

## ABSTRACT

Result of the experimental investigations of absorption of laser pulses in amorphous (a-) and crystalline (c-) As<sub>2</sub>S<sub>3</sub> films are presented. The optical transmission hysteresis and reversible film photodarkening at interband excitation of a-As<sub>2</sub>S<sub>3</sub> films in a blue-green spectral region are reported. It was suggested that the nonlinear light absorption could be explained by taking into account the light interaction with nonequilibrium localized lattice vibrations anharmonically coupled with the extended phonons. The measurements of peculiarities of the pulse absorption in crystalline As<sub>2</sub>S<sub>3</sub> films can confirm the proposed explanation.

## 1. INTRODUCTION

The interest in the study of nonlinear propagation of laser pulses in noncrystalline semiconductors is determined not only by the new fundamental physical mechanisms present in these materials, which can appear in the strong fields of the laser pumping, but also by a wide spectrum of possible applications in optoelectronic devices and optical computing. Additionally, the nonlinear optical effects in noncrystalline semiconductors are studied to a much less extent than in the crystalline ones. Promising effects are optical bistability and optical hysteresis, on the basis of which it is possible to build fast-response, all-optical switching and logical elements (see, for example, ref. 1).

In a number of works some of the light induced reversible changes of the chalcogenide glass (ChG) optical constants were studied considering the nonlinear transmission of focused CW laser radiation through thin film samples<sup>2</sup>. A reversible nonlinear change of the ChG transmittance, an optical bistable light transmission and the photocurrent, the transmission, the reflection coefficients periodic oscillations in time were observed. The material returns to its initial transparent state if the laser is switched off. It was not possible to find the same regimes of the light transmission in crystalline analogous. This fact indicates that the clue to understand the physical mechanism lying at its base, is connected with the amorphous nature of the ChG. In spite of a considerable number of works, up to now there are no reliable data about the physical processes, describing adequately the nonlinear interactions of the CW laser radiation with ChG. All the proposed physical models do not permit to give a single qualitative description (to say nothing of a quantitative one) of the nonlinear propagation of CW radiation in ChG films<sup>2</sup>.

The understanding of the complex physical phenomena, taking place in noncrystalline semiconductors depends in a significant degree on the possibility of their quantitative exploration with a sufficient short time resolution. By reducing the laser pulse duration down to picoseconds or femtoseconds, it is possible to exclude or to lower the influence of some processes, for example, the laser heating of the sample, and to investigate the mechanism of the nonlinear or nonstationary interaction of light with the noncrystalline semiconductor. The dynamic of the nonlinear absorption of light pulses with nanoseconds, picoseconds, and femtoseconds durations is surveyed in ref. 2. This absorption exhibits a maximum amplitude during the excitation pulse and relaxes, as a rule, with several time constants. A characteristic peculiarity of the induced transient absorption in ChG is the nonlinear dependence of the absorption coefficient on the light intensity, which shows a threshold-like dependence.

In present work the results of an investigation of the optical hysteresis and nonlinear light absorption at interband excitation of a-As<sub>2</sub>S<sub>3</sub> films with short laser pulses (300K) are described. The physical mechanisms, which can contribute to the nonlinear absorption in chalcogenide glass under pulsed excitation, are discussed. It was suggested that the

interband nonlinear light absorption could be explained by taking into account the light interaction with nonequilibrium phonons. Our attention is devoted to characterize the light absorption in crystalline  $\text{As}_2\text{S}_3$  to demonstrate the validity of the proposed mechanism.

## 2. INVESTIGATED SAMPLES AND METHODS

Thin film samples of a- $\text{As}_2\text{S}_3$  (2 to 2.6  $\mu\text{m}$  thick) have been obtained by vacuum thermal evaporation method on transparent substrates. The linear light absorption coefficient of the a- $\text{As}_2\text{S}_3$  thin film at the laser radiation wavelength was determined from transmission spectra, while the film thickness was obtained by an interferometric method. The crystalline  $\text{As}_2\text{S}_3$  films (5 - 8  $\mu\text{m}$  thick) were obtained by cleavage from natural orpiment. Fig. 1 shows the optical transmission spectra for measured a- $\text{As}_2\text{S}_3$  and c- $\text{As}_2\text{S}_3$  samples.

