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Holographic recording of surface relief gratings in stilbene azobenzene derivatives at 633 nm

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Abstract. Holographic recording in stilbene azobenzene derivatives by He-Ne 633 nm laser light has been experimentally studied. It was found that surface relief gratings (SRG) can be recorded by red light. Usually shorter wavelengths are used to induce the trans-cis photo-isomerization in organic materials. SRG with 2 µm period and an amplitude of 130 nm have been recorded with 0.88 W/cm² light in about 20 minutes in amorphous films of 3-(4-(bis(2-trityloxy)ethyl)amino)phenyl)-2-(4-(2-bromo-4-nitrophenyl)diazanyl)phenyl)acrylonitrile spin-coated on glass substrates. Self-diffraction efficiency up to 17.4% and specific recording energy down to 114 J/(cm²%) were measured. The recorded SRG were stable as proved by subsequent AFM measurements. The photo-induced changes in absorption spectra did not reveal noticeable signs of trans-cis transformations. Rather, spectrally uniform bleaching of the films took place. We conclude that a photothermally stimulated photo-destruction of chromophores is responsible for the SRG recording. The recording of stable SRG in the stilbene azobenzene derivatives we studied is accompanied by the recording of relaxing volume-phase gratings due to the photo-orientation of chromophores by the linearly polarized recording light. It should also be noted that holographic recording efficiency in stilbene azobenzene derivatives exhibit an unusual non-monotonic sample storage-time dependence presumably caused by the peculiarities of structural relaxation of the films.

1. Introduction
Holographic recording in stilbene azobenzene derivatives by He-Ne 633 nm laser light has been experimentally studied. Azocompounds are among the most efficient materials for holographic recording [1,2,3,4] that we have studied [5,6]. Commonly, blue and green light is used for recording in these materials because the absorption spectra of azocompounds have maxima at these wavelengths [1]. In this case a trans-cis-trans transformation [1,2] of the material under laser radiation takes place. In the red spectral range absorption is considerably lower yet recording is possible [5, 6]. The mechanism of such recording is unclear and this fact creates the motivation for further research. Discovery of efficient materials for optical recording of information in the red part of spectrum will allow using cheaper red lasers for recording instead of more expensive UV, blue and green lasers. As is known from laser theory, the lasing processes dictates that energy requirements scales as $\sim \lambda^{-4}$ where $\lambda$ is the wavelength of the laser radiation. Besides, with red light higher-quality of volume-

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holographic optical elements can be achieved because of the more homogeneous exposure through the volume.

In this paper, holographic grating (HG) recording at 633 nm has been experimentally studied in organic molecular glasses of stilbene azobenzene derivatives. The HG recording efficiency was measured as a function of the sample storage time before recording. The photo-induced changes in absorption spectra were measured. Atomic force microscope (AFM) measurements were made as well. It was found that efficient surface-relief grating (SRG) recording is possible and that material relaxation has a strong and non-monotonic influence on the holographic recording efficiency.

2. Samples

We have studied different chemical compositions of stilbene azobenzene derivatives. However, in this paper we describe only the results for the most efficient composition whose full chemical designation and chemical structure is given in figure 1. Stilbene azobenzene derivative films were applied to glass substrates by spin-coating. The chromophore substance was dissolved in dichloromethane. A drop of the solution was placed on the rotating glass plate where it was distributed rather evenly. After evaporation of dichloromethane the film formed. Absorption spectrum of the sample is shown in figure 2.

