Structural transformations and optical absorption spectra of Sb_xSe_{1-x} films

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Abstract

Thermo- and photostimulated processes of crystallization and amorphization of Sb_xSe_{1-x} films ($0.20 \le x \le 0.70$) as well as their optical absorption spectra are studied. The effect of thermal annealing on the optical absorption spectra of the films is investigated and the temperatures T_t of their transition to the crystalline state are determined. T_t is shown to decrease with x. At the transition from the amorphous to the polycrystalline state transition the whole spectral range ($0.60 \le \lambda \le 2.70$ μm) decreases non-selectively, which is related to the transformation of the film structure. The transmission spectra of the amorphized areas are similar to the spectra of freshly-evaporated films. The threshold intensities of crystallization and amorphization of Sb_xSe_{1-x} films are determined.

Keywords: crystallization, amorphization, optical absorption spectra, phase transition, structural transformations

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Introduction

Photothermal processes are used for optical recording and erasing in storage discs, where the absorbed light energy is converted into heat and results in a thermostimulated phase transition in to a photosensitive medium. As a rule, the transition is accompanied by an essential change of a wide variety of physical properties [1–3]. The amorphous state ↔ crystalline state reaction is efficient. Non-crystalline antimony chalcogenides (Sb–S and Sb–Se systems), possessing high crystallizability, are promising photosensitive media for the reversible photorecording.

Here we present the results of the studies of thermo- and photostimulated processes of crystallization and amorphization of Sb_xSe_{1-x} ($0{,}20 \le x \le 0{,}70$) films and their optical absorption spectra.

Experimental

Amorphous Sb_xSe_{1-x} films were obtained by thermal sputtering in $5 \cdot 10^{-6}$ Torr vacuum on glass substrates. The composition, evaporated in the vacuum, was synthesized from elemental Sb and Se in evacuated quartz ampoles in accordance with the technique, described in [4]. The film thickness in the course of evaporation was measured from interference-modulated optical absorption of the film at the wavelength $\lambda = 1.15$ μm, and after the evaporation – using an MP-4 interferential microscope, and was 0.3 μm (in the study of thermal annealing) and 0.10–0.05 μm (for experiments with nanosecond laser pulses).

The study of the freshly-evaporated Sb_xSe_{1-x} films by polarization microscopy have shown the absence of a dispersive structure, typical for the polycrystalline state, and qualitative electron

diffraction analysis has revealed no extreme reflexes.

Thermal annealing of the films was carried out in an ampoule with argon atmosphere with an average heating rate of 10 K/min. To study the optical absorption in the course of thermal annealing, the sample, located in a special heating cell, was illuminated by a light beam with λ = 0.9 μm from the output slit of a monochromator or by collimated radiation of a semiconductor GaAs-laser with λ = 0.83 μm. The samples were heated with a constant rate V=3.50 K/min. The amorphous-to-polycrystalline phase transition temperature T_{ph} was determined for the given V, the transition being identified by the sharp decrease of the film optical absorption and qualitatively estimated by polarization microscope observation.

Photocrystallization of amorphous films was achieved by a focused to ~ 1.0 μm (λ=0.63 μm) and determined from the change of reflectance, defined from the power of the partially reflected exciting radiation. The exposing pulse power is 15–40 mW, decreasing with the increase of antimony concentration in the Sb_xSe_{1-x} films.

The optical absorption spectra of the samples were studied in the wavelength range $0.60 \le \lambda \le 2.70$ μm on a VSU–2P spectrometer. All measurements (except thermal annealing) were carried out at room temperature..

The photoinduced amorphization of the crystallized Sb_xSe_{1-x} films was achieved by a single YAG:Nd^{3+} laser pulse, incident on the film through the substrate, with λ = 1.06 μm and duration τ = 15 ns. The threshold values of the incident light intensity for the beginning of the amorphization and for the formation of ablative discontinuities in the film differ by a factor of about 3, thus imposing essential restrictions on the uniformity of the intensity distribution over the light spot and the film depth. In order to reduce this non-uniformity (d = 2 mm) a diffuser was applied, and relative uniformity of the beam intensity over the film depth was achieved by a choice of the film thickness (≤ 0.10 μm).

Results and discussion

The studies of the optical absorption spectra have shown that the absorption edge of the fresh amorphous films is located near λ=1.0 μm and has a trend to red shift at the increase of Sb content in the film composition.

At the thermal annealing of fresh amorphous films a monotonous decrease of optical transmittance at the wavelength λ=0.90 μm is observed (Fig.1), its major part being irreversible in temperature and evidently related to the irreversible thermally induced changes of the film structure before crystallization. When the phase transition temperature T_{ph} is achieved, the film transmittance shows a stepwise decrease, accompanied by a disperse structure typical for the polycrystalline state, appearing in the polarizational microscope. The non-selective decrease of the transmittance in the whole spectral range ($0.60 \le \lambda \le 2.70$ μm) occurs (Fig. 2, curves 1 and 2) at the amorphous-to-polycrystalline state transition of the film.

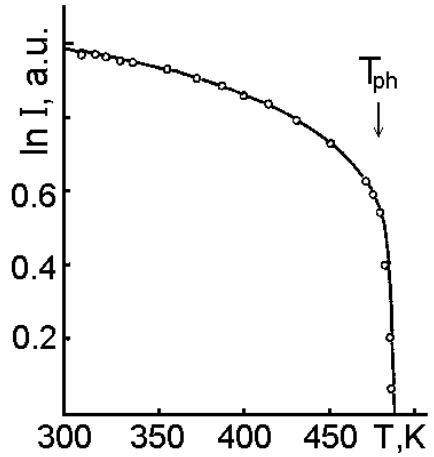

Fig.1. Optical transmittance variation at the wavelength λ = 0.90 μm for the fresh amorphous $Sb_{0.65}Se_{0.35}$ film in the course of thermal annealing.

