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OPTICAL MEDIA FOR INFORMATION RECORDING BASED ON AMORPHOUS LAYERS OF Sb-Se-In SYSTEM

V. M. Rubish*, P. P. Shtets, V. V. Rubish, D. G. Semak, B. R. Tsizh[a]

Uzhhorod National University, 54 Voloshin Street, 88000 Uzhhorod, Ukraine
[a]L'viv State Academy of Veterinary Medicine, 50 Pekars'ka Street, 79010 L'viv, Ukraine

Photocrystallization, amorphization and conditions for optical information recording on amorphous layers of Sb–Se–In system (Sb-Se and Sb_2Se_3–InSb section) are reported. The influence of thermal annealing on the structure and properties of films is evidenced.

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For primary optical recording and erasure the photothermal processes in which the absorbed light energy is transformed into heat and causes thermally stimulated phase transition in a light-sensitive medium are widely used in memory discs. The reversible recording on active layers of chalcogenide materials is mainly performed by using „amorphous state I ↔ amorphous state II" (reaction 1) and „amorphous state ↔ crystalline state" (reaction 2) transitions [1–3]. The redistribution of chemical bonds with the change in the short- and middle-range atomic orders of amorphous state takes place during the reaction 1 [4–5] and optical properties of light-sensitive layers (transmission, refraction, refractive index) are strongly influenced.

The most studied media in which under irradiation the reaction 1 is realized are the media based on arsenic chalcogenides possessing a high ability to photostimulated structural transformations [1,6]. The optical media in which recording – re-recording is performed by the reaction 2 are less studied. In this aspect non-toxic light-sensitive layers based on antimony chalcogenides are of great interest.

In an earlier paper [7] we reported on the peculiarities of preparation and properties of glassy antimony chalcogenides.

Here we report the results of the studies of glass-forming, amorphization range and the information recording conditions for the amorphous layers of Sb–Se–In system (Sb–Se and Sb_2Se_3–InSb sections were studied). The critical rates Q of the melt cooling are calculated in order to predict the formation of glasses and amorphous films in the Sb–Se–In system, to estimate the effect of various kinetic and thermodynamic factors on the glass-forming and amorphization process, as well as to determine the conditions of their obtaining. The critical cooling rates Q, at which during the whole period of cooling only a very small fraction ($z = 10^{-6}$) of its volume can crystallize, were calculated according to the Uhlmann approach [1] based on the Kolmogorov-Avraami equation

$$z = \pi I U^3 \tau^4 / 3$$

Here I is the homogeneous nucleation rate, U – the crystal growth rate. According to [7] the exposition time, τ, during which at the temperature T the fraction of the crystalline phase reaches the value z, is given by

* Corresponding author: Rubish@iss.univ.uzhgorod.ua

$$\tau = \frac{3\pi A^3 \eta}{3T}\left\{\frac{3z}{\pi n}\exp\left(-\frac{16\pi\alpha^3 \Delta H_m T_m^4}{3RT^3\Delta T^2}\right)^{-1}\left[1-\exp\left(-\frac{\Delta H_m \Delta T}{RTT_m}\right)\right]^{-3}\right\}^{1/4} \quad (1)$$

Here A is the elementary displacement of the crystal-glass interface, α – a dimensionless coefficient, equal to about 0.2 for chalcogenides [8], R – the gas constant, T_m – melting temperature, ΔH_m – variation of enthalpy at crystallization, $\Delta T = (T_m - T)$ – the liquid overcooling temperature, n – number of molecules per unit volume, η – the viscosity of the non-assocoated liquid with spherical particles of a diameter d. For the investigated samples the value of η at T = 293 K from the interval $T_m - T_g$ (T_g is the glass-forming temperature) was estimated from the Williams–Landel–Ferry equation [9]

$$\eta = \eta_g \exp\left(-\frac{1}{f_g}\frac{T-T_g}{T-T_0K_0}\right) \quad (2)$$

where η_g – is the melt viscosity at T_g, which for the majority of glasses is equal to 10^{12}–10^{13} Pa·s, f_g – the fraction of fluctuation free volume at T_g, $K_0 = (1 + 1/\ln f_g)$ – a dimensionless coefficient, weakly dependent on the glass nature ($K_0 = 0.68$). The solution of Eq.(1), the determination of the minimal value τ_{min} and the corresponding overcooling value ΔT_{min}, from vhich Q was estimated ($Q = \Delta T_{min}/\tau_{min}$), were perfomed by the method, given in [10].

