Dark relaxation of holographic gratings in azobenzene and chalcogenide films

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Abstract. Studies of transmission holographic grating (HG) relaxation (recorded with s-s, p-p, s-p, L-L, L-R laser beam polarizations) have been carried out in organic molecular azobenzene glassy films W-50 and W-75, and in chalcogenide glassy a-As$_2$S$_3$ film. Results previously obtained with azobenzene molecular glassy K-RJ-9 films also are used for comparison. HG with the periods of 0.50, 2.0 and 8.6 μm were studied in these films. It is found that recording efficiency in the same sample depends on both recording polarizations and HG period. The HG stability in the course of relaxation also depends on these factors. Anticorrelation has been observed of HG recording efficiency and stability. Recording was efficient with p-p or L-R polarizations at 2.0 μm HG period whereas it was stable with s-s L-L polarizations at 8.6μm HG period. As a rule, HG stability was higher in the samples with higher glass transition temperature. The HG dark (relaxational) self-enhancement of HG was observed in the case of W-75 (L-R polarizations, 0.50μm; s-s polarizations, 8.6μm) and in previously studied K-RJ-9 (p-p polarizations, 8.6μm) samples. Relaxational changes in diffraction efficiency are explained in terms of post-recording mass transfer under the influence of photoinduced spatially periodic mechanical stress.

1. Introduction
Relaxation processes in disordered materials after the optical irradiation are much less studied than photo induced processes [1]. However, they are important both from fundamental point of view as well from the point of view of applications. As mentioned by O.N.Oliveira, Jr, J.Kumar, L.Li and S.K.Tripathy [2] with respect to organic amorphous films “Perhaps the most important unexplained problem is the post writing evolution which can be due to the mechanical relaxation that has not been treated in any of the models”. Relaxation studies of optical recording in information storage materials are practically significant to establish the possible information storage time. They are also important for production of holographic optical elements. Previously we have experimentally investigated the relaxation of holographic gratings (HG) in fresh amorphous chalcogenide As$_2$S$_3$ films [4]. A strong relaxational (dark) self-enhancement (RSE) of holographic gratings up to 18 times was found. After that no strong RSE was found in other materials, to our knowledge. Are a-As$_2$S$_3$ films unique in this respect? Recently we also have explored the relaxation of HG in azobenzene molecular K-RJ-9 [(5,5,5-triphenylpentyl 4-(4-(bis(5,5,5-triphenyl-pentyl)amino) phenyl diazenyl) benzoate] molecular glassy film [1]. RSE of HG was found there. Interestingly, RSE of HG was more pronounced in reflection mode readout rather than in the transmission mode readout.

In this paper, we have experimentally studied the dark relaxation of transmission HG in two azobenzene molecular glassy films synthesized in our faculty and in one amorphous chalcogenide film varying recording beam polarizations and HG period. It was found that these factors indeed influence...
the relaxation. Besides, the glass transition temperature of the sample was found to have a strong effect. RSE of HG was observed in some cases but not as strong as in [4]. The observed HG relaxation properties are discussed in terms of post writing mass transfer initiated by mechanical stress periodically distributed in space after the HG recording. Previously reported results [1] partially also are included in discussion for generality.

2. Experiments and results
Studies of transmission holographic grating relaxation (recorded with s-s, p-p, s-p, L-L, L-R laser beam polarizations) have been carried out in organic molecular azobenzene glassy films W-50, W-75, and in a chalcogenide glassy a-As$_2$S$_3$ film (the latter provided by Dr.J.Teteris from the Institute of Solid State Physics, University of Latvia). The precise chemical notation of the films and the chemical structure of molecules of azobenzene films are given in Figs.1 and 2. Films were spin-coated onto the glass substrates. Amorphous chalcogenide As$_2$S$_3$ film was thermally evaporated onto the glass substrate. Its bandgap was $E_g=2.39$ eV, corresponding to $\lambda=519$ nm. Glass transition temperature $T_g$, long wave length absorption band maximum location, $\lambda_{\text{max}}$, and thickness of the samples, $d$, are given in the Table 1. There, data for the sample K-RJ-9 studied previously in [1] are also included for comparison and for further discussion.

