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**DYNAMIC HOLOGRAMS IN AMORPHOUS SEMICONDUCTORS AND  
AZOBENZENE OLIGOMERS**

Summary of Promotion Thesis

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**CONFIRMATION**

I confirm that this promotion thesis, submitted to Riga Technical University in fulfillment of the requirement for the degree of Doctor of Physics, is my own work. The promotion thesis has not been submitted for a scientific degree to any other university.

Dmitrijs Saharovs.....

Date: .....

The promotion thesis was written in Latvian and consists of an introduction, 12 chapters, conclusions and bibliography, containing 71 figures and 12 tables, 154 pages in total. The first six chapters are a review of the literature. The bibliography includes 173 sources.

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## GENERAL DESCRIPTION OF THESIS

### Introduction

This research is focused on two perspective material classes for optical recording - amorphous chalcogenide semiconductors and azobenzene compounds.

Hologram recording using sub-band gap radiation ( $h\nu > E_g$ ) is interesting from a theoretical and practical point of view. In this case, the spectrum part with low absorption is used, so the hologram is recorded also in the depth of the sample, not only on the surface.

Organic materials are being actively researched as recording materials because they allow for a wider change of their properties comparing with inorganic ones. Azobenzene compounds are among the most efficient holographic recording materials.

Azobenzene compounds have an interesting practically useful property - photoisomerization. *Trans*- and *cis*- molecules of isomers have different absorption spectra and size (which causes change of the electric dipole molecule moment). The recording mechanism of red light in these materials (where absorption is low) is not clear yet, which caused the motivation to study this area.

Theoretical interest is stimulated by unclear microscopic surface relief grating formation processes depending on the structure of a material and on the recording radiation parameters. Different mechanisms have been proposed which allow to explain achieved results, but surface relief grating formation process is still not fully clear yet. Practical interest is caused by possibility of direct (without etching or development) recording of effective surface gratings in azopolymers enabling production of surface relief holographic optical elements such as gratings with a period smaller than wavelength, waveplates, antireflection surfaces, switching units for optical wave guides and so on [18, 52].

### Aim of the research

The aim of this work was the experimental research of elementary dynamic holograms - holographic grating recording in a-As<sub>2</sub>S<sub>3</sub> amorphous chalcogenide films and in azobenzene compound films, which belong to two different classes of materials – to inorganic and organic materials in the red region of spectrum – as well as to clarify their recording characteristics and recording processes, to perform the comparison of the studied materials, as well as to evaluate application possibility.

### Tasks of the research

1. Research the holographic recording process in a-As<sub>2</sub>S<sub>3</sub> films with focused and unfocused He-Ne laser 632.8 nm light.

2. Research the holographic recording process in the films of different azobenzene compounds with focused and unfocused He-Ne laser 632.8 nm light.
3. Experimentally identify possibilities of realization of one of the more complicated holographic recording methods – focused four-wave mixing in a-As<sub>2</sub>S<sub>3</sub> and azobenzene compound films, comparison of these possibilities.
4. Experimental study of the dependence of recording efficiency on chromophore concentration and on chromophore connection to the matrix in the azobenzene compounds.
5. Study of the possibility of the relief hologram recording in both material classes with red light.
6. Comparison of the studied materials in the context of experimental data and literature.

## Techniques of the research

The following techniques were used in the current research.

1. Recording of elementary holograms with parallelogram scheme, using focused beams and changing the period.
2. Recording in the four-wave mixing geometry.
3. Surface relief study by atomic-force microscope before and after the recording process.
4. Measurements of the absorption spectra.
5. Measurements of optical parameters of the films (transmission and reflection coefficients), researching changes of these.
6. Analysis of relevant literature.
7. Theoretical calculations.

## Scientific novelty

1. It is experimentally found that effective recording of holograms with focused sub-band gap ( $h\nu=1,96$  eV) red light in a-As<sub>2</sub>S<sub>3</sub> films is possible and properties of such recording differs from the band gap recording and from the sub-band gap unfocused recording. Sub-band gap recording mechanisms have been offered.
2. Holographic recording efficiency dependence on the chromophore bonding to the matrix and chromophore concentration is clarified in azobenene compounds.
3. It has been found experimentally that effective relief surface grating recording is possible with red light (632.8 nm) in stilbene azobenzene compounds, which indicates the possibility of *trans-cis* photoisomerization.
4. It is established that efficiency of holographic recording in stilbene azobenzene compounds is a nonmonotonic function of the sample's age.

## Statements to be defended

1. It has been found experimentally that dynamic hologram recording in a-As<sub>2</sub>S<sub>3</sub> films by sub-band gap light ( $h\nu < E_g$ ) differs by physical properties significantly from recording by band gap light ( $h\nu \geq E_g$ ).
2. Focused sub-band gap hologram recording in a-As<sub>2</sub>S<sub>3</sub> films is more effective (with higher diffraction efficiency and lower recording energy) than unfocused one. Recording mechanisms differ also.
3. Covalent bonding of chromophore groups to the matrix in the azobenzene oligomers generally is more effective than dispersing, but nevertheless azobenzene oligomer films with large enough dispersed chromophore groups concentration can have almost the same holographic recording efficiency as films with covalently bonded chromophores.
4. In compounds where dialkylaminazobenzene chromophore groups are dispersed in a polystyrene matrix, a threshold of chromophore groups concentration in the material exists (between 0.01 and 0.04 mol/l) below which holographic recording not observed.
5. Effective relief surface grating production is possible (with amplitude 113 nm) by red light ( $\lambda=632.8$  nm) in stilbene azobenzene compounds.

## Practical value of the research

The practical value of the research is defined by information obtained during research. It allows making the conclusion that focused recording in a-As<sub>2</sub>S<sub>3</sub> films can be used for producing stable three-dimensional holographic elements like gratings, diffractive lenses, wave guides and combined elements as well as long term information storage. Stilbene azobenzene compounds can be used for producing of surface relief diffractive optical elements by red light. The advantage of this method comparing with lithographical methods is the lack of necessity of etching. The achieved results allow more effective search of the new optical light-sensitive materials.

## Approbation

The content of the promotion thesis is reflected in the following publications:

1. Ozols A., Saharovs Dm., Reinfelds M. Holographic recording in amorphous As<sub>2</sub>S<sub>3</sub> films at 633 nm// Journal of Non-Crystalline Solids. – 2006. - Volume 352. – pp. 2652-2656.
2. Saharov Dm., Ozols A., Kampars V., Kokars V., Kreicberga J., Ratyeva S. Influence of chromophore group concentration on the holographic properties of spin-coated azobenzene oligomers// Latvian Journal of Physics and Technical Sciences. – 2006. – Volume 2. – pp. 59-65.

3. Saharov D., Ozols A., Kampars V., Kokars V., Kreicberga J., Ratyeva S. Effect of bonding type and concentration of chromophore groups on the holographic properties of azobenzene oligomers// Scientific Proceedings of Riga Technical University. Series: Material Science and Applied Chemistry. – Rīga: RTU, 2006. – Volume 12. – pp. 45-55.
4. Saharov D., Ozols A. Focused four-wave mixing in a-As<sub>2</sub>S<sub>3</sub> and azobenzene oligomer films. Scientific Proceedings of Riga Technical University. Series: Material Science and Applied Chemistry. – Rīga: RTU, 2006. – Volume 13. – pp. 34-41.
5. Ozols A., Saharov Dm., Kampars V., Kokars V., Kreicberga J. Ratyeva S. Holographic properties of azobenzene oligomers with differently bonded chromophore groups// Physica Status Solidi (c). – 2007. – Volume 4. – pp. 1360-1363.
6. Ozols A., Saharov D. Sub-bandgap light hologram recording in amorphous chalcogenides// Proceedings of SPIE. – 2007. – Volume 6596. – pp. 65961C-65966C.
7. Saharov D., Ozols A., Kokars V., Kampars V., Mezinskis G., Maleckis A., Pludons A. Jansone M. Relaxation effect of stilbene azobenzene derivatives on their holographic properties// Journal of Physics: Conference Series. – Rīga: RTU, 2007. – Volume 93. – p. 012029.
8. Kokars V., Maleckis A., Saharov D., Ozols A., Kampars V. Synthesis and holographic efficiency of the derivatives of 3-[4-[bis-(2-hydroxyethyl) amino]phenyl]-2-{4-(4-nitrophenylazo)phenyl]acrylonitrile// Organic Chemistry. Proceedings of Scientific Conference, dedicated to the 85th anniversary of the Department of Organic Chemistry Kaunas University of Technology. – Kaunas: Technologija, 2007. – pp. 30-32.
9. Saharov D., Ozols A., Kokars V., Kampars V., Mezhinskis G., Maleckis A., Pludons A., Rutkis M. The *trans-cis* photoisomerization possibility of stilbene azocompounds by red light of He-Ne laser// Scientific Proceedings of Riga Technical University. Series: Material Science and Applied Chemistry. – Rīga: RTU, 2008. – Volume 18. – pp. 26-34.
10. Ozols A., Reinfelds M., Saharov Dm., Kundzins K., Kampars V., Kokars V. Holographic recording of surface relief gratings in tolyle-based azobenzene oligomers// Thin Solid Films. – 2008. – Volume 516. – pp. 8887-8892.
11. Saharov D., Ozols A. DFWM of focused laser beams in a-As<sub>2</sub>S<sub>3</sub> and azobenzene oligomer films// Journal of Material Science: Materials in Electronics. – 2009. – Volume 20. – pp. S395-S399.
12. Ozols A., Saharov D., Kokars V., Kampars V., Maleckis A., Mezinskis G., Pludons A. Holographic recording of surface relief gratings in stilbene azobenzene derivatives at 633 nm// Journal of Physics: Conference Series. – 2010. – Volume 249. – p. 012055.



The results of the thesis were declared at the following scientific conferences:

