

## Effect of molybdenum doping on photoinduced changes of the properties of As<sub>3</sub>S<sub>7</sub> films

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### Abstract

**Subject of study.** This study examines the influence of Mo metal concentration on the properties of As<sub>3</sub>S<sub>7</sub> films when exposed to continuous laser radiation. **Aim of study.** This study aims to investigate the impact of Mo metal concentration on the photodarkening and photoresist properties of As<sub>3</sub>S<sub>7</sub> films. **Method.** The photodarkening process was performed by subjecting the films to continuous radiation with a wavelength of 445 nm. The transmission spectra of the samples were measured using a fiber spectrophotometer. The surface of the films was examined using an optical microscope. To assess the photoresist effect, radiation with a wavelength of 532 nm was employed, along with a solvent comprising a solution of C<sub>8</sub>H<sub>19</sub>N in C<sub>6</sub>H<sub>5</sub>CN. **Main results.** The degree of photodarkening decreased with increasing Mo concentration. In the original film a 10% decrease in transmission was observed, whereas at the highest metal concentration, the change in transmission approached zero. Additionally, the study demonstrates that the solubility rate ratio of exposed to unexposed films decreases at higher metal concentrations. **Practical significance.** The results of this study hold practical significance in the development of devices that utilize changes in the phase state of chalcogenide glass films.

**Keywords:** photodarkening, photoresist, chalcogenides, thin films, laser exposure, As<sub>3</sub>S<sub>7</sub>, molybdenum

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## 1. INTRODUCTION

Chalcogenides, specifically sulfur (S), selenium (Se), and tellurium (Te) compounds, have extensive applications as optical elements for infrared (IR) radiation [1, 2]. They are also utilized in the development of memory elements with phase change capabilities [3] and X-ray medical sensors [4]. Moreover, chalcogenides play an active role in the development of photovoltaic elements [5] and photocatalytic devices [6]. A key characteristic of chalcogenide substances is the presence of lone pair electrons occupying the top of the valence band. Although these electrons do not actively participate in covalent bonding, they can be excited by various stimuli, such as temperature [7], photons [8], and electric fields [9]. This unique property enables a wide range of adjustments to the characteristics of chalcogenides.

Chalcogenide glasses demonstrate several notable photoinduced effects, including reversible photostructural changes (photodarkening) and photoinduced anisotropy. The occurrence of these phenomena and the stability of the material depend on factors such as the concentration of lone electron pairs and the bond configuration.

Doping chalcogenide materials with transition metals is a common approach to modifying their various characteristics. One extensively studied chalcogenide system is the binary  $As_xS_{100-x}$  [10]. This system is often alloyed with metals like Ag [11] and Cu [12] to enhance material conductivity, and with Mn [13], which among other effects, enhances the magnetic properties. The presence of vacant d-orbitals in transition metals enables their interaction with the electrons of the lone pairs in the doped matrix. Consequently, the concentration of these electrons is altered [14], leading to changes in phase transition properties, photodarkening, and parameters of the material as a photoresist.

Therefore, it is crucial to investigate the impact of alloying metal concentration on these properties. In this study, we focused on Mo, a commonly used transition metal for chalcogenide doping [15]. The chalcogenide matrix consisted of a thin film of  $As_3S_7$ . Laser radiation serves as a convenient tool for examining phase transition properties, specifically the kinetics of photodarkening. This technique enables rapid and localized manipulation of the material structure.

The aim of this study was to explore the influence of the Mo metal concentration on the photodarkening of  $As_3S_7$  films under the action of laser radiation. In addition, the correlation between the photodarkening of the films and their resistance to the solvent was studied.

## 2. METHODS AND MATERIALS

In this study, chalcogenide films of arsenic sulfide  $As_3S_7$  doped with molybdenum in various concentrations were fabricated. The films had a thickness of  $500 \pm 5$  nm. The film fabrication methodology is described herein.

