PHYSICS AND CHEMISTRY OF SOLID STATE
V. 24, No. 1 (2023) pp. 197-201

Section: Physics

DOI: 10.15330/pcss.24.1.197-201

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 24, № 1 (2023) С. 197-201

Фізико-математичні науки

PACS:42.40.Eq

ISSN 1729-4428

O. Paiuk[1], A. Meshalkin[2], A. Stronski[1], E. Achimova[2], C. Losmanschii[2], V. Botnari[2], A. Korchovyi[1], M. Popovych[1]

Direct magnetic and surface relief patterning using carbazole-based azopolymer

[1]V.E. Lashkaryov Institute of Semiconductors Physics, NAS in Ukraine, Kyiv, Ukraine, paiuk@ua.fm
[2]Institute of Applied Physics, Chisinau, Moldova

The results on using of carbazole-based azopolymer layers (Polyepoxypropylcarbazole: Methyl Red with magnetic particles of Fe_2SO_4) for the recording of 1-D and 2-D surface relief gratings are presented in this report. Morphology study using AFM and MFM of obtained structures has shown their good quality. Surface relief gratings with profile height up to 1.2 μm were obtained during the holographic recording using blue laser. Along with surface relief grating it was shown the direct formation of magnetic relief. Possibility of simultaneous direct fabrication of surface and magnetic relief by optical holographic recording using azopolymer thin films as recording media was shown.

Keywords: azopolymer, polyepoxypropylcarbazole, methyl red, thin films, recording media, holographic gratings, direct recording, surface and magnetic relief.

Received 16 November 2023; Accepted 22 March 2023.

Introduction

Recently, research and the development for new recording media on the base of non- crystalline photosensitive materials have been actively carried out [1-3]. Of particular interest are carbazole-containing copolymers, which could be used for photoinduced formation of surface reliefs [4-6]. Versatile optical elements (refractive elements [7], optical storage elements [8-10]) can be fabricated using such media. Carbazole-containing polymers can be used for both optical and electron-beam recording, which may be of interest for the implementation of combined recording [11]. To increase the light sensitivity of recording materials, their optical sensitization is of great importance [12-14]. Various dyes and additives can be used as spectral sensitizers.

Photostimulated changes in optical and physical properties are the basis for recording and optical information storage [1,3,8]. Substantial materials motions (induced by photoisomerization reactions of azobenzene molecules) can be obtained under light exposure of azopolymers. Carbazole-based azopolymers under the influence of laser irradiation exhibit changes in thickness, transmission, provide ability to form surface relief's, high resolution and possibility of optical elements fabrication such as photonic crystals, broad-band antireflection coatings, diffraction gratings, nanostructured polarizers, microlens arrays, holograms, plates, etc. [3]. Carbazole-containing azopolymers are good light-sensitive materials due to high refractive index modulation, high resolution, low absorption for visible and infrared light, high signal-to-noise ratio and good stability of parameters in the environment. However, this recording material is primarily sensitive to the ultraviolet region of the spectrum. Therefore, the problem of expanding the spectral photosensitivity into the visible region of the spectrum to adjust it to the wavelength of recording is topical. To expand the spectral sensitivity, it is necessary to use the optical sensitization of the polymeric recording layer by introducing a dye that has absorption in the desired region of the spectrum.

Exposure by interference intensity pattern is usually used to fabricate diffraction gratings [15-17]. Selective etching usually is used for the surface relief formation

[1,3,15]. Direct fabrication (without a step of selective etching) of gratings by interference pattern exposure was shown in [18-20].

The results on using of carbazole-based azopolymer layers for the direct recording of surface relief gratings are presented in this report.

I. Experiment

Polyepoxypropylcarbazole:Methyl Red (PEPC:MR) with magnetic particles of Fe_2SO_4 was synthesized. As a photosensitizer, the azopolymer contained azodye Methyl Red.

PEPC thin films were fabricated using spin coating. Experiments were carried out at room temperature. Two-beam spectrophotometer SPECORD M40 in the range of wavelengths of 450–900 nm was used for the recording of PEPC:MR films transmission spectra which showed good transparency in the VIS region (Fig.1, curve 1).

