in experimental digital holographic printer

Direct write digital hologram viewed at different angles, shows information represented by the different angular images of three-dimensional scene. The proposed experimental method, using only a single wavelength laser, can create several types of transmission holograms (Fig. 4): full color Rainbow, white achromatic (black and white), including laser light visible transmission hologram (H1 original). Therefore formed hogels are shown in a liquid crystal SLM modulator, which is illuminated by single nanosecond (48 ns) duration laser pulse.
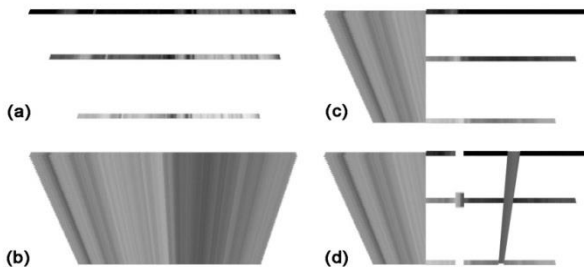

Fig. 4. Single hogel *SLM* views prepared for digital hologram diffractive microrelief structures recording**:** a – color hologram; b – achromatic hologram; c – hybrid hologram (comprising achromatic / color elements); d – hybrid hologram (comprising various elements)

Modulated object beams then focused to photoresist surface by special large numerical aperture objective. Following this, object beam light modulation of digital holographic printer is performed.

Modulated object laser beam intersected with reference beam at the surface of DNQ-novolac photoresist at close proximity of special objective waist, and by means of light interference records used *SLM* pixels hologram – hogel. Exposed hogel *h* in this case contains information about corresponding pixel of *SLM* display and information about angular light intensity distribution (Fig. 5).
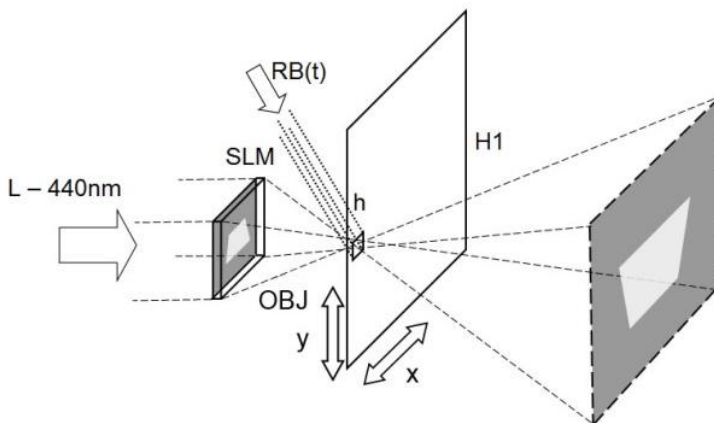

Fig. 5. Experimental holographic printer hogel formation layout

During the exposure, while pulsed laser synchronized with *SLM*, the glass plate (coated with photoresist) moves during recording with a constant velocity in the *y* direction. When one line of hogels is recorded, the plate moves in the *x* direction parallel to the drawing plane by the distance of one hogel size, i.e. by 100 μm. The next line of hogels is exposed by moving the plate in the opposite direction. The entire process is repeated until the desired size area is covered with hogels. The final digital transmission image grating is obtained when the defined photomaterial area is covered with hogels and each of these areas carries the modulated information from the SLM (identical to that which would be transferred during a conventional analogue H_1–H_2 optical transfer).

In all investigated diffraction grating recording cases white square images are formed, which in achromatic holograms due to achromatic angle looks like a trapezoid (see Fig. 5) (Zhang, 1996).

In order to effectively form diffraction structures and estimate diffraction efficiency of microrelief values made by digital holographic

method with values of an analogue method, light intensity ratio between object and reference beam is equalized (1:1).

Digital holographic grating formation feasibility investigation. At the beginning, the holograms were formed using 200×200 µm hogel size. However, a distance of 30–50 cm the hologram pixelated structure is visible. Therefore, the printer optical scheme was modified and the resolution of holographic printer was increased by twice – 100×100 µm hogels were formed. High-quality holograms were formed after the increase of image resolution.

Furthermore, it was decided to check an object and reference beam ratio influence onto diffraction intensity of difraction structures formed in photoresist by digital method (Fig. 6)
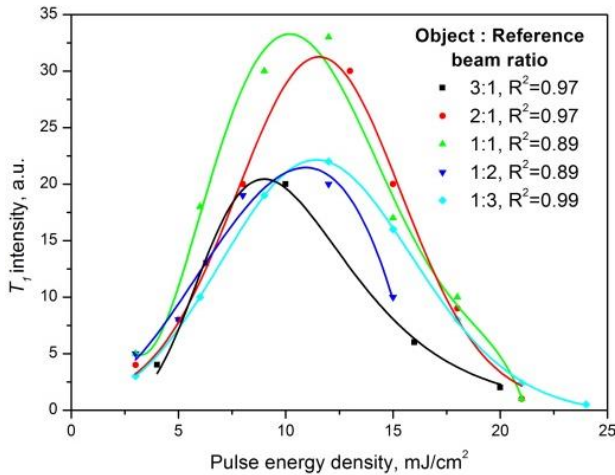

Fig. 6. Diffraction grating intensity T_1 dependence on pulse energy density at different object and reference beam ratio

The resultant curves of diffractive intensity vs exposure pulse energy density for various ratios show that the best results are achieved at 1:1 object to reference beam ratio or when the reference beam is greater than object beam by ratio 2:1.

Besides, the optical efficiency of microrelief in DNQ-novolac exposed with single pulse by digital method depends on the duration of chemical treatment (Fig. 7).
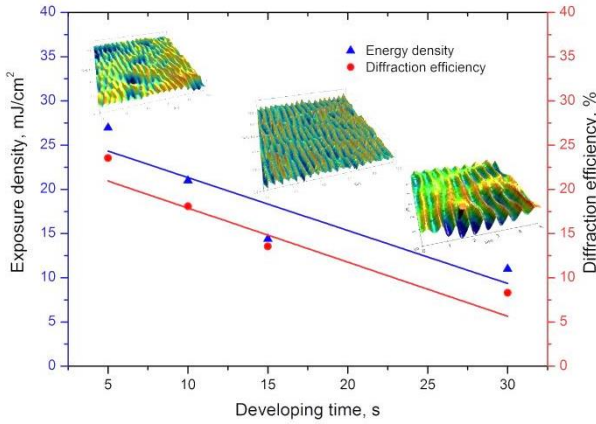
Fig. 7. Dependence of exposure density, difraction efficiency of microrelief structures formed by digital method and their 3D topographic image on the development time

The maximum DE value, ca. 23 % was obtained at pulse energy density of 25-30 mJ/cm^2 and 5 s development time. The increase of development time up to 30 s decreases DE value almost 3 times – down to ~8 % (Fig. 8).
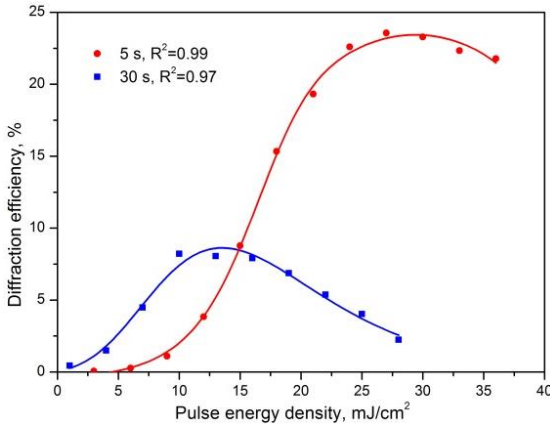

Fig. 8. Diffraction efficiency of surface microrelief structures formed by digital method dependence on SP energy density at different processing time

After development, the diffraction grating structures periodic grooves and ridges are obtained, where a distinctive feature emerges and disappears through individual lines of relief modulation (Fig. 9).

