

FORMATION OF DIRECT SURFACE RELIEF
IN PHOTOCHROME-CHALCOGENIDE COMPOSITESA. Gerbreders^{1,2}, J. Teteris¹¹Institute of Solid State Physics, University of Latvia,
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A method for preparation of thin triple composite films of organic polymer-chalcogenide-photochromes is described, the photo-induced changes of optical properties and holographic recording are considered. The films were obtained from solutions of arsenic sulphide, azobenzene Disperse Red 1, spiropyran, and organic polymers in organic solvents. The solutions were spread over glass or quartz substrates; the thickness of dry films was 3–10 μm . The absorption spectra of the prepared films were studied and analyzed. The holographic recording of diffraction gratings was performed by laser lines of 325 nm, 442 nm and 532 nm. During recording the diffraction efficiency was measured simultaneously in the transmission and reflection modes. The relief formation on the film surface was observed and the profile of the gratings formed was analyzed using AFM microscope. The influence of photoisomerization and photo-induced mass transport on the surface relief formation process is discussed.

Key words: *arsenic sulphide, Disperse Red 1, spiropyran, polymer-photochrome composite, polymer-photochrome-chalcogenide composite, holographic grating, surface relief.*

1. INTRODUCTION

Chalcogenide thin films are well known as the recording media that have been widely applied for a long time in different areas for information storage and reproduction. For micro- and nano-relief formation in the films, selective etching is mostly used. In this work, we describe the chalcogenide materials as a system for direct relief formation under light radiation without selective etching.

The results of recent publications [1, 2] devoted to studying this process in chalcogenide films, in particular at holographic recording, have shown that the relief formation in pure chalcogenide films is possible at a high value of exposure (approx. 5 kJ/cm² and higher). We suggested that direct relief formation is possible at a lower exposure if the composite material on chalcogenide and polymer base is used. Such materials have already been used for holographic records [3].

A thin film of composite from the engineering point of view can be considered as a homogeneous photoresist, allowing its optical properties to be varied. Furthermore, chemically such a composite is solid solution of chalcogenide in a polymeric matrix. In our previous work [4] we showed the difference in

chemical composition of illuminated and non-illuminated areas of the composite. In our opinion, the interaction of chalcogenide particles with electric field leads to a mass transport in the films. Under radiation the structure of chalcogenide particles might change; corresponding changes in their dipole moments occur, which result in stress appearance and particle movement in the film.

We suggested that another type material – with a large difference in dipole moments in illuminated and non-illuminated areas – can activate the mass transport in a composite and increase the diffraction efficiency of a grating. As such material, organic photochromes can be used. Besides, the direct relief formation was observed in the photochrome-polymer films [5,6].

Figure 1 shows two types of organic photochromes (from numerous types existing): Disperse Red 1 (DR1) and spiropyran, and the respective photoisomerization mechanisms. The former is an azobenzene compound whose photoisomerization mechanism can be described as *cis-trans* recombination regarding the N=N bond. The dipole moments of *cis*- and *trans*-forms are 6 D and 9 D, respectively [6].

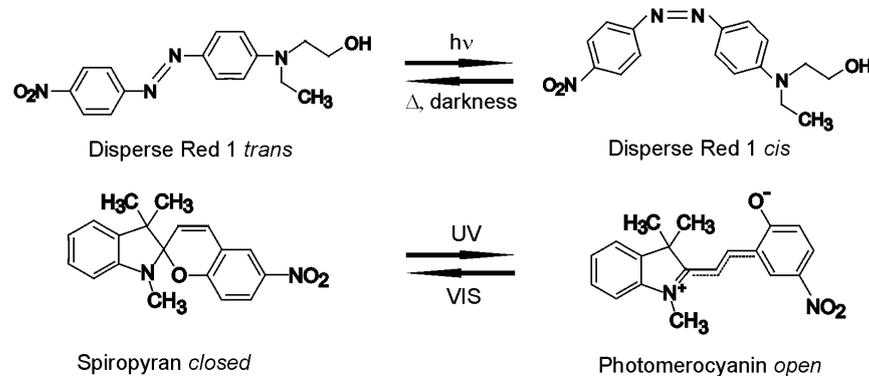


Fig. 1. Disperse Red 1, spiropyran and mechanisms of their photoisomerization.

