# Enhancement of photosensitivity in azo-epoxy resists for direct holographic recording

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Azo-epoxy resist is promising material for direct holographic recording due to good photosensitivity and possibility to modify structure of molecule during synthesis – obtained polymer polymerization index easily can be changed by varying curing temperature and curing time. Produced photoresist had properties similar to low-weight molecular glasses. In this work 4-Aminoazobenze, Disperse Orange 2 and epoxy resin bisphenol A diglycidyl ether were used. Surface relief grating formation by direct holographic method was performed in obtained resists. Surface relief grating post-recording self-enhancement process was investigated. It allows to increase a depth of surface relief grating after holographic recording, using physical method – uniform light illumination. It decreases time and required exposure for recording, making holographic recording more effective because grating formation is less affected by vibrations and noises.

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## 1. Introduction

The practical usage of holographic diffractive elements depends on holographic media research and development. Recently many groups studied different new materials for direct holographic recording [1-5]. The main disadvantage of studied photosensitive materials is low photosensitivity. Several materials are promising like azo-dye covalently attached to polymer matrix or organic low-weight molecular glasses, but synthesis of these materials is difficult, reaction outcome can be different in each synthesis and obtained compounds are rather expensive. Azo-epoxy films could solve these problems, since photosensitivity of azo-epoxy films is good and can be improved by adding different compounds and changing holographic recording conditions; synthesis of azo-epoxy films is easy, but reaction outcome is defined and does not change [6-7]. Glass transition temperature $T_g$ of film is one of the parameter determining mass transport effectiveness in a thin film. In azo-epoxy films $T_g$ can be controlled by film curing time or azo-dye and epoxy concentration, allowing to select optimal conditions for films preparation and obtain more effective mass transport in synthesised film.

In this paper we discuss the possibility to enhance photosensitivity of azo-epoxy glass by adding second azo-dye in the media and applying assisting light [8-9] to the film during holographic recording. We performed self-enhancement process [10] of surface relief grating (SRG). It allows obtaining higher modulation of SRG by shorter holographic recording, thus SRG formation is not inhibited by vibration and non-stability of recording system.

## 2. Experimental

Experiments were performed by two beam holographic set-up (Fig. 1) [6]. Grating period was set to $\Lambda$ = 1 μm. Assisting light of laser 3 (Ls3), but it hasn't been used in all experiments. For self-enhancement process studies, one of recording beam was closed by shutter.

Azo-epoxy films for holographic recording were synthesised. Synthesis of azo-epoxy AAB:BADGE (4-Aminoazobenzene: Bisphenol A diglycidyl ether) films is described in previous paper [6]. In this research we added second azo-dye to the synthesis - DO3 (Disperse Orange 3, purchased at Sigma-Aldrich and used as received) [11].

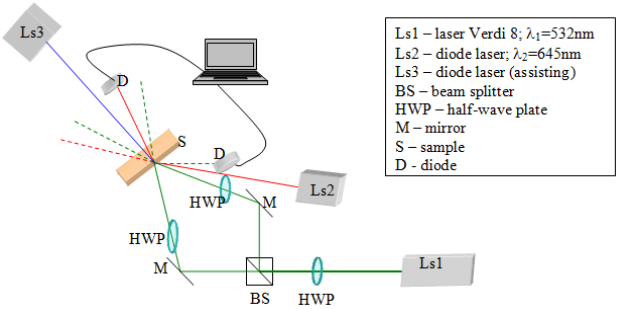


*Fig. 1. Experimental set-up for holographic recording*

Molar concentration of azo-dye and epoxy resin was 2:1. Samples with DO3:AAB ratio 10%:90%, 20%:80%, 30%:70% and 50%:50% of required azo-dye concentration regarding to epoxy resin were made.

## 3. Results and discussion

It is possible to obtain SRG with modulation up to 500 nm in AAB:BADGE films. Nevertheless photosensitivity of the film at $\lambda$ – 532 nm is not good enough and recording time is too long for practical application. In this work we studied possibilities to improve photosensitivity by adding DO3 azo-dye in different ratio [12]. Obtained results can be seen in Fig. 2. Recording with exposure of $E$ = 205 J/cm$^2$ in the media without DO3 resulted in SRG with modulation of $h$ = 225 nm according to AFM data. The best result were obtained in sample with DO3 content of 20%, where the same exposure produced SRG with modulation of $h$ = 305 nm (Fig. 3).