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Exposing of photoresist with pulsed laser at 48 ns single pulse duration, photoresist actually encounters peak exposure power, which can be calculated according to the formula $P = E_i/t$ (E_i is laser pulse energy and t is laser pulse duration).
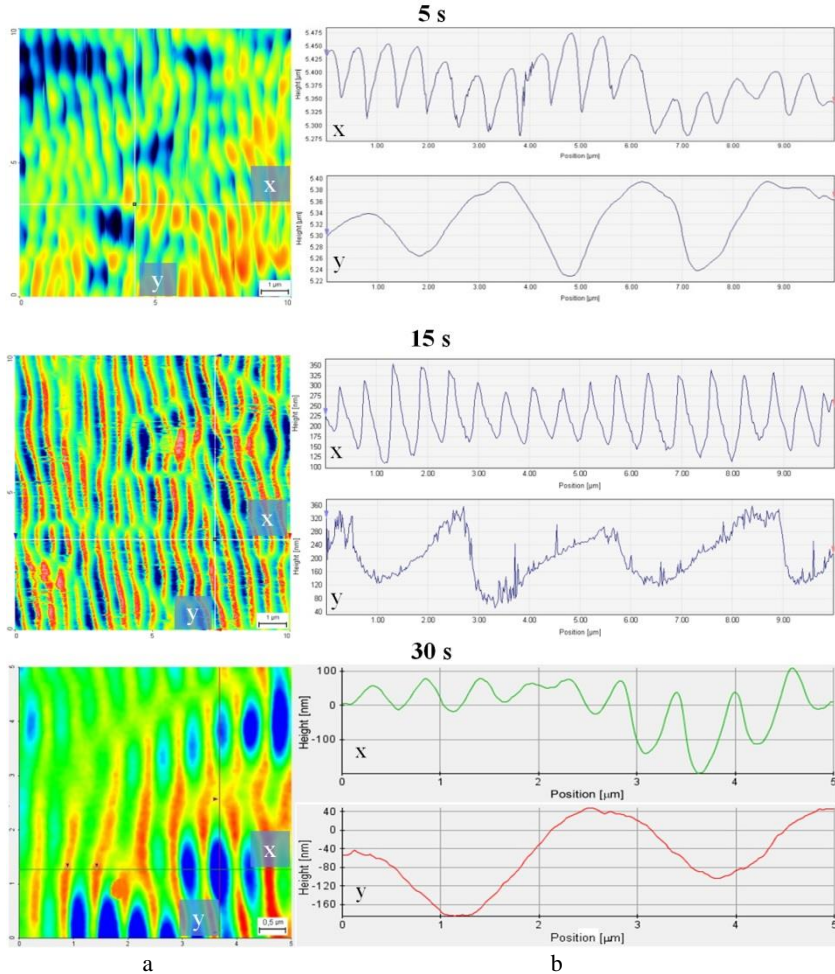

Fig. 9. Surface AFM topography (a) and profilograms (b) of microrelief structures formed by digital method depending on processing time

In the case of 48 ns pulse duration and 15 mJ/cm^2 single pulse energy density positive DNQ-novolac photoresist feels ~312 kW/cm^2 pike power light fluence. When photoresist absorbs such dense laser light, DNQ

photolysis reaction proceeds, i.e. DNQ decomposes into nitrogen and unstable radical. The nitrogen gas release creates a sudden gas pressure increase in material volume. Through 1 µm thickness positive photoresist layer nitrogen molecules inherent diffusion time at diffusion coefficient of ~10^{-7} cm^2/s reaches ~0.1 s (Bogdanov, 1987). It can be assumed that because of pressure, N_2 gas penetrates at microrelief surface and forms micropores, which irreversibly modifies the photoresist surface topography. At short development time (less than 5 s), developer penetrates into the photoresist surface only at low depth at higher energy density zones. However, at increased processing time – 15 or 30 s, through resulting micropores developer penetrates into deeper layers of the photoresist simultaneously affects the unexposed photoresist areas, also.

Digital holographic printer quality and its suitability for master-original origination on the surface of DNQ-novolac were evaluated by printing deep three-dimensional color holograms (Fig. 10).
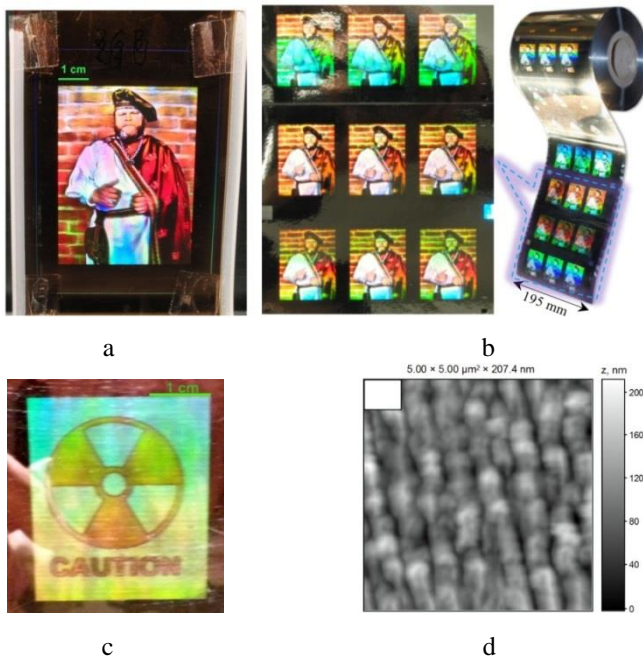

a   b

c   d

Fig. 10. Color Rainbow holograms printed on DNQ-novolac (S1805) surface by pulsed laser SP method and their replicas made on metallized PET surface: a, b – hologram „Fellow" master original (45 x 62 mm), and their replicas; c, d – hologram „Caution" (30 x 40 mm) master original and their PET replica surface topography

The image of digital hologram was formed on surface of nickel from which working master-stamp and embossed holograms were produced. It was revealed that the hologram replicas produced by embossing methods showed identical surface topography (to hologram original), which varied only by surface roughness.

DNQ-novolac patterned by single pulse nanosecond light was compared with exposure by multipulse expose regime. The best DE results of single pulse were achieved at highest energy densities (25-30 mJ/cm^2) and short (5 s) processing times, while at exposure by nanosecond pulse-trains the highest (~90 %) DE values were obtained at lower total energy densities (~17-20 mJ/cm^2) and longest 30 s processing time. The exposure energy density and time differences could be related to the light-sensitive material (diazonaphthaquinone) photolysis reaction elements and its transformation time, which affects Reciprocity law, photoresist coating topography assuring a different percolation zone for developer penetration.

Nanoparticles influence to DNQ-novolac composition exposure by various methods. Previous studies have shown that nanoparticles (NPs) affect DNQ-novolac resin properties illuminated by UV light sources. It was revealed that the nanoparticles change microrelief surface morphology and optical properties, markedly improve optical lithography resolution (Marques-Hueso, 2010). Therefore, it was interesting to determine the impact of nanoparticles addition in to DNQ-novolac composition on the exposure by pulse and continuous wave lasers.
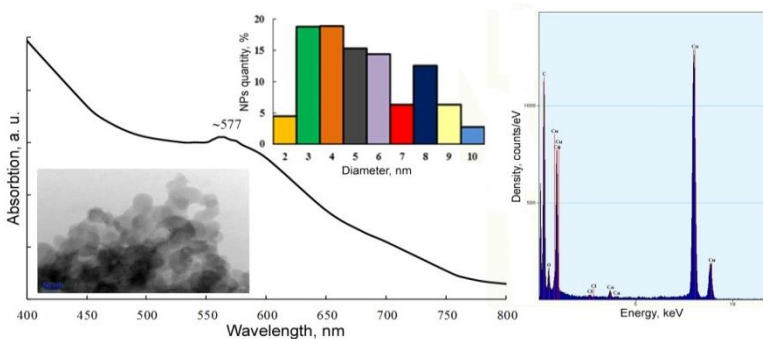
Ag and Cu nanoparticles colloidal solutions obtained by chemical reduction methods in water, ethanol or chloroform were used. In Fig.11 synthesized metal nanoparticles images and size distribution is presented. Ag and Cu nanoparticles of various forms were obtained, although the majority of them have a spherical shape.