As concerns spiropyran, it has another photoisomerization mechanism: tautomerization to the photomerocyanine form. The dipole moments of spiropyran and photomerocyanine differ more considerably – 7.5 D and 13.6 D, respectively [6], which is the main reason why we have chosen spiropyran as one of the additives for the composite.

2. EXPERIMENTAL

When preparing the optically homogeneous chalcogenide-polymer composites some problems arise. Low solubility of chalcogenide in organic solvents and poor compatibility with the majority of polymers restrict the production possibilities for a wide range of composites. Quite often, coagulation of chalcogenide particles takes place at drying a composite film, which results in preparation of a composite film possessing high optical scattering. To improve the optical transparency of the films, Disperbyk-161 copolymer (made by *BYK-Chemie GmbH*) with free amine groups (as additive for prevention of pigment coagulation) was used, which made it possible to obtain transparent composite films with As₂S₃

concentration up to 60% (wt) in relation to the polymer. Originally, it had been planned to use Disperbyk 161 as uniform polymer for all composites; however, in dry spiropyran – Disperbyk 161 films the optical homogeneity was not achieved.

Crushed arsenic sulphide was dissolved in a mixture of organic solvents (N,N-dimethylformamide and diethylamine, 9÷1 (wt) accordingly). Dissolution took place in a conical retort using an interfusion magnetic mixer, at room temperature (RT) for several days. A 10% (wt) solution of arsenic sulphide was mixed with a 30% (wt) solution of Disperbyk-161 polymer (as a solvent a mixture of methoxypropylacetate and butylacetate, 6÷1 (wt) was used) in such proportion that after a film's drying the mass concentration of arsenic sulphide on the substrate was 28, 40, 50 and 60% (wt).

As photochrome, DR1 (*Aldrich, CAS 2872-52-8*) was chosen. Powder of DR1 was dissolved in N,N-dimethylformamide at RT. A 5% (wt) solution of DR1 was mixed with a 30% (wt) solution of polymer Disperbyk-161 and with Disperbyk-161+As₂S₃ solution in such proportion that after drying the mass concentrations of components on the substrate were: 5% (wt) DR1 + 60% (wt) Disperbyk-161 and 5% (wt) DR1 + 35% (wt) As₂S₃ + 60% (wt) Disperbyk-161, respectively.

In a like manner, the spiropyran (*Aldrich, CAS 1498-88-0*) was dissolved in chloroform at RT. A 5% (wt) solution of spiropyran was mixed with poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) $M_w = 50\ 000\text{--}80\ 000$ (GPC) (CAS 27360-07-2), poly(vinyl acetate) $M_w = 500\ 000$ (CAS 9003-20-7) and poly(methyl methacrylate) $M_w = 350\ 000$ (CAS 9011-14-7) dissolved in chloroform. The solutions were mixed in such proportion that after drying the mixtures on a substrate the concentration of spiropyran in the polymer would make 5% (wt). Besides, to the solution with spiropyran and poly(vinyl acetate) a 10% As₂S₃ solution in organic solvents was added (as described above), in such a proportion that after drying the mixtures on a substrate the concentration of arsenic sulphide in the composite would be 1% (wt). For studying the transmission spectra of composite in the UV region in more detail, a composition with a 1% wt. spiropyran concentration in poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) was prepared.

Films from composite solutions were produced using a BYK Gardner GmbH applicator. The liquid layer was 30, 60, 90 and 120 μm thick; as substrates, glass and quartz plates were used. To improve the moistening, to the As₂S₃ and Disperbyk 161 solution a surfactant was added (less than 0.01% (wt)) before application. The As₂S₃ films were dried in an oven at the temperature of 303 K for 30–40 min. The DR1 containing films were also dried in an oven at the temperature of 423 K for 3 h. Similar drying at the same temperature but for 30 min. was done for spiropyran containing films. The thickness of dry films was 1.5–9 μm (determined using a Veeco Dektak 150 surface profiler).

