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Kinetics of photo-darkening and -bleaching in amorphous $As_{20}Se_{80}$ layers: temperature dependence

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Photo-darkening (PD) and surface relief (SR) recording is applicable for fabrication of photonic elements in amorphous chalcogenides. While SR in $As_{20}Se_{80}$ layers was found very efficient, the influence of PD on recording and thermal stability need to be established. Thermally activated transient and reversible components of PD were detected. From temperature dependent characteristic times of recording and erasing for both PD components rather low activation energies (17 and 13 meV) for the recording process and high activation energies (210 and 90 meV) for erasing were determined. The mechanisms of relevant processes and stability of optical relief recording are discussed.

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1. Introduction

Light-induced changes of optical parameters (absorption and refraction) and other characteristics of amorphous chalcogenide layers (structure, micro-hardness, viscosity, chemical stability) were widely investigated for various arsenic- and germanium chalcogenide films and used for optical, holographic recording of different optical elements (see for example [1-3] and references therein).

One of the most investigated and measurable manifestation of such variation of optical parameters is photo-darkening (PD) [1–5]. The PD effect was described as the photo-induced conversion of some structural units from the ground state into some upper metastable state, in which they absorb light [1, 6, 7], and as the narrowing of optical band gap due to the broadening of band-tails, characteristic for chalcogenide glasses with increasing local structural disorder. The photo-bleaching (PB) at the same time relates to structural ordering, decrease of disorder in the films, obtained in highly non-equilibrium conditions (see for example [8]). Anyway, the basic role of photon-stimulated changes in defect states and related localized structural changes of the glass network are taken into account both for PD and PB. Due to the parallel changes of optical absorption ($\Delta\alpha$) and refraction (Δn), which can be read-out in optical transmission or reflection modes, PD may be used for amplitude-phase optical recording. Besides the PD and PB, the volume change seems to be important for recording of phase-modulated structures. These are known as small thickness variation in illuminated spots (up to 0.1%) and giant profile variations, caused by mass-transport in non-uniformly irradiated layers, as well as surface rippling, which appears even under homogeneous illumination [9].

The PD effect is usually reversible: the original transmission of the layer can be restored after annealing near the glass transition temperature T_g [1,2,10-14]. This reversibility is assigned to the metastable nature of the excited state. Annealing restores original film structure and thus eliminates PD. When such a sample, usually stabilized after deposition or recovered to initial stable state by thermal annealing, is exposed to band gap illumination at lower temperature, it again undergoes photo-structural transformations, which leads to the red shift of the optical absorption edge for ΔE and to the increase of the refractive index.

In addition to metastable PD, which persists after the light is switched off and can be removed by annealing, transient effects of PD and PB were observed in amorphous films during irradiation [4, 15-19]. The transient part of the PD decays rapidly on cessation of the illumination, leaving only the normally observed metastable effect.

PD was mainly studied at room temperature, however, its temperature dependence was also reported [20, 21]. Tanaka [7] analysed how red shift, ΔE, of chalcogenides depends on temperature and found its universal dependence versus T_i/T_g where T_i is the temperature of illumination.

Efficiency of PD and thus the recording of PD-based optical elements was found to be dependent on the thin film composition, temperature and irradiation conditions. The PD decreases with increasing temperature and increases with increasing content of As in As-Se glasses, being maximal near As_2Se_3, for As-Se based compositions: variation of relative optical transmission at room temperature is about 80% for As_2Se_3 and about 5% for $As_{20}Se_{80}$ [21]. At the same time, the highest efficiency of holographic recording of surface relief gratings in As_xSe_{100-x} films was found for a-Se and $As_{20}Se_{80}$ [22, 23]. Now $As_{20}Se_{80}$ films are considered as promising materials for optoelectronics due to their applicability for efficient direct formation of stable photonic elements, such as surface relief gratings, waveguides, microlenses, etc. They can be recorded using He-Ne laser (λ=633 nm) due to the optimal absorption at corresponding optical band gap.

At room and higher temperatures the most effective recording mechanism is lateral mass transport, which results in formation of surface reliefs, however, at lower temperatures noticeable contribution in the recording efficiency can give PD. Despite this, the kinetic parameters of PD and PB, which accompany the geometrical relief formation and erasing, as well as their possible role in the mass transport were not investigated.