![Fig.1. Sample W-50 –azobenzene molecular glassy film: 2-(2-(4-(4-(bis(2-(trityloxy)ethyl) amino) phenyl)diazenyl) styryl)-6-styryl-4H-pyran-4-ylidene)-2H-indene-1,3-dione. Donor group is on the left side from the azobenzene, acceptor group is on the right side.](image1)

![Fig.2. Sample W-75 (also IWK-2D) – azobenzene molecular glassy film: 2-(3-(4-(4-(bis(2-(trityloxy)ethyl) amino)phenyl)diazenyl) styryl)-5,5-dimethylcyclohex-2-enylidene). . Donor group is on the right side from the azobenzene but the acceptor group is on the left side.](image2)

| Sample       | W-50 | a-As$_2$S$_3$ | W-75 | K-RJ-9 |
|--------------|------|--------------|------|--------|
| $T_g$, $^\circ$C | 176  | 187          | 105  | 66     |
| $\lambda_{\text{max}}$, nm | 478  | 519          | 504  | 457    |
| $d$, $\mu$m   | 1.5  | 12           | 3    | 2      |

HG with the periods ($\Lambda$) of 0.50, 2.0 and 8.6 $\mu$m were studied in these films. Recording wavelength was 532 nm and the readout wavelength was 632.8 nm. Recording light intensity was 1.76 W/cm$^2$, the recording beam powers were equal. The main experimental setup is shown in Fig.3.
Fig. 3. The main experimental setup for HG recording and readout in the case of circular recording beam polarizations. Other wave plates were inserted in the case of other polarizations. A photo diode was measuring the diffracted beam power, the B-photo diode was measuring the incident beam power. Their ratio gave the diffraction efficiency.

The experimental procedure was as follows. First, HG were recorded until the maximum diffraction efficiency (DE) or (in the case of samples W-50 and a-As$_2$S$_3$) until the maximum self-diffraction efficiency [5] was reached. Then DE at 632.8 nm (DE$_{initial}$) was measured in all cases and the relative DE $\xi = DE/DE_{initial}$ was monitored periodically during the relaxation time in the dark. The experimental relative DE relaxation time dependences are presented in Figs. 4-8. Polarizations C-1 and C-2 in Figs. 4, 5 corresponded to L-L and L-R, respectively, but they were slightly elliptical for technical reasons.

Fig. 4. Sample W-50. Relative DE relaxation time dependences for different recording polarizations. $\Lambda = 2.0 \mu$m.

It is seen from Figs. 4-8 that relaxation curves were changing non-monotonically, with oscillations. DE relaxation behaviour depended on recording beam polarizations. In some cases of the sample W-75 RSE was observed. DE relaxation time dependences for sample K-RJ-9 has been presented in our previous study [1].
Fig. 6. Sample W-75. Relative DE relaxation time dependences for different recording polarizations. Λ = 0.50μm.

Fig. 7. Sample W-75. Relative DE relaxation time dependences for different recording polarizations. Λ = 2.0μm.

Fig. 8. Sample W-75. Relative DE relaxation time dependences for different recording polarizations. Λ = 8.6 μm.

The obtained results are summarized in Tables 2-7. There, the initial DE, the mean square deviation σ of relative DE and the extremal relative DE deviation Δξextr = ξextr-1 are given. The mean square deviation was calculated according to the formula

$$\sigma = \sqrt{\frac{1}{N} \sum_{n=1}^{N} (\xi_n - 1)^2}$$

where N is the number of experimental points for each DE relaxation curve.

| Table 2. DE relaxation parameters of the sample W-50 at Λ = 2.0 μm. |
|---------------------------------------------------------------|
|                  s-s    |   p-p    |   s-p    |   L-L    |   L-R    |
| initial, %       | 4.0      | 10.1     | 5.2      | 7.0      | 17.0     |
| σ               | 0.15     | 0.055    | 0.066    | 0.041    | 0.066    |
| Δξextr          | -0.22    | -0.10    | -0.13    | -0.08    | -0.14    |

| Table 3. DE relaxation parameters of the sample a-As₂S₃ at Λ = 2.0 μm. |
|---------------------------------------------------------------|
|                  s-s    |   p-p    |   s-p    |   L-L    |   L-R    |
| initial, %       | 17.0     | 17.0     | 5.7      | 15.0     | 13.0     |
| σ               | 0.15     | 0.088    | 0.21     | 0.051    | 0.12     |
| Δξextr          | -0.25    | -0.15    | -0.37    | -0.07    | -0.15    |
### Table 4. DE relaxation parameters of the sample W-75 at \( \Lambda = 0.50 \) μm.

|          | s-s | p-p  | s-p  | L-L  | L-R  |
|----------|-----|------|------|------|------|
| DE\(_{\text{initial}}\), % | 0.085 | 1.1  | 0.0070 | 0.093 | 0.14 |
| \( \sigma \)  | 0.22 | 0.12 | 0.46  | 0.10  | 0.33 |
| \( \Delta \xi_{\text{extr}} \) | -0.27 | -0.21 | -0.55 | 0.13  | 0.37 |

