Effect of holographic grating period on its relaxation in a molecular glassy film

A Ozols, P Augustovs, V Kokars, K Traskovskis, and D Saharov

Faculty of Material Science and Applied Chemistry, Riga Technical University, Azenes iela 14/24, LV-1007, Riga, Latvia

E-mail: aozols@latnet.lv

Abstract. Holographic grating (HG) relaxation has been experimentally studied in 5,5,5-triphenylpentyl 4-((4-(bis(5,5,5-triphenylpentyl)amino)phenyl)diazemyl)benzoate molecular glassy film for HG periods (\(\Lambda\)) of 0.50, 2.0 and 8.6 \(\mu\)m. A strong effect of HG period on its relaxation is found manifesting itself differently in the volume and on the surface. The volume part of HG is fairly stable during 40 days if \(\Lambda > 0.50\) \(\mu\)m whereas the surface part of HG (most probably, surface relief grating) exhibits relaxational self-enhancement which is maximal at \(\Lambda = 8.6\) \(\mu\)m. It is proposed that thermostimulated directional mass transfer in the process of relaxation can be responsible for this relaxational self-enhancement. Weak HG recording and relatively fast HG decay takes place at \(\Lambda = 0.50\) \(\mu\)m. Therefore, effective chromophore photoorientation domain of about 0.2 \(\mu\)m is supposed.

1. Introduction

Azobenzene-containing materials have found numerous applications in optoelectronic devices, including those based on hologram recording [1-4]. However, the relaxation processes after the hologram recording has been studied much less than the recording itself [5]. The studies of relaxation processes are not only practically important. They are also of large physical interest because rheological processes, especially in disordered media, are far from clear. Relaxational (dark) self-enhancement (RSE) of holograms is an unexpected manifestation of rheological processes after the hologram recording. It was for the first time reported by R.G.Brandes et al in 1970 in bromide-doped As-S films [6]. Further RSE was reported and studied in additively-coloured KBr crystals [7] and a-As\(_2\)S\(_3\) films [8]. Detailed studies of RSE in undoped a-As\(_2\)S\(_3\) films have been made by A.Ozols et al [7]. Record diffraction efficiency increase up to 18 times in a relaxation process was found there. RSE of holographic gratings was later reported and studied also in Bi\(_{12}\)Ti\(_{0.76}\)V\(_{0.24}\)O\(_{20}\) crystals [10], in dichromated gelatin and polyvinyl alcohol films [11], and in photopolymers [12].

In this paper, we have experimentally studied holographic grating (HG) relaxation in an azobenzene molecular glassy thin film choosing different HG periods. The obtained results show that relaxation processes strongly depend on HG period and that relaxation processes are different in the volume and on the surface. Noticeable RSE was observed only on the surface.

1 To whom any correspondence should be addressed.
2. Samples and experiments

Two 2 \mu m thick samples of 5,5,5-triphenylpentyl 4-((4-(bis(5,5,5-triphenyl-pentyl)amino) phenyl) diazenyl) benzoate molecular glassy film (briefly \textbf{K-RJ-9} film) were identically prepared by spin-coating and used for experiments. Their glass transition temperature was \( T_g = 66^\circ \text{C} \). Film consisted of molecules bound together by weak van der Waals forces. Chemical structure of molecules is shown in Fig.1. In Fig.2 absorption spectrum is presented. \textbf{K-RJ-9} molecule is a push-pull molecule of donor-acceptor type consisting of central \(-\text{N}=\text{N}-\) azochromophore groups surrounded by donor \((\text{=N})\) and acceptor \((\text{ester O} = \text{C-O})\) groups. This molecular structure enables intramolecular charge transfer facilitating \textit{trans-cis} photoisomerization.

We have used the following experimental procedure. First, full HG recording was made by two equal power symmetrically incident 532 nm laser beams monitoring both transmission self-diffraction efficiency (SDE\(_t\)) and reflection self-diffraction efficiency (SDE\(_r\)) to evaluate the efficiency of recording and its time scale (Fig.3). Self-diffraction efficiencies were defined in the following way: 

\[
\text{SDE}_t = \frac{P_{dt}}{P_i}, \quad \text{SDE}_r = \frac{P_{dr}}{P_i}
\]

where \( P_{dt} \) and \( P_{dr} \) are the beam powers diffracted in the plus first transmission and reflection orders, respectively, for the upper recording beam, \( P_i \) is the incident lower recording beam power.