1. 21. zinātniskā konference, veltīta Starptautiskajam Fizikas gadam, 2005. gada 7.-9. februārī, Rīga, Latvija. (Saharovs D., Ozols A., Reinfelds M. Hologrāfiskais ieraksts amorfās  $\text{As}_2\text{S}_3$  kārtiņās ar He-Ne lāzeru// Referātu tēzes, 51. lpp.)
2. International Student Conference „Developments in Optics and Photonics“, April 30 – May 1, 2005, Riga, Latvia. (Saharovs D., Ozols A., Kampars V., Kokars V., Kreicberga J., Ratyeva S., Ozols A., Reinfelds M. Holographic recording in azobenzene oligomers// Abstracts, p. 30.)
3. 1<sup>st</sup> Conference on Advances in Optical Materials, October 12 – 15, 2005, Tucson, Arizona, USA. (Ozols A., Saharovs D., Reinfelds M. Holographic recording in amorphous  $\text{As}_2\text{S}_3$  films at 633 nm// Abstracts, p.47.)
4. 2<sup>nd</sup> Latvian Conference „Functional Materials and Nanotechnologies“, March 27 – 28, 2006, Riga, Latvia. (Saharov D., Ozols A., Kampars V., Kokars V., Kreicberga J., Ratyeva S. Effect of chromophore group concentration on the holographic properties of spin-coated azobenzene oligomers// Abstracts, PO – 30, p. 64.)
5. 10<sup>th</sup> Europhysical Conference on Defects in Insulating Materials, July 10 – 14, 2006, Milano, Italy. (Ozols A., Saharov D., Kampars V., Kokars V., Kreicberga J., Ratyeva S. Holographic properties of azobenzene oligomers with differently bonded chromophore groups// Abstracts, p. 317.)
6. 10<sup>th</sup> European Conference on Organised Films, August 20 – 24, 2006, Riga, Latvia. (Ozols A., Reinfelds M., Saharov D., Kundzins K., Kampars V., Kokars V. Holographic recording of surface relief gratings in tolyle-based azobenzene oligomers// Abstracts, p. 72.)
7. 5<sup>th</sup> International Conference „Advanced Optical Materials and Devices“, August 27 – 30, 2006, Vilnius, Lithuania (Ozols A., Saharov D. Sub-bandgap light holographic recording in amorphous chalcogenides. Abstracts, p.101.)
8. Latvijas Universitātes Cietvielu fizikas institūta 23. zinātniskā konference, veltīta LU profesora Ilmāra Vītola 75 gadu atcerei, 2007. gada 13. – 15. februāris, Rīga, Latvija. (Saharovs D., Ozols A., Kokars V., Kampars V., Maļeckis A., Jansone M. Stilbēna azobenzola atvasinājumu hologrāfiskā efektivitāte// Referātu tēzes, 43. lpp.)
9. International Baltic Sea Region Conference „Functional Materials and Nanotechnologies 2007“, April 1 – 4, 2007, Riga, Latvia. (Saharov D., Ozols A., Kokars V., Kampars V., Mezinskis G., Maļeckis A., Pludons A., Jansone M. Relaxation effect of stilbene azobenzene derivatives on their holographic properties// Abstracts, p. 48.)
10. International Conference on Optical and Photonic Materials and Applications, July 30 – August 3, 2007, London, UK. (Saharov D., Ozols A. DFWM of focused laser beams in a- $\text{As}_2\text{S}_3$  and azobenzene oligomer films// Abstracts, p. PO49.)

11. International Baltic Sea Region Conference „Functional Materials and Nanotechnologies 2008“, April 1 - 4, 2008, Riga, Latvia (Ozols A., Saharov D., Kokars V., Kampars V., Mezinskis G., Maleckis A., Pludons A., Rutkis M. Spectroscopic studies of the red light surface relief grating recording in stilbene azobenzene derivatives// Abstracts, p.71.)
12. 16<sup>th</sup> International Conference on Defects in Insulating Materials ICDIM-2008, August 24 – 29, 2008, Aracaju, SE, Brazil. (Ozols A., Saharov D., Kokars V., Kampars V., Maleckis A., Mezinskis G., Pludons A. Holographic recording of surface relief gratings in stilbene azobenzene derivatives at 633 nm// Abstracts, p. A021.)

## SYNOPSIS OF THESIS

**In the first chapter holographic foundations, principles of hologram creation are described, elementary hologram classification is proposed. The main parameters of holographic materials and gratings are described. Theoretical foundations of thin, thick and surface relief grating production are given.**

Two coherent and interfering beams are used for the holographic grating production. Single-mode laser beams are used usually. These are closer to ideal plane wave and interference of these beams in general cause periodic modulation of light intensity and polarization, which change the optical properties of light-sensitive material accordingly, when this material is located in the area of interference. Spatial modulation of material's optical parameters is photoinduced production of diffractive grating.

The goal of classification is representing the main properties of different types of holograms. Holograms that differ by one parameter may have completely different properties. A generally accepted, single classification of holograms does not exist today, so at this research an attempt is made to divide elementary holograms into types and to give them definitions. Elementary hologram is defined as hologram which is made by interference of two plane of spherical waves. It needs to be noticed that this classification is conditional and hologram types may be mixed. Elementary hologram classification is given in the table 1. The importance of holographic material and grating parameters is conditional and depends on application. The main parameter of holographic grating is diffraction efficiency:

$$\eta_m = \frac{P_m}{P}, \quad (1)$$

where  $\eta$  is diffraction efficiency,  $m$  is diffraction order and  $m = 0, \pm 1, \pm 2, \dots$ ,  $P_m$  – power of light diffracted in  $m$ -th order,  $P$  – readout beam power. Usually, diffraction efficiency is expressed in percents and is defined in the first order. Important parameters are grating period, spatial frequency and resolution. As light-sensitivity criteria in the photography the parameters of darkening curve are used. The darkening curve is optical density function of exposure. Such criteria are useful for amplitude media only. Holographic light-sensitivity criteria are universal. Diffraction efficiency dependence on exposition may be complicated, so many holographic light-sensitivity parameters are used and the main of them is specific recording energy [56]. Specific recording energy corresponding to maximal diffraction efficiency is used often (see formula (7)).

Diffraction of the readout beam occurs in the hologram also. It is defined not only by media thickness and hologram features, but also by other parameters. If it is possible to describe the propagation of light in hologram by the laws of geometrical optics, this is called Raman-Nath diffraction. If different diffractions orders interact in hologram, this is called Bragg diffraction.

Table 1

## Classification of elementary holograms

	Criteria	Feature	Type name
1	Type of the recorded interference pattern in the material	Interference of spherical waves with various radii, interference pattern is Fresnel-zone plate	Fresnel
		Interference of spherical waves with identical radii or two plane waves. Interference pattern is sinusoidal grating of straight lines	Fourier
2	Readout beam parameters that are modulated in the hologram	Amplitude	Amplitude
		Phase	Phase
3	Disposition of the recording beams relative to recording media	Sample and reference beams directed from one side	Transmission
		Sample and reference beams directed from opposite sides	Reflection
4	Diffraction type in the hologram	Raman-Nath diffraction	Thin
		Bragg diffraction	Thick
5	Changes of registered parameters during the readout process	No change	Stationary
		Change	Dynamic
6	Usage of polarization modulation of the recording beams	Not used, parallel polarizations of the recording beams	Scalar
		Used, orthogonal polarizations of the recording beams	Vectorial (Polarization)

Parameters that allow distinguishing thin and thick holograms also are important. Klein's parameter is used often [14]

$$Q = \frac{2\pi\lambda d}{n_0 \Lambda^2}, \quad (2)$$

where  $d$  is absolute thickness of hologram in units of length,  $\lambda$  is readout beam wavelength,  $n_0$  is average refraction index of recording material,  $\Lambda$  is grating

period.  $Q < 1$  corresponds to the thin gratings and Raman-Nath diffraction,  $Q > 10$  corresponds to the thick gratings and Bragg diffraction.

**In the second chapter degenerate four-wave mixing and phase conjugation is described, theoretical explanations with gratings and nonlinear polarization are given, major applications are examined.**

Four-wave mixing generally means the interaction of four light waves with different frequencies and propagation directions in nonlinear media [5]. If frequencies of the incident light waves are equal, this is degenerate four-wave mixing. This method may be used for phase conjugation which allows compensate optical signal distortions or produce conjugate mirror. Four-wave mixing also can be used for optical signal amplification.

**In the third chapter the laser beam focusing process is described, quantitative relations are given. The influence of aberrations and focusing limit of optical system are considered.**

Every optical system has finite focusing limit which is defined by diffraction. It names diffraction limit. Diffraction limit defines the minimal cross-section area of the beam and maximal intensity. The beam with minimal dimensions can be obtained focusing a beam where distribution of intensity in cross-section follows the Gauss law. In such beam the intensity distribution in cross-section does not change with distance from the focal waist in laser resonator, also in the Gauss beams the phase of wave is the same in all cross-section points.

Lens aberrations greatly worsen the properties of focusing systems. For monochromatic collimated laser beam which propagates along the axis of a lens' spherical aberration brings larger distortion. The spherical aberration conduces to the following effect: the beams from a point source fall down to the lens in different distances from the axis and do not converge at the focus. As the result the image of point looks like circle with blurred borders.

**In the fourth chapter the structure and optical properties of amorphous chalcogenide semiconductors as well as photoinduced processes in these are observed. Holographic recording mechanisms in amorphous semiconductor films are also described.**

Amorphous state is solid state of substance when isotropy of the mechanical, thermal, electrical and other properties is observed and the substance has no defined melting point. These characteristics result from the absence of long-range order in the amorphous state. Amorphous substances have short-range order, which exists in a scale of molecules dimensions (the first coordination sphere) [60].

Generally, amorphous chalcogenide semiconductors  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  with halogens, tellurium, selenium or silver dopants are used for hologram recording.

Chalcogenide semiconductors have electronic conductance, its magnitude is  $10^{-13} - 10^{-16} \Omega^{-1}\text{m}^{-1}$ . These glasses may consist of two or more components. Amorphous semiconductors have wider optical transmission range (approximately from 1 up to 25  $\mu\text{m}$ ) than crystalline ones. Its transparency maximum is located in the infrared range [57].

For holographic recording in amorphous semiconductors phase transitions are used. The properties of different phases differ dramatically, so it can be used for information recording with high signal/noise ratio.

Six principles of optical recording are used [63]:

1. Crystallization of amorphous substance
2. Thermoamorphization of crystal
3. Photochemical transformation in the “chalcogenide – metal” system.
4. Recording “amorphous phase 1 – amorphous phase 2”
5. Evaporation of amorphous substance
6. Photoelectrochemical etching of the films

The first four principles are reversible. Using these repeated recording and erasing are possible. For holographic recording mainly various photophysical processes in amorphous state are used (without transition to the crystalline state).

There are known various mechanisms of photosensitivity which can be used for holographic recording. These are photoinduced structural changes, relaxational structural changes, recharging of localized states, photoinduced anisotropy [25, 27].

The main recording mechanism for stable holographic recording in the amorphous chalcogenide semiconductor films is photoinduced structural changes. It is known that this is metastable atom shifting because of chemical bonds breaking [40, 27]. That shifting is possible because atomic lattice is not solid and fixed like in crystals and have little coordination number  $Z$ . The condition of lattice elasticity is  $Z < 2.40 \pm 0.06$  [17]. For  $\text{a-As}_2\text{S}_3$  film there is  $Z = 2.4$  [50].

The sub-band gap light is radiation where photon energy corresponds to this formula:

$$h\nu < E_g, \quad (3)$$

where  $h$  is Plank's constant,  $\nu$  is frequency of radiation and  $E_g$  is band gap.

The recording with sub-band gap light can be explained by three mechanisms: photoinduced relaxation structural changes, photoinduced recharging of D-centers and photoinduced orientation of D-centers [31]. D-centers conception was introduced by Mott and Davis [19]. In the  $\text{As}_2\text{S}_3$  films  $\text{D}^0$  centers are  $\text{S}_1^0$  or  $\text{S}_3^0$  atoms,  $\text{D}^+$  centers are  $\text{S}_3^+$  atoms and  $\text{D}^-$  centers are  $\text{S}_1^-$  atoms, where lower indices mean coordination numbers and higher mean charges. The defects of sulphur atoms are activated mainly by sub-band gap light, which breaks Van Der Waals chemical bonds.

**The fifth chapter is devoted to azobenzene compounds. Properties of the organic compounds, structures of organic polymers and oligomers are described in brief. Also described are photoinduced processes in the organic materials, electron donor and electron acceptor groups' significance in the azocompounds. The trans-cis isomerization in azobenzene compounds is reviewed.**

The variety of organic compounds is connected with carbon's specific abilities, comparing with other chemical elements. The carbon is able to make bonds with majority of various elements. This feature is connected with carbon's almost electroneutral character and ability to make covalent bonds. Carbon atoms also can connect each other, forming various carbon chains. Some elements also can form chains, but not as long. [20, 51].

Polymers are natural and synthetic compounds, its molecules consist of large amount of repetitive atom groups ( $10^2 - 10^3$ ), which are connected and make long straight or branching chains [59].