a
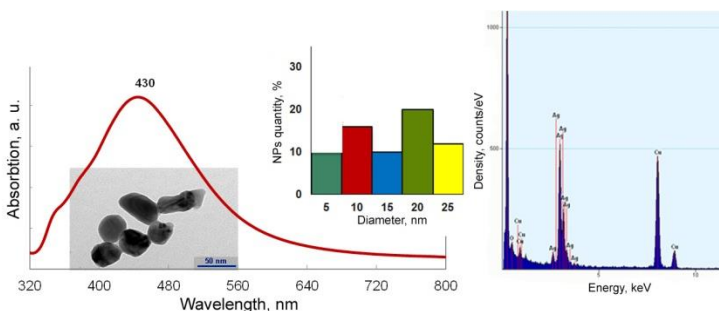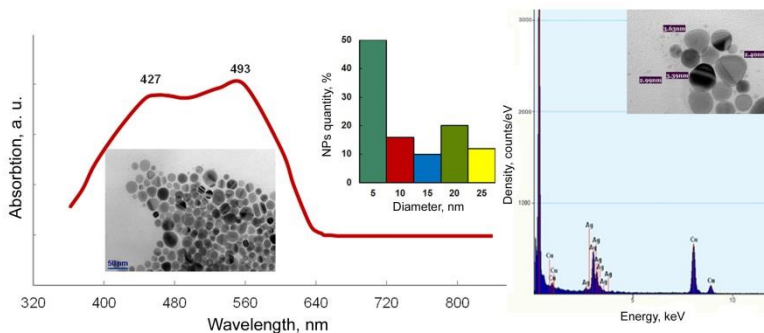
Fig. 11. Metal nanoparticle TEM images, size distribution histograms, UV-VIS spectra (left) and EDS spectra (right): a – Ag NPs in aqueous solution, b – Ag NPs in chloroform solution, c – Cu NPs in ethanol solution

DNQ-novolac resin UV-VIS investigations show absorption bands attributed to the molecules of DNQ and novolac, but also the maximum corresponds to absorption of azo compounds resulted by interaction of novolac resin with DNQ was observed (Sheats, 1998) (Fig. 12). No absorption bands were observed after mixing of of SiO_2 or TiO_2 nanoparticles in the range of 300-800 nm.
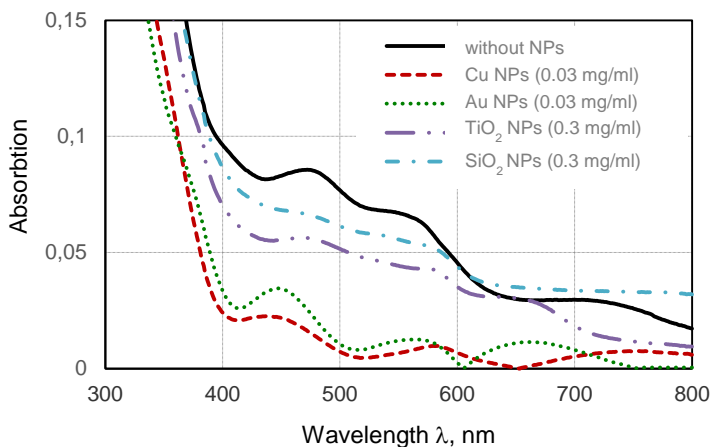
Fig. 12. UV-VIS absorbtion spectra of DNQ-novolac and its nanocomposites

Meanwhile, intensity of absorbtion maximums inherent for DNQ-novolac compositions decreases by mixing these metal oxide nanoparticles, which proves their influence on DNQ-novolac resin optical properties. In the nanocomposites with Au and Cu nanoparticles absorption spectra inherent bands to DNQ, novolac and their interaction remain, but also localized surface plasmon resonance due to the effect related to metal nanostructures is observed.

Previous studies showed (Pudlauskaitė, 2013) that metal (Ag, Cu) nanoparticles in DNQ-novolac composition interacts with nitrile groups via coordination bonds.

For the evaluation of structural changes of DNQ-novolac caused by Au NPs and SiO_2 and TiO_2 nanoparticles, FT-IR investigation was applied (Fig. 13). Novolac is characterized by a broad band at 3485 cm^{-1} range assigned to OH groups and at 2920 cm^{-1} attributed to the C–H deformational vibrations of phenol group. The peak at 2165 cm^{-1} is attributed to the valence vibrations of $C=N_2$ groups of in 2-diazo-1-naphthoquinone structure (Wei, 2015). A peak at 1512 cm^{-1} can be attributed to the aromatic ring C=C band vibrations, while 1467 cm^{-1} band – to benzene ring C=C vibrations due to the methylene bridge –CH_2– (Polnajšek, 2005). The high-intensity peak at 1275 cm^{-1} wavelength range assigned to asymmetric bending vibrations of phenolic groups C–C–OH. The DNQ-novolac absorption spectrum visible at band 1040 cm^{-1} can be attributed to the bending vibrations of aromatic ring C–H in plain. The band at 792 cm^{-1} belongs to the C–H bond vibrations in diketone molecule, which in the case of nanocomposites shifts to 810 cm^{-1} (Rongben,

1990). A peak at 548 cm^{-1} is due to the =C–C–C stretching vibration of the ethyl phenyl componets.
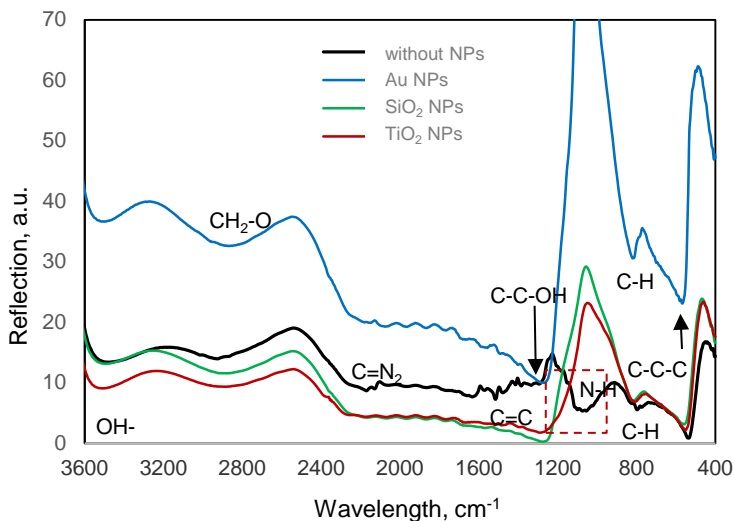

Fig. 13. FT-IR analysis spectrums of various NPs/DNQ-novolac nanocomposites

   Due to the low nanoparticles concentration, new absorption bands are not visible or they are low intensity and overlap with appropriate bands of DNQ-novolac. However, in nanocomposites spectra at the range of 1200-975 cm^{-1} change can be observed, because the band related to the aromatic ring vibrations at 1040 cm^{-1} disappears. This spectrum band is associated with vibrations of C–H group and N=CH groups, the intensity of which changes due to the interaction with nanoparticles. Comparision of nanocomposites spectra shows that changes are not related with types of nanoparticles (metal or metal oxide nanoparticles).

   DNQ-novolac nanocomposites exposed by pulsed laser and digital method. In the case of nanoparticles mixing the efficiency of diffraction structures formed by digital method at low processing duration deteriorates from DE ~ 23% down to DE ~ 21% (Fig. 14, a). Therefore, in order to determine the influence of nanoparticles, sample processing time was extended up to 30 s (Fig. 14, b). Investigations show that processsing time differs depending on the nanoparticles type.
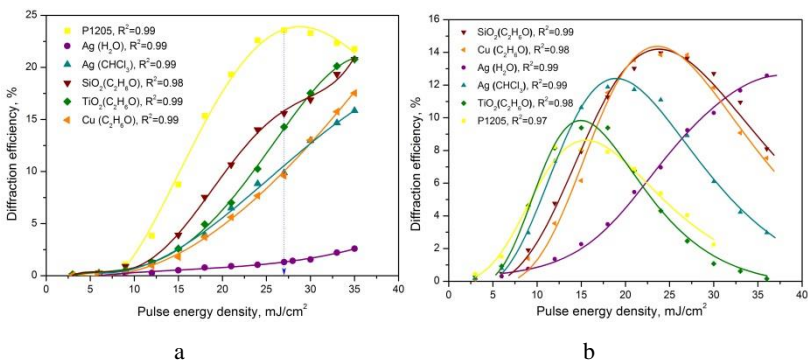
20

Fig. 14. DNQ-novolac nanocomposites microrelief formed by digital method DE dependence vs pulse energy density at different processing time: a – 5 s; b – 30 s

DNQ-novolac samples with SiO_2 and TiO_2 NPs processed at 30 s almost all exposed area was washed by developer.

