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LASER PULSE EFFECTS IN Se-S GLASSY THICK FILMS

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Amorphous thick films in the system Se-S have been prepared by splat-cooling. Local irradiation of the films with laser pulses of various intensities and wavelengths were carried out. The effects induced by laser pulses with special emphasis to the eutectic composition $Se_{42}S_{58}$ were investigated by optical microscopy and before and after annealing of the films. For low density of power incident on the film, a local photo-darkening effect is observed. For mean power density the photo-darkened region increases. For high power density a considerable destructive effect appears, which determine the appearance of clusters of bubbles after annealing the film at the softening temperature.

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1. Introduction

Thick non-crystalline films in the system Se-S have been obtained by quenching the corresponding melts to room temperature. The photo-structural effects induced in the Se-S films are accompanied by modifications of the position of the absorption edge and of the refractive index [1]. For high incident power the accompanying thermal effect induces crystallization and local evaporation. The annealing effect after irradiation, with the formation of small bubbles, suggested using these films in designing a new type of optical memory device with $Se_{0.975}S_{0.025}$ [2].

In this paper we report the results of a study of the effect of laser pulses on the thick Se-S films, with special emphasis on the eutectic composition, prepared in non-crystalline state by splat cooling.

2. Experimental

Homogeneous composition in the system Se-S were prepared by encapsulating the mixture of selenium (99.999 Hoboken sulfur 99.9, Romanian Trade Mark) in evacuated Pyrex ampoules followed by heating at ~220 ^{o}C. The ampoules were maintained for 2 hours at this temperature and were shaked from time to time. Then the melts were quenched on a copper block covered by a tungsten foil. Glassy films of thickness ~ 0.1-0.2 mm were obtained. The following Se_xS_{1-x} compositions were prepared: (x= 0.25; 0.42, 0.5; 0.6; 0.8; 0.9). Red, dark-red and gray films were obtained, as a function of composition. All the films exhibited plasticity, related to the non-crystalline structure, as proved by optical inspection and x-ray diffraction.

Then the films were pressed between two ordinary glass plates when heated at 100^{o} C, in order to get uniform thinner films to be used as targets for laser pulses. All the films are stable at temperatures of ~ –10 ^{o}C. At room temperature some compositions with high sulfur content are stable for ~ 2-4 weeks, then they crystallize.

Two pulsed lasers were used for the investigation of the photo-induced effects in glassy Se-S films:

- a ruby laser working in relaxed regime with the pulse length of τ = 500 μs, λ = 0.6943 μm.

- a YAG-Nd laser with τ = 10 ns (working in the regimes: nanopulse (14 mJ/pulse) and double pulse (28 mJ/pulse) λ = 1064 nm.

The spot can be adjusted in the range: 10 μm - 1000 μm. The examinations of the laser pulse effects were performed in a Leitz-Orthoplan-pol microscope.

A considerable attention was paid to the sample with the eutectic composition in the system: $Se_{0.42}S_{0.58}$. This composition exhibits the lowest melting temperature (T_t = 105 ^oC) [3] and the highest stability in the glassy state.

3. Results

Under the action of light the glassy chalcogenides from the system changes the position of the fundamental absorption edge, and, therefore, of the transparency [4]. This is the so-called photo-darkening effect.

Laser pulses of variable total energy were applied on the Se-S films. As a consequence, the irradiated zone suffered transformations and a latent image of the spot was registered. In time, the image develops under the form of a darkened zone. The experimental data for the composition $Se_{0.42}S_{0.58}$ are given in Table 1.

Table 1. Ruby laser pulse effect on $Se_{0.42}S_{0.58}$ glassy film.

Pulse energy (mJ)	Spot diameter (μm)	Observed photo-darkening
< 100	-	Absent
200	23	after 24 h
330	80	after 24 h
580	300	after 3 h
750	350	after 1 h
980	400	immediately

The minimum energy of the pulse (200 mJ) corresponds to a threshold for the induced photo-structural effects. It is observed a strong correlation between the size of the photo-transformed region and the total energy of the laser pulse. This behavior can be explained by the thermal induced effect of photo-transformation around the zone of pulse impact. An induced crystallization seems to be responsible for the photodarkening of the sample.

In order to prove this transformation, a thin film was irradiated on a broad area and the transformation of the $Se_{0.42}S_{0.58}$ material was investigated by X-ray diffraction.