In this paper, we study temperature dependence of PD kinetics in amorphous $As_{20}Se_{80}$ films, as well as the kinetics of thermal erasing of PD at various temperatures. We have detected that both transient and reversible components of PD are thermally activated. We determined characteristic times of recording and erasing for both PD components at various temperatures and found rather low activation energy for the recording process and higher activation energy for PD erasing. The activation energy for erasing of the metastable PD component turns out the same as for the photo-induced (PI) diffusion mass transport, which is responsible for formation of surface reliefs. We suggest this indicates that decomposition of the metastable PD sites occurs during at the PI diffusion event. These data can be used to forecast the stability of recorded amplitude-phase reliefs and so of the fabricated photonic elements.

2. Experimental

The $As_{20}Se_{80}$ chalcogenide films were deposited by thermal evaporation of bulk glass in vacuum at 10^{-5} Torr pressure onto microscope glass slides, kept at room temperature. The rate of deposition was between 10 and 20 nm/s, and the layer thicknesses were 2.5 μm (measured by Ambios XP-1 profile meter). The glass transition temperature, T_g, of this composition is rather low 377 K [24].

For kinetic studies of PD we used a beam of a laser diode (λ= 635 nm, P = 10 mW). The spot of 1 mm in diameter was illuminated by an expanded and uniform laser beam, thus the incident intensity of the recording beam was 1.27 W/cm^2. All experiments were carried out in a special cryostat, cooled by liquid nitrogen vapour and complemented by a heater. Variations of optical transmission and reflection with time were measured by a Thorlabs PM-100 power meter using a probe beam of a He-Ne laser, (P=0.01 mW, λ= 633 nm), which did not affect the results of the measurements. The same setup was used for studies of thermal erasing kinetics.

3. Results and discussion

3.1. Kinetics of PD

The changes of optical transmission (Fig. 1.) at the PD process in $As_{20}Se_{80}$ amorphous films were measured at different temperatures in the range of 80 - 290 K. At higher temperatures no essential variation of transmission with illumination time was detected. Due to the redshift of the absorption spectra with increasing temperature, the absorption coefficients α increase with increasing temperature at any given wavelength in the spectral range of investigations.

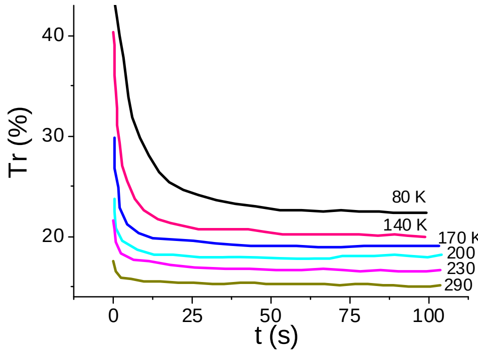

Fig. 1. PD kinetics (transmission) in $As_{20}Se_{80}$ layers at different temperatures

The presented data on transmission (*Tr*) variation during PD are normalized to the same incident power taking into account the reflection, which also varies with time and temperature. Variation of transmission, ΔTr, from its initial value to saturation decreases with increasing temperature, with ΔTr being a maximum at 80 K in our experiments, small at 290 K and almost not measurable at higher temperatures. With the time of illumination, the absorption coefficients increase, resulting in a large PD at lower temperatures. In contrast, the rates of *Tr* variation under illumination are rather small at low temperatures and increase at higher temperatures.

Exponential fitting of the curves in Fig. 1 results:

$$Tr(t) = Tr_0 - A_{r1}\left[1-\exp(-t/\tau_{r1})\right] - A_{r2}\left[1-\exp(-t/\tau_{r2})\right], \qquad (1)$$

where Tr_0 is the initial transmission, $A_{r1} > 0$, $A_{r2} > 0$, τ_{r1} and τ_{r2} are the fitting parameters. It is important that there are two characteristic times, τ_{r1} and τ_{r2}, which describe the PD recording. The two characteristic times, τ_1 and τ_2, detected during PD indicate the presence of both the transient (dynamical) PD and the metastable (erasable) PD components in our investigated composition.