For all films, including those of pure polymer and pure arsenic sulphide, the transmission spectra were measured by the Ocean Optic HR4000CG spectrometer. Measurements of transmission spectra for pure organic polymer and spiropyran films were performed with the films on quartz substrate.

The holographic gratings with a period of $\Lambda = 1 \mu\text{m}$ were recorded by two symmetrical laser beams of equal intensity with linear horizontal polarization (p-p). For As_2S_3 and DR1 containing films the 442 and 532 nm lasers were used, with the beam intensity being in the range 0.79–0.86 W/cm^2 . The readout of the transmission diffraction efficiency was made at the Bragg angle using semiconductor laser beams: 640 nm for the 442 nm recording laser, and 673 nm for the 532 nm recording laser. The second-order maximum of the recording beam was employed for measuring the efficiency of reflection diffraction.

For spiropyran-containing films the holographic gratings with a period of $\Lambda = 1 \mu\text{m}$ were recorded by two symmetrical laser beams of equal intensity with linear horizontal polarization (p-p), using 325 nm (beam intensity $2 \times 1.8 \cdot 10^{-4} \text{ W}/\text{cm}^2$) and 532 nm (beam intensity $2 \times 1.4 \cdot 10^{-3} - 2 \times 4.2 \cdot 10^{-2} \text{ W}/\text{cm}^2$) lasers. The readout of transmission diffraction efficiency was made at Bragg's angle using a 640 nm semiconductor laser beam (for the 325 nm recording laser) at the 2nd order maximum of recording beam (for the 532 nm recording laser). Immediately before recording by the 532 nm laser, the samples were illuminated by a 375 nm laser beam (intensity 0.01 W/cm^2) for 5 min.

After recording, the surface relief of the samples was analyzed using an Atomic Force Microscope (AFM).

To study the relief formation, the films of compositions 5% (wt) DR1 + 60% (wt) Disperbyk-161 and 5% (wt) DR 1+35% (wt) As_2S_3 +60% (wt) Disperbyk-161 were irradiated by a cylindrical lens focused laser beam with wavelength 532 nm and intensity 11 W/cm^2 . The linear sizes of focused light spot were $35000 \times 25 \mu\text{m}$. The profile of irradiated area was studied using the Veeco Dektak 150 profiler.

3. RESULTS AND DISCUSSION

Figures 2–4 show transmission spectra obtained while studying the compositions: arsenic sulphide/Disperbyk 161, DR1/arsenic sulphide/Disperbyk 161 and spiropyran/arsenic sulphide/polyvinylacetate. The spectra are displayed in such a manner that one can see the influence of components on the general transmission spectra of composites. We therefore could make composites forming the spectral characteristics by changing concentration and proportion of the components. Besides, as Fig. 5 shows, the spectrums of spiropyran composites are changing under UV-light (at a relatively low exposition of 0.36 J/cm^2) due to the transfer to a photomerocyanine form, which goes most intensively at illumination of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate)/spiropyran film by the 325 nm laser.

The results of holographic recording in composites, namely, the diffraction efficiency dependence on the exposure can be seen in Figs. 6 and 7. If we compare these graphs, it is obvious that simultaneous presence of arsenic sulphide and DR1 in the composite increases the diffraction efficiency in comparison with materials containing only one photosensitive material. Almost the same picture can be observed for the composite film of spiropyran/arsenic sulphide in PVA (Fig. 8). In this case we tried to record the grating in the photomerocyanine form (more detailed description is published in [7]). Figure 8 shows the dependence of the diffraction efficiency maxima on the recording beam intensity. The top curve corresponds to spiropyran/arsenic sulphide in PVA.