The used methods permitted to measure sinchronously the temporal shape of incident laser pulse ( $I_0$ ) and transmitted ( $I$ ) one. A coumarin 102 flash-lamp pumped dye laser generated pulses of a 0.6  $\mu\text{s}$  duration (at FWHM) with a smooth temporal shape. The light quanta energy (in the spectral range of the used dye laser  $\Delta\hbar\omega \sim 2.53 - 2.75$  eV) corresponds to the strong absorption spectrum of the a- $\text{As}_2\text{S}_3$  ( $\hbar\omega > E_g$ ,  $E_g = 2.4$  eV), where the absorption coefficient  $\alpha \geq 10^4$   $\text{cm}^{-1}$ . The incident and the output laser radiation were registered by coaxial vacuum photoelements (time resolution  $< 10^{-9}$  s) and an oscilloscope. All experiments were done at the room temperature.

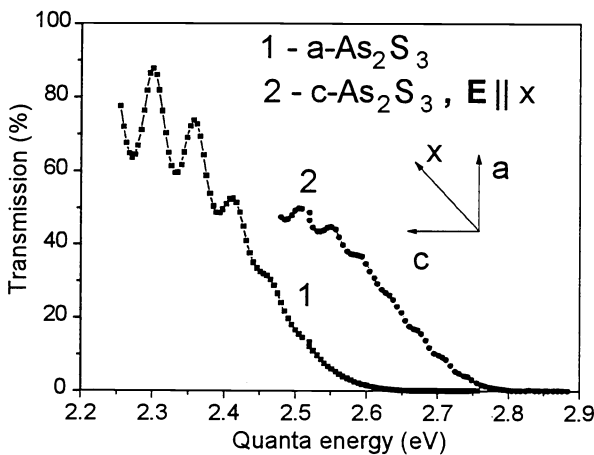


Fig. 1. Optical transmission spectra of a- $\text{As}_2\text{S}_3$  film (thickness 2.6  $\mu\text{m}$ ) and of c- $\text{As}_2\text{S}_3$  (thickness 5  $\mu\text{m}$ ) sample.

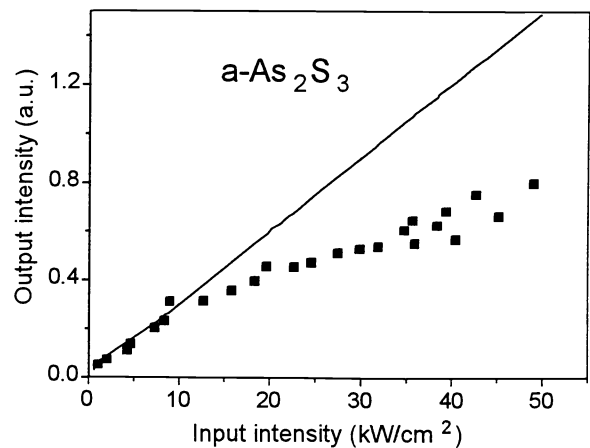


Fig 2. Full line: continuation of low intensity light transmission. Symbols: nonlinear light transmission of a- $\text{As}_2\text{S}_3$  film (thickness 2.6  $\mu\text{m}$ ) versus input pulse intensity;  $\hbar\omega = 2.58$  eV.

## 3. EXPERIMENTAL RESULTS

When the input light (with  $\hbar\omega \geq E_g$ ) pulses intensity was relatively low the transmission of the a- $\text{As}_2\text{S}_3$  film decreased according to the usual Beer law (linear transmission). However, increasing the incident light intensity over some characteristic threshold value ( $I_t = 10 - 15$   $\text{kW}/\text{cm}^2$ ) leads to a nonlinear light transmission by the film (Fig. 2). The increase of the photoinduced absorption coefficient up to 1.8 times was measured.