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![Chemical structure of a K-RJ-9 molecule.](image1)

![Absorption spectrum of K-RJ-9 in methylene chloride (CH\(_2\)Cl\(_2\)) solution.](image2)

![The first experimental setup.](image3)

![The second experimental setup.](image4)
Second, transmission HG with the periods ($\Lambda$) of 0.50, 2.0 and 8.6 µm were recorded with two equal symmetrically incident 532 nm laser beams and read out simultaneously by a 632.8nm beam until the maximum readout light transmission diffraction efficiency (DE) defined as $DE_t = \frac{P_{dt}}{P_i}$ ($P_{dt}$ being the light power diffracted in the minus first transmission order, $P_i$ being the incident light intensity) was reached (Fig.4). Simultaneously, reflection DE ($DE_r = \frac{P_{dr}}{P_i}$) was measured, here $P_{dr}$ being the light power diffracted in the plus first reflection order. After the recording, $DE_t$ and $DE_r$ were continuously monitored during about 30 minutes. Further, $DE_t$ and $DE_r$ measurements of recorded HG were repeated during 40 days.

Klastech DENICAFC 532-300 diode pumped solid state laser ($\lambda_1 = 532$ nm) with a coherence length exceeding 100 m was used for HG recording. Recording light intensity was 0.40-0.46 W/cm$^2$. Melles Griot 25LH928-230 He-Ne gas laser ($\lambda_2 = 632.8$ nm) was used for HG readout. Readout beam power varied in the 0.27-1.8 mW, mainly it was 0.50 mW. It was proved not to influence HG. All the diffracted light powers was measured by Ophir Laserstar laser power meter and stored in the PC memory. Diffraction efficiency time dependences in characteristic cases are presented in the next section. All the measurements started from zero at 30 seconds. The estimated measurement errors did not exceed 5%.

3. Results and discussion
The main experimental results are presented in Figs.5-11.

![Fig. 5. Transmission SDE exposure time dependence. $\lambda_1 = \lambda_2 = 532$ nm, $\Lambda = 2.0$ µm.](image)

![Fig. 6. Reflection SDE exposure time dependence. $\lambda_1 = \lambda_2 = 532$ nm, $\Lambda = 2.0$ µm.](image)

![Fig. 7. Transmission DE exposure (until the green arrow) and relaxation (after the arrow) time dependences. $\lambda_1 = 532$ nm, $\lambda_2 = 633$ nm, $\Lambda = 2.0$ µm. This quasiconstant relaxation was observed also further 24 minutes (not shown).](image)

![Fig. 8. Reflection DE exposure (until the green arrow) and relaxation (after the arrow) time dependences. $\lambda_1 = 532$ nm, $\lambda_2 = 633$ nm, $\Lambda = 2.0$ µm. This quasiconstant relaxation was observed also further 24 minutes (not shown).](image)
**Fig. 9.** Transmission DE exposure (until the green arrow) and relaxation (after the arrow) time dependences. \( \lambda_1 = 532 \text{ nm}, \lambda_2 = 633 \text{ nm}, \Lambda = 0.50 \mu \text{m}. \) This quasiconstant relaxation was observed also further 24 minutes (not shown). Note the weak oscillatory recording behaviour! It was impossible to measure \( \text{DE}_r(t) \) for such a small grating period because the +1st and higher diffraction orders do not exist.

**Fig. 10.** Transmission DE relaxation time dependences for the gratings periods of 2.0 \( \mu \text{m} \) (blue rectangles), 8.6 \( \mu \text{m} \) (red triangles) and 0.5 \( \mu \text{m} \) (black circles). In the case of 0.5 \( \mu \text{m} \) period 100 times larger \( \text{DE}_t \) values are shown. Rectangles, triangles and circles are experimental points. Lines are to guide the eye.

**Fig. 11.** Reflection DE relaxation time dependences for the gratings periods of 2.0 \( \mu \text{m} \) (blue rectangles) and 8.6 \( \mu \text{m} \) (red triangles). Rectangles, triangles and circles are experimental points. Lines are to guide the eye.

The \( \text{DE}_t(t) \) and \( \text{DE}_r(t) \) dependences at \( \Lambda = 8.6 \mu \text{m} \) were qualitatively the same as for \( \Lambda = 2.0 \mu \text{m} \). Therefore, they are not shown to save the restricted space.

The following observations can be made from Figs. 5-11 supported also by other curves not shown.