### Table 5. DE relaxation parameters of the sample W-75 at \( \Lambda = 2.0 \) μm.

|          | s-s | p-p  | s-p  | L-L  | L-R  |
|----------|-----|------|------|------|------|
| DE\(_{\text{initial}}\), % | 0.81  | 9.9  | 0.70 | 8.0  | 24.0 |
| \( \sigma \)  | 0.10 | 0.23 | 0.23 | 0.27 | 0.25 |
| \( \Delta \xi_{\text{extr}} \) | 0.09  | -0.31 | 0.35 | -0.30 | -0.33 |

### Table 6. DE relaxation parameters of the sample W-75 at \( \Lambda = 8.6 \) μm.

|          | s-s | p-p  | s-p  | L-L  | L-R  |
|----------|-----|------|------|------|------|
| DE\(_{\text{initial}}\), % | 1.63 | 4.7  | 0.74 | 4.4  | 8.5  |
| \( \sigma \)  | 0.074 | 0.20 | 0.19 | 0.10 | 0.088 |
| \( \Delta \xi_{\text{extr}} \) | -0.11 | 0.32 | -0.36 | 0.14 | 0.10 |

### Table 7. DE relaxation parameters of the sample K-RJ-9 in the case of p-p recording polarizations for three HG periods (DE\(_{\text{initial}}\) values are taken from [1]).

|          | \( \Lambda = 0.50 \) μm | \( \Lambda = 2.0 \) μm | \( \Lambda = 8.6 \) μm |
|----------|------------------------|------------------------|------------------------|
| DE\(_{\text{initial}}\), % | 0.21 | 23 | 9.5 |
| \( \sigma \)  | 0.86 | 0.91 | 0.15 |
| \( \Delta \xi_{\text{extr}} \) | -0.98 | -0.37 | 0.18 |

### 3. Discussion of the observed regularities

Let us analyse the effects of HG period (\( \Lambda \)), recording beam polarizations and of materials glass transition temperature (\( T_g \)) on the recording efficiency characterized by DE\(_{\text{initial}}\) and recording stability characterized by DE deviations \( \sigma \) and \( \Delta \xi_{\text{extr}} \). Lower deviations correspond to higher HG stability.

#### 3.1. Effect of HG period on the recording efficiency

Arrangement of HG periods (in micrometres) in the decreasing DE order for different polarizations gives the following sequences. W-75, s-s: 8.6, 2.0, 0.50; p-p: 2.0, 8.6, 0.50; L-L: 2.0, 8.6, 0.50; L-R: 2.0, 8.6, 0.50. K-RJ-9, p-p: 2.0, 8.6, 0.50. As seen, the most efficient HG period depends on recording polarizations. Most often optimal is \( \Lambda = 2.0 \)μm.

#### 3.2. Effect of recording polarizations on its efficiency

Arrangement of polarizations in the decreasing DE order gives the following sequences. W-75, \( \Lambda = 0.50 \) μm: p-p, L-R, L-L, s-s, s-p; \( \Lambda = 2.0 \) μm: L-R, p-p, L-L, s-s, s-p; \( \Lambda = 8.6 \) μm: L-R, p-p, L-L, s-s, s-p. W-50, \( \Lambda = 2.0 \) μm: L-R, p-p, L-L, s-s, s-p. Amorphous As\(_2\)S\(_3\), \( \Lambda = 2.0 \) μm: p-p, s-s, L-L, L-R, s-p. The most efficient recording polarizations depend on the material and HG period. Yet, in most cases they are L-R or p-p. L-R polarizations most often are the most efficient in azobenzene films thus supporting the azochromophore orientation mechanism in the light electrical field.
3.3 Effect of HG period on the recording stability

Arrangement of periods in the increasing $\Delta \xi_{\text{extr}}$ order gives the following sequences. W-75, $s-s$: 8.6, 2.0, 0.50; $p-p$: 0.50, 8.6, 2.0; L-L: 0.50, 8.6, 2.0; L-R: 8.6, 2.0, 0.50. As seen, HG are the most stable in the case of 8.6 and 0.50 $\mu$m HG periods. As a rule, these HG periods do not coincide with the most efficient HG recording period.