As a result of the nonlinear light absorption a change of the time profile of the laser pulses was recorded at the output of the a- $\text{As}_2\text{S}_3$  sample (Fig. 3). The change of the time profile of the laser pulses leads to hysteresis-like dependencies of

the output light intensity (passed through the sample) on the corresponding value of the input (Fig. 4). The extension of the optical hysteresis loop increases (changing its shape) with the input light intensity up to the damage of the sample surface ( $> 200 \text{ kW/cm}^2$ ).

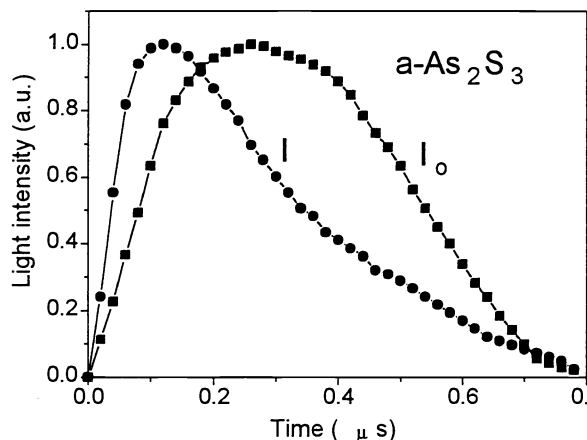


Fig. 3. Oscillograms of incident ( $I_o$ ) and transmitted ( $I$ ) pulses; film thickness  $2.6 \mu\text{m}$ ,  $\hbar\omega = 2.58 \text{ eV}$ .

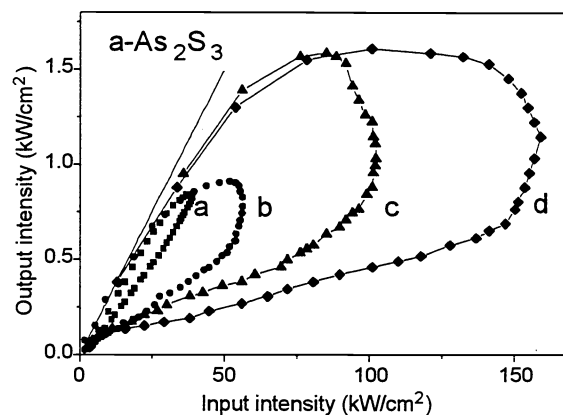


Fig. 4. Hysteresis dependencies of output light intensity versus input one. Incident pulse peak intensity ( $I_o$ ): 40 (a), 55 (b), 105 (c), and  $160 \text{ kW/cm}^2$  (d). Film thickness -  $2.6 \mu\text{m}$ ,  $\hbar\omega = 2.58 \text{ eV}$ .

The kinetics of the film induced darkening in the field of laser pulses can be determined from the laser pulse oscillograms at the input and output of the sample. Fig. 5 presents the curve of the transmission change (in per cents) during the film irradiation by a laser pulse. The characteristic times of the setting in of the new light absorption quasiequilibrium state (corresponding to the horizontal part in Fig. 5) in the field of laser pulses were measured. They are less than  $0.5 \mu\text{s}$  and do not exceed the duration of the laser pulses.

The photoinduced increase of the  $\text{a-As}_2\text{S}_3$  light absorption coefficient in the field of the laser pulses has a reversible character, i.e. the medium fully restores its initial transmission state after the ending of the laser pulse, and if the same place of the sample is irradiated with another laser pulse the effect can be completely repeated.

So, the most characteristic peculiarities of the measured nonlinear light transmission in  $\text{a-As}_2\text{S}_3$  are the following: a nonlinear increase of the light absorption coefficient; the threshold character of the nonlinear transmission; the change of the time profile of the laser pulses, leading to a hysteresis-like transmission dependence; the characteristic time constants of the photoinduced darkening, which does not exceed the laser pulse duration; the independence of the photostructural transformations. These results correlate with the analogous measurements in  $\text{As}_2\text{Se}_3$ ,  $\text{AsSe}$ ,  $\text{GeSe}_2$  chalcogenide glass films<sup>2,3</sup>.