Between monomers and polymers are oligomers [59]. The oligomers have properties typical for both monomers and polymers. The amount of atom groups is not large: from several to several hundreds.

The photoinduced processes in organic materials are more various than in inorganic and these are connected with the following processes:

- a) phototransfer of electron
- b) phototransfer of proton
- c) *trans-cis* photoisomerization
- d) redistribution of  $\pi$ - and  $\sigma$ - bonds
- e) rearrangement of molecular fragments
- f) bond breaking
- g) dimerization and polymerization reactions [40, 62].

Azocompounds are organic compounds containing a group of two nitrogen atoms which are connected by a double bond and each of these is connected with other parts of the molecule with the C-N bond [61]. For example, azomethane  $\text{CH}_3 - \text{N} = \text{N} - \text{CH}_3$  or aromatic azocompound azobenzene  $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$ .

Bonds conjugation is one of the most important intramolecular interaction types of atoms and bonds. It is based on atomic electron orbital overlapping. The main sign of conjugation is common distribution of  $\pi$ -electrons density in the conjugated molecular system. In the molecules with conjugated double bonds  $\pi$ -electrons form the united electron cloud, which belongs to whole electron chain. As a result the mobility of  $\pi$ -electrons (delocalization degree) grows and excitation energy of the molecule decreases [58].

Substituent addition to the conjugation chain (for example, to azobenzene rings) causes spectroscopic changes. Pull-push system is characterized by electron acceptor substituent from one side and electron donor substituent from the other side. Such configuration makes  $\pi$ -bond polar, constant electric dipole moment is

generated, which brings additional part in the dipole moment of the whole molecule. Major dipole moments respond to more expressed nonlinear properties [54].

The absorption spectra of azocompounds explain the theory of chromaticity of organic compounds. The main idea of this theory is that ability of organic substance to absorb light is determined by special electronic states, which are formed in the long enough conjugated chains of double bonds with connected electron donor and electron acceptor groups [58].

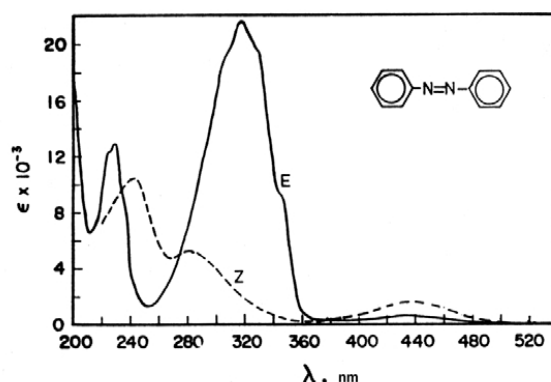


Fig. 1. Absorption spectra of E- (*trans*-) and Z- (*cis*-) isomers in  $C_2H_5-OH$  solution [41]

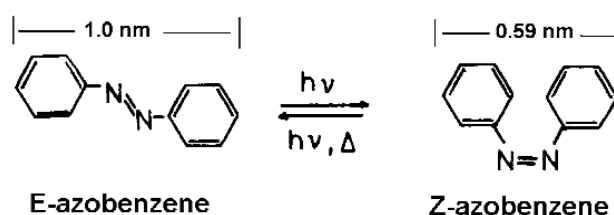


Fig. 2. E- (*trans*-) and Z- (*cis*-) isomers with dimensions  
The dipole moment increased from 0 to approx. 3 Debye [41, 54].

The important property of azobenzene is isomerization. Isomerization is the main photoreaction for the major part of azocompounds [41]. Azocompounds have two geometric isomers: *trans*- and *cis*- forms. By changing spatial form the absorption spectrum is changed (fig .1) and dimensions of the molecule (fig .2). Isomerization reaction can be excited by light and heat.

**In the sixth chapter surface the relief grating recording in azobenzene compounds and amorphous semiconductors, as well as the recording mechanisms of surface relief holograms, are described.**

The first surface relief gratings were recorded in polymers with high glass-transition temperature, but by relatively low intensities [12, 13 and 36]. Later researches [4, 49] showed that in such obstacles surface relief is generated mainly



by photoinduced mass transport with insignificant thermal effect. It is fully photonic process.

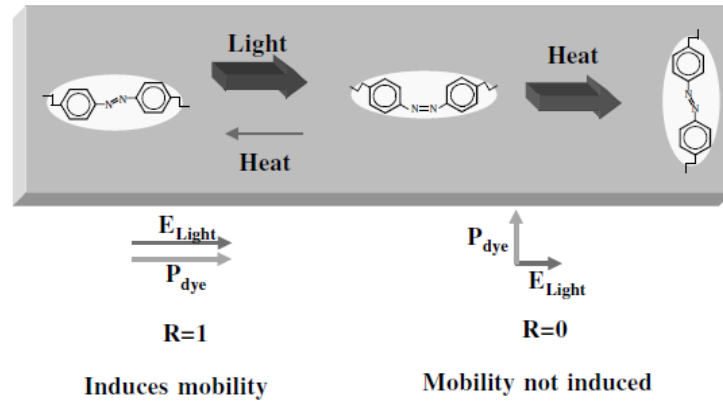


Fig. 3. Molecular reorientation is a consequence of the *trans-cis* isomerization cycles [41]

This process is based on the azobenzene chromophore isomerization possibility under influence of light. In the fig. 3 is shown that orientation of molecule follows the photoisomerisation and thermal relaxation from high-energy *cis*- form to low-energy *trans*- form.

The theoretical models interpret the forming of surface relief gratings:

1. Free volume model or isomerization pressure model [2, 3]. The directing force for mass transport is the gradient of pressure, which is caused by chromophore photoisomerization in the interference pattern. The active isomerization process causes high pressure in the bulk and the viscoelastic flow of material takes place from high-pressure areas to the areas with lower pressure.
2. Gradient electric force model [15]. In the base of this is the influence of optically induced electric field on the chromophore molecules [1]. Time averaged density of the gradient force is described by the expression [15, 41, 54]:

$$\vec{f}(r) = \langle [\vec{P} \cdot \nabla] \vec{E} \rangle, \quad (4)$$

where  $\vec{P}$  is polarization,  $\vec{E}$  is the electric field of light,  $\langle \rangle$  means time average. The polymer chains obey the directing force in the direction where the component of the electric field gradient exists only and this force does not exist when the polarization of molecule is perpendicular to the gradient.

3. Mean-field theory [34]. Light orientates chromophores align the electric field direction. The dipoles attraction forces appear, which attract chromophores placed parallel each to other. The mass transport is possible only if chromophore molecules have parallel relative position.
4. Model of viscous mass flow [9, 43] is quite successful but does not describe the microscopic nature of the directing force. For the explanation of the

mass transport the hydrodynamics theory is used. The dynamics of the surface relief grating are described analytically as a function of the film thickness and wave number of the interference pattern. Authors of this model believe that the analysis of the grating geometry can be helpful for clarification of causes of the mass transfer.

5. Asymmetric diffusion model [16] is based on assumption that the exited molecules containing chromophores are moved due to *trans-cis* photoisomerization from illuminated areas to dark ones. The movement of molecules describes the diffusion equation. Diffusion flow includes the probability multiplied by chromophore quantity, which cross the given area at one time unit. The flow is introduced into diffusion equation and its solution gives the chromophore density distribution and the modulation of surface.
6. Permittivity gradient model. Photoinduced changes of permittivity produce force, which is proportional to light intensity and gradient of permittivity. This force realizes mass transfer to the opposite direction of gradient.

$$\vec{\mathbf{f}} = -\frac{\varepsilon_0}{2} \vec{\mathbf{E}}^2 \nabla \varepsilon, \quad (5)$$

where  $\vec{\mathbf{E}}$  is electric field of light,  $\varepsilon$  is permittivity [54].

Beginning with 1971 when J. Feinleib and colleagues [6] discovered photoinduced crystallization in the amorphous semiconductors, density, solidity, chemical reactivity, dissolution speed, photoinduced changes of the electrical and optical properties were discovered too [33, 44, 45, 46]. It was shown that the big set of chemical and structural changes can be induced by the band gap radiation. The photoexiting of charge carriers and nonradiative relaxation lead to the breaking of chemical bonds, polymerization, relaxation of the mechanical tensions and corresponding structural changes [45, 46]. Photostructural changes in the chalcogenide glasses are clarified by fast photoexcited localization of the charge carriers, by low energy defect pairs with alternation of valences and by atoms with low coordination numbers, which change its positions and configuration of chemical bonds [7].

Also a different photochemical mechanism is known – surface photooxidation. It can be used for surface relief modulation in the chalcogenide amorphous semiconductors [10]. This mechanism is working by the band gap radiation. The surface photooxidation leads to the decrease of thickness of the film in the brighter illuminated areas.  $\text{As}_2\text{O}_3$  microcrystals remain in the less illuminated areas after the exposition. These crystals change absorption of the material [21].

Light radiation can change not only physical properties of the material, but also chemical ones, specifically dissolution speed by inorganic alkaline and organic solvents [8]. The dissolution speed is dependent on the state of amorphous semiconductor film, chemical composition of the film and the solvent [47].

Photoinduced volume changes can be used to produce surface relief gratings [39, 48] by holographic method and to produce microlenses [11].

**In the seventh chapter the sample preparation processes and the experimental technique are described.**

The samples of amorphous semiconductors have been prepared in the laboratory of optical recording in the institute of Solid State Physics of the University of Latvia by the thermal evaporation of raw material and vapor deposition on the glass header at the room temperature. Thin films with thicknesses from 3 to 10  $\mu\text{m}$  were produced by this way, controlling the thickness by the interferometric measurement during the deposition process.

The samples of azocompounds have been prepared in the Chemistry department in the faculty of Materials Science and Applied Chemistry of RTU. First of all solutions of azocompounds have been prepared. The solution of polymer or oligomer consists of the investigated material, the film forming polymer and the solvent. The solutions with different concentrations of a polymer are prepared. The films are prepared by spin-coating after the solution is ready. Polymer solution distributes evenly on the glass header and a film forms after the solvent evaporates.

During the experiments optical (transmission coefficient, spectral), holographic (in two and four wave interaction geometry), atomic force microscopic measurements were performed.