The precursors used were  $As_3S_7$  bulk glass particles synthesized by melt quenching and  $(NH_4)_2MoS_4$  powder, which were dissolved in propylamine. The resulting solutions were thoroughly mixed in a ratio of 1:5, 1:2, 2:1, and 5:1 and left to homogenize and react with each other for 24 hours. Thin layers were applied through centrifugation. The prepared thin films were placed in a vacuum furnace preheated to 200 °C, purged with pure gaseous argon, and rapidly evacuated to a residual pressure of 1 Pa. The layers were annealed for 2 h and then cooled to room temperature. The choice of  $As_3S_7$  material instead of stoichiometric  $As_2S_3$  was motivated by a faster dissolution rate in the preparation of initial solutions, which takes several hours compared to several days for  $As_2S_3$ . Furthermore, the  $As_2S_3$  solution precipitates in air, thereby complicating its handling.

The compositions of the obtained films are presented in Table 1, and the obtained films are shown in Fig. 1. An increase in the concentration of molybdenum led to darkening of the film.

To reveal the dependence of the film photosensitivity on the metal concentration, we used the experimental setup shown in Fig. 2. For irradiation, a source of continuous laser radiation with a wavelength of 445 nm (violet light) was utilized. The chosen wavelength falls within the intrinsic absorption region of the films to minimize the change in absorption of the incident radiation during exposure to the film. A light source was placed at an angle of 45° to the normal of the sample. An AvaSpec ULS4096CL-EVO spectrophotometer was placed in line with the light source behind the film to measure the spectral transmission of the sample during processing. The beam size was 4.5×0.6 mm with a Gaussian intensity distribution in its cross section. The laser radiation power density ( $q$ ) was varied from 8 to 25 W/cm<sup>2</sup>. The samples were exposed to the impact for a duration of 5 minutes, and the spectrophotometer readings were recorded at one-minute intervals.

To study the effect of Mo concentration in As-S glasses on dissolution resistance, we utilized a 10% solution of  $C_8H_{19}N$  in  $C_6H_5CN$ , which is an optimal solvent for such thermally deposited resists. The film was exposed for 90 min to continuous-wave laser radiation with a power of 100 mW and a wavelength of 532 nm (green light). The illumination spot had a diameter of 3 mm. The film dissolution rate was determined from the results of interferometric measurements.

**Table 1. Composition of As-S-Mo films**

Proportions	As, %	S, %	Mo, %
5:1 1:5	31.8	65.6	2.6
2:1 1:2	25.1	67.8	7.1
1:2 2:1	11.4	74.1	14.6

1:5 5:1	5.6	75.0	18.6
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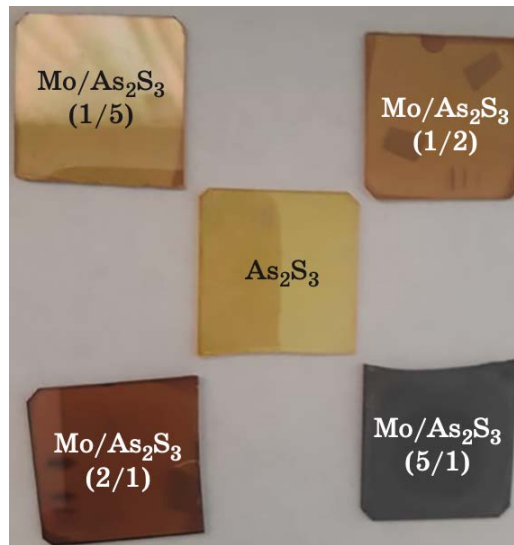


Fig. 1. Study samples.