The value of T_{ph} in Sb_xSe_{1-x} films decreases with the antimony content in their composition

(from 497 K for $Sb_{0.40}Se_{0.60}$ to 463 K for $Sb_{0.70}Se_{0.30}$). Reflectance measurements at $\lambda = 0.63$ μm for Sb_xSe_{1-x} films have shown that the crystallization and photocrystallization is most effective for the layers with $x \geq 0.40$. The difference in the film reflectance in the amorphous and polycrystalline state is maximal at $x = 0.65$. The photocrystallization of the amorphous films occurs under continuous laser light ($\lambda = 0.63$ μm) whose intensity $\mathbf{I}_l$ exceeds a certain threshold value $\mathbf{I}_t$. For the 0.3-μm thick $Sb_{0,65}Se_{0,35}$ film the value of I_t is $\sim 3 \cdot 10^3$ W/cm^2.

The experiments on photoinduced amorphization of crystallized Sb_xSe_{1-x} films have shown that no changes of the optical properties are observed until a certain threshold intensity of the incident light $\mathbf{I}_1$ is achieved. After recording with $\mathbf{I} > \mathbf{I}_1$ in the incident film distinctly separated islands of an other phase with higher optical transmittance are revealed. With the increase of the laser pulse intensity the fraction of these islands in the record area increases.

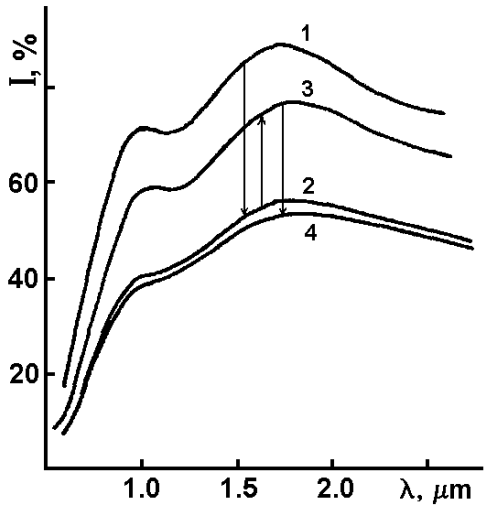

Fig. 2. Optical transmittance spectra of $Sb_{0.65}Se_{0,35}$ film: 1 – fresh film; 2 – the film after thermal annealing; 3 – area, recorded by a nanosecond laser pulse; 4 – record area after the repeated annealing of the film.

The presence of the threshold intensity for the photothermal reactions, in particular, the crystalline-to-amorphous state transition, is also reported in the studies of other authors [3,5].

The disperse structure of the polycrystalline background, surrounding the islands, is not observed in the islands themselves. The transmittance spectrum of the amorphized area is somewhat intermediate between the spectra of the fresh and crystalline films (curve 3 in Fig. 2), approaching with the increase of $\mathbf{I}$ to the transmittance spectrum of the fresh film (curve 1 in Fig. 2). At $\mathbf{I} \geq \mathbf{I}_2 \approx 3\mathbf{I}_1$, besides the islands of the other phase, a considerable number of ablative holes appears in the film. For Sb_xSe_{1-x} films from within the composition range $0.55 \leq x \leq 0.70$ no qualitative difference in the phenomena is revealed. The typical values of $\mathbf{I}_1$ and $\mathbf{I}_2$ for the samples of this interval are $4 \cdot 10^6$ and $1.4 \cdot 10^7$ W/cm^2, respectively.

At subsequent thermal annealing the areas of the new phase disappear, merging with the polycrystalline background, and only ablative holes remain as traces in the recorded areas. The transmittance spectrum of the record area looks like curve 4 in Fig. 2, practically coinciding with the crystalline film spectrum before the recording (curve 2 in Fig. 2). In the repeated record-erasure cycles the described effects are reproduced qualitatively and quantitatively.

The non-selective reduction of optical transmittance under thermal annealing (curves 1, 2 in Fig. 2) was also observed in [6] and is evidently related to the transition of the uniform film to the polycrystalline state with a possible separation of phases (Sb, Sb_2Se_3). The formation of heterophase composition is the general feature of many photothermal reactions of the amorphous-to-crystalline state transition. Meanwhile, in [6] during the X-ray analysis of $Sb_{0.40}Se_{0.60}$ crystalline films no reflexes, corresponding to crystalline Sb, Se, Sb_2Se_3 or relevant oxides have been found, and the observed series of reflexes was explained by the formation of a new metastable compound Sb_2Se_3. However, the available results are still insufficient to provide an unambiguous conclusion on the mechanism and the final products of the photothermal processes.

The transmittance spectrum of the polycrystalline film after nanosecond laser recording (curve 3 in Fig. 2) is a superimposement of the transmittance spectra of the crystalline part of the film (curve 2 in Fig. 2) and the part of the film, comprised by the new phase island. The approaching of the record area spectrum to the fresh film spectrum (curve 1 in Fig. 2) at the increase of the island fraction in the record area means the transmittances and the structure of the islands and the fresh films are rather closer. The transformation of the record area spectrum at the repeated annealing (curve 4 in Fig. 2) is explained by the return of the islands to the crystalline phase.

The described transition is reversible and can be repeated, providing multi-cycling of optical recording and erasure.

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