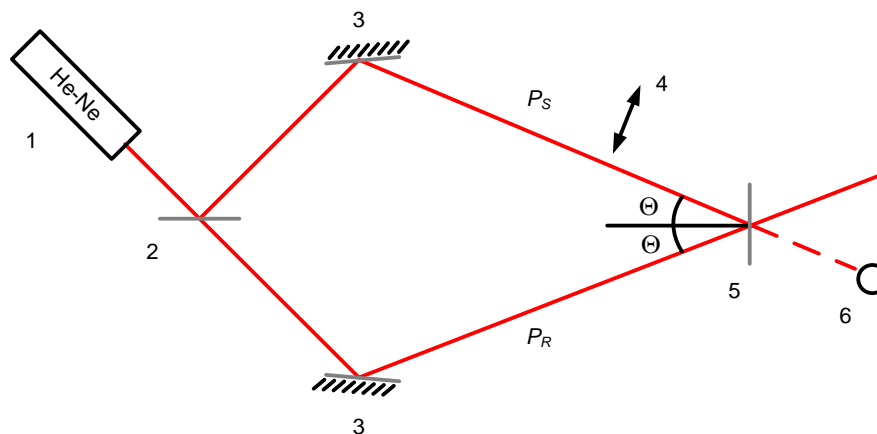


Fig. 4. Recording scheme by unfocused beams for the direct measurements of diffraction efficiency

*1 – laser; 2 – beam splitter; 3 – mirror; 4 – shutter; 5 – sample; 6 – sensor;*

*$P_S$  and  $P_R$  – laser beams;  $\Theta$  – angle of incidence, which determines the period of the holographic grating.*

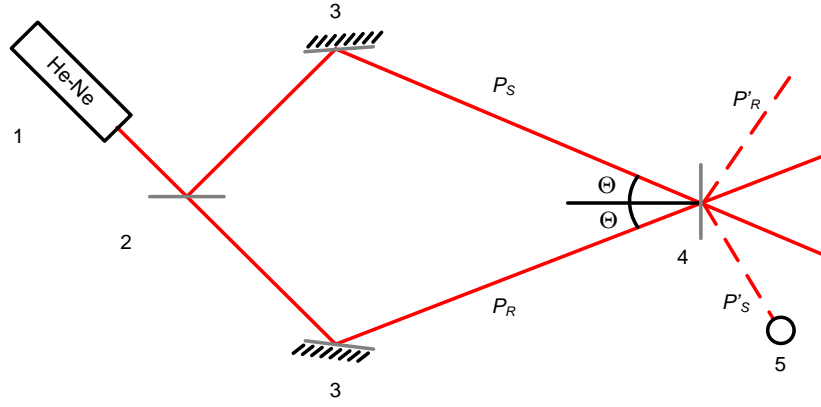


Fig. 5. Recording scheme by unfocused beams for the indirect measurements of diffraction efficiency using self-diffraction

*1 – laser; 2 – beam splitter; 3 – mirror; 4 – sample; 5 – sensor;  $P_S$  and  $P_R$  – laser beams;  $P'_R$  and  $P'_S$  – diffraction maximums;  $\Theta$  – angle of incidence, which determines the period of the holographic grating.*

Holographic recording schemes are shown at fig. 4 and fig 5. The period of a diffraction grating has been calculated using formula:

$$\Lambda = \frac{\lambda}{2 \sin \Theta}, \quad (6)$$

where  $\Lambda$  is period of the holographic grating,  $\lambda$  is wavelength of the recording laser,  $\Theta$  is angle of incidence.

According to the measurement results graphs have been plotted, which shows the dynamics of diffraction efficiency during the exposure time. For each attempt when diffraction efficiency was registered specific recording energy have been calculated:

$$W_{\max} = \frac{It}{\eta_{\max}}, \quad (7)$$

where  $W_{\max}$  is specific recording energy,  $I$  is light intensity,  $t$  is the exposure time for the first maximum of diffraction efficiency,  $\eta_{\max}$  is the first maximum of diffraction efficiency. The intensity has been calculated according to the formula:

$$I = \frac{4(P_1 + P_2)}{\pi (2r_0)^2}, \quad (8)$$

where  $I$  is average intensity of laser radiation,  $P_1$  and  $P_2$  – powers of the recording laser beams,  $2r_0$  – the diameter of laser beam.

In the case of fast diffraction efficiency changes during the exposure time (interrupting one of the recording beams and reading out the meterage influence on the recording process was observed) the scheme shown at the fig. 5 have been used, where the self-diffraction efficiency were measured directly.

Self-diffraction efficiency (*SDE*) is defined as:

$$SDE = \frac{P_d(k = -2, l = -1)}{P_s}, \quad (9)$$

where  $P_d(k = -2, l = -1)$  is the power of self-diffracted beam (see fig. 6). It is defined by the sum of two complex amplitudes: complex amplitude of the minus first diffraction order of  $P_S$  beam and complex amplitude of the minus second diffraction order of  $P_R$  beam.  $P_S$  is readout beam. If  $P_R=0$ , then self-diffraction efficiency is equal to the diffraction efficiency. Self-diffraction efficiency is used to estimate the diffraction efficiency.

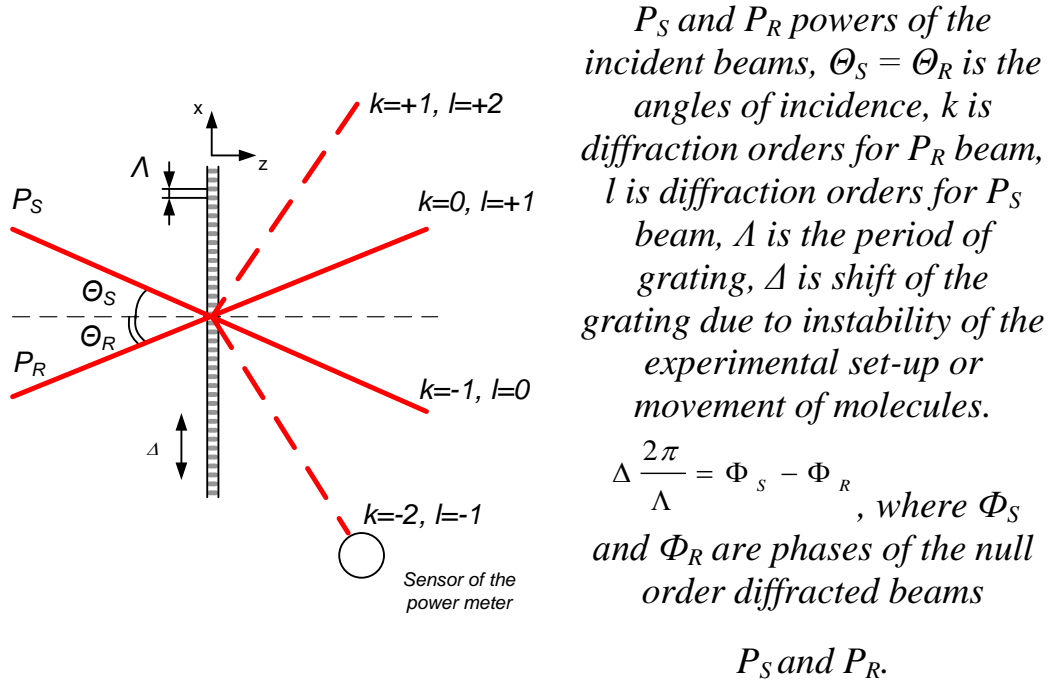


Fig. 6. Detailed recording and read-out scheme

According to the calculations, which have been made using the thin hologram theory [22] self-diffraction efficiency and diffraction efficiency are connected by the following expression:

$$SDE = DE_{(-1)} + \frac{P_R}{P_S} DE_{(-2)} + 2 \left( \frac{P_R}{P_S} DE_{(-1)} DE_{(-2)} \right)^{1/2} \cos(\Phi_S - \Phi_R + \Phi_{S(-1)} - \Phi_{R(-2)}), \quad (10)$$

where  $P_R$  and  $P_S$  are powers of the recording beams,  $DE_{(-1)}$  is the diffraction efficiency of the minus first order,  $DE_{(-2)}$  is the diffraction efficiency of the minus second order of  $P_R$ ,  $\Phi_S$  and  $\Phi_R$  are the phases of zeroth orders of diffracted  $P_S$  and  $P_R$ ,  $\Phi_{S(-1)}$  is the phase of the minus first order of  $P_S$  and  $\Phi_{R(-2)}$  is the phase of the minus second order of  $P_R$ .

In the degenerate four-wave mixing experiments He-Ne laser LGN-222 with wavelength 632.8 nm has been used. For weak enough recording intensity the holographic approximation can be used. [28]. Experimental set-up is shown at the fig. 7. Experiment was performed by the following way. The beams  $P_1$  and  $P_2$  recorded elementary transmission hologram (holographic grating) in the sample.

Reflected from the mirror 12 beam diffracts in the recorded dynamic grating. Diffracted beam  $P_1'$  is directed to the sensor of power meter 9 by beam splitter 8.

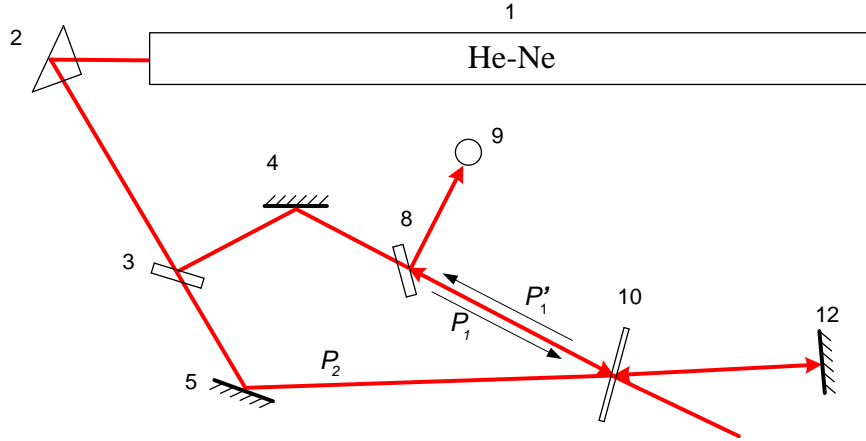


Fig. 7. Experimental set-up for the unfocused measurements in the four-wave geometry

*1 – laser, 2 – prism, 3 and 8 – beam splitter, 4, 5 and 12 – mirrors, 9 – sensor of the power meter, 10 – sample.*

If the beams are focused by lenses new parameters appear: the focal length  $f$  and the distance between parallel beams  $l$  (fig. 8). Performing trigonometric transformations of (6) and expression from fig. 8 it is possible to derive a formula for the calculation of grating period in the case of focused beams:

$$A = \frac{\lambda}{2} \sqrt{1 + \frac{4f^2}{l^2}}, \quad (11)$$

where  $A$  is grating period (see expression (6)),  $\lambda$  is wavelength,  $f$  is focal length,  $l$  is the distance between parallel beams.

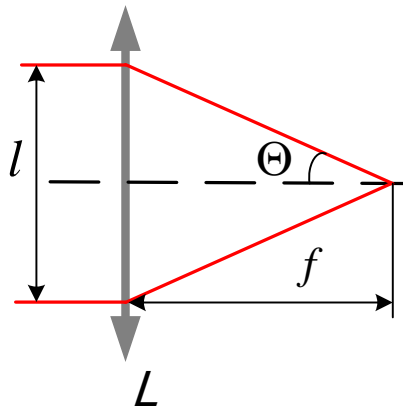


Fig. 8. Focusing geometry

*$L$  – lens,  $\tan \Theta = \frac{l}{2f}$ , where  $l$  is distance between beams,  $f$  is focal length of the lens,  $\Theta$  is the angle of incidence.*

The efficiency of holographic recording in the case of four-wave mixing is described by the inverted wave efficiency (IWE):

$$\text{IWE} = \frac{P_1'}{P_1}, \quad (12)$$

where  $P_1'$  is power of the inverted beam,  $P_1$  is power of the incident beam (fig. 7 and 9).

Specific recording energy is calculated for the maximal IWE:

$$W_{\max} = \frac{It}{\text{IWE}_{\max}}, \quad (13)$$

where  $W_{\max}$  is specific recording energy,  $I$  is intensity of laser radiation (see formula (8)),  $\text{IWE}_{\max}$  is maximal inverted wave efficiency,  $t$  is the time for achieving  $\text{IWE}_{\max}$ .