The calculations have shown that in order to obtain Sb_xSe_{1-x} glasses ($0.01 \le x \le 0.05$) one requires the cooling rates ~ 10–30 K/s. With the increase of Sb content in the glasses Q increases (e.g., for obtaining $Sb_{0.10}Se_{0.90}$ glassy alloy the rate of ~ 80 K/s is required, and for $Sb_{0.25}Se_{0.75}$ alloy – ~ 250 K/s). Having applied such alloy cooling rates, we have obtained in evacuated quartz ampoules Sb_xSe_{1-x} ($x \le 0.25$) glassy alloys. These glasses possess enhanced crystallizability [8]. In In–Se system the glass-forming range extends to 12 at.% In.

Glassy Sb_2Se_3 can be obtained only at the cooling rates ~ 10^3 K/s. Such rates can be achieved by the alloy spinning or its thermal sputtering onto a cool substrate [11]. The latter technique enabled Sb_xSe_{1-x} amorphous films with antimony content up to 70 at.%, possessing high photocrystallizability, to be obtained. Similar rates are required for obtaining non-crystalline alloys of Sb_2Se_3–InSb section ($Q = 1.0\cdot10^3$–$2.5\cdot10^3$ K/s). Thus determined ranges of glass-forming and amorphization in Sb–Se–In system are shown in Fig.1. At such cooling rates amorphous $(Sb_2Se_3)_x(InSb)_{1-x}$ layers with InSb content up to 80 mol.% can be obtained. The amorphization range includes also $In_{0.35}Sb_{0.45}Se_{0.20}$ alloy, which is the most efficient for information recording.

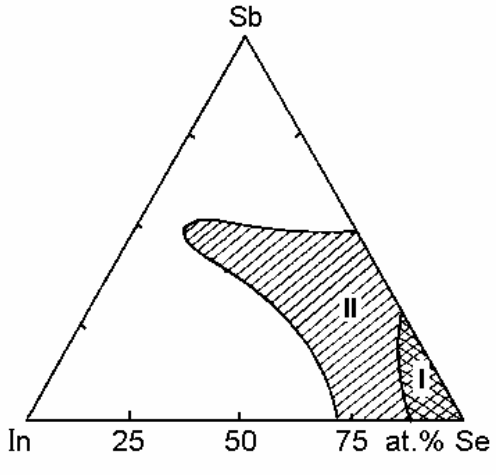

Fig. 1. Glass-forming range (I) and amorphization range at $Q = 10^3$ K/s (II) in the Sb–Se–In system.

Amorphous Sb_xSe_{1-x} films with $0.40 < x < 0.70$ were obtained by thermal sputtering in the vacuum of 5×10^{-6} Torr onto glass substrates. The film thickness in the course of sputtering was measured by interference-modulated optical absorption of the film at the wavelength $\lambda = 1.15$ μm, and after the sputtering – by an interference microscope MII-4 and was 0.3 μm (at the studies of thermal annealing) and 0.1–0.05 μm (for the experiments with nanosecond laser pulses).

Thermal annealing of the films was carried out in an ampoule with argon atmosphere, the average heating rate being 3.50 K/min. For the given heating rate the temperature T_{ph} of the amorphous film phase transition to the policrystalline state was determined, corresponding to a sharp decrease of the film optical absorption at the given wavelength $\lambda = 900$ nm [12]. The compositional dependence T_{ph} of Sb_xSe_{1-x} films is given in Fig. 2. With increasing content of antimony in the composition of films the phase transition temperature is seen to decrease.

Photocrystallization of the amorphous films was achieved by a focused beam of He-Ne laser ($\lambda = 632.8$ nm) and determined from the reflectance variation. The studies enabled us to show that the maximal difference of reflectances for the films in the crystalline and amorphous states was reached for the films with $x = 0.65$.

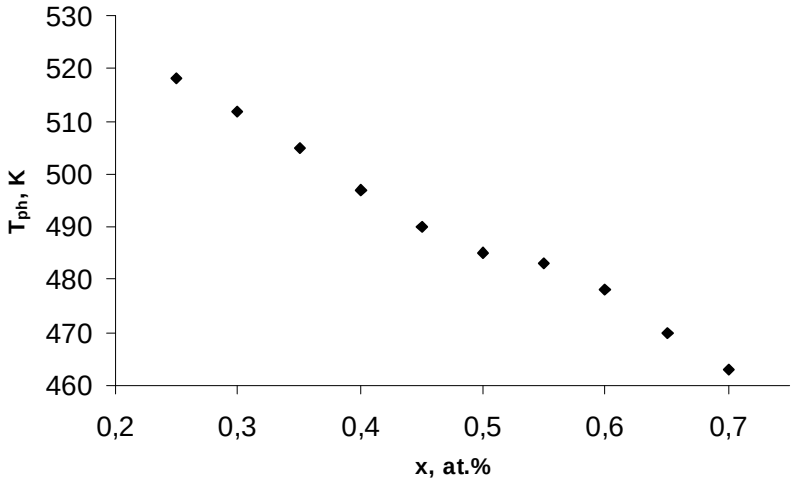

Fig. 2. The compositional dependence T_{ph} of Sb_xSe_{1-x} films.