Fig. 1 shows the results.

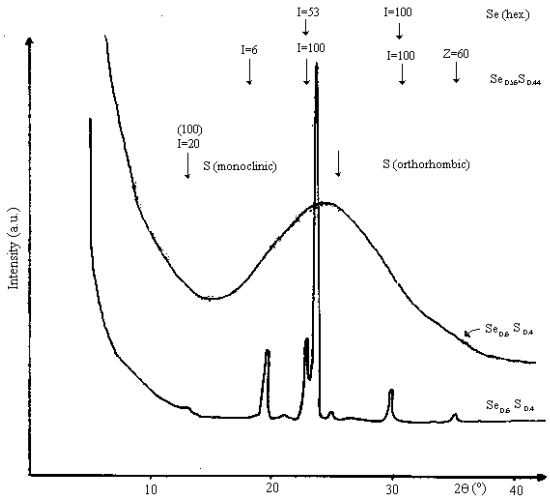
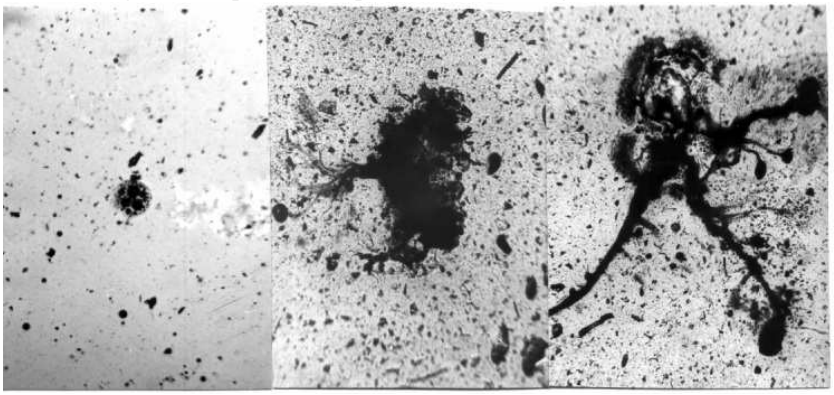


Fig. 1. X-ray diffraction before and after laser pulse irradiation and storage in dark for several days.

As a general observation, the photo-transformation of the glassy films advances in time and the advancing speed is increased by the macroscopic defects in the films (e.g. cracks, see Fig. 2c). The greatest stability against the advancement in time of the crystallization is manifested in the film of composition $Se_{42}S_{58}$. Low temperature storage determines a good stability of all the films.

Fig. 2 shows the general aspect of the photo-darkened regions in $Se_{42}S_{58}$ films.



a b c

Fig. 2. Photograph of the darkened regions obtained by ruby laser pulse irradiation of a $Se_{42}S_{58}$ glassy film: a- 200 mJ (spot diameter:10 μm); b – 580 mJ; c – 750 mJ.

In the following stage of the research we have studied the effect of high-energy laser pulse on the Se-S films.

Fig. 3 shows the effect of the pulse with 980 mJ on a $Se_{42}S_{58}$ glassy film. The high power density changed considerably the region of the pulse impact (to a size of ~60-100 μm). A central crater is clearly seen. A diffusion of sulfur or even a release of this element outside the central crater is suggested. Some dark spots around the central crater are probable due to the strong thermal effects of the laser pulse.

Then, the film was subjected to thermal annealing at a temperature of ~ 100 ^{0}C. A strong transformation of the film takes place, while the central crater seems to preserve its feature: the dark spots around the crater transform in nearly perfect round bubbles, of size 10-40 μm (Fig. 4). The bubbles are very stable in time, and, due to the perfect transparency of every bubble, the cluster of bubbles defines a zone of transparency in the film.

The formation of transparent bubbles can be explained by a phase separation in the darkened zone. Some phases (e.g. sulfur) evaporates very easily during heating and, as a result of vapour pressure, it is formed in the film a disk filled with sulfur vapour. By cooling at room temperature, sulfur crystallizes at the margins of the disc, the inner part remaining empty.