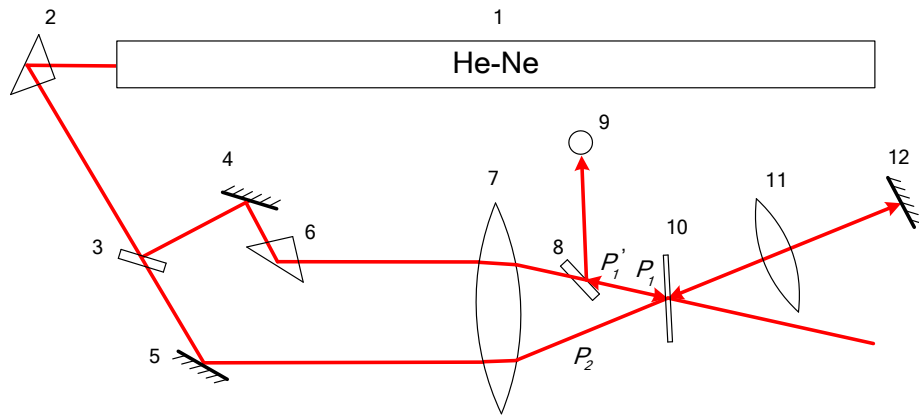


Fig. 9. Experimental set-up for the focused measurements in the four-wave geometry

*1 – laser, 2 and 6 – prisms, 3 and 8 – beam splitters, 4, 5 and 12 – mirrors, 7 and 11 – lenses, 9 – sensor of the power meter, 10 – sample.*

Surface relief grating holographic measurements have been performed using scanning atomic force microscope NT-MDT Model Smena-A (Russia) in the case of toluy azobenzene oligomer samples and using SPM II VEECO (USA) for other samples. In the first case the measurements were performed in the institute of Solid State Physics of the University of Latvia, in the second case in the faculty of Materials Science and Applied Chemistry of RTU.

**In the eighth chapter the experiments of focused and unfocused recording of holographic gratings in  $\text{As}_2\text{S}_3$  films by He-Ne laser at 632.8 nm wavelength are described.**

The fig. 10 shows that the recording by focused beams is more effective than by unfocused ones. Higher diffraction efficiencies and lower specific recording energies were achieved for gratings with 1.4  $\mu\text{m}$  period. Higher recording

intensities gave higher diffraction efficiencies and lower specific recording energies, i.e. better recording efficiency (at least for gratings with periods less than 5  $\mu\text{m}$ ), than lower recording intensities. The best holographic parameters achieved for focused recording  $\eta_{\text{max}} = 14.9\%$  and  $W_{\text{max}} = 216 \frac{\text{J}}{\text{cm}^2 \%}$ , but for unfocused  $\eta_{\text{max}} = 0.11\%$  un  $W_{\text{max}} = 72400 \frac{\text{J}}{\text{cm}^2 \%}$ . The dependence of maximal diffraction efficiency on grating period differs too. In case of focused recording there is maximum at  $\Lambda = 1.4 \mu\text{m}$ . In case of unfocused recording two maximums were observed: at 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$  [26]. The annealing of samples reduces the diffraction efficiency:  $\eta_{\text{max}} = 0.92\%$ ,  $W_{\text{max}} = 10300 \frac{\text{J}}{\text{cm}^2 \%}$ .

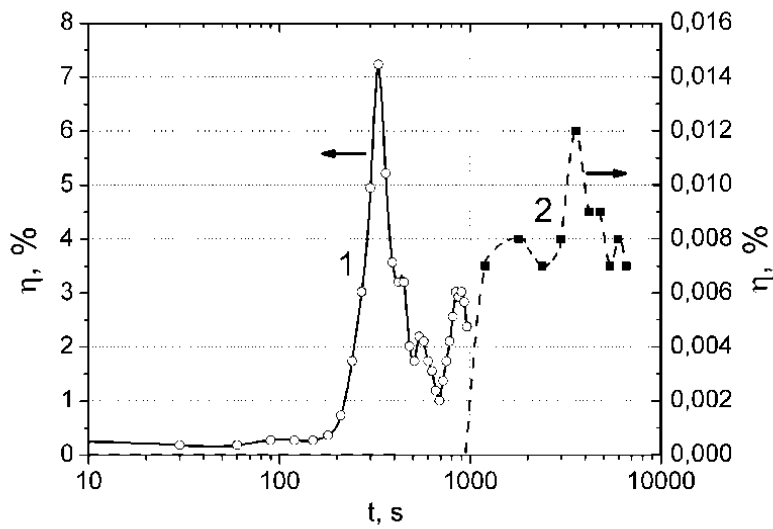


Fig. 10. Diffraction efficiency vs exposure time for holographic grating with 1  $\mu\text{m}$  period  
*Curve 1 – focused beams,  $I=14 \text{ W/cm}^2$ ; curve 2 – unfocused beams,  $I=0.58 \text{ W/cm}^2$ . Experimental points for focused recording are circles, for unfocused - squares. As seen, scales differ considerably [32].*

Experimental results authenticate that, most probably, focused and unfocused recording in  $\text{As}_2\text{S}_3$  using 632.8 nm light is made with different mechanisms [31, 32]. To explain the results three mechanisms were offered: structural changes due to photostimulated relaxation, generation and recharging of D-centers under the influence of light and photoorientation of D-centers [31, 32].

Focused recording is more effective than unfocused due to different concentration of D-centers. This concentration in amorphous  $\text{As}_2\text{S}_3$  is approximately  $10^{17} \text{ cm}^{-3}$  [19] and only these active centers take part in the unfocused recording. Concentration of D-centers grows together with intensity due to generation of these centers (recharging of D-centers).



Photoinduced relaxation structural changes take place in the soft atom configurations, whose concentration is approximately  $10^{21} \text{ cm}^{-3}$  [55] and which is activated by intensive focused light.

**In the ninth chapter the experimental research of four-wave mixing in amorphous  $\text{As}_2\text{S}_3$  and azobenzene oligomer films is described.**

The four-wave mixing has been realized in amorphous  $\text{As}_2\text{S}_3$  and azobenzene oligomer films. Experimental results for a- $\text{As}_2\text{S}_3$  and the compound [4-((4-nitrophenyl)diazenyl)-*N,N*-bis(2-(tetrahydro-2H-pyran-2-iloxy)ethyl)benzamine are shown at fig. 11 and 12 as well as at table 2.

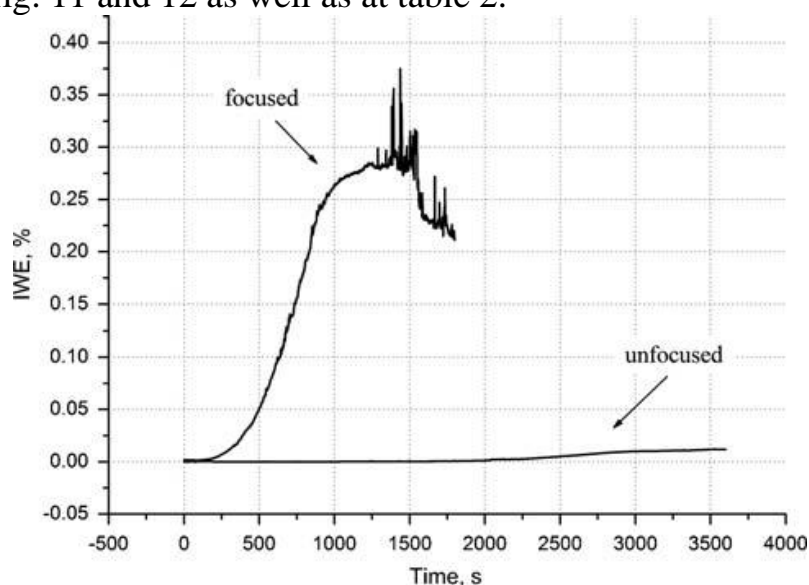


Fig. 11. Inverted wave efficiency vs exposure time for amorphous  $\text{As}_2\text{S}_3$  sample

*The intensities of recording light were  $I=44 \text{ W/cm}^2$  for focused four-wave mixing and  $I=0.80 \text{ W/cm}^2$  for unfocused [37].*

It is obvious that inverted wave efficiency of focused recording is higher and the process is faster than unfocused one. Inverted wave efficiency decreases after large enough exposure time because the changes of refractive index reach saturation [42].

Recording process occurs faster in azobenzene oligomers than in  $\text{As}_2\text{S}_3$ . The specific recording energy is lower for unfocused four-wave mixing in azobenzene oligomers and for focused recording in amorphous  $\text{As}_2\text{S}_3$  (see table 2). Such effect can be explained by the recording mechanisms difference in different materials. In amorphous  $\text{As}_2\text{S}_3$  there occurs orientation of D-centers during unfocused recording and photostimulated relaxational structural changes together with generation and recharging of D-centers during the focused recording [32]. The recording mechanism in azobenzene oligomers are the chromophore group orientation perpendicularly to the electric field vector of polarized light [23, 37].

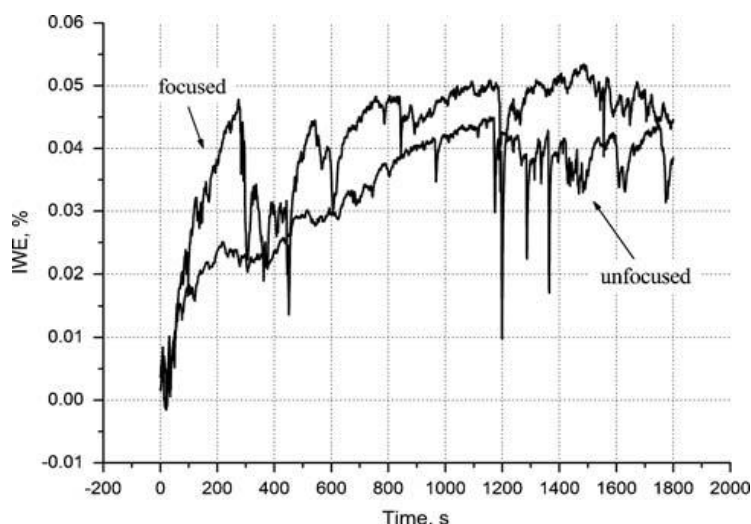


Fig 12. Inverted wave efficiency vs exposure time for the sample of azobenzene oligomer with chromophore concentration 0.12 mol/l

*The intensities of recording light were  $I=47 \text{ W/cm}^2$  for focused four-wave mixing and  $I=0.57 \text{ W/cm}^2$  for unfocused [37].*

The great energy consumption in four-wave mixing can be explained by the following way. Probably that in case of focused recording temperature in the recording area increases significantly like in a-As<sub>2</sub>S<sub>3</sub> [42] because both materials have comparable thermal conductivity (379 mW/m·K for a-As<sub>2</sub>S<sub>3</sub> and 80 mW/m·K for polystyrene [37, 53]. Chromophore groups of azobenzene oligomers are dispersed in polystyrene matrix and chromophore amount in the sample is significantly less than amount of polystyrene).

Table 2

Inverted wave efficiency  $IWE_{\max}$  and specific recording energy  $W_{\max}$  for different samples of azobezene oligomers (ABO) and recording conditions

Material	Recording	$IWE_{\max}$ , %	$W_{\max}$ , kJ/(cm <sup>2</sup> %)
a-As <sub>2</sub> S <sub>3</sub>	focused	0.285	190
	unfocused	0.012	234
ABO; C=0.1 mol/l	focused	0.045	1197
	unfocused	0.030	25.3
ABO; C=0.12 mol/l	focused	0.053	1316
	unfocused	0.047	8.6

The molecules of chromophore in the heated recording area are subjected to photoinduced orientation by linearly polarized light and influence of heating, which initiate the opposite effects. As the result, the inverted wave efficiency in

azobenzene oligomer is lower than in a-As<sub>2</sub>S<sub>3</sub> where rising of temperature stimulates structural relaxation (for focused recording).

