

PACS numbers: 42.70.Nq; 42.65.Re
DOI: 10.1070/QE2001v031n05ABEH001964

Formation of microstructures in As_2S_3 by a femtosecond laser pulse train

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***Abstract*. Irradiation of the As_2S_3 chalcogenide glass by a train of focused femtosecond laser pulses from a master oscillator based on a Ti:sapphire crystal results in the formation of submicron structures in the bulk of the sample with modified optical properties. The minimum exposure time for producing such microstructures does not exceed 1 μs. A model based on two-photon absorption of laser radiation and local heating of the sample material is proposed for this phenomenon.**

Keywords: *As_2S_3 chalcogenide glass, photorefractive effect, femtosecond light pulses.*

In recent years, femtosecond lasers have been used widely for irradiation of various materials to obtain micron and submicron structures [1 – 5]. One of the advantages of using femtosecond pulses lies in the suppression of heat-conduction processes and a consequent decrease in the size of such structures. A distinguishing feature of femtosecond radiation is its high intensity, which makes it possible to realise the nonlinear mechanism of exposure and also helps in minimising the size of the obtained structures. In addition, nonlinear processes (such as ionisation and two-photon absorption) makes it possible to create 3D structures [1, 2], which is of prime importance for applications such as photonic crystals, 3D memory, etc.

In a number of works published in recent years, femtosecond laser pulses were used for producing 3D microstructures during photopolymerisation [1, 2] or ionisation of the sample material [4, 5]. However, wide avenues are still open for studying the optimisation of the conditions of exposure leading to the maximum rate of 'recording' of structures and their microminiaturisation, as well as new 'nonlinear' materials which would make it possible to optimise the process of microstructure formation.

In this paper, we study the effect of a femtosecond laser pulse train on the semiconductor As_2S_3 chalcogenide glass. The source of radiation was a Ti:sapphire laser generating a train of 75-fs pulses at $\lambda \approx 0.8$ μm with a mean power $P_{in} \leqslant 200$ mW, pulse repetition rate $F = 81$ MHz (pulse energy $W_p \leqslant 2.5$ nJ).

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Received 21 March 2001
Kvantovaya Elektronika **31** (5) 398 – 400 (2001)
Translated by Ram Wadhwa

Laser radiation was focused with the help of an aspheric lens of focal length $f = 6.24$ mm at a depth 0.3 – 0.8 mm inside the sample. The diameter $2r_0$ of the spot at the focus of the lens, estimated by measuring the diameter of the incident beam, was found to be 2.2 μm, and the corresponding Rayleigh length l_R was ~ 24 μm. This made it possible to attain an intensity $I \approx 10^{12}$ W cm^{-2} at the lens focus at the maximum incident energy. The radiation intensity in the sample was varied by using an attenuator consisting of a half-wave plate and a polariser.

The sample placed on a three-coordinate table was in the form of a polished parallelepiped of size 15 mm × 15 mm × 5 mm. An optomechanical modulator placed in front of the sample provided a variation of the exposure from a few nanoseconds to tens of seconds with a pulse leading edge steepness of the order of a nanosecond. The energy of laser pulses incident on the sample and transmitted through it was monitored by calibrated photodiodes with a nanosecond time resolution. The emergence of the region of a modified material in a sample was observed through an optical microscope. The time required for the appearance of microstructures was determined from the variation (decrease) in the amplitude of the output signal from the pho{wtodiode used for measuring the transmitted energy.

If the energy of the incident pulses exceeds a certain threshold value, the exposure of an As_2S_3 sample to a train of focused femtosecond pulses results in the formation of a region with a modified refractive index, which was observed through a microscope. The emergence of such microstructures was accompanied by a decrease in the energy of laser pulses transmitted through the sample. The exposure time required for the formation of such regions depended on the energy of the incident pulses and decreased with increasing energy. For an exposure time close to the time required for the emergence of the modified region, the resulting structure had a visible diameter $d \leqslant 1$ μm, while its length in the direction of propagation of the incident radiation was found to be $l = 4 - 5$ μm. Upon an increase in the exposure time, the modified region started expanding towards the incident radiation and its diameter increased gradually. The modification of the sample material was irreversible and was preserved after the termination of exposure.