1. \( \text{SDE}_t(t) \) and \( \text{SDE}_r(t) \), kinetic dependences are markedly different.
2. HG recording at \( \Lambda = 0.50 \mu \text{m} \) is much weaker and with oscillatory \( \text{DE}_t(t) \) dependence when compared to the cases with \( \Lambda = 2.0 \mu \text{m} \) and \( \Lambda = 8.6 \mu \text{m} \) (Figs. 7-9).
3. All HG are practically stable immediately after the recording during 30-40 minutes, as shown by kinetic \( \text{DE}_t(t) \) and \( \text{DE}_r(t) \) curves Figs.5-9).
4. HG relaxation as judged by \( \text{DE}_r(t) \) dependences strongly depend on HG period \( \Lambda \) (Fig.10):
1) fast (in 10 days) decay in the case of $A = 0.50 \mu m$;  
2) nonmonotonical HG relaxation in the case of $A = 2.0 \mu m$;  
3) slight increase in the case of $A = 8.6 \mu m$.

5. HG relaxation as judged by $\text{DE}_r(t)$ dependences also depend on $A$ but in different fashion when compared to $\text{DE}_r(t)$ case. RSE takes place and it is much more pronounced for $A = 8.6 \mu m$ than for $A = 2.0 \mu m$ (Fig.11). In 10 days $\text{DE}_r(t)$ increases more than 1.4 times $A = 8.0 \mu m$ whereas it is approximately constant at $A = 2.0 \mu m$.

6. Diffraction efficiency dependences on HG period are different for transmission and reflection cases: $\text{DE}_r(A = 2.0 \mu m) > \text{DE}_r(A = 8.6 \mu m)$ whereas $\text{DE}_r(A = 2.0 \mu m) < \text{DE}_r(A = 8.6 \mu m)$ (Figs. 10 and 11).

We know from literature [2,4,13] and our previous experiments (e.g., [14]) that HG recording in azocompound films at 532 nm is based on trans-cis photoisomerization including chromophore photoorientation perpendicularly to light electric field vector and mass transfer. Repeated trans-cis-trans photoisomerization cycles soften the matrix, especially near the surface [13].

From observations 2 and 4 we conclude that spatial resolution limit of our K-RJ-9 film is close to 0.5 $\mu m$. Therefore, we suppose that effective photoreorientation domain is about 0.2 $\mu m$ (a little bit less than $A/2$ if we suppose that there should be at least two photoreorientation domains per period to have recording) and it is much larger than the size of molecule (about 30 Å) due to the cooperation motion of molecule’s environment.

Observations 1, 4, 5, 6 show that photoinduced HG recording processes and HG relaxation processes are different at the surface (determining mainly SDE, and DE) and in the volume (determining mainly SDE, and DE). Thus a HG consists of two components-surface HG, most probably surface-relief grating (SRG), and volume grating. SRG are recorded on the surface, and volume phase gratings in the volume. This situation was observed also in our previous experiments with other azocompound films [15]. It was reported in amorphous chalcogenide As-S-Se films, too [16].

Thermostimulated cis-trans isomerization and the motion of molecules due to the dipolar interactions and under influence of mechanical stresses caused by HG recording (cis-isomer is bulkier than trans-isomer[4]) are, most probably, the main relaxation processes of HG. Motion of molecules in our K-RJ-9 film is facilitated by fact that this is a molecular glassy film in which molecules are bound together only by weak van der Waals forces. As a result, directional mass transfer is possible enhancing SRG. The possibility of such process is considered also by O.N. Oliveira, J.Kumar, L.Li and S.K. Tripathy in 2002 [4]. However, it should be confirmed by AFM measurements.

Higher DE, at $A = 8.6 \mu m$ when compared to $A = 2.0 \mu m$ (observation 6) can be explained by the specific backward diffraction properties of SRG [17].

RSE properties of our K-RJ-9 film are quite different from those of a-As$_2$S$_3$ film [9]. RSE in a-As$_2$S$_3$ is much stronger. DE increase up to 18 times was observed at $A = 1.0 \mu m$. In K-RJ-9 film RSE takes place only at reflection, and DE increase only up to 1.5 times was observed at much larger period of $A = 8.6 \mu m$. RSE in a-As$_2$S$_3$ is initiated by glassy layer network crosslinking during the HG recording by photoinduced structural changes, and it is explained by periodically distributed stress relaxation model. Compressive stress produced in HG maxima pushes unfilled sites towards minima thus causing density modulation proportional to $1/A$ [9]. No such dependence is found in K-RJ-9 film, thus the role of a mechanical stress is different.

4. Conclusions
HG period strongly influences its relaxation. This effect is different at the surface (corresponding to the SRG) and in the bulk (corresponding to the volume grating).
RSE of SRG is found whereas volume gratings are fairly stable during 40 days if the HG period is not less than 2.0 μm. It is proposed that directional mass transfer in the process of relaxation can be responsible for RSE of SRG. However, this proposal should be confirmed by AFM measurements.

Fast HG decay and weak HG recording takes place at 0.5 μm HG period. Therefore, we suppose that effective photoreorientation domain is about 0.2 μm.

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