![Figure 1. The structural formula of the studied most efficient composition 3-{4-[bis(2-trityloxyethyl)amino]fenyl}-2-{4-{(2-bromo-4-nitrophenyl)diazenyl}phenyl}acrylonitrile.](image)

3. Experimental measurements

The holographic measurements were made with the setup shown in figure 3. Two equally strong He-Ne laser beams $P_R$ and $P_S$ symmetrically incident on the sample recorded the transmission HG. A LGN-222 type He-Ne laser (produced in Ukraine) operating in TEM$_{00}$ mode with horizontal linear polarization was used for recording and readout at $\lambda$=632.8 nm. The diffraction efficiency (DE) could not be measured directly due to the fast oscillations of diffracted-beam power that were observed during exposure. Therefore, the measurements had to be made without interruption of one beam. Therefore, we have measured self-diffraction efficiency (SDE) at $PR \neq 0$, $PS \neq 0$ instead of DE. Light power measurements were made using a Gentec Solo power meter (Canada). The measurement results were stored in its memory and processed after the recording. This registration method allowed us to measure fast SDE changes during the exposure.
Figure 2. Absorption spectrum of the sample with chemical composition shown in figure 1. \( D \) is optical density, \( \lambda \) is wavelength. Vertical thick line shows the 632.8 nm line of the He-Ne laser by which the recording and readout of HG were made. Absorption maxima are red-shifted in comparison with azobenzene [1] to be more red-light sensitive.

Figure 3. Experimental set-up. 1- laser; 2 – beam splitter; 3 - mirrors; 4 – sample; 5 – photodetector; \( P_S, P_R \) – incident beams; \( \Theta \) – angle of incidence; \( P'_S, P'_R \) – diffracted beams; \( \Lambda \) – period of the recording interference pattern and the HG.

We defined SDE according to the formula:
\[
SDE = \frac{P_d(k=-2,l=-1)}{P_i},
\]

where \( P_d(k=-2,l=-1) \) is the sum of the minus-first-order diffracted power of the \( P_S \) beam and of the minus-second-order diffracted power of the \( P_R \) beam, \( P_i \) is the incident readout light power. If \( P_R = 0 \), SDE=DE. A detailed optical scheme explaining the recording and readout processes is given in figure 4. The connection between SDE and DE is discussed below.

Non-focused laser beams with a 1/e^2 (defined by the intensity decrease from the centre) diameter of 1.5 mm were directed to the same point on the sample and formed interference pattern there. The holographic grating period was 2 \( \mu \)m. It was calculated according to the formula

\[
\Lambda = \frac{\lambda}{2 \sin \Theta},
\]

where \( \Lambda \) is the holographic grating period, \( \lambda \) the recording light wavelength, \( \Theta \) the angle of incidence of the recording beams. The graphs of the SDE exposure time dependences were created using measurements results.

For each SDE graph the specific recording energy \( W_{\text{max}} \) [J/cm^2%/] was calculated according to the formula

\[
W_{\text{max}} = \frac{\eta I t}{\eta_{\text{max}}},
\]
where $I$ is the average recording light intensity, $t$ is the exposure time corresponding to the maximal DE $\eta_{\text{max}}$ (actually, maximal SDE, see below). The average recording light intensity was defined by the formula

$$I = \frac{4(P_R + P_S)}{\pi d^2},$$  \hspace{1cm} (4)

where $P_S$ and $P_R$ are the powers of the recording beams, $d$ is the $1/e^2$ laser beam diameter. The recording light intensity varied from 0.74 to 0.98 W/cm².

As mentioned, the self-diffraction efficiency (SDE) was used to estimate the diffraction efficiency (DE). According to calculations made on the basis of thin-hologram theory [7] SDE and DE are related by the expression

$$SDE = \frac{P_R}{P_S} DE_{(-1)} + \frac{P_R}{P_S} DE_{(-2)} + 2 \left( \frac{P_R}{P_S} \right) DE_{(-1)} DE_{(-2)} \left( \frac{1}{2} \cos(\Phi_S - \Phi_R + \Phi_{S(-1)} - \Phi_{R(-2)}) \right),$$  \hspace{1cm} (5)