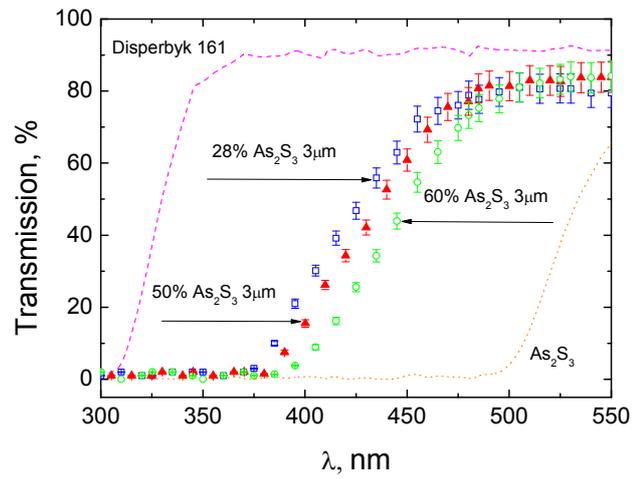


Fig. 2. Transmission spectra of As_2S_3 /Disperbyk 161 composite films at different As_2S_3 concentrations.

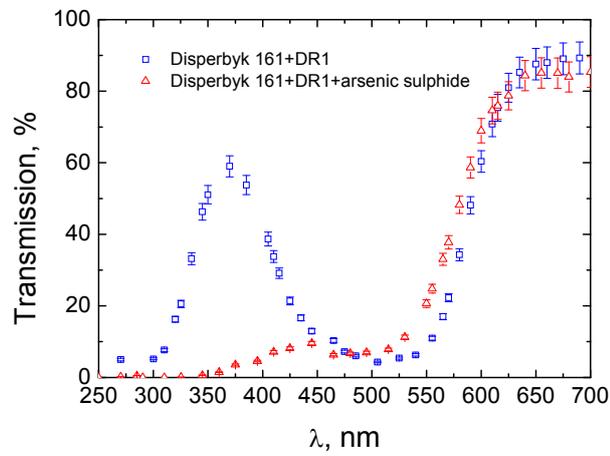


Fig. 3. Transmission spectra of the Disperbyk 161+DR1 composite films with and without As_2S_3 .

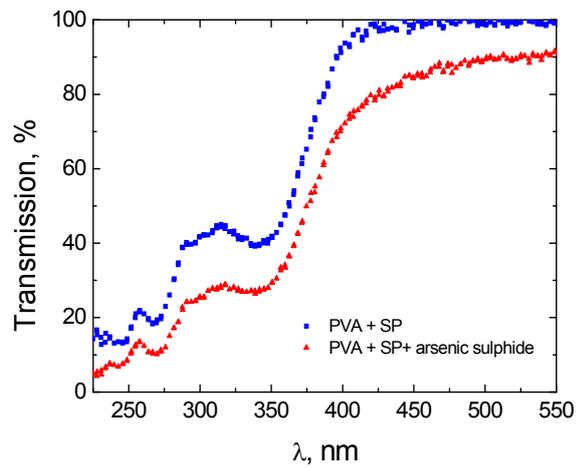


Fig. 4. Transmission spectra of the PVA+SP composite films with and without As_2S_3 .

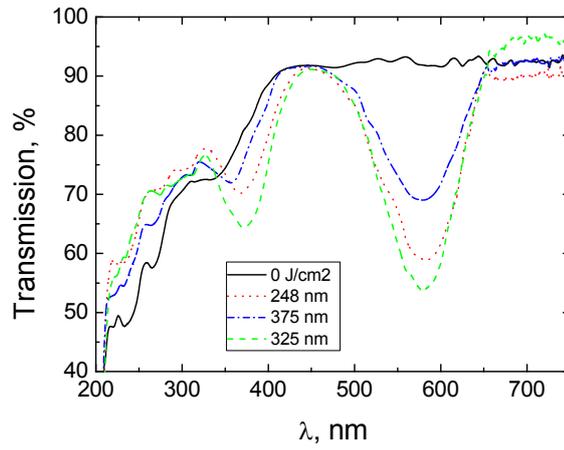


Fig. 5. Transmission spectra of spiropyran-poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) composite before (black line) and after (faltering lines) illumination by different UV-lasers ($E = 0.36 \text{ J/cm}^2$).