DNQ-novolac nanocomposites exposed by digital method behaviour depends on the nanoparticle type (Fig.15, a). AFM analysis showed that nanoparticles modified photoresist microrelief structures are characterized by deeper surface relief (Fig.15, b).
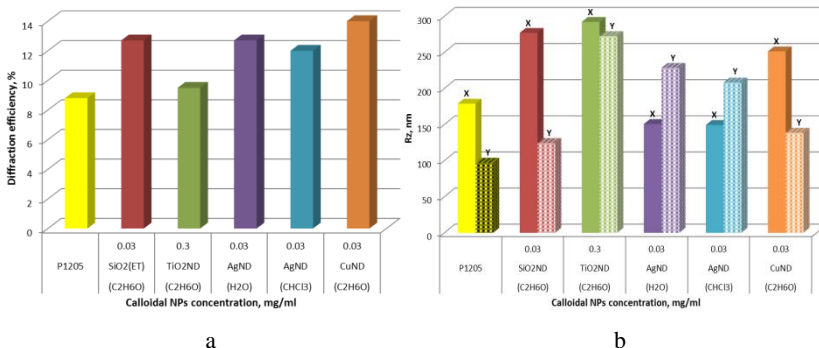

Fig. 15. Nanoparticle type influence to maximum DE values (a) and arithmetic average height R_z (b), exposing samples in digital method at different processing time (SiO_2 NPs – 10 s, TiO_2 NPs – 15 s, all other – 30 s)

On microrelief surface of positive photoresist modified by SiO_2 and Ag NPs aqueous colloid, chaotically located nanostructures are visible (Fig. 16, a, b – I, III). These structures could be related to nanoparticle aggregates, because the structural studies showed that SiO_2 nanoparticles and Ag nanoparticles tend to aggregate in aqueous medium.
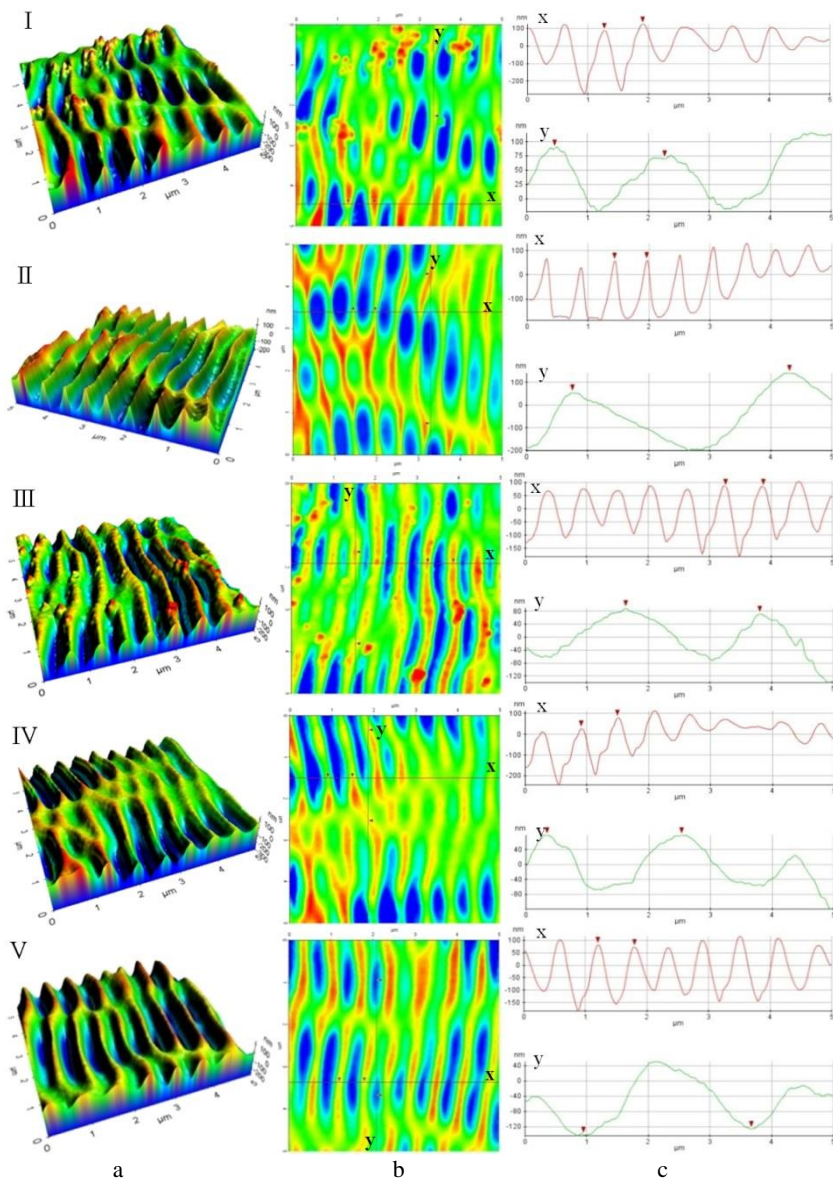
Fig. 16. DNQ-novolac nanocomposites diffractive structures patterned in digital method microrelief AFM topographic 3D (a), 2D (b) images and their profilograms (c): I – SiO$_2$ NPs; II – TiO$_2$ NPs (C = 0.3 mg/ml); III – Ag (H$_2$O) NPs; IV – Ag (CHCl$_3$) NPs; V – Cu NPs (C = 0.03 mg/ml)

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DNQ-novolac modified by TiO_2 NPs characterized by different surface topography. In this case, the obtained "blade" type microrelief, grating surface grooves are dominated in both x and y directions. It can be assumed that it is associated with NPs concentration resulting light scattering and a large nanoparticles refractive index, which is about 1.7 times higher than the DNQ-novolac refractive index. It is obvious that NPs can change roughening degrees of diffraction structures.

DNQ-novolac composites exposed by analogue method multipulse regime. For investigations, the pulse energy density of 260 µJ/cm^2 was chosen, at which the highest DNQ-novolac diffraction efficiency was achieved. Nanocomposites with metal nanoparticles were processed for 30 s, while in the case of SiO_2 NPs and TiO_2 NPs processing proceeds NPs at 10 s and 15 s, respectively.

According to the AFM investigations can be predicted that microrelief geometrical parameters and profile shapes are dependent on the nanoparticles type (Table 1).