Ganjoo and Shimakawa [15, 16] discussed existing models of PD and concluded that the dynamics of PD can be described well in terms of configurational-coordinate (CC) diagram [1], based on a double-well potential with a barrier separating the ground and photo-induced states. To describe the metastable (reversible) PD kinetics we assume, following Refs. [4, 15, 16], that the films contain clusters, which act as potential sites for PD. The PD sites are formed under illumination and associated with these clusters. Before illumination, there exist N_m clusters in the ground state. The number (N^{ms}) of the metastable PD sites grow with time as:

$$\frac{dN^{ms}}{dt} = G - \frac{N^{ms}}{\tau_r} - \frac{N^{ms}}{\tau_e}, \qquad (2)$$

where G is the generation rate of clusters in excited state, τ_r and τ_e are characteristic times for recording and erasing, respectively. At low temperatures, when one can neglect thermal erasing, all N_m^{ms} clusters will be in excited state after τ_r and one can put $dN^{ms}/dt = 0$. Then we have $G = N_m^{ms} / \tau_r$ and Eq. 2 can be rewritten as

$$\frac{dN^{ms}}{dt} = \frac{N_m^{ms}}{\tau_r} - \frac{N^{ms}}{\tau}; \quad \tau = \frac{\tau_r \tau_e}{\tau_r + \tau_e} \qquad (3)$$

Similar consideration can be applied for transient PD. Absorption of a photon breaks a pnictogen-chalcogen bond, *P-C*; then electron drops from the P_2 state to the C_1 state (subscripts show number of neighbouring atoms), giving rise to a P_2^+- C_1^-- pair. This pair of charged, undercoordinated defects is potentially unstable and after reconstruction more stable possible defect pairs can be formed [25]. Under continuous illumination, number of all these defects does not vary with time. Their steady state concentrations depend on the defects' lifetimes, which in turn depend on temperature. Each of these defects can locally modify the band gap and the linear additivity of the "local" optical gaps gives the effective total optical gap in the illuminated state, which is responsible for PD. Depending on the lifetime of the defects, which can change the band gap, one can distinguish transient and reversible PD that are caused by unstable and more stable defects, respectively. Then the current total number of absorption sites is

$$N(t) = N_0 + N^{ms}(t) + N^{tr}(t), \qquad (4)$$

where N_0 is number of absorption centres before illumination, $N^{tr}(t)$ is the current number of transient absorption centres, which can be calculated using equation

$$\frac{dN^{tr}}{dt} = \frac{N_m^{tr}}{\tau_{r1}} - \frac{N^{tr}}{\tau_1}; \quad \tau_1 = \frac{\tau_{r1} \tau_{e1}}{\tau_{r1} + \tau_{e1}} \qquad (5)$$

Here, τ_{r1} and τ_{e1} are characteristic times for recording and erasing, of transient PD, respectively, N_m^{tr} is maximal number of defects, which can act as potential sites for transient PD.

Solutions of Eqs. (3) and (5) with initial condition $N^{ms}(0) = N^{tr}(0) = 0$ are:

$$N^{ms}(t) = N_m^{ms}\left[1 - \exp\left(-t/\tau\right)\right] \qquad (6)$$

$$N^{tr}(t) = N_m^{tr}\left[1 - \exp\left(-t/\tau_1\right)\right] \qquad (7)$$

The number of PD centres $N(t)$ is proportional to additional absorption induced by light, $\Delta\alpha$, i.e.

$$\begin{aligned} \alpha &= \alpha_0 + \Delta\alpha_{tr} + \Delta\alpha_{ms} = \\ &= \alpha_0 + \alpha_m^{tr}\left[1 - \exp(-t/\tau_1)\right] + \alpha_m^{ms}\left[1 - \exp(-t/\tau)\right] \end{aligned} \qquad (8)$$