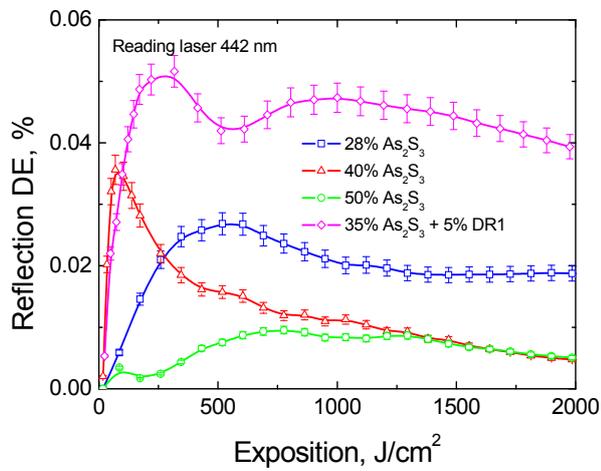


Fig. 6. Reflection (measured at 442 nm) diffraction efficiency vs. the recording exposition (recording laser 442 nm; polymeric matrix – Disperbyk 161).

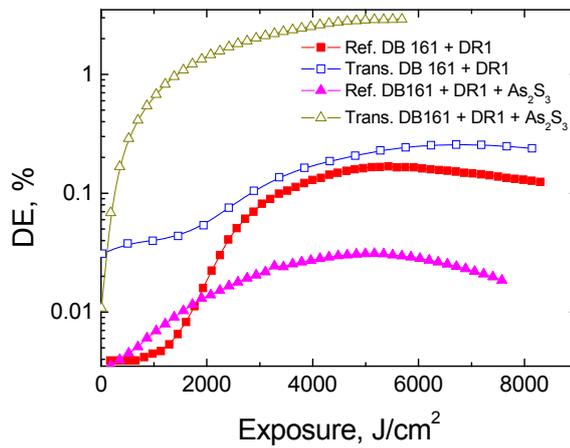


Fig. 7. Transmission (at 640 nm) and reflection (at 532 nm) diffraction efficiency vs. recording exposition (recording laser 532 nm; polymeric matrix – Disperbyk 161).

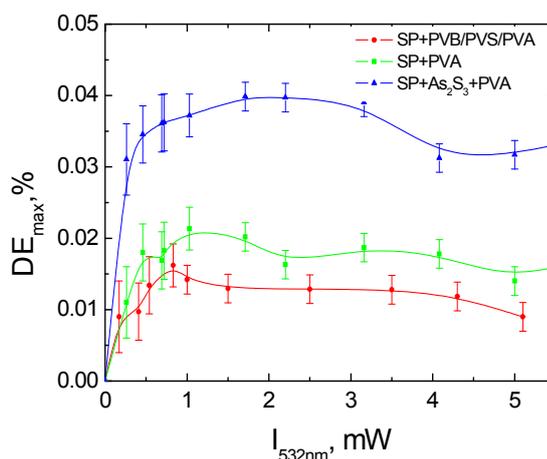


Fig. 8. Dependence of transmission diffraction efficiency maximums on the recording beam intensity (recording and reading lasers 532 nm).

An important question to be answered is: how does a grating form in composite films? We suggested that the particles of chalcogenide at the point of maximum recombine in another amorphous modification, as shown, e.g., in [8]. At the same time, photochrome particles recombine to another isomerization form. The polymer molecules usually do not change at wavelengths greater than 350–400 nm.