Table 1. Diffraction gratings DE and surface morphology parameters of various DNQ-novolac nanocomposites formed by analogue method in MP regime

NP colloid	NPs C, mg/ml	DE, %	Profile form	R_z, nm	R_q, nm	R_a, nm	R_{sk}	R_{ek}
ma-P1205	-	88		462,70	224,58	207,28	-0,12	1,39
SiO_2 (C_2H_6O)	0,3	70		484,73	187,97	172,64	-0,30	1,44
TiO_2 (C_2H_6O)	0,3	64		395,29	191,40	173,01	-0,63	1,70
Ag (H_2O)	0,03	69		473,96	192,90	183,19	-0,35	1,30
Ag ($CHCl_3$)	0,03	87		623,43	256,50	238,80	-0,41	1,40
Cu (C_2H_6O)	0,03	90		503,29	206,39	194,41	0,00	1,27
Au (C_2H_6O)	0,02	82		617,94	272,84	260,81	-0,04	1,17

The influence of nanoparticle amount on the DNQ-novolac microrelief geometrical parameters are presented in Fig. 17. As can be seen, DE values only slightly depends on the NPs amount. In the case of low Ag nanoparticles concentration (0.005 mg/ml) relatively high gratings DE (82 %) is obtained with effective exposure zone ($EEk_{80\%}$) in the range of 35-45 mJ/cm^2 energy densities (Fig. 18, a). An increase of Ag NPs concentration up to 0.015 mg/ml increases diffraction efficiency up to 90 % and shiftes its maximum towards higher energy densities ($EEk_{80\%}$ – 44-67 mJ/cm^2). In this case $EEk_{80\%}$ area becomes significantly wider by 4 times (Fig. 18, b).
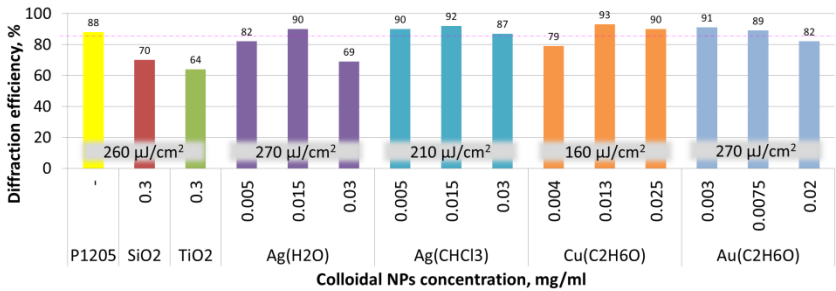
Fig. 17. Dependence of microrelief structure DE upon NPs colloidal solution type and concentration at different SP energy density (dashed line shows maximal unmodified photoresist efficiency)

However, an increase of Ag NPs amout up to 0.03 mg/ml, DE decreases down to 69 % (Fig. 18, c). In this case, instead of the usual Gaussian type of microrelief, the flattened pikes are visible and grating surface profile is close to a trapezoidal shape. The ratio between grating bottom and top is 1:2 (Fig.19, a, b).
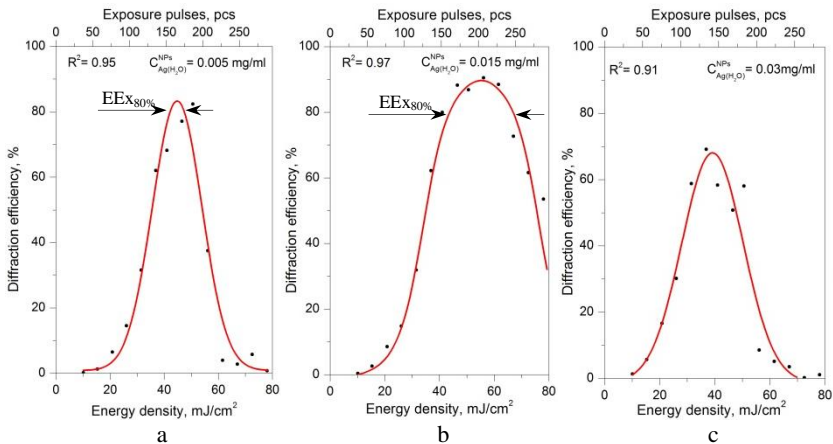
Fig. 18. DE dependence of iffraction gratings formed by pulsed laser in MP regime on pulse energy density at different Ag NPs concentration in aqueous colloid solution: a − $C = 0.005$ mg/ml, b − $C = 0.015$ mg/ml, c − $C = 0.03$ mg/ml

<p style="text-align:center">a   b</p>

<p style="text-align:center">c   d</p>

Fig. 19. Diffraction gratings AFM topography (a, c) and profilogram images (b, d) formed by pulsed laser in MP regime in aqueous DNQ-novolako/Ag NPs (a, b) and DNQ-novolako/Cu NPs (c, d) nanocomposites

It can be assumed that the microrelief peak irregularity is related to Ag NPs aggregation and flattening is associated with laser light scattering (in most cases Mi and Rayleigh scattering).

Similar diffraction efficiency results of diffraction structures formed in MP regime are obtained in the case of DNQ-novolac modified by aqueous Cu NPs colloids. The microrelief with flattened pikes was obtained (Fig. 19, c, d). At highest Cu NPs amount (0.03 mg/ml) the ratio of grating base and flat top is 1:3. Microrelief is symmetrical and slightly deeper than that formed in unmodified photoresist.

Diffraction grating formed at 210 $\mu J/cm^2$ SP energy density in DNQ-novolac compositions modified by Ag NPs in organic colloids characterized by low exposure energy density ($\sim$22 mJ/cm^2) and higher efficiency of diffraction structures (DE $\sim$ 90 %) (Fig. 20). An increase of Ag NPs concentration (0.015 mg/ml) narrows $EEk_{80\%}$ energy density zone in $\sim$ 1.5 – 2 times.
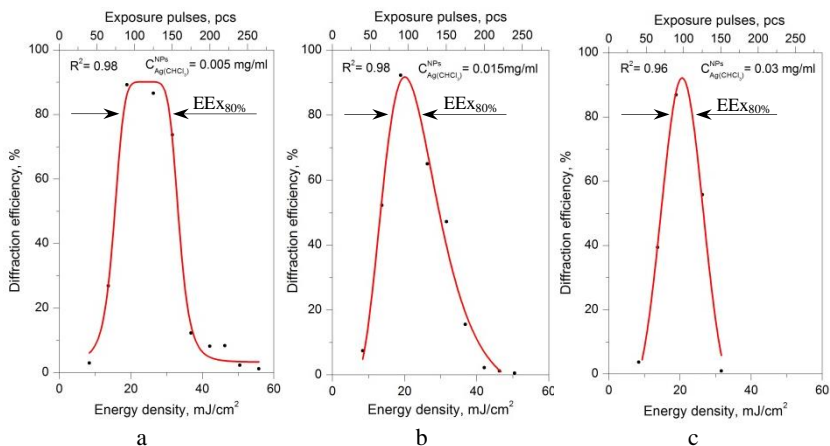
Fig. 20. DE dependance of diffraction gratings formed by pulsed laser in MP regime on pulse energy density at different Ag NPs concentration in organic medium: a – 0.005 mg/ml, b – 0.015 mg/ml, c – 0.03 mg/ml

Surface relief is symmetrical and about ~1.3 times deeper (R_z ~623 nm) compared to the profile formed in unmodified photoresist (Fig. 21, a, b).
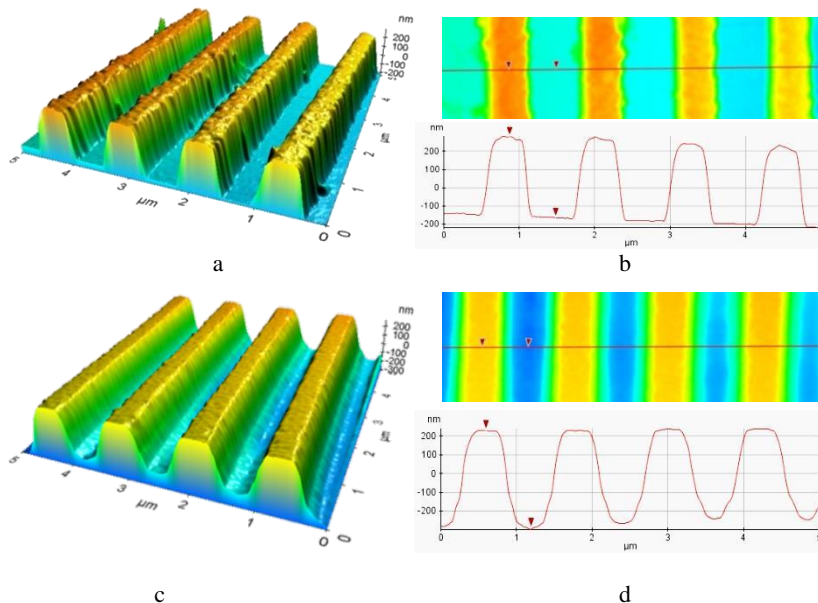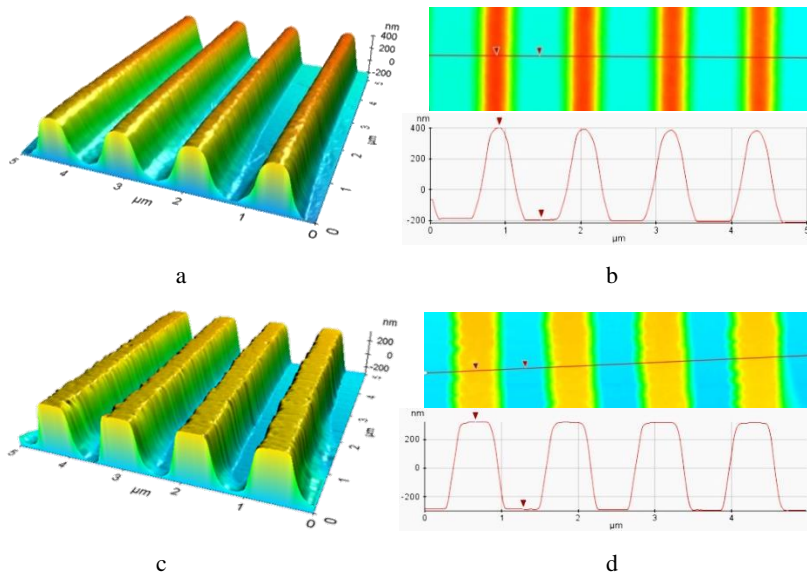