Exposure of the As_2S_3 sample to continuous Ti:sapphire laser radiation with the same average power did not produce any visible changes in it. Exposure of the sample to femtosecond pulse trains (with a train repetition rate ~ 100 Hz), which did not produce microstructures during the passage of a train, also did not lead to the formation of regions with modified properties. However, an increase in

the duration of a pulse train did lead to the emergence of microstructures, thus indicating that relaxation from the action of a pulse train occurs in the interval between such trains (~ 10 ms).

Fig. 1 shows the dependence of the energy of the first pulse from a train passing through the sample (before the formation of a modified region in it) on the energy of the incident pulses. One can see that the deviation of this dependence from a linear one increases with the incident pulse energy. Since the angle of vision of the receiving equipment was large, the scattered radiation was collected, at least for not-too-large scattering angles. Thus, the observed departure from linearity was associated with the absorption, which amounted to $\sim 40\,\%$ at the maximum incident energy. The dependence of the time of appearance of microstructures with modified properties on the incident pulse energy is shown in Fig. 2 (the solid curve in the figure corresponds to the dependence $\sim 1/W_p^2$). Note that the minimum time τ_{min}^{exp} required for the formation of microstructures in our experiments was of the order of 300 ns (corresponding to a train of ~ 25 femtosecond pulses).

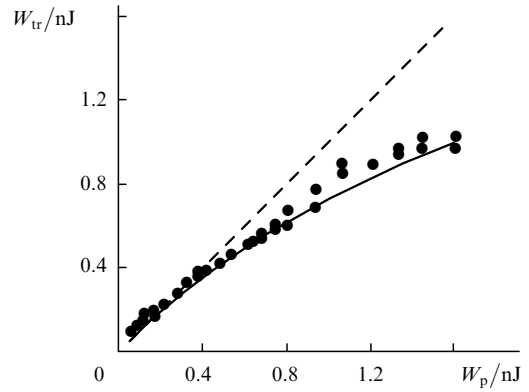

Figure 1. Experimental dependence of the energy W_{tr} of the first transmitted pulse from a pulse train on the incident pulse energy (circles) and its approximation (solid curve), as well as the linear dependence $W_{tr} = W_p$ (dashed line).

The following model is proposed for explaining the experimental results obtained in our work. Upon two-photon absorption of laser radiation (the band gap in As_2S_3 is $E_g \approx 2.55$ eV, and the energy of a laser photon is ~ 1.55 eV), electrons from the valence band are transferred to the conduction band. During the subsequent energy relaxation in the conduction band and recombination of electrons back to the valence band, most of the energy spent on ionisation is transformed into heat. The luminescence losses upon photoexcitation of As_2S_3 at room temperature are insignificant [6].

Persistent exposure of the sample to femtosecond pulses leads to its local heating. The heating is localised because the heat-conduction-controlled time τ_T of spreading of the region of energy release of characteristic size r_0 is $\sim r_0^2/\chi \sim 5$ μs, where $\chi = 4 \times 10^{-4}$ cal cm^{-1} K^{-1} is the thermal diffusity of As_2S_3 [7]. Thus, heat conduction is insignificant for most of the data presented in Fig. 2. In our view, the emergence of visible microstructures is associated with the heating of the sample to the temperature of softening (melting point) of the chalcogenide glass and its subsequent solidification. The observed changes in the optical properties are apparently caused by the emergence of mechanical stresses in the sample material during its softening and subsequent solidification and (or) local variations in the microstructure of the glass occurring as a result of this.

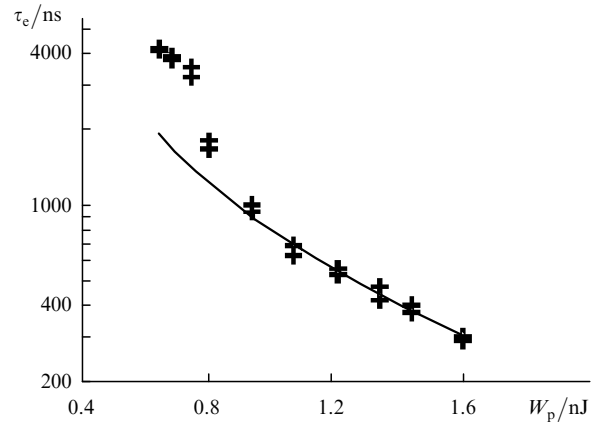

Figure 2. Experimental dependence of the microstructure appearance time on the incident pulse energy (crosses), as well as the dependence $\sim 1/W_p^2$ (solid curve).