Four-wave mixing can have many applications: research of materials, wave front inversion, optical information processing, real-time processing of images, creation of the coherent infrared and vacuum ultraviolet radiation sources, fiber and free-space optical communications.

**The tenth chapter is devoted to the dependence of azobenzene oligomers' holographic properties on the connection of chromophore groups' to the matrix and on their concentration.**

Organic materials allow more tailoring of its properties comparing with inorganic ones. Azobenzene compounds are perspective class of materials in this sense. It is confirmed by the properties of azobenzene and the great amount of publications devoted to this theme. Holographic research in the red region of spectrum is significant from theoretical and practical points of view. On the theoretical part the recording mechanism is not clarified enough that is responsible for recording process when absorption is low. On the practical part the recording in that region of spectrum allows to achieve higher diffraction efficiencies and to use cheaper lasers. In the current thesis two material groups were researched. The first group was azobenzene chromophores, which were covalently bonded to the oligomer matrix (the main chain of molecule). In that case two matrices were used: modified by toluyl and modified by hexamethylene polyurethane. The second group was azobenzene chromophores dispersed in polystyrene matrix without covalent bonds. The main results are combined in the fig. 13 and 14 and in the tables 3 and 4. The dynamics of diffraction efficiency during recording process was slightly unstable, with several maximums (see fig. 13 and 14). It was expressed more for the second type of the samples. With aim to express recording efficiency in different samples possibly more objectively four parameters were used:

- 1) Maximal diffraction efficiency of all maximal values achieved in different measurements ( $\max \eta_{\max}$ ).
- 2) Minimal specific recording energy ( $\min W_{\min}$ ).
- 3) Average value calculated from maximal diffraction efficiencies of different measurements ( $\overline{\eta}_{\max}$ ).
- 4) Average value of specific recording energies ( $\overline{W}_{\max}$ ) (which corresponds to maximal diffraction efficiency in a single measurement  $\eta_{\max}$ ) (see table 4).

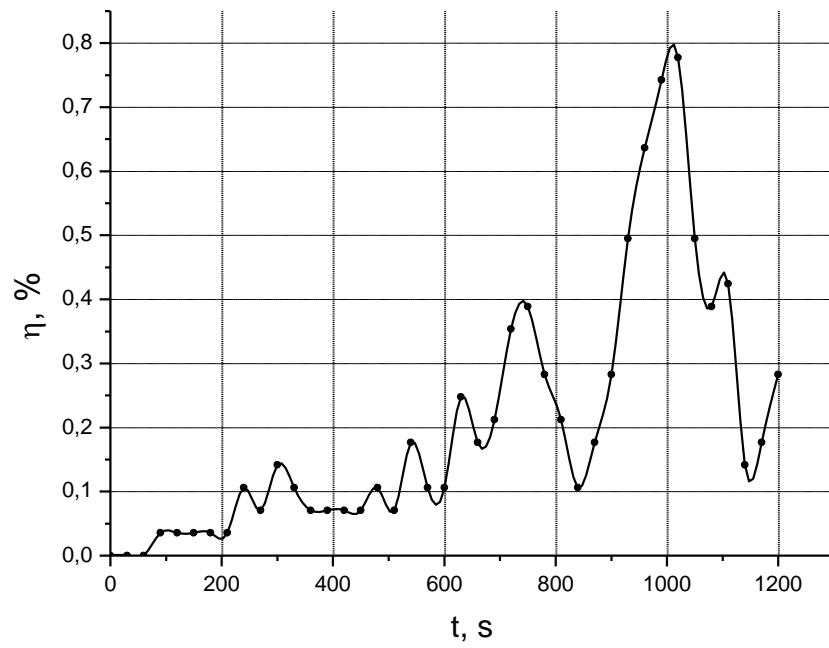


Fig. 13. Diffraction efficiency vs exposure time for the sample No. 1 from table 3

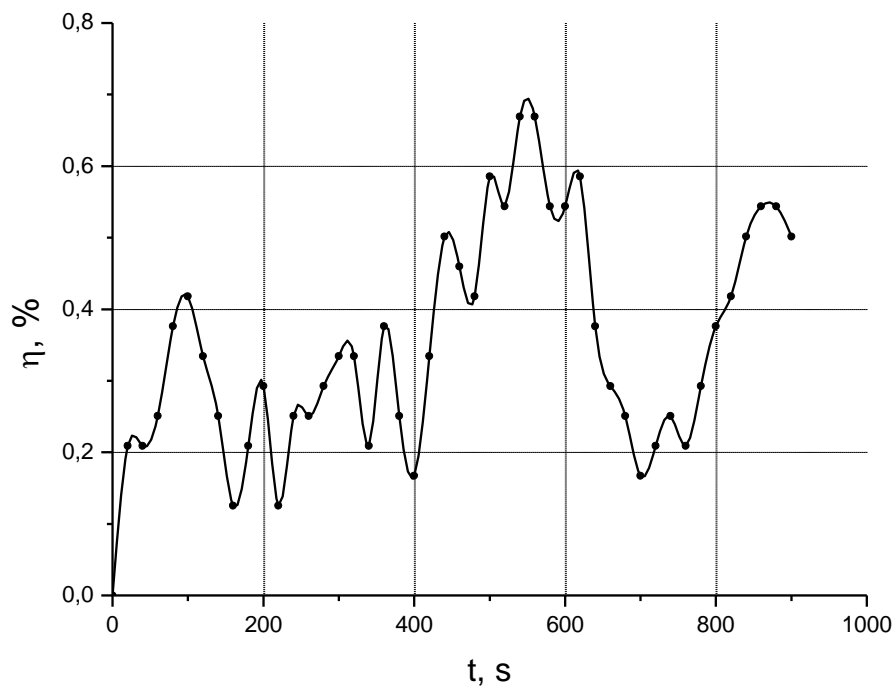
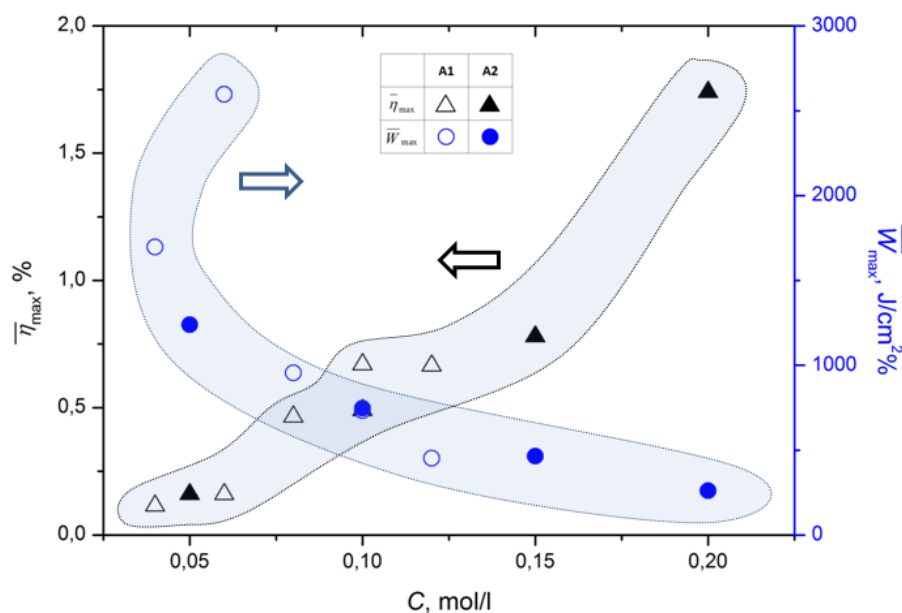


Fig. 14. Diffraction efficiency vs exposure time for the sample "A2[125]" from table 4

Table 3

Holographic parameters for the first type of the samples  
*HM*- hexamethylene, *Tl* - toluyl,  $\lambda_{max}$  – wavelength of the absorption maximum,  
 $D_{max}$  – optical density at the absorption maximum,  $\eta_{max}$  maximal diffraction  
efficiency,  $W_{max}$  – specific recording energy for  $\eta_{max}$

Sample	Matrix	Chromophore	$\lambda_{max}$ , nm	$D_{max}$	$\eta_{max}$ , %	$W_{max}$ , J/(cm <sup>2</sup> %)
1	HM	Paranitrofenylazobenzene	470	3.7	0.8	1071
2	HM	4-nitronapthylazobenzene	500	4.2	2.1	62
3	Tl	4-nitronapthylazobenzene	500	4.7	0.26	2626
4	HM	9,10-anthraquinone- $\alpha$ - azobenzene	417	2.4	0	--
5	Tl	9,10-anthraquinone- $\alpha$ - azobenzene	415	2.5	0	--
6	Tl	$\beta$ -chlorine-9,10- anthraquinone- $\alpha$ - azobenzene	550	3.6	0	--
7	HM	$\beta$ -chlorine-9,10- anthraquinone- $\alpha$ - azobenzene	420	2.1	2.9	260



15. att. Average diffraction efficiencies and specific recording energies vs azochromophore concentration in the polystyrene matrix

Data from table 4 shows that there is a threshold of diffraction efficiency between chromophore concentrations 0.01 and 0.04 mol/l. For the greater concentrations recording efficiency grows up to maximal concentration 0.2 mol/l, after which

crystallization begins. Existence of the threshold can be explained by cooperative interaction of chromophores. Fig. 15 shows that increase of concentration causes increase of diffraction efficiency and decrease of specific recording energy.

Table 4

Holographic parameters of the second type of the samples and chromophore concentration

*Chromophore group A2 has been used to achieve higher than A1 concentration in the polystyrene matrix; C – concentration of azochromophore,  $\lambda_{max}$  – wavelength of the absorption maximum,  $D_{max}$  – optical density at the absorption maximum,  $max\eta_{max}$  – maximal achieved diffraction efficiency,  $minW_{max}$  – minimal achieved specific recording energy,  $\bar{\eta}_{max}$  - average of maximal diffractions efficiencies,  $\bar{W}_{max}$  - average value of the specific recording energies (which corresponds to  $\eta_{max}$ ).*

Notation of sample	C, mol/l	$\lambda_{max}$ , nm	$D_{max}$	$max\eta_{max}$ , %	$minW_{max}$ , J/(cm <sup>2</sup> %)	$\bar{\eta}_{max}$ , %	$\bar{W}_{max}$ , J/(cm <sup>2</sup> %)
A1[112]	0.005	482	0.55	0	--	0	--
A1[113]	0.006	482	0.63	0	--	0	--
A1[115]	0.007	480	0.74	0	--	0	--
A1[116]	0.010	480	1.02	0	--	0	--
A1[117]	0.040	487	3.6	0.12	616	0.115	1696
A2[129]	0.050	502	3.7	0.19	1081	0.16	1239
A1[121]	0.060	500	3.8	0.22	3127	0.16	2596
A1[119]	0.080	508	3.9	0.52	733	0.465	956
A1[91]	0.100	490	3.9	0.42	1540	--	--
A1[123]	0.100	500	3.9	0.78	610	0.67	732
A2[128]	0.100	510	3.8	0.9	425	0.49	746
A1[125]	0.120	436	4.3	0.68	329	0.665	452
A2[127]	0.150	500	3.9	1.39	183	0.78	464
A2[130]	0.200	500	3.9	2.30	31	1.74	260

Pursuing the aim to characterize the recording efficiency by one number a parameter which combines the specific recording energy and the diffraction efficiency was introduced in this thesis. It is recording efficiency factor – REF and it is calculated as follows:

$$REF = \frac{\eta_{max}}{W_{max}}, \quad (12)$$

where  $\eta_{max}$  is maximal diffraction efficiency and  $W_{max}$  is specific recording energy, which corresponds to maximal diffraction efficiency. Fig. 16 shows the recording efficiency factor dependence on the concentration of azochromophore in the sample.