The peculiarities of the pulse absorption in  $\text{c-As}_2\text{S}_3$  film were measured to compare the behavior of crystalline and amorphous  $\text{As}_2\text{S}_3$  samples in powerful field of laser pulse. In the case of  $\text{c-As}_2\text{S}_3$ , the wavelength of the laser generation was changed to  $\lambda = 450 \text{ nm}$  to have the similar excitation conditions. The orientation, corresponding to the minimum of the light transmission of  $\text{c-As}_2\text{S}_3$  thin films (the light electric vector  $E$  is directed in the middle between  $a$  and  $c$  axes of the crystal<sup>4</sup>) was chosen to get the absorption coefficient  $\alpha = 7.3 \cdot 10^3 \text{ cm}^{-1}$ , comparable with amorphous material one. Fig. 6 shows the dependence of the output laser pulses peak intensity versus input one. As a result of measurement no dependence (in limits of experimental error  $< 20\%$ ) of light absorption in  $\text{c-As}_2\text{S}_3$  from pulse intensity was revealed.

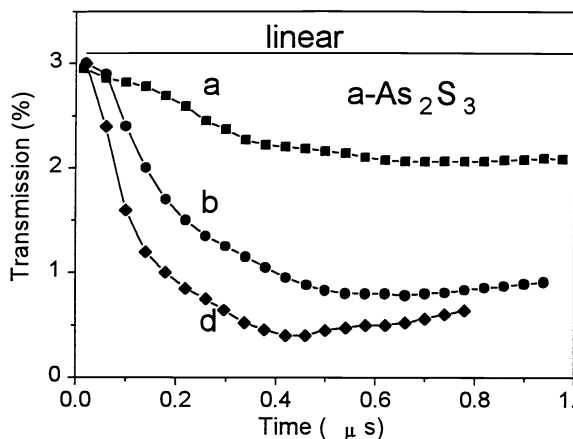


Fig. 5. Kinetics of the a-As<sub>2</sub>S<sub>3</sub> darkening during the pulse irradiation. The parameter values - the same as in the Fig. 4.

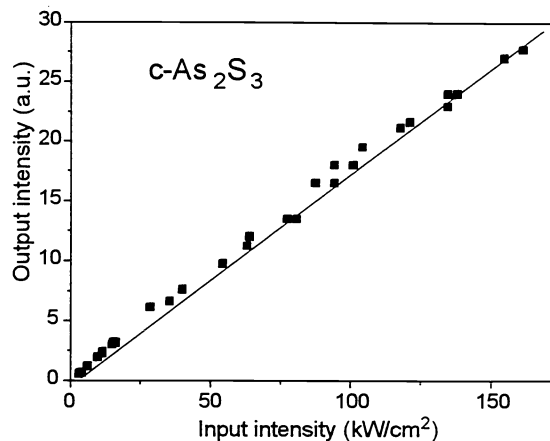


Fig. 6. The output laser pulses peak intensity versus input peak intensity in c-As<sub>2</sub>S<sub>3</sub> film (thickness 5 μm),  $\hbar\omega = 2.75$  eV.

#### 4. DISCUSSION

A distinct peculiarity of the amorphous semiconductors is the presence of a high ( $10^{16}$ - $10^{19}$  cm<sup>-3</sup>) density of the localized states in the optical bandgap. As a rule, in the literature the nonlinear light absorption peculiarities in the amorphous semiconductor transparency region are connected with carrier occupation and redistribution on these states<sup>2</sup>. In a number of works this mechanism is also proposed for the explanation of the laser pulse nonlinear absorption at the amorphous semiconductor interband excitation<sup>2,5,6</sup>. However, the laser pulses nonlinear absorption at amorphous semiconductor interband excitation, described in this work, cannot be explained on the basis of the occupancy and redistribution of the carriers on the localized states with their next excitation in the conduction band. It is conditioned by the fact that the probability of the transitions "localized state-band" is some orders lower than the interband optical transition probability. Consequently, it is rather difficult to experimentally distinguish such a low contribution to the absorption (at the same light wavelength) from the interband absorption. This is even more difficult because the optical absorption spectrum of the investigated film and the energy dependence of the density of states in the optical bandgap have a monotonous dependence in energy.