Fig. 21. Diffraction gratings AFM topography (a, c) and profilogram images (b, d) formed by pulsed laser in MP regime in organic DNQ-novolac/Ag NPs (a, b) and DNQ-novolac/Au NPs (c, d) nanocomposites

In all tested concentrations of Au NPs, diffraction efficiency values exceeded 80 %, while the maximum DE value ~ 91 % was obtained at lowest nanoparticle concentration (0.003 mg/ml) and at wide energy density $EEk_{80\%}$ zone (from 46 to 72 mJ/cm^2). Au NPs concentration increase results in $EEk_{80\%}$ zone width decrease without significant changes in DE value.

AFM test shows flattened pikes, deep and symmetrical microrelief (Fig. 21 c, d). Au NPs in DNQ-novolac composition are dispersed homogeneously.

Thus, DNQ-novolac nanocomposite optical properties are influenced by the nanoparticle, which leads to the light scattering in intense MP exposure. Scattered light enters into the interference minimums (dark) zones and results in the illumination of directly not exposed zones, which assures photoresist solubility and formation of flattened microrelief pikes.

CONCLUSIONS

1. Holographic printer was created using low output energy (~1 mJ) single wavelength pulsed nanosecond laser, and utilizing digital holography method working by the light interference principle. This printer in one step directly onto light sensitive material allows the obtaining of a deep 3D holographic transmission surface-relief holograms: color rainbow, achromatic (black and white), only laser light visible holograms (invisible), animated, and combined (rainbow/achromatic/invisible).

2. New direct write printer hologram recording speed on the positive photoresist surface is about 10 times higher than similar surface relief originators, because using pulsed nanosecond laser mechanical vibration does not affect the exposure process. Therefore, during new exposure, the standard "start-stop" exposure regime is not applicable and photoresist coated glass plate moves at a constant speed. It allows the elimination of a time-sensitive and quality-degrading mechanical hologram recombination process, because in proposed method holograms are recombined optically directly on the same photoresist plate.

3. During the formation of diffraction structures by digital printer directly on to positive photoresist surface, microrelief modulation takes place at different grating periods not only in x and y directions, but also periodically changing diffractive structure depth modulation in the z direction. Diffractive structures periods and depth modulations are directly dependent on the information used for object beam modulation (holographic object).

4. The holographic printer diffractive structure formation directly onto positive photoresist regimes have an influence on their quality:

- the highest hologram diffraction efficiencies are obtained at an equal intensity ratio between interfering beams (1:1);
- diazonaphthoquinone-novolac photoresist chemical treatment time directly affects microrelief diffractive efficiency and surface relief formed by pulsed laser single pulses. Shortening developing time from 30 s to 5 s leads to microrelief diffraction efficiency increase by 3.8 times and its depth increase by 1.6 times.

5. Diffraction structures can also be recorded exposing diazonaphthoquinone-novolac in multipulse regimes using low output energy (≤ 1 mJ), weak energy densities ($130 - 700$ $\mu J/cm^2$) and separate pulse-trains (10-300 pcs.) of nanosecond laser. Nanosecond laser and multipulse regime formed diffraction structures processing time, diffraction efficiency and microrelief topography depends not only on pulse-train accumulated energy density, but also on pulse quantity and single pulse energy density.

6. In the case of nanosecond exposure to obtain high quality (DE >90 %) microrelief requires >20 times higher optimal exposition energy density due to times differences between nanosecond laser pulse duration and DNQ-novolac photolysis reaction intermediate products transformation.

7. Hologram originals created by developed digital holographic printers based on pulsed laser can be successfully used for industrial deep holographic images replication on polymeric films via thermal imprinting method. It is determined that new deep holographic images increase first security level for current security holograms.

8. The nanoparticles (Au, Ag, Cu, TiO_2 and SiO_2) affect DNQ-novolac resin optical properties and chemical structure:
- aromatic ring vibrations, the peak positions and intensity changes in the infrared absorption spectrum show that the nanoparticle ions with nitrile groups form coordination bonds;
- at UV wavelength diapason absorption bands of DNQ molecules, novolac and their derivatives are greatly reduced by adding silica and titanium dioxide nanoparticles;
- metal (Au, Cu) nanostructures do not change DNQ-novolac composition attributed absorption band intensity, but in this case, there are localized surface plasmon resonance. Plasmon peak position shows that nanoparticles tend to aggregate.

9. Exposing DNQ-novolac nanocomposites with pulsed laser at single pulse regime, it was determined that nanoparticles adsorbed on the surface have an influence on the light scattering and nanocomposite surface properties, affecting formed microrelief developing time and its quality:

- addition of 0.3 mg/ml of SiO_2 and TiO_2 nanoparticles $2 - 3$ times reduces the development time;
- due to the scattering and high TiO_2 refractive index ($n = 2.7$) exposed by single pulse microrelief shape changes and "blade" type microrelief profiles are obtained;
- DNQ-novolac nanocomposites with metal (Ag, Au, Cu) nanoparticles formed microrelief diffractive efficiency at 30 s developing time is by $1.5 - 1.7$ times higher comparing to that formed in unmodified composition.

10. Exposing DNQ-novolac modified with Ag, Au, Cu nanoparticles in multipulse regime, it was determined that microrelief diffractive efficiency slightly increases (up to 5 %) and microrelief deepens by $8 - 30$ %. Change of laser energy density can change nanocomposite formed microrelief profile shape. Microrelief assumes unusual trapezoidal profile after exposition of DNQ-novolac modified with Ag, Cu and Au nanoparticles.

11. Nanoparticles significantly worsen microrelief optical properties and geometrical parameters formed by a continuous wave laser on DNQ-novolac nanocomposite layers. Nanoparticles initiate light scattering, therefore, during exposure, unexposed zones are also affected, and during developing, the exposed zones of nanocomposites layers are completely washed to the substrate (e. g. glass). Due to the increase of unexposed zone solubility, depending on nanoparticle type in $7 - 50$ % microrelief diffraction efficiency decreases, relief depth values and profile grooves takes a flat shape.