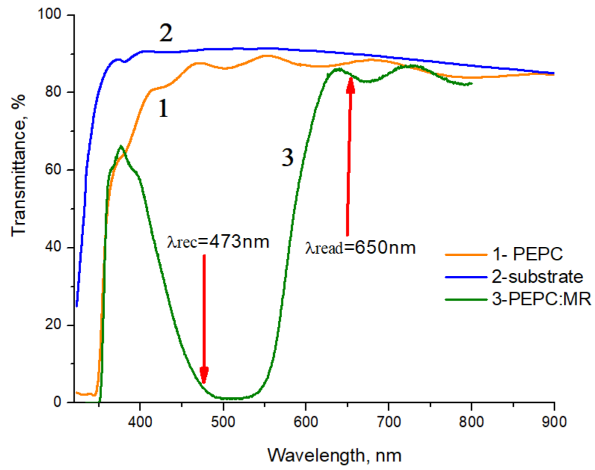


Fig.1. Transmission spectra of PEPC:MR films. 1- PEPC, 2 – substrate transmission, 3 – transmission of PEPC:MR.

By arrows are indicated the wavelength positions used for the gratings recording and diffraction efficiencies measurement. Addition of methyl red provided necessary increase of absorption (curve 3 Fig.1) and sensitivity on the recording wavelength (473 nm), with high transmittance on the reading wavelength (650 nm).

Films thickness was measured using atomic-force microscopy and interference microscope MII-4. Optic Meter program was used for processing of the obtained photographed interference patterns. Thicknesses of films were within 1-3 μm. Atomic Force Microscope (AFM) was used for study of surface relief and morphology of the recorded gratings. Magnetic Force Microscope (MFM) was used for study of magnetic relief of obtained structures.

Holographic gratings (1-D and 2-D) were recorded by standard two laser beams setup with the use of (Fig. 2) linearly p-polarized beams of DPSS laser (I= 1700 mW/cm^2 and λ=473 nm). Intensity ratio of beams consisted 1:1, spatial frequency - 170 lines/mm (period ~ 6.0 μm). Dependence on recording light polarization of the grating relief formation processes was shown in previous works [2, 6]. In present work p-p- configuration of polarized light was used. Simultaneously with grating formation in-situ diffraction efficiency η measurements were carried out in order to obtain η dependence on time of recording.

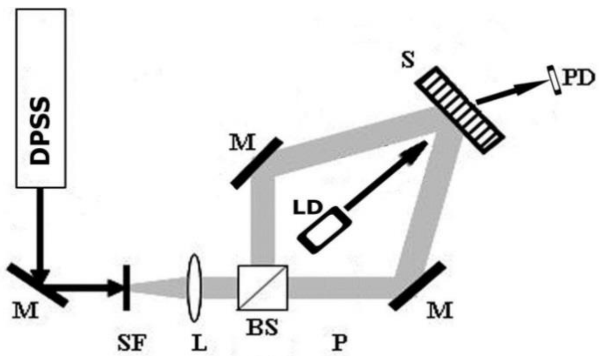
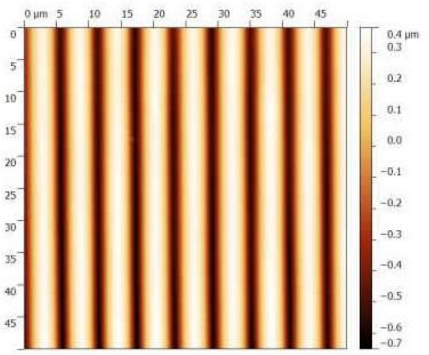


Fig.2.Experimental setup for gratings recording: LD, DPSS and PD are light emitting diode, laser, and registering unit, respectively, BS- beamsplitter, M – flat mirrors, SF and L - collimator, S – sample (registering media).

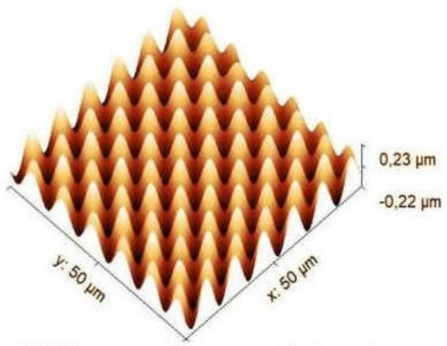
Dependence of the grating formation on exposure time was measured by detecting the intensity of first-order diffraction beam (in transmission) using normally incident light of laser diode (650 nm). Intensities ratio of the first order diffracted beam and the transmitted out of the grating beam was taken as diffraction efficiency value η.