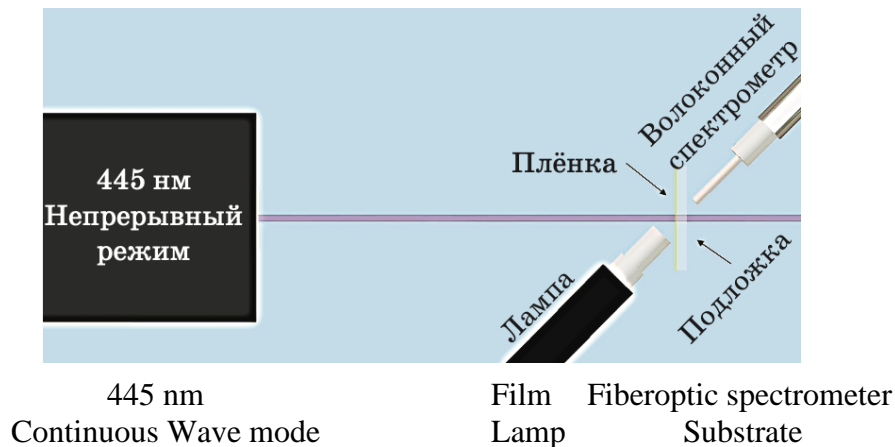


Fig. 2. Scheme of the experimental setup.

### 3. DISCUSSION OF THE RESULTS

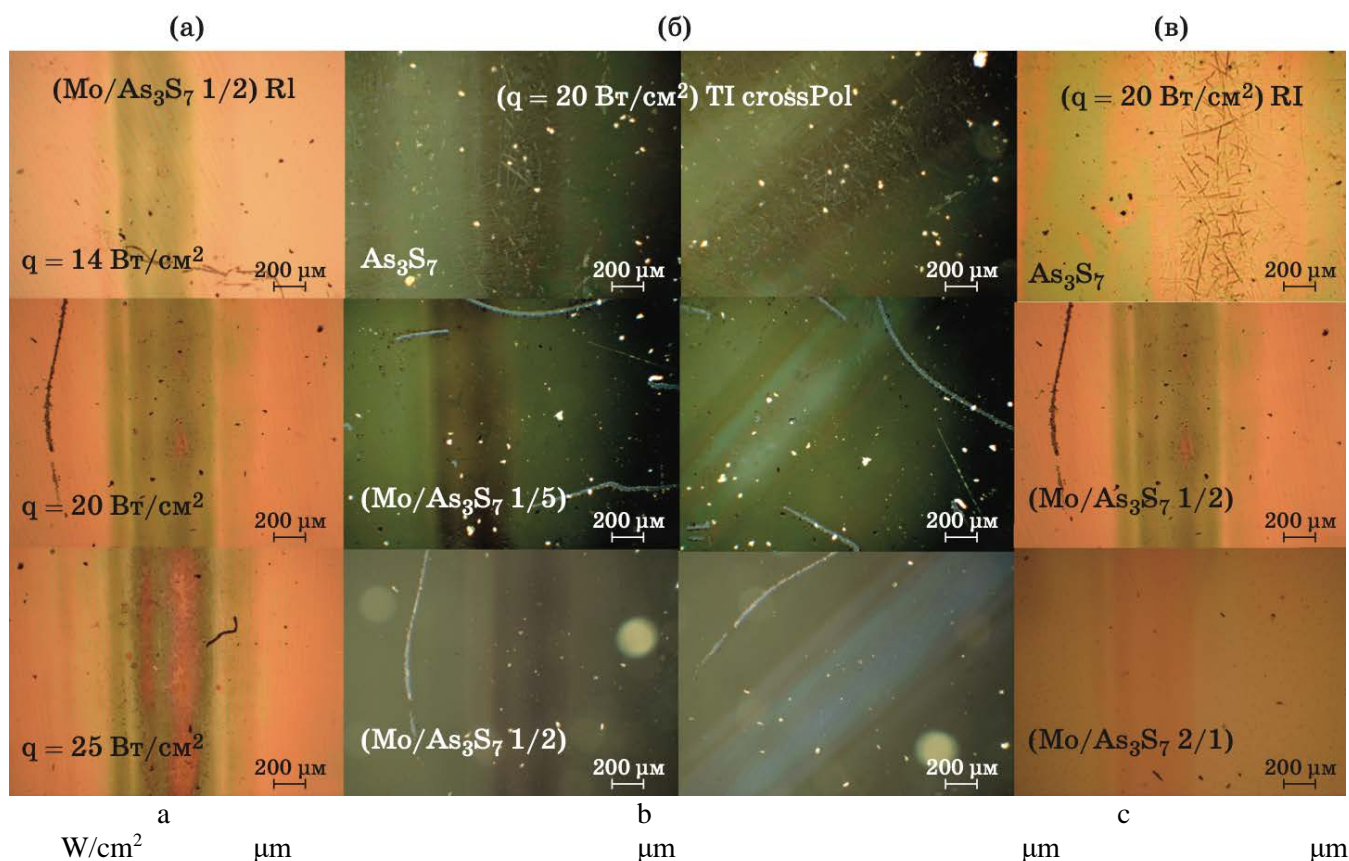
The areas modified under the action of violet light were examined using optical microscopy in bright field mode with reflected (RI) and transmitted light (TI). As the laser power density increased, the film darkened in the reflected light mode (Fig. 3a). At the highest  $q$  value of  $25 \text{ W/cm}^2$  in the center of the region, the film began to break down. In the presence of Mo in transmitted linearly polarized light with a crossed polarizer and analyzer, the modified regions changed their brightness when the sample was rotated, which indicated the appearance of an anisotropy in the optical properties (Fig. 3b). In this case, with an increase in the Mo concentration, the sensitivity of the film to radiation decreased (Fig. 3c). At a  $q$  value of  $10 \text{ W/cm}^2$ , the surface of the  $\text{As}_3\text{S}_7$  sample began to break down even without photodarkening, and cracks appeared in the affected area. Doping with Mo prevented cracking and instead caused darkening under radiation, with the degree of darkening decreasing as the metal concentration increased.