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PRESENTATION OF SCIENTIFIC RESULTS IN CONFERENCES

Internationa conferences

1. **Practical Holography XXVII**: Materials and Applications, 2013 (San Francisco, USA) – *oral presentation*
2. **Baltic Polymer Symposium** 2013 (Trakai, Lithuania) – *poster presentation*.
3. **Practical Holography XXVIII**: Materials and Applications, 2014 (San Francisco, USA) – *oral presentation*.
4. **Radiation Interaction with Materials**: Fundamentals and Applications 2014 (Kaunas, Lithuania) – *oral presentation*.
5. **11th International Conference on Nanosciences and Nanotechnologies (NN14),** 2014 (Thessaloniki, Greece) – *poster presentation*.
6. **Optical Society of Korea Summer Meeting** 2015 (Gyeongju, South Corea) – *invited talk.*
7. **Practical Holography XXX**: Materials and Applications, 2016 (San Francisco, USA) – *invited talk.*
8. **Practical Holography XXXI:** Materials and Applications, 2017 (San Francisco, USA) – *invited talk.*

National conferences

1. **Pramonės inžinerija** 2016 (Kaunas, Lithuania) – *poster presentation*.

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REZIUMĖ

Dėl savo išskirtinių savybių lazeriai yra neatsiejama optinės holografijos ir optinės litografijos dalis. Tobulėjant lazeriams, kartu tobulėja įvairūs holografiniai difrakcinių struktūrų formavimo metodai, nuo kurių priklauso struktūrų kokybė ir panaudojimo galimybės. Holografiniais metodais suformuotos difrakcinės struktūros yra vis plačiau naudojamos įvairiose srityse, pavyzdžiui, optiniai elementai karinei pramonei, duomenų laikmenų kaupikliai, holografinė topografija, reklamos ir holografiniai apsaugos elementai.

Holografinių elementų, suformuotų polimeruose panaudojimas yra gana platus: nuo elementarių ženklų leidimams, kvietimams, bilietams į masinius renginius (koncertus, sporto varžybas, konferencijas, forumus ir pan.) iki naudojimo produktų pakuočių dekoravimui, akcizinių žymių, vertybinių popierių, piniginių banknotų, asmens tapatybės kortelių ir pasų, vizų ir kitų griežtos apskaitos dokumentų apsaugos. Holografinių apsaugos elementų struktūra priklauso ir nuo panaudojimo srities. Sudėtingos kompleksinės struktūros elementai, kurie turi optiškai kintamus apsauginius efektus (mikrotekstus, optiškai kintamas žymes, paslėptus elementus ir kt.), yra dažniausiai skirti kontroliuojančioms tarnyboms. O sąlyginai nesudėtingos, pirmos pakopos saugos lygio holografinės struktūros elementai (pavyzdžiui, skirtingas vaizdo gylis, kintamos spalvos), skirti atskirti produktų klastotes ir suprantami eiliniam žmogui.

Esant laisvam prekių judėjimui, vis dažniau yra nustatoma prekių su suklastotais prekių ženklais. Tobulėjant apsaugos elementų technologijoms bei įrangai, tobulėja ir klastojimo įranga bei didėja jos mastai, o įmonės gamintojos patiria milžiniškų nuostolių. Todėl specifinių holografinių difrakcinių struktūrų formavimo metodų, tinkančių ir apsaugos elementų gamybai tobulinimas, yra aktualus darniai ekonomikos plėtrai. Taigi svarbu sukurti efektyvias, šiuolaikiškas holografines difrakcines struktūras, nesudėtingam klastočių indentifikavimui be papildomos įrangos ar priemonių.

Darbo tikslas ir uždaviniai

Darbo tikslas – sukurti didelės spartos efektyvų metodą, galintį formuoti šviesai jautriose polimerinėse medžiagose reljefines difrakcines struktūras, atstatančias gilų holografinį vaizdą bei ištirti formavimo režimų ir kompozicijos įtaką mikroreljefo optinėms savybėms ir morfologijai.

Darbo tikslui pasiekti reikia išspręsti šiuos uždavinius:
- pritaikyti skaitmeninės holografijos metodą reljefinių, gilaus vaizdo difrakcinių struktūrų formavimui impulsiniu lazeriu ir sukurti šviesos interferencijos principu veikiantį spausdintuvą;
- ištirti pozityvinio fotorezisto diazonaftochinono-novolakinės dervos pagrindu eksponavimo dėsningumus vienu nanosekundinio lazerio impulsu skaitmeniniu metodu;
- ištirti eksponavimo ir ryškinimo režimų įtaką fotorezistė suformuotų difrakcinių struktūrų geometriniams parametrams ir optinėms savybėms;
- palyginti difrakcinių struktūrų, suformuotų vienu impulsinio lazerio impulsu skaitmeniniu metodu, optinius parametrus su kitais metodais gautų struktūrų parametrais;
- ištirti diazonaftochinono-novolakinės dervos optinių savybių pagerinimo galimybę, kompoziciją modifikuojant įvairios prigimties nanodalelėmis;
- įvertinti skaitmeniniu metodu vienu impulsinio lazerio impulsu gautų gilių vaizdų difrakcinių struktūrų panaudojimo galimybę įspaudavimo metodu aukštos kokybės hologramų originalams polimerinėse plėvelėse gauti.

Darbo mokslinis naujumas ir praktinė vertė

Šiame darbe skaitmeninės holografijos metodas pritaikytas formuoti gilaus vaizdo reljefines vaivorykštines hologramas. Šis metodas užpildo trūkstamą nišą tarp analoginės holografijos ir elektroninės litografijos. Sukurtas skaitmeninis holografinis spausdintuvas, kuris, naudodamas vienos

bangos ilgio kietakūnį impulsinį nanosekundinį lazerį, veikiantis šviesos interferencijos principu, tiesiogiai pozityvinio fotorezisto sluoksnyje, vienu žingsniu ir vienu impulsu leidžia gauti gilaus vaizdo reljefines pralaidumo hologramas: spalvotas vaivorykštines, achromatines (nespalvotas), kombinuotas (vaivorykštines-achromatines) ir tik lazerinėje šviesoje matomas hologramas (paslėptas vaizdas). Naudojant šį metodą galima ir vaizdų animacija.

Pritaikytas metodas tinka apsaugos, pakavimo ir kitų aukštos kokybės hologramų originalų gamybai naudojant vieno bangos ilgio impulsinį lazerį. Turimais duomenimis šis metodas yra apie dešimt kartų spartesnis už kitus, šiuo metu egzistuojančius hologramų originalų gavimo metodus, nes aukštos kokybės hologramų originalų dauginimas atliekamas tiesiogiai optiniu metodu, atsisakant hologramų dauginimo terminiu įspaudavimu (hologramų rekombinacija).

Darbe pristatytas metodo panaudojimas difrakcinių struktūrų įspaudavimui plastikuose. Tai atveria naujas galimybes hologramų originalų gamyboje. Apjungiant gilių originalų vaizdų gavimo metodą su kitais, jau egzistuojančiais originalų kūrimo metodais, sukurti naujos kartos hibridinių apsauginių ir gilaus vaizdo hologramų originalų pavyzdžiai.

Ginamieji teiginiai

1. Gilaus vaizdo reljefines hologramas galima gauti skaitmeniniu holografijos metodu veikiant tiesiogiai šviesos interferencijos principu pozityvinio fotorezisto sluoksnį vienu, vieno bangos ilgio kietakūnio impulsinio lazerio impulsu.
2. Nanodalelėmis modifikuotose DNQ-novolako dangose impulsiniu lazeriu suformuoto mikroreljefo geometriniai parametrai ir optinės savybės priklauso nuo eksponavimo metodo ir režimų.

Disertacijos apimtis ir struktūra

Disertaciją sudaro darbo įvadas, literatūros apžvalga disertacijos tema, darbe naudotų metodų aprašai, tyrimo rezultatų apibūdinimai ir apibendrinimai, darbo išvados, naudotos literatūros ir publikacijų disertacijos tema sąrašai.

Darbas pristatomas pateikiant 80 paveikslų, 14 lentelių ir 169 literatūros šaltinius.
Bendra disertacijos apimtis – 114 puslapių.

Disertacijos aprobavimas

Pagrindiniai darbo rezultatai paskelbti 8 publikacijose, iš kurių 2 – žurnaluose, referuojamuose „Clarivate Analytics Web of Science" duomenų bazėje, 6 – kitų tarptautinių duomenų bazių leidiniuose be citavimo indekso (konferencijų pranešimų leidiniuose) bei 2 Lietuvos Respublikos patentai. Rezultatai pristatyti 8 tarptautinėse ir 1 respublikinėje konferencijose.