Structural modifications in As₂S₃ lead to loss of thermodynamic balance in a composite film. If the viscosity and polarity of the polymer allow the movement of photochrome and chalcogenide particles, the composite film structure puts in order accordingly the bands of minimum and maximum. This does not mean that the relief formation takes place – possibly, for this a movement of polymer macromolecules is required.

Figures 9a,b demonstrate the character of surface relief dependence on the contents of composite. The presence only of arsenic sulphide gives a “hole”, whereas the presence of DR1 and arsenic sulphide – a “hill”. The dependence of the relief height on the exposure for the 5%(wt)DR1 + 35%(wt)As₂S₃ + 60%(wt)Disperbyk-161 composite can be seen in Fig. 9c. We tried to make the experiment with two directions of the electric field vector (changing the beam polarization), but this affected only insignificantly the relief height. To reach the value of this parameter of about 100 nm (which is a usual height of relief obtained at selective etching of chalcogenide film [9]) an exposure on the order of 5 kJ/cm² is required. The maximum relief height might be 600 – 800 nm at the exposure of 25 kJ/cm².

Unfortunately, in spiropyran-containing composites we did not obtain a direct surface relief. This could be explained by the fact that spiropyran photoisomerization takes place at a very low exposure (less than 2–4 mJ/cm² [7]) At exposures greater than 50–100 J/cm² the spiropyran-containing composites possibly lose the photoisomerization properties because of chemical decomposition. This situation confirms our assumption that it is not enough to change the photoresist dipole moment for the direct relief formation in composites; for this, the movement or restructuring of polymer macromolecules is possibly required.