where $P_R$ and $P_S$ are the incident beams with equal power, $DE_{(-1)}$ is the minus first-order diffraction efficiency, $DE_{(-2)}$ is the minus second-order diffraction efficiency of $P_R$ beam, $\Phi_S$ and $\Phi_R$ are the phases of the zeroth-order diffracted $P_S$ and $P_R$ beams respectively, $\Phi_{S(-1)}$ and $\Phi_{R(-2)}$ are the phase of the first-order diffracted wave $P_S$ and the phase of the minus-second-order diffracted wave $P_R$. The first term of the sum in the expression is the diffraction efficiency that needs to be estimated. The third term describes the instability of the induced grating, that can be caused by equipment instability or (and) molecules moving under the influence of light. We have estimated that in our experiments the SDE values were in the range from 0.5 $DE_{(-1)}$ to 1.6 $DE_{(-1)}$.

The photo-induced changes of absorption spectra were measured to elucidate the recording mechanism. Measurements were performed with PERKIN ELMER Instruments Lambda35 UV-VIS spectrometer. There were 25 records made with a diameter of 1.93 mm in the sample area of 5x5 mm² to fit the entrance slit width of the spectrometer. Apart from holographic and spectral measurements the surface relief of the samples was studied with a scanning atomic force microscope, VEECO model SPMII (USA).

4. Results and discussion

The measurement results are presented in figures 5 to 7. The maximum SDE value was 17.4%. Small dips in SDE time dependences (figure 5) are due to the non-monotonic nature of the chromophore photo-orientation counteracted by thermal back reactions. Large dips are due to the small instabilities of the recording setup causing small shifts of the recording interference pattern with respect to the recorded grating. This behavior was repeatable and follows from the expression (5).

It is also seen from the figure 5 that the sample storage time before recording significantly influences the recording efficiency. There exists an optimal storage time that enables the maximum efficiency, i.e., the DE and SDE maximum, and the specific recording energy minimum. This optimal sample storage time is about 50 days for sample No2 for which the data are presented. At 66 days the efficiency has decreased noticeably. The optimal storage time varies even for different samples of the same chemical composition. For the composition studied in this paper (of the figure 1) it varied from 6 days to 51 day. The physical mechanism of the storage-time effect is not yet clear. We believe that it is due to the peculiarities of structural relaxation of stilbene azobenzene derivatives which form organic molecular glasses consisting of pure chromophores having a large free volume.

AFM measurements (figure 6) show that a surface-relief grating (SRG) is recorded. SRG amplitudes as high as 113 nm has been achieved. The maximum SRG amplitude achieved (in epoxy-based polymers) to-date is 160 nm [9]. SRG was stable during a year as shown by repeated AFM
measurements. To our knowledge this is the first SRG recording using red light. It should also be noted that HG recording results in a large increase in surface roughness. The average roughness increased from 11 nm to 85 nm for the samples we studied.

In contrast to SRG, DE and SDE decreased in the course of storage. Thus we have concluded that complementary volume phase gratings are recorded simultaneously with SRG and relax in the course of the HG storage over several months. The phase character of these additional volume HGs is shown below by the absorption spectra. The conclusion about the volume-phase gratings is supported by the DE calculations of SRG according to the formula

$$\eta = \frac{\tau}{3} \left[ \frac{\pi(n-1)d_{\text{max}}}{\lambda \cos \theta_i} \right]^2, \quad (6)$$

where \( \tau \) is the transmittance of the grating, \( n \) its average refractive index, \( d_{\text{max}} \) is the amplitude of thickness modulation, \( \lambda \) the readout wavelength, \( \theta_i \) is the readout beam incidence angle inside the medium. This formula (6) was derived by us on the basis of thin-hologram theory [7]. The calculation at \( \tau = 0.398, n = 1.5, d_{\text{max}} = 113 \text{ nm}, \lambda = 633 \text{ nm}, \cos \theta_i = 1 \) gives \( \eta = 1.04 \% \), which is much less than the maximum SDE value of 17.4 %.