For a quantitative comparison of our model with the experiment, we find first the two-photon absorption cross section using the experimental data presented in Fig. 1. For this purpose, we carried out numerical simulation of the propagation of a Gaussian beam of electromagnetic radiation (in space and time) within the framework of the parabolic equation taking the two-photon absorption into account. Comparison of the obtained theoretical dependence of the transmitted pulse energy on the energy of the incident pulse with the experimental dependence made it possible to determine the two-photon absorption cross section δ_2, which was found to be 8.5×10^{-32} cm^4 W^{-1}. We could not find in the literature any data for the two-photon absorption cross section at a wavelength $\lambda \approx 0.8$ μm, but the value obtained by us was found to be in reasonable agreement with the available values of δ_2 for other wavelengths: $\delta_2 \approx 3.2 \times 10^{-32}$ cm^4 W^{-1} for $\lambda = 1.064$ μm [8], and $\delta_2 \approx 1.75 \times 10^{-29}$ cm^4 W^{-1} for $\lambda = 0.696$ μm [9].

Let us estimate the sample heating in the focal region during two-photon absorption. The number of two-photon absorption events in unit volume per unit time is proportional [10] to the two-photon absorption cross section δ_2, concentration n_0 of the absorbing molecules, and the square of the intensity I_0 at the focus. In this case, the energy released in a unit volume at the focus during the time τ_p of action of a pulse is $\Delta W \approx \delta_2 n_0 \tau_p I_0^2$. For a pulse repetition rate F, the energy release rate per unit volume is

$$\frac{dW}{dt} \approx \delta_2 n_0 \tau_p I_0^2 F. \qquad (1)$$

The microstructures observed in As_2S_3 are formed when the absorbed energy becomes sufficient to heat the material of the sample to its melting point T_m. The time τ_e of the emergence of microstructures can be determined from the relation

$$\delta_2 n_0 \tau_p I_0^2 F \tau_e = c_p \rho T_m, \quad (2)$$

obtained by integrating Eqn (1), where $c_p = 0.46$ J g^{-1} K^{-1} is the specific heat and $\varrho = 3.2$ g cm^{-3} is the density of As_2S_3 [7]. The dependence $\tau_e \sim 1/I_0^2 \sim 1/W_p^2$ following from Eqn (2) is shown in Fig. 2 and is found to be in good agreement with the experimental data for $\tau_e \leqslant 1$ μs. Apparently, the departure from the inverse quadratic dependence at low energies of the incident pulse is due to heat-conduction losses, which necessitate a large energy contribution, and hence large values of the microstructure formation time. Substituting the maximum pulse energy W_p into Eqn (2), we obtain $\tau_e \approx 0.4$ μs, which is close to the experimental value $\tau_{min}^{exp} = 0.3$ μs (see Fig. 2).

The proposed model of two-photon absorption and subsequent local heating of the sample also explains the experimental fact concerning the absence of microstructures in samples exposed to continuous radiation (due to the absence of two-photon absorption). The heat-conduction-controlled cooling of the focal region of the sample, occurring during the intervals between separate femtosecond pulse trains, explains the absence of sample material modification after exposure to several pulse trains if the energy of a pulse in the train is lower than the value required for modification of the material.

Thus, a relatively simple Ti:sapphire master oscillator of femtosecond pulses can be used to produce modified material structures of submicrometer size in a sample of As_2S_3 exposed to focused low-intensity laser radiation. The time required for the formation of microstructures is inversely proportional to the square of the laser pulse energy, and was found to be smaller than one microsecond in our experiments ($\tau_{min}^{exp} \approx 0.3$ μs). The model proposed by us is based on two-photon absorption of laser radiation with a subsequent local heating of the sample material and provides a noncontradictory explanation for the entire body of the experimental data. A quantitative agreement between the experimental data and the results of our model was obtained by measuring the two-photon absorption cross section at the wavelength $\lambda = 0.8$ μm.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (Grant Nos 98-02-17013 and 99-02-17257).

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