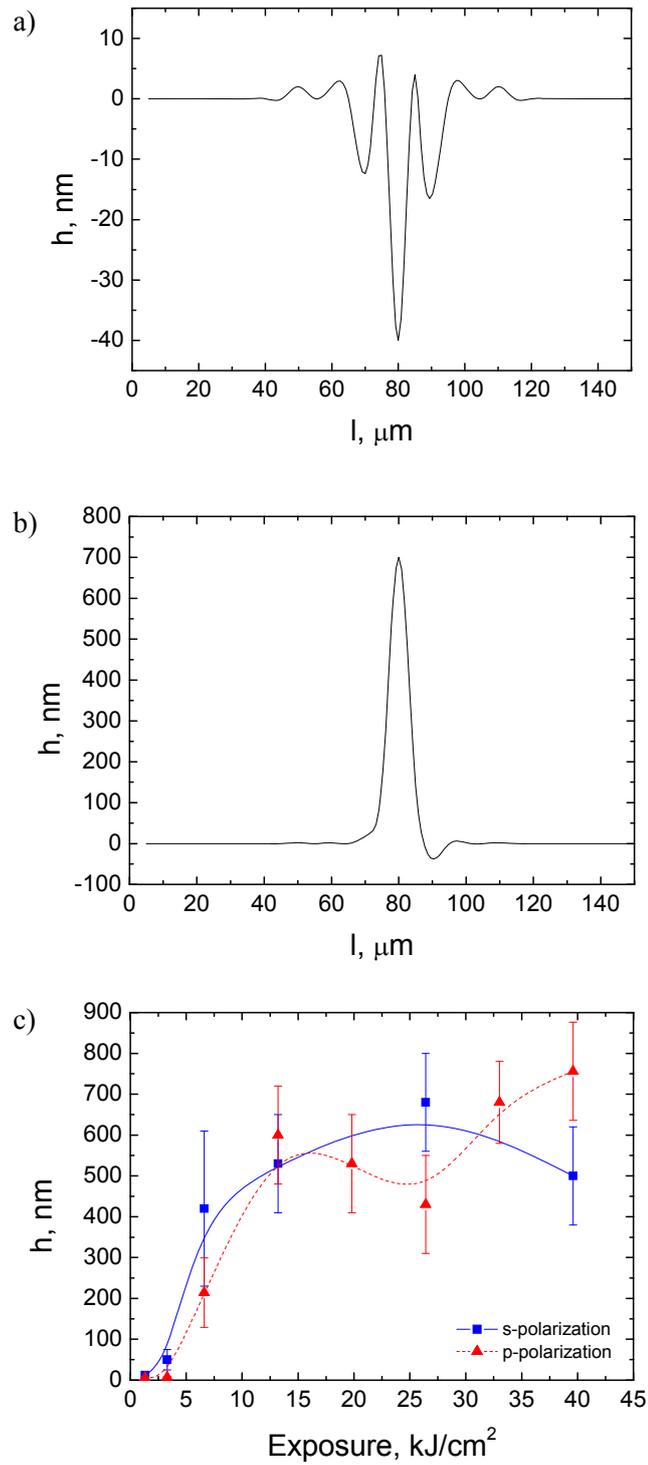


Fig. 9. The relief after laser irradiation of composites through cylindrical lens by laser beam 532 nm:
 a) profiles of relief for 40% As₂S₃ + 60% Disperbyk161 composite;
 b) profiles of relief for 5% DR1+35% As₂S₃+60% Disperbyk161 composite;
 c) exposure dependence of the relief height for 5% DR-1 + 35% As₂S₃ + 60% Disperbyk161 composite.