II. Results and Discussion

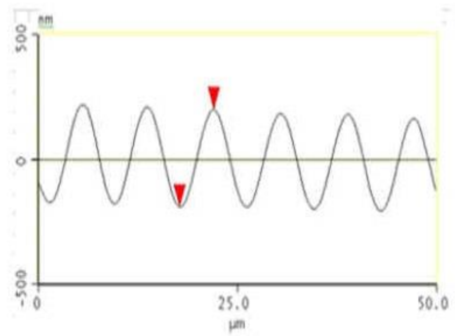
AFM image of the directly recorded holographic diffraction grating (without selective etching) with the use of PEPC:MR films is shown in Fig.3. Relief heights of the recorded gratings were within 0.3-1.2 μm, that gives relief modulation depth h/d ~ 0.05 – 0.2 (h – relief height, d – grating period – 6 μm). Images of gratings in Fig.3-5 show that holographic surface relief gratings with relatively large thickness modulation could be obtained by direct one-step holographic recording without any subsequent processing steps using PEPC layers as recording media. It is also necessary to note that p-p polarization configuration allows to achieve surface relief grating with the largest amplitude up to 50% of original film thickness. In photosensitive azopolymer materials vectorial mass transport during formation of photoinduced surface pattern is known to depend on the excitation wavelength, distribution of intensities and light polarization [1, 6]. Very interesting results were obtained in MFM microscopy studies of the obtained gratings. Amorphous chalcogenides and various photosensitive polymers being non-crystalline materials can be easily doped [16, 19, 21, 22]. Introduced admixtures change physical and chemical (magnetic, optical luminescent, etc.) properties of substances [21]. Such changes enabled to provide direct simultaneous recording of surface and magnetic relief with the use of such substances [23]. Fig. 4 – 5 show that similar result can be obtained with the use of PEPC:MR films with Fe_2SO_4 particles. MFM and AFM images (Fig.4 and 5) show correlation between grating surface relief and distribution and value of magnetic field.



a – 2-D AFM figure of the recorded grating (d~ 6.0 μm)



b – 3-D AFM image of the recorded grating



c – grating profile

Fig.3. AMF image of fabricated grating (d~ 6 μm) obtained with the use of PEPC:MR films: a – 2-D image, b– 3-D image, c – grating profile.

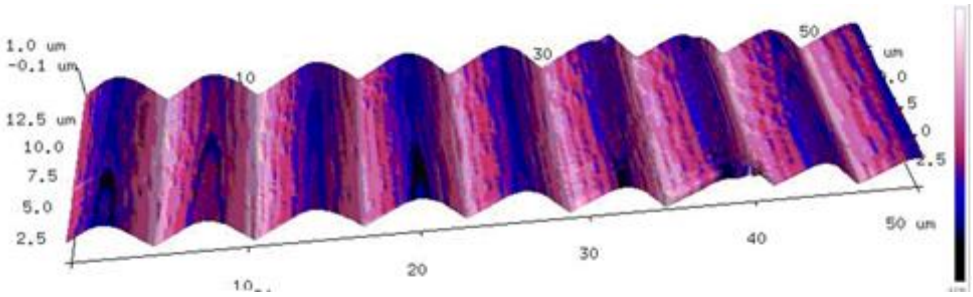


Fig. 4.AFM image of gratings surface relief and MFM image map (overlapped, colour image, right scale bar) of grating fabricated using PEPC:MR films with Fe_2SO_4 particles [24].