Fig. 4 depicts the transmission spectra of the films at two different time points: the initial moment of exposure (Fig. 4a) and that after 5 min of exposure (Fig. 4b). Upon exposure of the films to laser irradiation, the spectral lines exhibited a shift toward the infrared (IR) region of the spectrum.

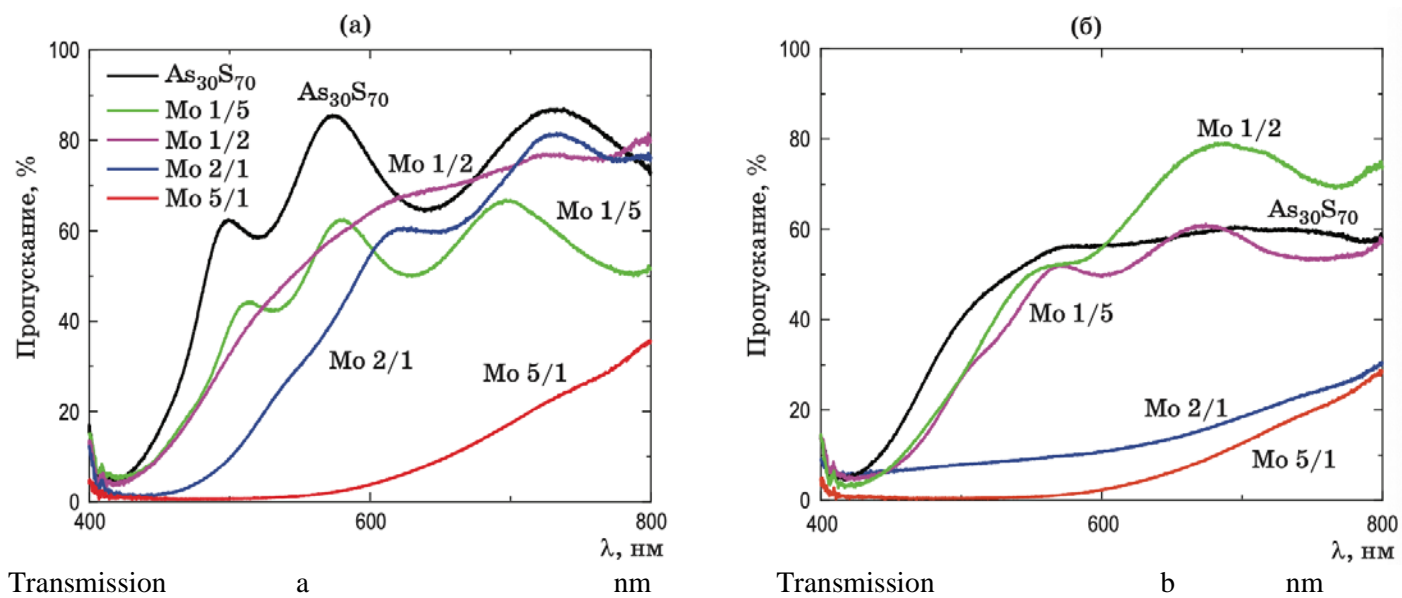
Fig. 5a shows the transmission spectra of the initial  $\text{As}_3\text{S}_7$  film (black curve) and the film during laser irradiation with a power density  $q = 8 \text{ W/cm}^2$  (blue curve). Additionally, Fig. 5b shows the region of the spectrum from 490 to 510 nm. An intense peak near 445 nm corresponds to the wavelength of laser radiation. The largest shift of the spectral curves occurred within 1 min. After the end of irradiation, the curve shifted again towards shorter wavelengths (blue curve). A similar result was observed for all films and for all power densities.