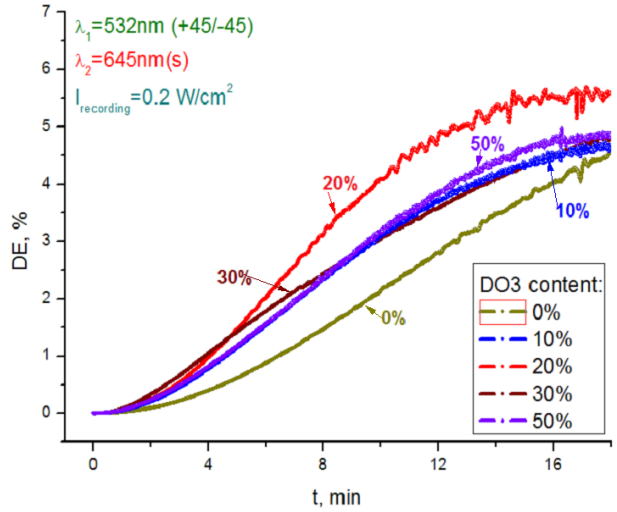


*Fig. 2. Diffraction efficiency of SRG on reflection mode measured by recording beam ($\lambda$ = 532 nm) in films with different DO3 concentration (colour online)*

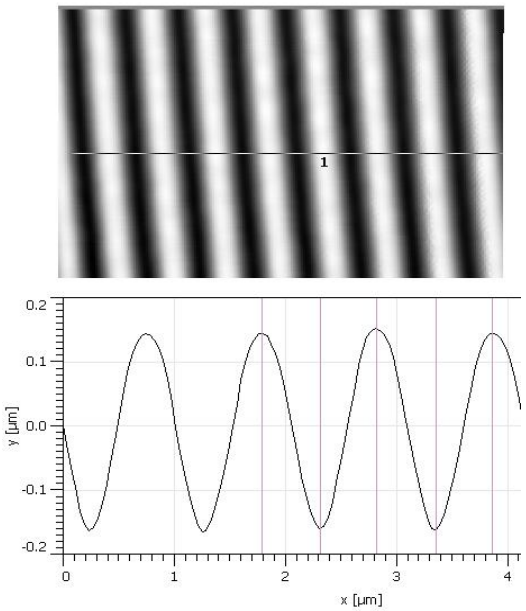


*Fig. 3. SRG profile in AB:DO3:BADGE film with DO3 concentration 20%. Corresponding DE - the red line in Fig. 2*

Adding DO3 to AAB:BADGE film increases absorption of recording beam wavelength $\lambda$ = 532 nm and SRG formation become more effective.

Improvement in photosensitivity was observed if DO3 content was less than 20%; holographic recording was more effective. Further increment of DO3 concentration leads to decrement of incident light penetration depth due to higher absorption of recording beam wavelength; this inhibits SRG formation process due to thinner film layer is involved in SRG formation.

It should be noted, that bulk DO3 dye content is 90% and some impurities have been filtered out during synthesis. DO3 solubility in acetone, which has been used as solvent, is low and actual DO3 concentration can be lower than represented, undissolved DO3 azo-dye could be filtered out with impurities, this is why curves for DO3 content of 30% and 50% in Fig. 2 are similar.

Adding DO3 improves photosensitivity of azo-epoxy film, still further improvements are required. We studied possibility to decrease exposure for SRG holographic recording by applying assisting light [9]. Assisting light beam is incoherent to recording beam and comes from other laser Ls3 (in Fig. 1). Holographic recording was performed by *p-p* polarized recording beam and assisting light was set to perpendicular polarization state – *s* [13]. Using assisting light with wavelength $\lambda_3$ = 491 nm exposure for holographic recording decreased from 120 J/cm$^2$ to 20 J/cm$^2$ (Fig. 4).

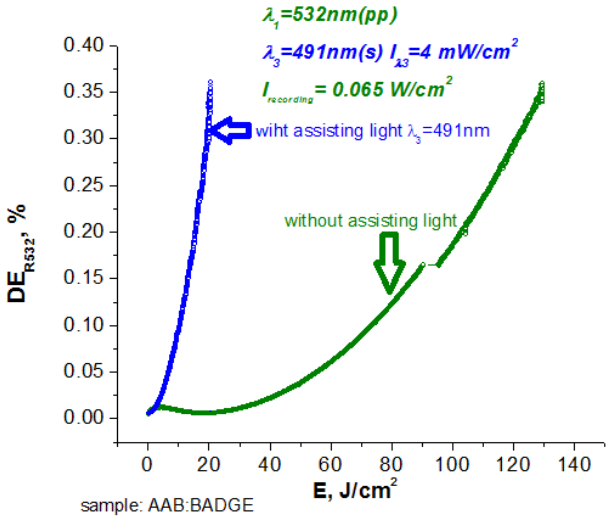


*Fig. 4. Green line – recording without assisting light; blue line – with assisting light $\lambda_3$ = 491 nm (colour online)*