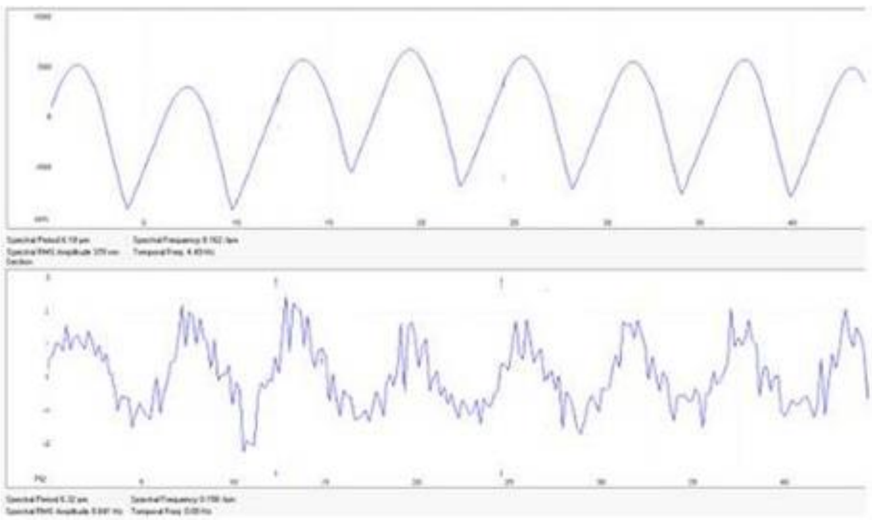


Fig.5. AFM and MFM profiles of grating (shown in Fig.4) directly recorded with the use of PEPC:MR films with Fe_2SO_4 particles.

Nanoparticles redistribution in photopolymer nanoparticle-dispersed matrix as a result of light exposure observed in [25, 26] may also be mechanism of the magnetic relief formation in layers of PEPC:MR with Fe_2SO_4 particles. Direct magnetic relief recording simultaneously with the recording of surface relief by interference pattern using PEPC:MR with Fe_2SO_4 particles as recording media provide possibility for magnetic memory applications and fabrication of optical elements with combination of unique properties.

Conclusions

Holographic grating recording by a direct, one-step process (recording wavelength 473 nm) using polyepoxypropylcarbazole (PEPC): methyl red layers with magnetic particles Fe_2SO_4 was shown in this work. Diffraction efficiency values in transmission of the fabricated gratings were ~ 34%. Simultaneous surface and magnetic relief recording using as recording media polyepoxypropylcarbazole (PEPC) layers: methyl red with Fe_2SO_4 magnetic particles was shown. Obtained results have shown that PEPC films can be used for the fabrication of high quality optical elements with unique properties using changes of films properties after doping and laser irradiation (changes in absorption, transmission, reflection, in thickness, in magnetic and other physical properties) and for information recording.

Acknowledgements:

Authors appreciate partial financial support from ANCD projects 20.80009.5007.03 & 21.80013.5007.1M and bilateral Moldova-Ukraine project 17.80013.5007.03/UA.

Paiuk Oleksandr – Candidate of Physical and Mathematical Sciences;
Meshalkin Alexexei – Senior Scientific Researcher;
Stronski Alexander – Senior Scientific Researcher, Doctor of Physical and Mathematical Sciences;
Achimova Elena – Associate Professor, Doctor of Physical and Mathematical Sciences;
Losmanschii Constantin – PhD student;
Botnari Vladislav – Engineer;
Korchovyi Andriy – Candidate of Physical and Mathematical Sciences;
Popovych Mykhailo – PhD student.

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О. Паюк[1], А. Мєшалкін[2], О. Стронський[1], Є. Акімова[2], К. Лошманський[2], В. Ботнарі[1], А. Корчовий[1], М. Попович[1]

Пряме формування магнітного та поверхневого рельєфу на основі карбазолвмісногоазополімеру

[1]*Інститут фізики напівпровідників ім. В.Є. Лашкарьова, НАН України, Київ, Україна,* paiuk@ua.fm
[2]*Інститут прикладної фізики, Кишинів, Молдова*

У роботі представлено результати дослідження шарів карбазолвміснихазополімерів (поліепоксипропілкарбазол: метиловий червоний з магнітною домішкою Fe_2SO_4) для створення 1-D та 2-D поверхнево рельєфних решіток. Проілюстровано гарну якість отриманих структур на основі результатів досліджень морфології поверхні з використанням АСМ та МСМ. За допомогою синього лазера в процесі голографічного запису отримано поверхнево рельєфні решітки з висотою профілю рельєфу до 1,2 μm. Разом з утворенням поверхнево рельєфної гратки показано пряме формування магнітного рельєфу решітки. Продемонстровано можливість одночасного прямого формування поверхневого та магнітного рельєфу при оптичному записі решіток на тонких плівках азополімеру.

Ключові слова: азополімер, поліепоксипропілкарбазол, метиловий червоний, тонкі плівки, голографічні решітки, прямий запис, поверхневий і магнітний рельєф.