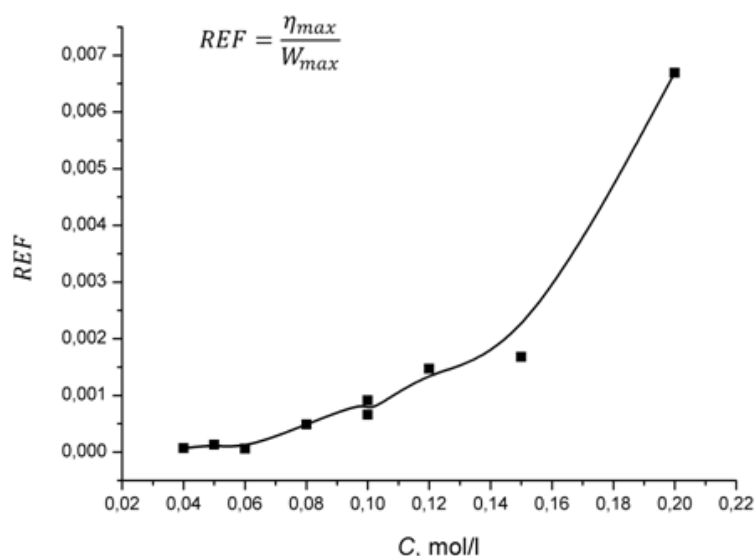


Fig. 16. Recording efficiency factor vs chromophore (A1 and A2) concentration in polystyrene matrix

**The eleventh chapter is devoted to studies of surface relief grating recording in azobenzene compounds and analysis of achieved results.**

Blue and green light is used for recording in azobenzene compounds usually, because absorption spectra of them have maximums in the blue and green regions [41]. In that case the *trans-cis* isomerization takes place under the influence of light [40, 41]. At the red region of spectrum absorption is significantly lower, but recording is possible yet [23, 29]. The mechanism of such recording is not clear entirely and this fact gave the motivation to continue research. In limits of the thesis, the recording of surface relief grating in the azobenzene oligomers with toluyll matrix was researched for recording using green 514.5 nm light of Ar<sup>+</sup> laser and in the stilbene azobenzene compounds using red light 632.8 nm of He-Ne laser. The possibility of surface relief gratings recording in azobenzene compounds by red light was discovered during the present research and has been noted by Latvian Academy of Sciences in 2008.

Two azobenzene samples (T2 and T3) have been prepared and placed on the glass substrate. In the both samples polyurethane matrix have been modified by toluyll oligomer (toluene diisocyanate) (n<500) with chromophore groups in side chains. The samples T2 and T3 differ by acceptor groups. Transmission holographic gratings with period  $\Lambda \approx 360$  nm have been recorded by two symmetrically incident beams of Ar<sup>+</sup> laser (Spectra Physics Model 171-09) with equal power and linear TE polarization at the wavelength  $\lambda_1 = 514.5$  nm. Recording intensity was  $I = 0.6$  W/cm<sup>2</sup>. Photoinduced changes have been measured by the spectrometer (Perkin Elmer Lambda 35 UV/VIS). Absorption has decreased at 480 - 500 nm and has increased near 360 nm. These changes indicate *trans-cis* transformation [41]. In addition the area under the lines decreased. Immediately

after the recording the first order diffraction efficiency  $\eta$  was measured at wavelength 632.8 nm with TM polarization and at wavelength 650 nm with TE polarization. Specific recording energy  $W$  was calculated also. For the sample T2  $\eta = 1.0\%$  ,  $W = 0.54 \frac{\text{kJ}}{\text{cm}^2 \%}$  at  $\lambda_2 = 632.8 \text{ nm}$  and  $\eta = 0.76\%$  ,  $W = 0.71 \frac{\text{kJ}}{\text{cm}^2 \%}$  at  $\lambda_2 = 650 \text{ nm}$ . For the sample T3  $\eta = 2.0\%$  ,  $W = 0.45 \frac{\text{kJ}}{\text{cm}^2 \%}$  at  $\lambda_2 = 632.8 \text{ nm}$  and  $\eta = 1.5\%$  ,  $W = 0.60 \frac{\text{kJ}}{\text{cm}^2 \%}$  at  $\lambda_2 = 650 \text{ nm}$ . Accuracy was 3% for diffraction efficiency and 8% for specific recording energy.

Microscopic measurements (with microscope NT-MDT Model Smena-A) have shown that surface relief grating formed in the recording area. Maximal relief amplitudes were 27 nm for the sample T2 and 35 nm for the sample T3. An example of surface relief and profile are shown at fig. 17 and 18. Repeated after four years measurements have shown that the relief has remained.

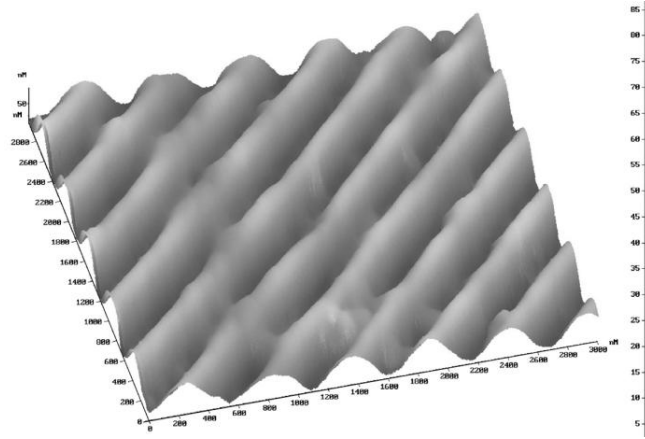


Fig. 17. Surface relief grating recorded in the sample T3 [30]

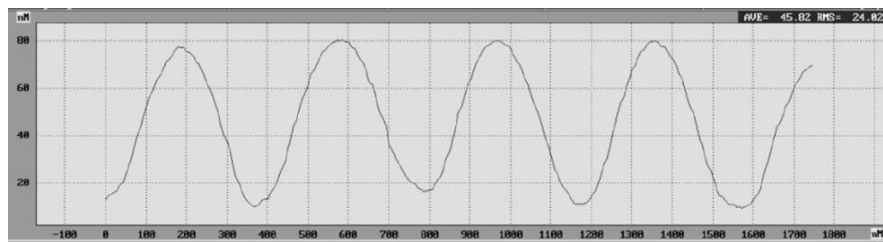


Fig. 18. The profile of surface relief grating in the sample T3 [30]

Holographic gratings using 632.8 nm light with TM polarization were recorded also. The changes of the absorption spectrum and the relief have not been observed in this case. These records were more effective, but less stable. For the

sample T2  $\eta_{\max} = 7.9\%$  ,  $W_{\max} = 0.42 \frac{\text{kJ}}{\text{cm}^2 \%}$  and for the sample T3  $\eta_{\max} = 4.2\%$  ,

$W_{\max} = 0.086 \frac{\text{kJ}}{\text{cm}^2 \%}$  . The relaxation time of diffraction efficiency in the dark was approximately 30 hours. It is obvious that recording mechanisms are different for 514.5 nm and 632.8 nm [29].



The readout was realized by He-Ne laser 632.8 nm differently polarized light: linear TE, linear TM, counter orthogonal polarizations (see table 5). The first and zeroth diffraction orders of diffraction efficiency were measured for through-passing and reflected beams [30].

These measurements have been made immediately after the recording and have been repeated after four years. Diffraction efficiency has decreased significantly, but surface relief grating has remained [30]. This fact shows that amplitude and phase gratings were recorded in the sample simultaneously. Such recording process can be explained by mean-field recording mechanism and chromophore photodegradation mechanism. The covalently bonded acceptor group of bromine increases recording efficiency.

Table 5

Diffraction efficiency dependence on polarization  
at 632.8 nm for the sample T3 [30]  
*OCP-1 and OCP-2 are orthogonal circular polarizations.*

Diffraction efficiency, %	TE	TM	OCP-1	OCP-2
$\eta$	0.45	0.20	0.22	0.32
$\eta_r$	0.96	1.4	0.76	1.2
$\eta_{0t}$	14	23	16	17
$\eta_{0r}$	25	2.9	21	8.7

Strong diffraction efficiency dependence on polarization can be explained by the photoinduced anisotropy of film material. More effective, but unstable record by 632.8 nm light is, obviously, based on photoorientation and recharging processes of chromophores without *trans-cis* transformations.

Stilbene azobenzene compounds researched in the experiments were molecular glasses with stilbene fragments in the donor part of the azochromophore. During the experiments holographic gratings with period 2  $\mu\text{m}$  were recorded. Recording intensity was 0.88 W/cm<sup>2</sup>. Maximal self-diffraction efficiency achieved have been 17.4%. Efficiency of the recording process was dependent on the sample age. Optimal results have been achieved approximately after 50 days from sample preparation. Microscopic measurements showed relief in the recording area (see fig. 19). Amplitude of surface grating achieved 113 nm. Structure of the surface remained during a year, as repeated measurements have shown. Photoinduced absorption changes are shown in fig. 20. Photobleaching is observed mainly. As it is possible to see the absorption changes are very low at 632.8 nm, thus there exists phase record only. Fig. 20 shows that optical density decreases almost evenly in whole observed part of spectrum excluding small decrease approximately near 700 nm. In preference the even absorption decrease after the recording process can be explained by chromophore photodegradation, i. e. chromophore destruction under the influence of light during the recording

process. For example N-N bonds can be broken by 632.8 nm light [41]. Photoablation is possible too, but intensities significantly more than  $1 \text{ W/cm}^2$  are needed [41].

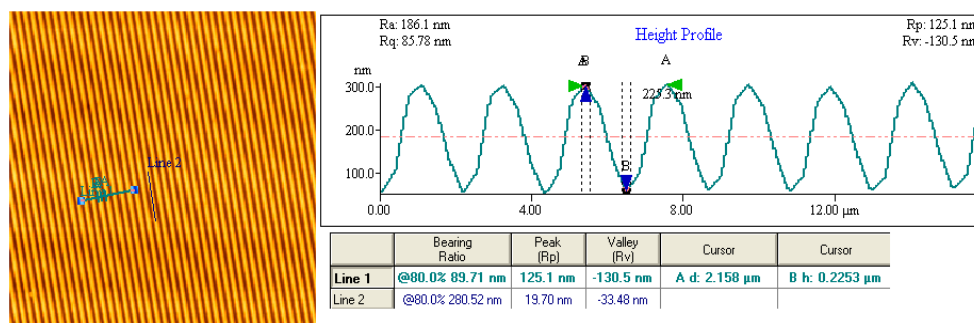


Fig. 19. Surface relief and it's profile in the center of recorded area  
Relief amplitude is 113 nm, maximal level changes – 226 nm.

Taking in account examined properties of the recording of surface relief holograms (including fact that record have been made by He-Ne laser TM polarized light) and known surface relief grating mechanisms, it is possible to make a conclusion that the gradient electric force, mean-field, asymmetric diffusion models and chromophore photodegradation mechanism are responsible for recording.