An effect of improved SRG formation depends on assisting light polarization state in respect to recording beam polarization, the wavelength of assisting light and its intensity [14]. Photosensitive media absorb assisting light more effectively and it contributes to photoinduced processes like photoisomerisation, dipole moment changes, viscosity, glass transition temperature $T_g$ of the material during holographic recording. Another effect of improvement could be connected to changes of refractive

indexes in illuminated and non-illuminated areas. Recording beams interference pattern aligns molecules in the material perpendicularly to light electric field vector (Fig. 5.1), thus photoinduced birefringence appears. For *p-p* polarization state in illuminated areas light refractive index will be $n_{||}$. Studied azo-epoxy films is considered as materials with positive birefringence, where refractive index relationship is $n_{\perp} > n_{||}$. Assisting light changes an alignment of azo-molecules (Fig. 5.2) and aligns them perpendicularly to electric field vector. Alignment changes depend on recording and assisting light intensity and their absorbance coefficient in the material.

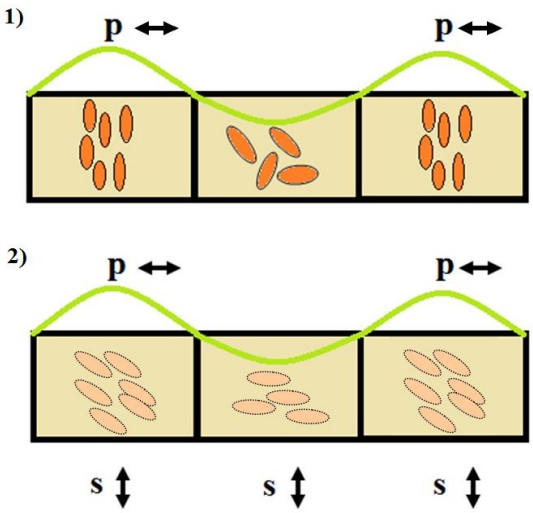


*Fig. 5. Molecules alignment in material 1) with p-p polarization state of recording beams; 2) with p-p polarization state of recording beams and s polarized assisting light*

Refractive index $n$ in recording beams interference pattern illuminated areas slightly increases $n > n_{||}$, but refractive index in recording beam non-illuminated areas becomes equal to $n_{\perp}$.

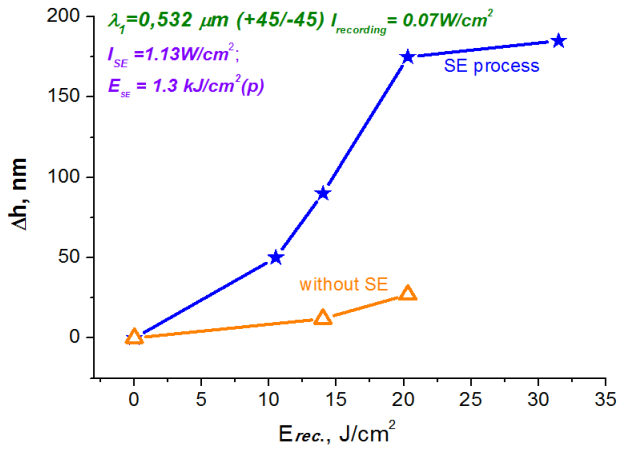


*Fig. 6. Self-enhancement process in AAB:BADGE films (colour online)*

It leads to more efficient SRG formation due to higher refractive indexes changes $\Delta n$ between illuminated and non-illuminated areas.

In Fig. 6 results obtained after self-enhancement process is shown [6]. After holographic recording one of recording beam was switched off, but parameters of other beam was changed – polarization state was set to *p*, but intensity was increased from $I = 0.035$ W/cm$^2$ to $I_{SE} = 1.13$ W/cm$^2$. Thus falling beam and its diffracted beam generates interference pattern in the volume and SRG formation goes on. On Fig. 6 orange line – depth of SRG after holographic recording; blue line – depth of SRG after self-enhancement process. Thus, we used exposure of $E = 20$ J/cm$^2$ for holographic recording (3$^{rd}$ point in orange line), and after exposure of $E_{SE} = 1.3$ kJ/cm$^2$ of produced by one beam, the depth of SRG increased 8 times.

## 4. Conclusion

In this paper we discuss possibilities of photosensitivity enhancement in azo-epoxy films for direct holographic recording. Adding DO3 into AAB:BADGE film increases absorption of recording beam wavelength and increase recording velocity, diffraction efficiency and the depth of SRG. If assisting light is added during holographic recording, required exposure can decrease 6 times. Assisting light changes material properties and contributes to SRG formation. Self-enhancement process of SRG was studied in azo-epoxy films. After short holographic recording, it is possible to obtain 8 time deeper SRG. Self-enhancement process can be used for large area diffractive grating productions, because during illumination by one beam SRG formation is not inhibited by vibration and non-stability of recording system like it is in holography.

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