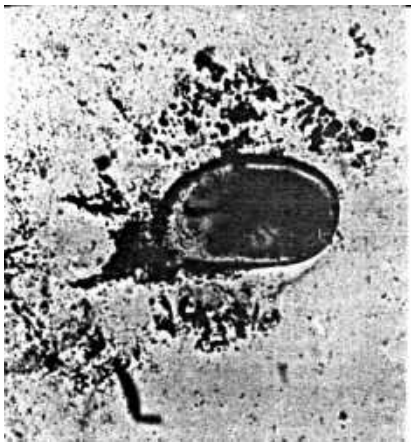


Fig. 3. Images of the film $Se_{42}S_{58}$ in the region of impact of a simple laser pulse (ruby) of energy 980 mJ immediately after impact.

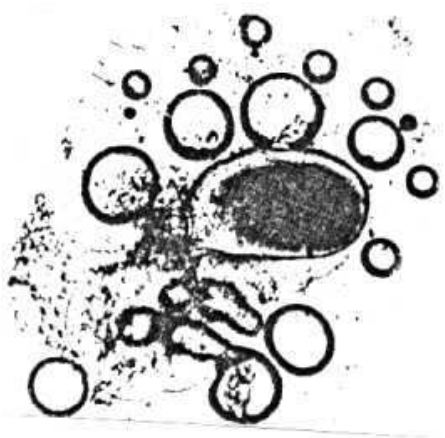
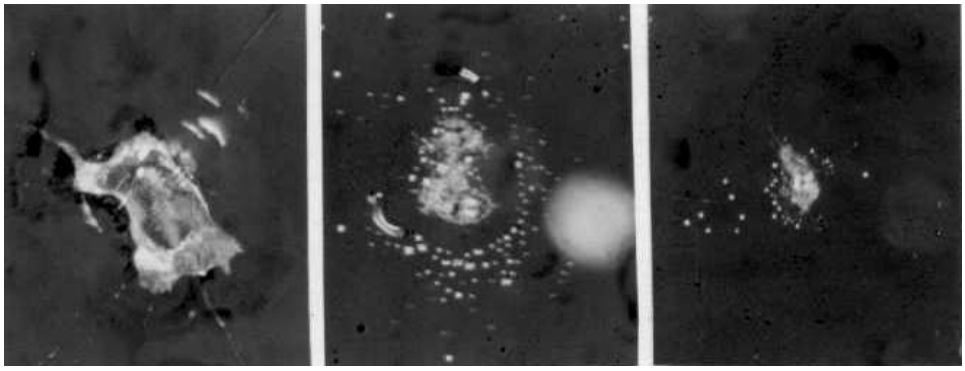


Fig. 4. The same region of the laser pulse impact, in $Se_{42}S_{58}$ film after heat treatment at ~100 ^{0}C.

The effect of the single pulse emitted by the YAG - Nd laser with the energy per pulse of 14 mJ and duration 10 ns (power per pulse : 1.4 MW; λ = 1064 nm) is shown in Fig. 5a.



a b c

Fig. 5. The effect of a single laser pulse on the eutectic composition $Se_{42}S_{58}$. (YAG-Nd laser λ = 1064 nm : τ = 10 ns); a) E = 14 mJ; b) E = 6.7 mJ; c) E = 3.8 mJ. Magnitude: 1 cm $\rightarrow$ 50 μm

The chalcogenide film ($Se_{42}S_{58}$) is strongly damaged on a region of 70 × 120 μm. The pulse has a diameter of ~ 50μm. Fig. 5b and c shows the effect of the laser pulse whose intensity was reduced by 48% and 27%, respectively. The dimensions of the central irradiated zone are 50 × 80 μm and 30 × 50 μm, respectively. The irradiated zone changes the colour from the red to yellow due probably to the release of sulphur during irradiation. In the same time, around the laser pulse impact region, groups of micro - bubbles appears. These micro - bubbles transform into large, stable bubbles during thermal annealing as in the case of the experiments with ruby laser pulses.

The experiments with laser pulses of different wavelengths show that moderate energies produce significant modifications in Se-S materials. The main aspects are the release of sulphur and the formation of bubbles. An irreversible optical memory based on the diffusion of light on bubbles is under study.

4. Conclusions

The results obtained by irradiation of glassy Se-S films by laser pulses allowed to conclude that it is possible to get transparent bubbles, which can be suggested to be used for an optical memory. The most important composition for the formation of the bubbles seems to be $Se_{42}S_{58}$. The minimum of the bubble size obtained by us was 10 μm and the maximum 40 μm. A control of the bubble size and, especially, finding the conditions for getting of only one bubble for a laser shot can ensure an optical RAM memory of enough high density : 10^8 bit/cm^2.

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