The nonlinear photoinduced darkening under laser pulses, described in the present work, is accompanied by photostructural transformations (with the  $E_g$  shift) only in freshly prepared (previously not illuminated) samples. The described photoinduced a-As<sub>2</sub>S<sub>3</sub> darkening in the laser field has another physical nature than the glass photostructural transformations<sup>2</sup>, because it is reversible (the initial ChG film light transmission sets completely in during 1 to 100 μs<sup>2,3</sup>). It was experimentally shown that the peculiarities of the laser pulse nonlinear absorption are the same in previously darkened (by other light pulse) a-As<sub>2</sub>S<sub>3</sub> film.

It is impossible to explain the laser pulses nonlinear transmission by the homogeneous heating of the a-As<sub>2</sub>S<sub>3</sub> films. The temperature coefficient of the optical absorption edge shift ( $dE_g/dT$ ) in these compounds is about  $5 \cdot 10^{-4}$  eV K<sup>-1</sup>. Therefore, to change the absorption light coefficient in the absorption edge region, by an amount equal to the one revealed in the experiment (up to 1.8 times), it is necessary to heat the a-As<sub>2</sub>S<sub>3</sub> sample to a temperature considerably exceeding the temperature of the material softening. Moreover, an analogous laser pulses nonlinear absorption has also been registered at light quantum energies, considerably exceeding the a-As<sub>2</sub>S<sub>3</sub> optical band gap ( $E_g$ ), where the contribution of the temperature shift of the absorption edge on the light transmission change is smaller.

In the investigated ChG samples the interband linear and nonlinear light absorption coefficients depend on the temperature<sup>2,3</sup>. Consequently, a considerable role in the interband light absorption is played by the transitions with a simultaneous participation of light quanta and phonons. In noncrystalline materials the local-density fluctuations result in strong vibration scattering, and in localization of the excited vibrational modes with energies above the mobility edge  $\omega_c$ <sup>6</sup>. There is also a large inelastic phonon scattering rate caused by anharmonic coupling between the extended state phonon ( $\omega < \omega_c$ ) and localized vibrational modes with frequencies  $\omega > \omega_c$ . The additional phonons can be generated as a result of the hot carrier (created by the light) energy dissipation. It is not very difficult to estimate that the number of created phonons due to the energy dissipation of hot carriers is of the same order as the number of the equilibrium phonons using laser pulse energy density in the range 1 to 10 mJ/cm<sup>2</sup>. We suggest that the optical transmission hysteresis in a-As<sub>2</sub>S<sub>3</sub> can be explained, as in the case of a-As<sub>2</sub>Se<sub>3</sub>, a-AsSe, a-GeSe<sub>2</sub><sup>2,3</sup> by the mechanism of the interband light absorption with participation of nonequilibrium localized lattice vibrations anharmonically coupled with the extended phonons. This is confirmed by the measurements (in the same conditions as for a-As<sub>2</sub>S<sub>3</sub>) of the peculiarities of pulse absorption in c-As<sub>2</sub>S<sub>3</sub> films, where the local-density fluctuations are absent. As a result of measurements no dependence of light absorption in c-As<sub>2</sub>S<sub>3</sub> from pulse intensity was revealed.

## 5. CONCLUSIONS

Result of the investigations of the nonlinear absorption of short laser pulses in a-As<sub>2</sub>S<sub>3</sub> films have been described. The most characteristic peculiarities of the measured nonlinear light transmission in a-As<sub>2</sub>S<sub>3</sub> are the following: a nonlinear increase of the light absorption coefficient; the threshold character of the nonlinear transmission; the change of the time profile of the laser pulses, leading to a hysteresis-like transmission dependence; the characteristic time constants of the photoinduced darkening, which does not exceed the laser pulse duration; the independence on the photostructural transformations. A physical mechanism of nonlinear light absorption in amorphous semiconductors, taking into account the interaction with nonequilibrium phonon modes, was suggested for explanation of the experimental results.

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