IŠVADOS

1. Panaudojant impulsinį mažos išvadinės energijos, vieno bangos ilgio nanosekundinį lazerį ir skaitmeninės holografijos metodą, sukurtas šviesos interferencijos principu veikiantis spausdintuvas, kuris vienu etapu, tiesiogiai šviesai jautrios medžiagos sluoksnyje įrašo skaitmenines, gilaus vaizdo reljefines hologramas. Sukurtu spausdintuvu galima suformuoti vienspalvius, spalvotus, achromatinius ir kombinuotus hologramų originalus ne tik matomus paprasta akimi, bet ir paslėpto vaizdo hologramas, matomas tik lazerio šviesoje.

2. Sukurto spausdintuvo hologramų įrašymo vienu etapu metu pozityvinio fotorezisto paviršiuje sparta yra apie 10 kartų didesnė už panašius reljefinių originalų spausdintuvus, nes naudojant impulsinį nanosekundinį lazerį mechaninės vibracijos neturi įtakos eksponavimo procesui. Todėl šio proceso metu nenaudojamas įprastas „start-stop" eksponavimo režimas. Fotorezisto plokštelė juda pastoviu greičiu, leidžiančiu atsisakyti ilgo ir reljefo kokybę bloginančio mechaninio hologramų dauginimo proceso, o jas dauginant optiniu metodu tiesiogiai fotorezisto plokštelėje.

3. Formuojant difrakcines struktūras skaitmeniniu spausdintuvu tiesiogiai pozityvinio fotorezisto sluoksnyje nustatyta, kad mikroreljefo moduliacija vyksta x ir y kryptimis ne tik skirtingais gardelių periodais, bet ir neperiodiškai kintančia struktūrų gylio moduliacija z kryptimi. Suformuotų difrakcinių struktūrų moduliacijų periodiškumai ir reljefo gyliai tiesiogiai priklauso nuo objektinio pluošto moduliacijai naudojamos informacijos (holografinio objekto).

4. Tiriant difrakcinių struktūrų formavimo skaitmeniniu spausdintuvu tiesiogiai pozityvinio fotorezisto sluoksnyje režimus nustatyta, kad didžiausias hologramų difrakcinis efektyvumas gaunamas esant vienodam interferuojančių pluoštų intensyvumo santykiui (1:1). Fotorezisto DNQ-novolako cheminio ryškinimo trukmė turi didelę įtaką impulsiniu lazeriu vienu impulsu suformuotų mikrostruktūrų difrakciniam efektyvumui ir paviršiaus reljefui. Trumpinant ryškinimo trukmę nuo 30 s iki 5 s mikroreljefo difrakcinis efektyvumas padidėja 3,8 karto, o gylis – 1,6 karto.

5. Tiriant impulsinio lazerio eksponavimo įtaką difrakcinių struktūrų kokybei nustatyta, kad struktūros gali būti įrašomos eksponuojant DNQ-novolako fotorezistą impulsiniu lazeriu ir daugiaimpulsiniu režimu su mažos išvadinės energijos (≤ 1 mJ), mažų energijos tankių (130–700 $\mu J/cm^2$) bei atskirų (10–300 vnt.) nanosekundinio lazerio impulsų voromis. Gauta, kad nanosekundiniu lazeriu, daugiaimpulsiu režimu suformuotų difrakcinių struktūrų ryškinimo trukmė, difrakcinis efektyvumas ir mikroreljefo topografija, priklauso ne tik nuo impulsų voros prikaupiamo galutinės energijos tankio, bet ir nuo vienetinio impulso energijos tankio ir impulsų skaičiaus.

6. Tiriant DNQ-novolako eksponuoto impulsiniu ir nuolatinės veikos lazeriu režimų įtaką mikroreljefo savybėms nustatyta, kad geros kokybės (DE >90 %) mikroreljefui gauti nanosekundinės ekspozicijos atveju, dėl didelio nanosekundinio lazerio impulso trukmės ir DNQ-novolako fotolizės reakcijos tarpinių produktų virsmo trukmių skirtumo, reikalingas >20 kartų didesnis optimalios ekspozicijos energijos tankis.

7. Sukurtu skaitmeniniu holografiniu spausdintuvu, impulsiniu lazeriu gauti hologramų originalai gali būti naudojami pramoniniam gilaus vaizdo hologramų tiražavimui polimerinėse plėvelėse terminio įspaudavimo metodu. Šios gilaus vaizdo hologramos padidina dabartinį pirmos pakopos apsauginių hologramų saugos lygį.

8. Nanodalelės (Au, Ag, Cu, TiO_2 ir SiO_2) turi įtakos DNQ-novolako dervos optinėms savybėms ir cheminei struktūrai:
   • aromatinio žiedo virpesius atitinkančių smailių padėčių ir intensyvumo kitimas infraraudonųjų spindulių absorbcijos spektre rodo, kad nanodalelių jonai su nitrilo grupėmis sudaro koordinacinius ryšius;
   • UV bangų ilgių diapazone DNQ molekulių ir novolako bei jų sąveikos darinių absorbcijos juostų intensyvumas žymiai sumažėja, įmaišius silicio ir titano dioksido nanodalelių;
   • metalo (Au, Cu) nanostruktūros nekeičia DNQ-novolako kompozicijai priskiriamų absorbcijos juostų intensyvumo, tačiau šiuo atveju atsiranda lokalizuotų paviršinių plazmonų rezonansas. Plazmoninių pikų padėtis rodo, kad nanodalelės linkusios agreguotis.

9. Impulsiniu lazeriu vieno impulso režimu eksponuojant DNQ-novolako nanokompozitus nustatyta, kad dangos paviršiuje adsorbuotos nanodalelės turi įtakos šviesos sklaidai ir nanokompozito paviršiaus savybėms, lemiančioms suformuotų mikroreljefų ryškinimo trukmę ir jo kokybę:
   • įmaišius 0,3 mg/ml SiO_2 ir TiO_2 nanodalelių ryškinimo trukmė sutrumpėja 2 – 3 kartus;

- dėl sklaidos ir didelio TiO_2 nanodalelių lūžio rodiklio ($n = 2,7$) kinta mikroreljefo, gauto eksponuojant nanokompozitą vienu impulsu, forma – gaunamas „ašmenų" tipo mikroreljefo profilis;
- DNQ-novolako nanokompozituose su metalo (Ag, Au, Cu) nanodalelėmis suformuoto mikroreljefo difrakcinis efektyvumas, esant 30 s ryškinimo trukmei, yra 1,5–1,7 karto didesnis už mikroreljefo, suformuoto nemodifikuotoje kompozicijoje.

10. Daugiaimpulsiniu režimu eksponuojant DNQ-novolako su Ag, Au, Cu nanodalelėmis nanokompozitus nustatyta, kad nežymiai padidėja suformuoto mikroreljefo difrakcinis efektyvumas (iki 5 %), o mikroreljefas pagilėja 8–30 %. Keičiant lazerio energijos tankį, galima keisti nanokompozite suformuoto mikroreljefo profilio formą. Eksponuojant DNQ-novolako su Ag, Cu ir Au nanokompozitą, mikroreljefas įgauna nebūdingą trapecinį profilį.

11. Nanodalelės žymiai pablogina mikroreljefo, suformuoto nuolatinės veikos lazeriu DNQ-novolako nanokompozitų dangose, optines savybės ir geometrinius parametrus. Nustatyta, kad nanodalelės inicijuoja šviesos sklaidą, todėl eksponavimo metu yra paveikiamos ir neapšviestos fotorezisto zonos, kurios ryškinimo metu išplaunamos. Dėl padidėjusio neapšviestų zonų tirpumo priklausomai nuo nanodalelių tipo 7–50 % sumažėja mikroreljefo difrakcinio efektyvumo ir reljefo gylio vertės, o profilio įdubos įgauna plokščią formą.