Here, α_0, α_m^{tr}, and α_m^{ms} are the initial absorption, maximal transition contribution, and maximal contribution of the metastable PD, respectively. In Fig. 2. we present the experimental data on absorption variation during PD in comparison with that calculated using Eq. (8). The main fitting parameters were τ and τ_1. Values α_0, α_m^{tr} and α_m^{ms} can be easily determined from experimental data (Fig. 1). Values τ and τ_1 are presented in Arrhenius coordinates (Fig. 3.) and straight lines indicate that they are thermally activated. However, the activation energies of both transient and metastable PD recording times are rather low, 17 and 13 meV, respectively. As it follows from the above-mentioned model, the electron-hole pairs at photon-activated centres should overcome a barrier, which corresponds to the transition to the different local potentials, and this process is thermally activated. By other words, the capture of exited electrons by PD sites requires overcoming some potential barriers.

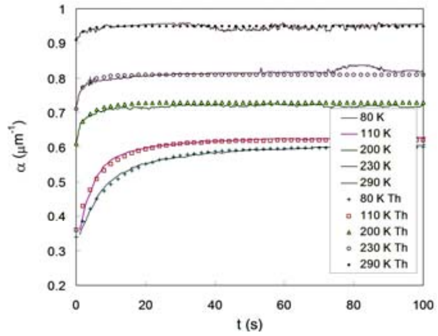

Fig. 2. Kinetics of PD at various temperatures: comparison of experimental data (lines) with theoretical calculations according to Eq. (8)

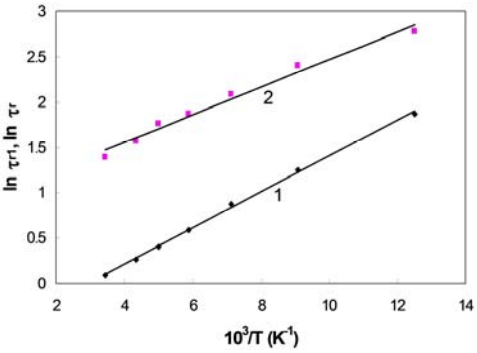

Fig. 3. Temperature dependences of recording times: 1 - for transient (τ_{r1}) and 2 - for metastable PD component (τ_r)

3.2. Kinetics of thermal PD erasing (thermal bleaching)

The kinetics of thermal erasing was studied in a temperature range 298 - 398 K, since at lower temperatures the process is too long for real-time experiments. In Fig. 4. one can see that the thermal erasing of PD also consists of two stages: at the first, a faster stage the transient component of PD is erased, whereas at the second stage the metastable component of PD is erased, faster at higher temperatures and the initial absorption coefficient, α_0 , for given temperature is recovered.

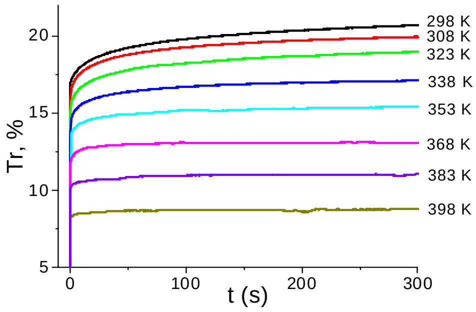

Fig. 4. Kinetics of thermal PD erasing at various temperatures

Number (N^{ms}) of the metastable PD sites (as well as the transient sites) decreases with time as:

$$-\frac{dN^{ms}}{dt}=\frac{N^{ms}}{\tau_e} \quad , \tag{9}$$

where τ_e is a characteristic erasing time at given temperature. Solution of Eq. (9) and similar equation for transient PD component results in the following variation of absorption coefficient with time:

$$\alpha=\alpha_0+(\alpha_{\max}-\alpha_m^{ms})\exp(-t/\tau_{e1})+(\alpha_m^{ms}-\alpha_0)\exp(-t/\tau_e) \tag{10}$$

Here, $\alpha_{\max}$ corresponds to maximum PD at given temperature, τ_{e1} is a characteristic erasing time of transient PD component. In Fig. 5. we compare experimental data on the thermal PD erasing with values α calculated using Eq. 10. Fitting parameters were τ_{e1} and τ_e. Values $\alpha_{\max}$ and α_m^{ms} can be easily determined from experimental curves.