The kinetics of photodarkening directly during exposure to radiation was analyzed in more detail. Dependences of the change in transmission  $dT = T_0 - T_i$  on the exposure time were constructed:  $T_0$  is the value of the initial transmission of the film at a wavelength of 500 nm and  $T_i$  is the transmission value at a wavelength of 500 nm at time  $t_i$ . The larger the value of  $dT$ , the greater the degree of photodarkening. This wavelength is approximate to the thickness of the samples, and therefore, the influence of interference effects associated with multiple re-reflection in thin films on the

transmission value was minimized.



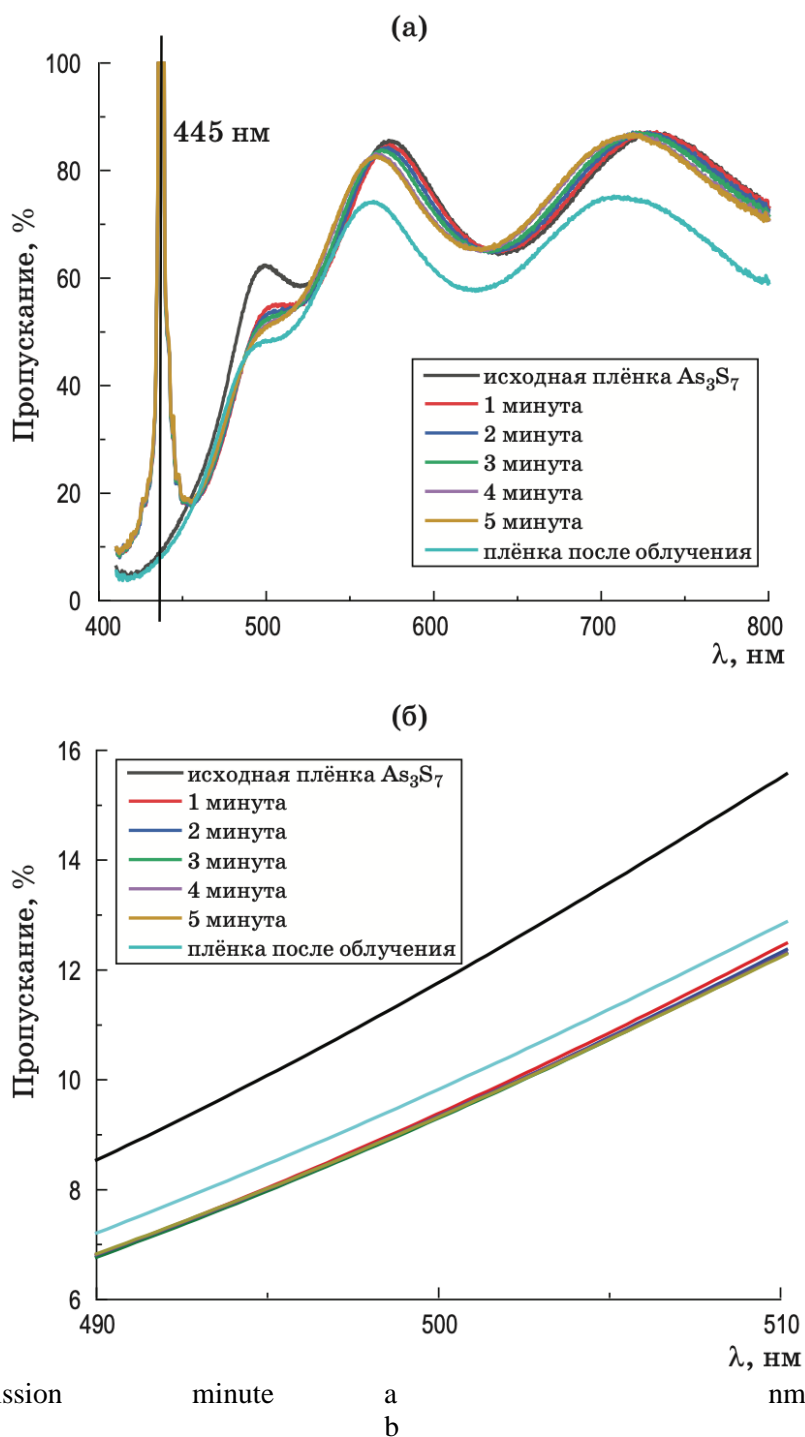
**Fig. 3.** Optical microscopy in reflection and transmission mode.