3.4 Effect of recording beam polarizations on its stability

Arrangement of the polarizations according to increasing $\sigma$, $\Delta \xi_{\text{extr}}$ gives the following sequences. W-75, $\Lambda = 0.50 \mu$m: $L-L$, $p-p$, $s-s$, $L-R$, $s-p$; $\Lambda = 2.0 \mu$m: $s-s$, $p-p$, $s-p$, $L-L$, $L-R$, $p-p$, $s-p$. W-50, $\Lambda = 2.0 \mu$m: $L-L$, $p-p$, $s-p$, $L-R$, $s-s$. Amorphous As$_2$S$_3$, $\Lambda = 2.0 \mu$m: $L-L$, $p-p$, $L-R$, $s-s$, $s-p$. One can see that the recording stability is the highest in the case of $L-L$ and $s-s$ polarizations. They do not correspond to the most efficient recording polarizations $L-R$ and $p-p$. In fact, we can speak about the anticorrelation of recording efficiency and stability in our experiments.

3.5 Effect of material’s glass transition temperature on the HG recording efficiency and stability

Fig. 9. Materials initial (maximum) DE and mean square deviation $\sigma$ of relative DE versus $T_g$ in the case of $p-p$ HG recording at $\Lambda = 2.0 \mu$m. The red curve (triangles) corresponds to $\sigma$, but the blue one (circles) to DE.

The tendency can be seen in Fig. 9 that the lower $T_g$ value of the material corresponds to the lower recording stability. This is an indication to the possible role of the mass transfer in the HG relaxation process because the lower $T_g$ corresponds to the lower viscosity. A similar $T_g$ dependence was recently observed in azobenzene molecular glassy films with respect to the stability of nonlinear optical second-order susceptibility [6].

3.6 Effect of the sample thickness on the recording stability

If one compares the DE deviations $\sigma$, $\Delta \xi_{\text{extr}}$ in the case of materials with close glass transition temperatures (Table 1) but with strongly different thicknesses such as W-50 and a-As$_2$S$_3$, one can easily see (Tables 2,3) that larger sample thickness facilitates lower stability.

3.7 HG relaxation mechanism

Non-monotonical DE changes after the recording which can be quite large (Figs. 4-8) are not because of the temperature changes in the laboratory. This temperature was monitored during the experiments and changed from 18.5 to 22.6°C. Calculations of thermally induced refractive index changes have shown that they are too small to cause the observed DE changes. Besides, no correlation was observed between the temperature and DE changes. In our opinion, material relaxation is responsible for DE changes. After the HG recording the film is thermodynamically unstable and tends to the thermodynamic equilibrium. The driving force behind the relaxation is the mechanical stress periodically distributed in space as already suggested in [2,4]. It arises during the HG recording due to
the trans-cis photoisomerization in azobenzene molecular glassy films [1,3,5], and due to the photoinduced As-As bond breaking and As-S bond formation in a-As$_2$S$_3$ film [4]. In the case of azobenzene films one reason of arising such stress distribution is that cis-isomer occupies larger space than trans-isomer [3]. This conclusion is supported by the observed tendency (see Sections 3.3 and 3.6) that larger HG stability corresponds to smaller sample thickness, $d$, and larger HG period, $\Lambda$. It is in accordance with structure perturbation theory [7] by which one can show that the mechanical stress increase due to HG is

$$\Delta \sigma = \text{const} \frac{d}{\Lambda}.$$ 

As the result, the thermostimulated rearrangement of azobenzene chromophores together with their environment takes place resulting in the mass transfer. HG recording stability dependence on $T_g$ supports this conclusion. Near the surface, there is enhanced cooperative segmental mobility and a reduced effective $T_g$ [8]. Therefore, post recording mass transfer is expected to be stronger on the surface than in the volume. Relaxation difference was indeed observed in transmission and reflection modes [1]. Efficient photo-induced mass transfer has also been observed in a-As$_2$S$_3$ films [9]. Charge transfer and the interaction of molecular dipoles may also take place.

RSE effect observed in this study was much weaker than in fresh a-As$_2$S$_3$ films [3]. The reason may be that photoinduced structural changes in fresh a-As$_2$S$_3$ films are much stronger than in relaxed a-As$_2$S$_3$ films used in this study and the structure changes in azobenzene molecular glassy films due to trans-cis photoisomerization. Of course, details of relaxation remain to be established in numerous further studies.

4. Conclusions
Holographic recording efficiency and stability depend on the material, HG period and recording beam polarizations.
Anticorrelation has been observed of HG recording efficiency and stability. Recording was efficient with $p$-$p$ or $L$-$R$ polarizations at 2.0 $\mu$m HG period whereas it was stable with $s$-$s$ or $L$-$L$ polarizations at 8.6$\mu$m HG period.
An approximate anticorrelation has been observed between recording stability and material’s glass transition temperature, $T_g$.
Relaxational self-enhancement (yet not large) of HG has been found in azobenzene molecular glassy films W-75 and K-RJ-9. In the latter case, also in the reflection mode.
HG relaxation in studied films mainly proceeds by post-recording mass transfer under the influence of mechanical stress.

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