**Figure 5.** Self-diffraction efficiency (SDE) exposure-time dependences for different sample No2 storage times (marked by arrows) before the recording. The recording light intensity was 0.88 W/cm².
Figure 6. Surface relief and its profile in the central area of the recording. The SRG amplitude is 113 nm, the maximum surface-relief change is 226 nm.

The photo-induced changes in absorption of the sample during holographic recording are shown in figure 7. Photo-induced bleaching is mainly observed. As can be seen, the absorption changes at 633 nm are negligible and a pure phase recording took place. At shorter wavelengths amplitude recording can take place as well.

Figure 7 shows that optical density has decreased almost uniformly over the spectrum, except for a little increase at long wavelengths beyond 700 nm. This is in contrast with known trans-cis spectral transformations in UV and visible bands [8]. Besides, the cis-trans back reaction usually proceeds on time scales from seconds to hours [1,8], and, therefore, it was finished when the absorption spectra were measured about two months after recording. Thus, we cannot exclude the trans-cis photo-isomerization and the mass transfer by electric gradient force [1] or other mechanisms but these seem unlikely at 633 nm. Yet, further experiments are needed to draw a conclusion about the contribution of photo-isomerization. Mostly uniform reduction of the absorbance after recording can be explained by the photo-degradation, i.e., by chromophore destruction under irradiation during the recording process. For example, N-N bonds can be broken by 633 nm photons [9]. Photoablation is also possible, but it needs recording intensities higher than 1 W/cm² [9].

Calculations show that photo-degradation in our experiments can be photo-thermally stimulated. The photoinduced temperature increase of a thin film on a bulk substrate by a CW laser in the center of the beam is [10]
\[ \Delta T = \frac{Klr}{k}, \quad (7) \]

where \( K \) is the absolute absorption coefficient, \( I \) is light intensity, \( r = d/2 \) is the laser beam radius, \( k \) is the heat conductivity of the film. In our case \( K = 0.64, I = 0.88 \text{ W/cm}^2, r = 0.965 \text{ mm}, k = 0.08 \text{ W/mK} \) (the value for polystyrene which we assumed to be approximately equal to the unknown heat conductivity of our film) and \( \Delta T = 69 \text{ K} \). Thus the temperature of sample can be close to the glass transition temperature \( T_g = 94^\circ \text{C} \) of the film if the room temperature is \( 20^\circ \text{C} \).

There are different possible recording mechanisms of the complementary volume- phase HG. The most probable is the photo-orientation mechanism [5,6,9]. Chromophore groups and fragments of molecules that have dipole moments can change their orientations and spatial positions under the influence of linearly polarized light. As a result, the refraction and absorption indices change. A spatially periodic density modulation accompanying photo-degradation can also contribute. Practical aspects of efficient red- light SRG recording include simpler and cheaper production of holographic optical elements – gratings, couplers, waveplates, antireflection coatings, etc.

5. Conclusions

Efficient stable SRG recording with the surface relief modulation amplitudes up to 113 nm has been achieved in stilbene azobenzene derivatives at 633 nm. To our knowledge, this is the first direct SRG recording with red light. Usually, UV, blue or green light is used.

Photo-induced absorption spectra changes are consistent with assuming that photo-thermally stimulated degradation of the films is the main recording mechanism. However, the contribution of trans-cis photo-isomerization cannot be excluded.

SRG recording is accompanied by volume-phase holographic grating (HG) recording that slowly relaxes in the course of the sample storage over several months. These volume HGs are, most probably, recorded due to the photo-orientation of chromophores by linearly polarized \( p \)-light.

Holographic recording efficiency in stilbene azobenzene derivatives is a non-monotonic function of the sample storage time. An optimal storage time exists after sample preparation that enables the maximum efficiency. This optimal storage-time is not uniquely determined by the chemical composition because even for the same composition it can be different. Most probably, this storage time effect is caused by peculiarities in the structural relaxation of stilbene azobenzene derivatives which form organic molecular glasses consisting of pure chromophores with a large free volume.

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