**Fig. 4.** Transmission spectra of all samples. a) Spectra before laser exposure, b) spectra after 5 minutes of laser exposure at  $q = 20 \text{ W}/\text{cm}^2$ .

Fig. 6a shows the  $dT$  dependence for the  $\text{Mo}/\text{As}_3\text{S}_7 \text{ 1/2}$  film at various  $q$  values. Observably, an increase in the power density of laser radiation, which altered the optical properties of the film, led to a rapid increase in the value of  $dT$  from 3.5% to 6.5% within 1 min. Over the next 4 min, the growth rate decelerated, and  $dT$  began to decrease, i.e., the transmission began to increase. This trend is attributed to a decrease in the film thickness. Characteristic dependencies were observed for all samples.

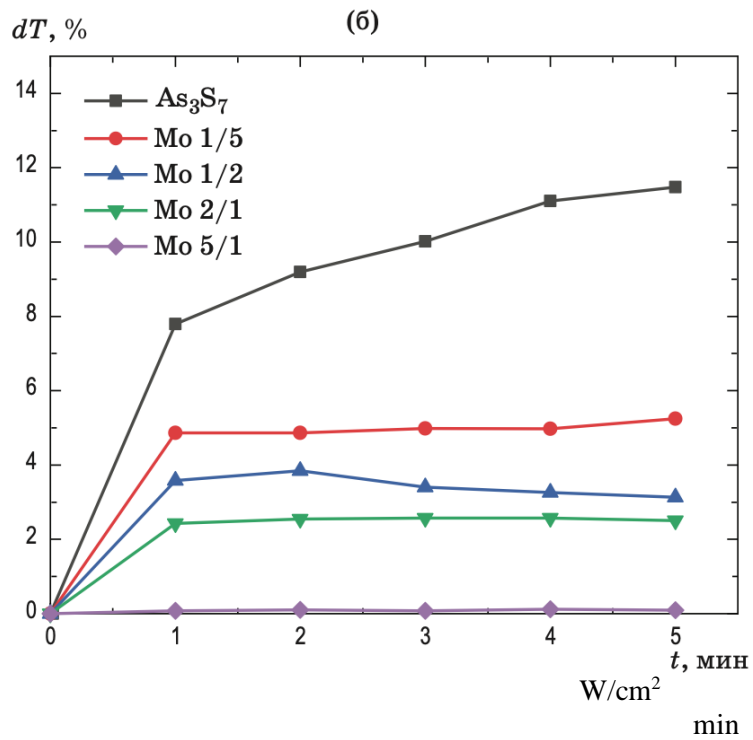