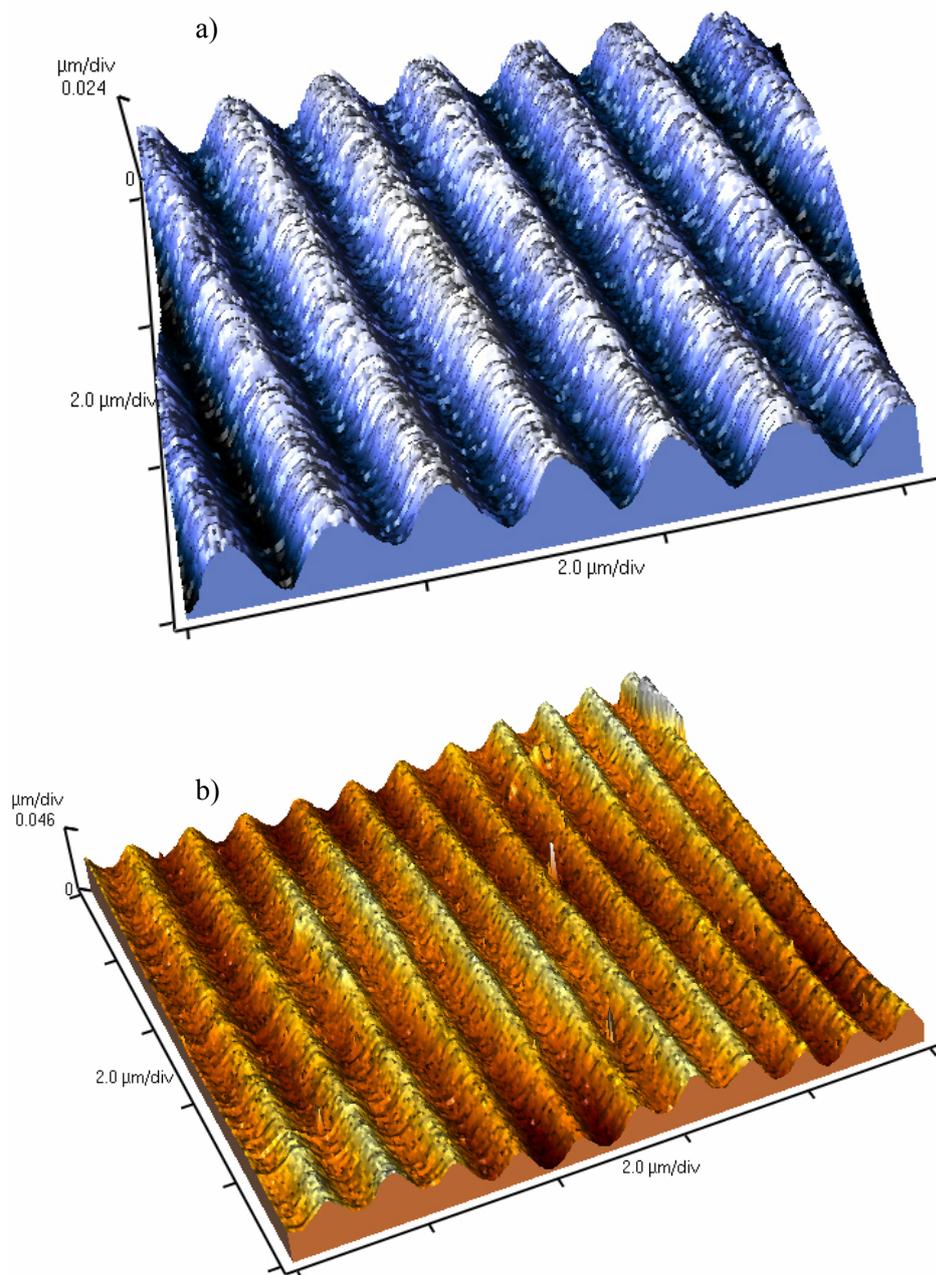


Fig. 10. AFM images of the surface relief holographic grating recorded by laser 532 nm in composites: 40% As_2S_3 – 60% Disperbyk161 (a) and 5% DR1 – 35% As_2S_3 – 60% Disperbyk161 (b); film thickness $\sim 5 \mu\text{m}$.

Figure 10 shows the AFM images of relief gratings obtained without selective etching procedure.

4. CONCLUSIONS

A composite material on the basis of arsenic sulphide, DR1 and copolymer Disperbyk-161 with different proportion of components and low optical scattering

has been obtained. The composite with addition of Disperse Red 1 has a higher value of transmission diffraction efficiency of gratings. The direct surface relief formation by holographic recording in the composites has been shown.

We have obtained composites with various concentrations of spiropyran, with and without presence of arsenic sulphide in various polymers (polyvinyl-acetate, polymethylmetacrylate and copolymer of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate).

The studies of the initial transmission spectra of composites and their changes induced by lasers of wavelengths of 248, 325 and 375 nm have revealed appearance of an absorption band in the spectral region of 475–650 nm with the maximum at 580 nm. The holographic recording of transmission gratings was performed; it has been shown that the diffraction efficiency increases in the presence of arsenic sulphide.

The conclusion is therefore that the composites with combination of arsenic sulphide and photochromes are more effective for diffraction recording.

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VIRSMAS RELJEFA VEIDOŠANĀS FOTOHROMA-HALKOGENĪDU KOMPOZĪTOS.

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K o p s a v i l k u m s

Šajā darbā tiek aprakstīta kompozītu polimēra-fotohroma-halkogenīdu plāno kārtiņu iegūšanas metode, kā arī izpētītas šo materiālu optiskās īpašības un hologrāfiskā ieraksta īpatnības. Kompozītu plānās kārtiņas tika iegūtas no arsēna

sulfīda, Disperse Red 1, spiropirana un polimēra Disperbyk-161 (ražots BYK-Chemie GmbH) šķīduma organiskajā šķīdinātajā. Šķīdumu uzklājām uz stikla un kvarca plāksnītēm, sausu kārtiņu biezums bija 3–10 μm. Šiem kompozītiem tika izpētīti un salīdzināti transmisijas spektri. Paraugos tika ierakstīti difrakcijas režģi ar viļņu garumiem 442 un 532 nm, rakstīšanas laikā izmērījām transmisijas un refleksijas difrakcijas efektivitāti. Tika izpētīta difrakcijas efektivitāte atkarībā no ekspozīcijas. Tika pētīta virsmas reljefu veidošanās uz kompozītu kārtiņām pēc to apstarošanas ar lāzerstarojumu 532 nm caur cilindrisku lēcu, noteikta reljefa augstuma atkarība no apgaismošanas ekspozīcijas. Difrakcijas režģi tika apskatīti ar AFM palīdzību.

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