In $(Sb_2Se_3)_x(InSb)_{1-x}$ system the difference in the reflectances of the crystallized and amorphous areas increases with InSb content increase and is maximal for $In_{0.35}Sb_{0.45}Se_{0.20}$ composition ($x = 0.30$). It should be noted that the reflectance difference in $(Sb_2Se_3)_x(InSb)_{1-x}$ films is several times higher than in Sb_xSe_{1-x} films.

Photoinduced amorphization of the crystallized films of the Sb–Se–In system was carried out by a single YAG:Nd^{3+}-laser pulse, reaching the film through the substrate with $\lambda = 1.06$ μm and duration $\tau = 15$ ns.

The studies of the conditions of optical information recording on the amorphous layers of $(Sb_2Se_3)_x(InSb)_{1-x}$ have shown that a 1-μm-focused laser beam ($\lambda = 750$ nm) results in the crystallization of the illuminated areas of the amorphous layer. The power of the exposing pulse P_{rec} is 5–18 mW, depending on the film composition, the lowest P_{rec} value being revealed for $(Sb_2Se_3)_{0.30}(InSb)_{0.70}$ film. In Sb–Se system the information is recorded only on the layers with Sb content not less than 25 at.% and at the laser light power, capable of burning holes in the active media (Table 1). Hence, the erasure of information in Sb_xSe_{1-x} films is also encumbered.

Table 1. Parameters of record-read-erase processes for the active reversible media.

Composition	P_{rec}, mW	λ, nm	P_r, mW	P_{er}, mW	K, %
$Sb_{0,25}Se_{0,75}$	40	680	10	–	5
$Sb_{0,40}Se_{0,60}$	30	680	5	–	10
$In_{0,15}Sb_{0,43}Se_{0,42}$	18	750	3	12	16
$In_{0,35}Sb_{0,45}Se_{0,20}$	5	750	1–2	8	43

The studies of videodisks by electron microscopy have shown that the crystallized videodisk tracks on the base of $(Sb_2Se_3)_{0.30}(InSb)_{0.70}$ alloy contain a 0.9–1.1-μm wide central stripe with the crystal grain size of 0.30 μm, and intermediary stripes, neighbouring with the amorphous tracks (Fig. 3). The width of the intermediary stripes is 0.32–0.35 μm, and the grain size in them (0.008–0.025 μm) increases towards the middle of the crystalline track. The distance between the closest boundaries of the central stripes of two neighbouring crystallized tracks is ~ 1.75–1.85 μm.

The amorphization of the crystallized films occurs under the erasing laser light of much higher power (Table 1). The structure and optical properties of the amorphized films are the same as those of the as-deposited films.

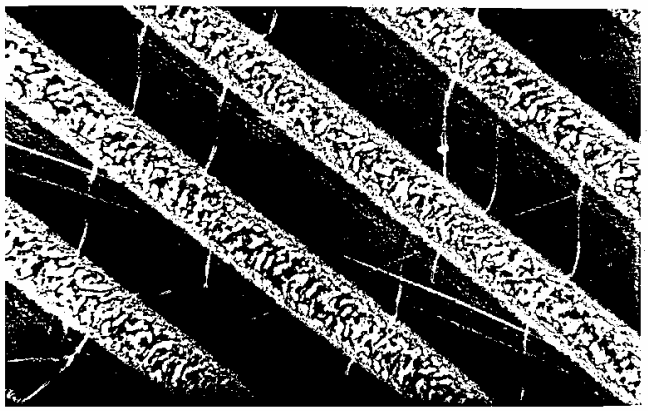

Fig. 3. Amorphous and crystallized areas of active layers of $(Sb_2Se_3)_x(InSb)_{1-x}$-alloy-based videodisks (multiplication ×11500).

The studies of the effect of thermal annealing on the structure and properties of $(Sb_2Se_3)_x(InSb)_{1-x}$ films have shown that annealing of the crystallized film at the temperature 640 K does not result in an essential change of its phase composition. Annealing of an amorphous area at the same temperature results in its crystallization with the emergence of the same metastable phase, as under the exposure to laser light. The relative stability of the crystalline and amorphous phases points out to the possibility of recording and re-recording of information and its durable storage.

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