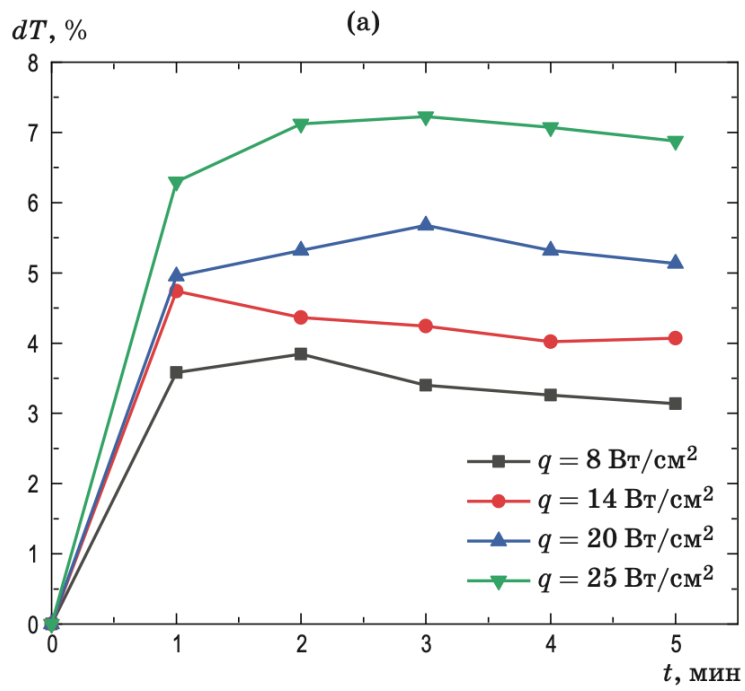
Fig. 6b shows the dependence of  $dT$  at a power density of  $q = 8 \text{ W}/\text{cm}^2$  for films with different Mo concentrations. The largest increase in  $dT$  was observed for the sample without Mo; in the first minute, the value rapidly increased to 8%, after which it increased monotonically to 11%. As the impurity concentration increased,  $dT$  decreased; for the sample with an impurity ratio of 5/1, the change in transmission was close to zero.



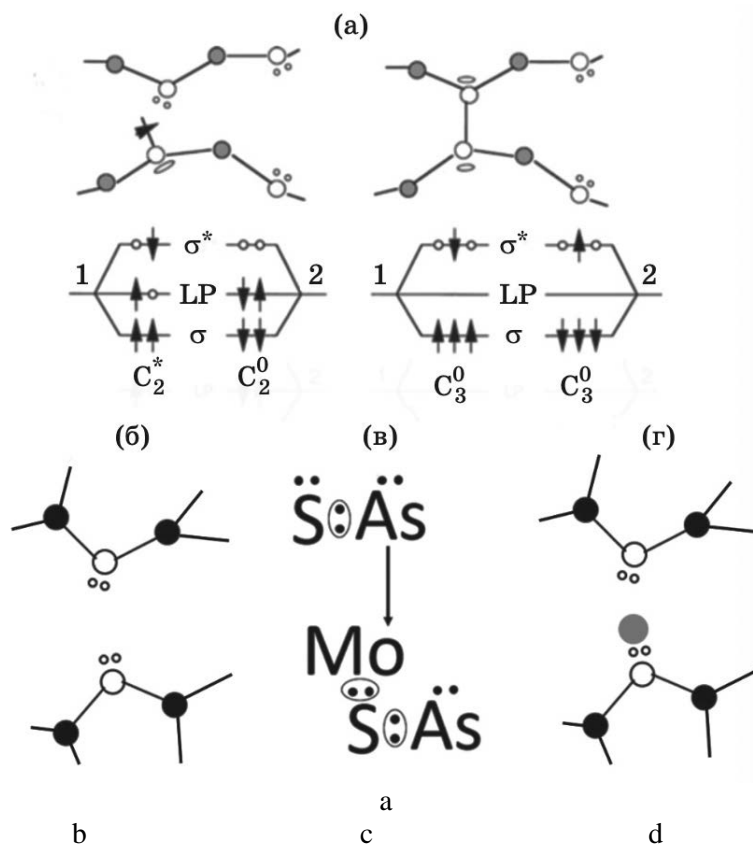
**Fig. 5.** Transmission spectra of the  $As_3S_7$  film exposed for 5 min to  $q = 8 \text{ W/cm}^2$ , a) spectrum section from 400 nm to 800 nm, b) spectrum section from 490 nm to 510 nm.