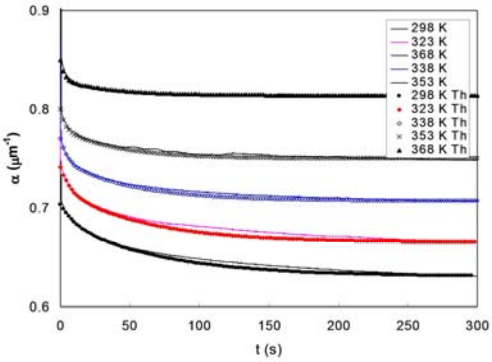

Fig. 5. Thermal erasing of PD: comparison of experimental data with α calculated using Eq.10

Characteristic times for erasing of transient and reversible components of PD are presented in Fig. 6. in Arrhenius coordinates. Activation energies of thermal PD erasing are 0.21 eV for transient and 0.09 eV for metastable PD components.

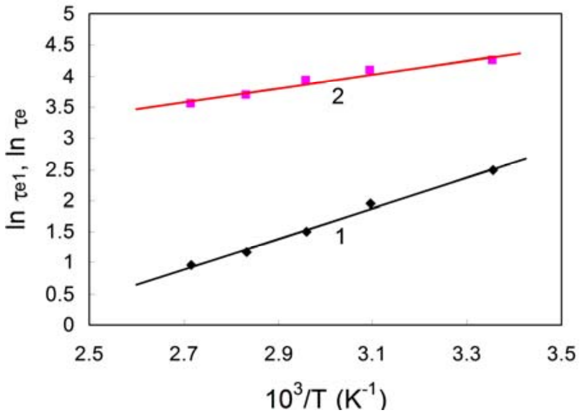

Fig. 6. Temperature dependences of erasing times: 1- for transient (τ_{e1}) and 2 - for metastable PD component (τ_e)

The activation energy of metastable PD erasing (0.09 eV) in our material is noticeably smaller compared to that in a-Se (0.78 eV) [12]. Probably it is connected with difference in structure, presence of inter-chain bonds with increasing As content in Se. It is unexpected that restoration of the initial ground state for transient PD component (time τ_{e1}) requires higher activation energy than for metastable PD (time τ_e).

Previously [26], we studied low temperature (at 77 K) holographic recording of surface relief gratings (SRGs) in the same, $As_{20}Se_{80}$ film composition. Grating formation under two-beam light illumination was caused mainly by lateral mass transfer, although contribution of PD in the diffraction efficiency (about 4 %) was also noticeable. But at room and higher temperatures such contribution (less as 1%) is small, the formation of surface grating due to the mass transport determines the diffraction efficiency of the grating and so the erasing of the metastable PD relief in a complex PD+SR grating does not influences essentially the efficiency of grating at higher temperatures. Estimates of diffusion activation energy of the SRG recording (when we compared recording rates at 77 and 300 K) gave us 0.09 eV, which coincides with that for erasing of metastable PD. Low diffusion activation energy of mass transfer was explained in assumption that Coulomb interaction between charges localized near the radiation defects (such as self-trapped exciton) and bounded with the diffusing atom deforms potential barrier for migration. Diffusion jump leads to recombination of electron and hole and the exciton disappears. We believe that the metastable PD sites are located near self-trapped excitons and erasing of metastable PD leads to their disappearing like this occurs as a result of photo-induced diffusion jumps.

4. Conclusions

Kinetics of PD in $As_{20}Se_{80}$ amorphous chalcogenide films was investigated in a temperature range 80 - 298 K and thermal PD erasing - in a range 298 - 398 K. Both the recording and erasing kinetics show transient and metastable (reversible) PD components and temperature dependence of both PD components can be approximated by Arrhenius law for thermally activated processes. The transient and metastable PD recording times are characterized by low activation energies (17 and 13 meV respectively). Thermal erasing of the transient and metastable components of PD occurs with activation energies 0.21 and 0.09 eV, respectively. The activation energy of thermal erasing of metastable PD component coincides with previously estimated activation energy of photo-induced diffusion mass transfer, which is responsible for the surface patterning. We suggest that erasing of metastable PD occurs as a result destroying of self-trapped excitons, near which the metastable PD sites are located.

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