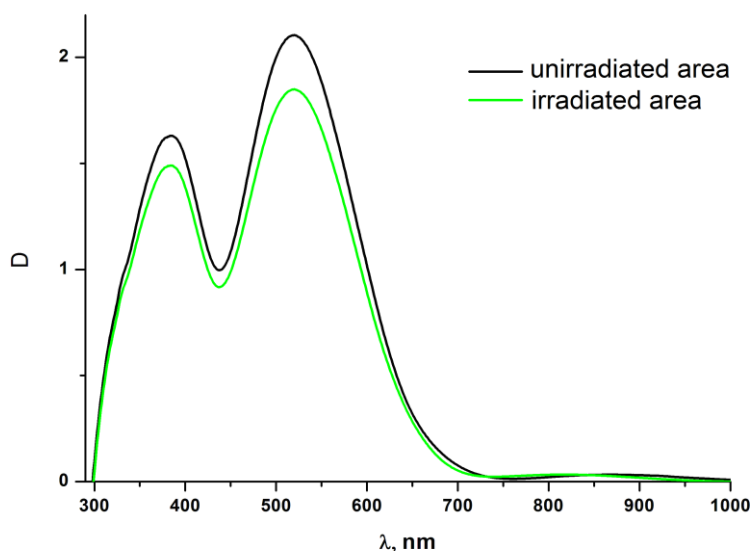


Fig 20. The photoinduced changes of the absorption spectrum in the sample No. 2 (**8a**) under the 632.8 nm light influence

The possibility of the latter is indicated by photobleaching and warming of the sample. *Trans-cis* isomerization under the red light's influence is possible. This possibility is confirmed by the further experiments [24]. Common action of many mechanisms is probable. Further researches are needed to specify surface relief grating recording mechanisms in the observable azobenzene compounds.

The practical importance of the effective recording at the red part of spectrum consists in availability of cheaper equipment and, as a result, cheaper production of holographic optical elements, antireflection films and others.

**The twelfth chapter contains information about relaxation peculiarities of stilbene azobenzene compounds obtained as part of the thesis.**

Mainly two samples of molecular glasses containing stilbene fragments in the electron donor part have been researched. The results of experiments are shown at the fig. 21 and table 6. It appears that fresh samples are not the most effective for holographic recording as generally think [35, 40]. Some optimal age of the sample corresponds to the most effective recording (maximal self-diffraction efficiency and minimal specific recording energy).

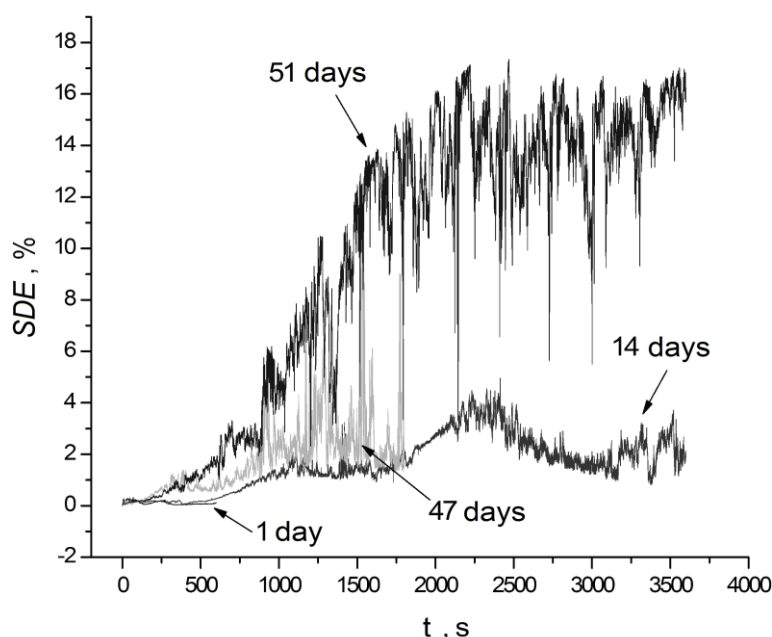


Fig. 21. Self-diffraction efficiency vs exposure time for the different ages of the sample No. 2 (**8a**)

*The recording process was more effective for older sample [38].*

The measurements have shown that recording efficiency in the samples of stilbene azobenzene is a nonmonotonic function of the sample age. An optimal time exists after which recording with maximal efficiency is possible. This time is independent on chemical composition because in experiments the time was different for different samples made of the same chromophore. Likely, this effect is conditional on relaxation features of the samples of azobenzene derivatives, because these samples consist of chromophore molecules with a lot of free volume between them.

In the end of the thesis the achieved results of current research have been combined, holographic efficiency of the researched materials has been quantitatively compared and conclusions have been formulated.

Table 6

Holographic recording efficiency dependence on chromophore concentration in polyvinylpyrrolidone and sample age for the 3-(4-(bis(2-(trifluoromethoxy)ethyl)amine)phenyl)-2-(4-(2-bromine-4-nitrophenyl)diazenyl)phenyl)acrylonitrile (**8a**)

$SDE_{max}$  is the maximal self-diffraction efficiency,  $W_{max}$  is the specific recording energy, which corresponds to  $SDE_{max}$ ,  $I$  is the intensity of recording light [38].

	6 days from preparation				7 days	
Sample designation	6,1	6,2	7,1	8	9	10
Mass concentration, %	100	100	95	70	35	20
$SDE_{max}$ , %	15.8	5.05	9.79	0.07	0.11	0.06
$W_{max}$ , J/cm <sup>2</sup> %	57	265	162	22651	13692	30068
$I$ , W/cm <sup>2</sup>	0.51	0.74	0.89	0.90	0.98	1.01
	66 days from preparation					
$SDE_{max}$ , %	0.23		0.35	0.04	0.03	
$W_{max}$ , J/cm <sup>2</sup> %	5175		4506	144	161	
$I$ , W/cm <sup>2</sup>	0.87		0.95	0.92	0.85	

## Conclusions

1. The holographic recording process by focused and unfocused sub-band gap He-Ne laser 632.8 nm light has been experimentally researched in annealed and unannealed a-As<sub>2</sub>S<sub>3</sub> films. It is ascertained that focused recording is more effective than unfocused one (14.9% and 0.11% diffraction efficiency, 0.216 kJ/cm<sup>2</sup>% and 72.4 kJ/cm<sup>2</sup>% specific recording energy) and properties of these differ considerably (two year lifetime of holographic grating and positive changes of refractive index in the case of focused recording, but only two day lifetime and negative changes of refractive index in the case of unfocused recording). The annealing of samples lowers recording efficiency by more than an order of magnitude.
2. Sub-band gap light recording in a-As<sub>2</sub>S<sub>3</sub> films differs from band gap recording. In the first case weak photoinduced bleaching of the film occurs, but in the second case expressed photoinduced darkening is observed. As known, structural phototransformation of the film occurs during the band gap recording. The results of sub-band gap light recording can be explained by photostimulated structural relaxation and by photoinduced generation and recharging of D-centers, but the results of unfocused sub-band gap recording can be explained by the photoorientation of D-centers and structural relaxation.
3. The recording process of holographic gratings by linearly polarized 632.8 nm light in films of different composition (azobenzene oligomers and stilbene azobenzene compounds) has been experimentally researched. It is established that in all cases dynamic phase holographic gratings have been recorded. Relaxation times of these gratings were from two days to a few years. The recording mechanism essentially is the photoorientation of chromophore group's dipole moment perpendicularly to the intensity of electric field of light. This mechanism also causes shifting of the connected molecular segments. Evidence in favor of this mechanism is instability of the recording and its phase character, expressed differences of the holographic gratings changing polarization of recording light, as well as expressed dependence of holographic recording properties on chromophore concentration.
4. The recording of holographic gratings by focused and unfocused beams have been realized in the four wave geometry in a-As<sub>2</sub>S<sub>3</sub> and azobenzene oligomer films [4-((4-nitrophenyl)diazenyl)-N,N-bis(2-(tetrahydro-2H-pyran-2-iloxy)ethyl)benzeneamine]. Focused recording in that geometry, as known, has been realized the first time. The higher inverted wave efficiency was achieved for both materials by focused recording. On the contrary, sensitivity is higher in the case of focused recording in a-As<sub>2</sub>S<sub>3</sub> films, but in the case of unfocused recording the samples of azobenzene compounds are more sensitive. This difference can be explained by the diverse influence of temperature growth on the recording mechanisms. Temperature growth

- stimulates structural relaxation in the  $\alpha$ -As<sub>2</sub>S<sub>3</sub> films, but detains the photoorientation of chromophores in the azobenzene samples.
5. The dependence of holographic recording efficiency on chromophore group connection type (covalent or dispersed) in azobenzene oligomers (toluyl or hexamethylene) to the matrix, or the main chain of oligomer, also the dependence on the chromophore group concentration in the samples of azobenzene oligomers on polyurethane and polystyrene basis is experimentally studied. It has been ascertained that connection of chromophore groups by the covalent bonds to the matrix is generally more effective and more elastic matrix with larger free bulk inside is desirable for better results. At the same time the efficiency of holographic grating recording is considerably dependent on chromophore group concentration and there exists a threshold the concentration between 0.01 and 0.04 mol/l. After achieving it the recording efficiency increases noticeably and approximately linearly. Existence of the threshold can be explained by cooperative interaction of the chromophore groups (for example due to interaction of dipole moments of the chromophore groups).
  6. Though covalent bonding of chromophore groups ensures higher recording efficiency in general, azobenzene oligomer films with dispersed chromophore groups with high enough concentration can be almost as effective. The advantages of dispersing are higher processability and higher standardization possibilities.
  7. In azobenzene films, where dialkylazobenzene groups are dispersed in a polystyrene matrix (without covalent bonds) the photosensibilization effect is observed. This effect is seen from increased photosensitivity in the holographic grating recording place after previous grating have been erased.
  8. The recording of holographic surface relief grating in films with azobenzene groups covalently bonded to a polyurethane matrix has been studied theoretically and experimentally. The matrix has been modified by covalently bonded toluyl (toluyldiisocyanate) oligomer, using 514.5 nm Ar<sup>+</sup> laser light. The amplitude of the holographic surface relief grating reached 35 nm. The conclusion is made that the recording process is explained by photoinduced mass transfer in accordance with chromophore photodegradation or mean-field mechanism, which is initiated by *trans-cis* photoisomerization.
  9. It is experimentally ascertained that organic molecular glasses on the base of stilbene azocompounds are potential materials for holographic information recording in the red region of spectrum (self-diffraction efficiency reaches 17%, surface relief modulation reaches 113 nm). As far as we know, the recording of surface relief holographic grating in organic materials by sub-band gap light is made for the first time. The unstable volume amplitude-phase holographic gratings are the main contributor to diffraction efficiency like in other researched materials. Most probably, the recording mechanisms of surface relief gratings in stilbene azocompounds

are the photothermal degradation of chromophores and trans-cis photoisomerization.

10. It is ascertained that holographic recording efficiency in stilbene azocompounds is a nonmonotonic function of the sample age. An optimal age of sample exists (approximately 50 days) when the holographic grating recording with maximal efficiency is possible. This period of time is not dependent on specific chemical composition. Most likely, such an effect is caused by the structural relaxation peculiarities of the samples, because stilbene azocompound films consist of chromophore molecules only and there is a lot of empty space between these molecules.

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