We suggest that the decrease in  $dT$  with an increase in the Mo concentration is attributed to a decrease in the number of lone pair electrons. As was experimentally demonstrated by the EXAFS [16] and **EPR ESR** [17] methods, photostructural transformations are initiated by the formation of dynamic bonds due to lone pairs of chalcogen atoms (Fig. 7a). Such atomic configurations present in undoped glass (Fig. 7b) disappear (Fig. 7d) due to the formation of Mo–S bonds involving empty d-orbitals of the transition metal and lone pairs of chalcogen atoms (Fig. 7c), leading to a decrease in their concentration, thereby reducing the sensitivity of the material to laser action.

Photodarkening in  $As_3S_7$  correlates with the change in solubility in various solvents, and chalcogenide glasses can be used as a photoresist [18]. The process is characterized by an extremely high resolution; in particular, elements with sizes up to 30 nm have been realized using synchrotron radiation [19]. Depending on the choice of solvent, both positive and negative photoresists can be produced on the basis of chalcogenide glasses. Table 2 summarizes the dissolution rate measurements of samples with different concentrations of Mo in both unexposed and exposed zones.



**Fig. 6.** Kinetics of  $dT$  change under laser exposure a) Mo/As<sub>3</sub>S<sub>7</sub> 1/2 film; b) power density 8 W/cm<sup>2</sup>.



**Fig. 7.** Molybdenum participation in the formation of chemical bonds. (a) Mechanism of formation of dynamic bonds between selenium atoms upon electronic excitation of lone-pair electrons (according to [16] and [17]), (b) As-S-As fragments in undoped glass, (c) scheme of bond formation Mo-S with the participation of lone pairs of sulfur; (d) in doped glass, a reduced concentration of lone pairs leads to a decrease in the concentration of photoinduced bonds between chalcogen atoms.

**Table 2. Dissolution rates of films with different Mo concentrations**

Film Proportion	<del>5/1</del> 1/5	<del>2/1</del> 1/2	<del>1/2</del> 2/1
Dissolution rate (unexposed region), nm/min	26	5.8	1.2
Dissolution rate (exposed region), nm/min	125	18.5	2.5
Ratio	4.6	3.2	2.1

Notably, the dissolution rate increases in the exposed films (positive photoresist). Moreover, the ratio of dissolution rates in the exposed and unexposed regions decreases in films with a higher Mo content. This finding corresponds to lower photodarkening in films containing a higher concentration of molybdenum.

#### 4. CONCLUSION

Our study demonstrates that the addition of molybdenum to glassy arsenic sulfide results in a reduction of the band gap, leading to a noticeable darkening of the sample. Despite the introduction of molybdenum, the doped samples retain the characteristic photostructural processes commonly observed in chalcogenide glasses, including photodarkening, photoinduced anisotropy, and changes in dissolution rates induced by light. Interestingly, the extent of these photostimulated changes diminishes as the concentration of molybdenum increases. This observation supports the hypothesis that the unshared electron pairs of chalcogen, which are involved in the formation of Mo-S bonds, are not involved in the material's response to electronic excitation.

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