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# Crystallization study of $(As_2S_3)_{100-x}(SbSI)_x$ amorphous films by the optical method

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**Abstract.** The results of isothermal and nonisothermal crystallization investigations of the $(As_2S_3)_{100-x}(SbSI)_x$ ($53 \le x \le 80$) thin films are given. It is shown that the films crystallization is accompanied by a sharp decrease in transmission. The phase structure arising in the matrix of films during crystallization corresponds to the structure of crystalline SbSI. The formation mechanism of nanocrystalline SbSI inclusions in the amorphous matrix is discussed.

**Keywords:** amorphous film, crystallization, transmission, structural transformation.

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## 1. Introduction

The study of kinetics and mechanisms of structural transformations, phase compositions, which arise during the crystallization of glasses and films, makes it possible to develop specific recommendations to improve their temperature and temporal stability, controlled change of properties under variations of chemical composition, conditions of obtaining, heat treatment and exposure, to enable their usage as elements of optoelectronics, holography, information recording systems and storage, ferroelectric memory. In this regard, amorphous films $As_2S_3$–SbSI present certain interest.

Due to their high sensitivity, amorphous films of arsenic sulfide are widely used as media for information optical recording, in creation of highly efficient holographic gratings, optical diffraction elements for various applications [1-4]. Antimony sulphoiodide (SbSI) is a well-known quasi-one-dimensional ferroelectric semiconductor [5].

Glasses of the $As_2S_3$–SbSI system containing more than 50 mol.% of SbSI have high crystallization ability. Crystallization of glasses is accompanied by a sharp change in the optical and dielectric parameters [6, 7]. The structure of the phase which occurs during the crystallization of glasses of the given system, corresponds to the structure of crystalline SbSI [6]. The size of needle-like crystalline inclusions of antimony sulphoiodide in the glassy matrix on the $As_2S_3$ basis can be controlled by changing the heat treatment regimes [6, 8] or laser exposure [9].

In this work, we have adduced the results of studying the processes of non-isothermal and isothermal crystallization of the $(As_2S_3)_{100-x}(SbSI)_x$ ($53 \le x \le 80$) thin films.

## 2. Experimental

$(As_2S_3)_{100-x}(SbSI)_x$ glasses were prepared using the vacuum melting method (0,01 Pa) of the relevant mixture of $As_2S_3$ and SbSI components preliminary synthesized from high purity elemental substances. Glassy $As_2S_3$ was obtained by cooling (for 48 h) a homogenized melt from 780 K in air. Polycrystalline SbSI was obtained by cooling (for 72 h) a homogenized melt from 900 K to room temperature. $(As_2S_3)_{100-x}(SbSI)_x$ melts were processed in the same manner for 24 h at 830-870 K. The melts were periodically stirred. Cooling of melts was carried out in the air ($53 \le x \le 70$) and into cold (273 K) water.

Thin films (thickness ~ 1-2 μm) were obtained by the method of vacuum evaporation of the present

composition glasses from quasi-closed effusive cells on cold silica substrates. The uniform thickness of layers was provided by planetary rotation of substrates.

Study of transmission spectra in the wavelength region 450-750 nm was carried out by means of «МДР-23» spectrometer at room temperature. The spectral resolution was no worse than $10^{-3}$ eV.

Investigations of the transmission temperature dependencies were performed using the equipment based on a spectrophotometer «СФ-46». Optical radiation is introduced into the thermostat through an optical fiber. Registration of the transmission change was performed at the wavelength of $\lambda$ = 0.85 μm. During the study of isothermal crystallization, the samples were placed into the thermostat, in which the stabilization of temperature within the range 300 – 500 K was ensured. During the study of the processes of non-isothermal crystallization of films, linear heating of films with different rates was carried out. In the first case, optical transmission change with time was registered at constant temperature exposure, the second case – transmission change with temperature.

### 3. Results and discussion

Investigation of non-isothermal crystallization of films $(As_2S_3)_{100-x}(SbSI)_x$ showed that the temperature dependence of transmission has a stepwise character (Fig. 1 and 2), and the transition temperature depends on the composition of films and the heating rate $q$.

The temperature range $\Delta T$ for the films of this system containing 70 and 80 mol. % of antimony sulphoiodide (Fig.1, curves 1 and 2), where the transmission decreases sharply, is 5-10 K. As the SbSI content decreases in the films, this interval increases (for example, up to 20-30 K, for films with $x$=53-55), and the relative transmission change in the films during crystallization decreases. The smallest transmission change is found for the film $(As_2S_3)_{47}(SbSI)_{53}$ (8-10%). The transition amorphous phase to crystalline phase is completely irreversible.

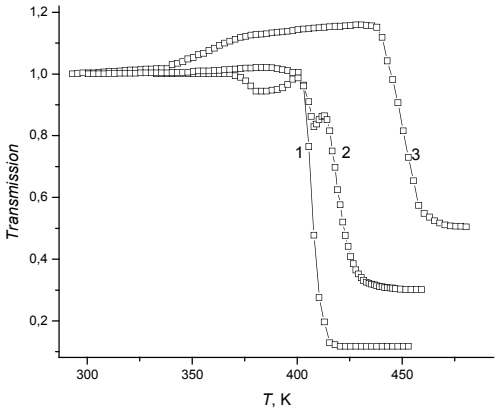


**Fig. 1.** Temperature dependences transmission of $(As_2S_3)_{100-x}(SbSI)_x$ films on $\lambda$=0.85 μm at $q$=1.28 K/min, $x$: mol.%: 1-80; 2-70; 3-55

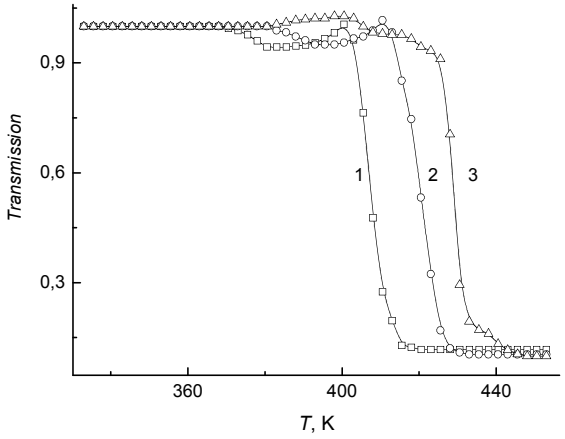


**Fig. 2.** Temperature dependences of $(As_2S_3)_{20}(SbSI)_{80}$ films at different $q$, K/min: 1-0.64; 2-1.28; 3-2.56

The increase of the heating rate leads to a shift of the transition temperature range of films into the crystalline state in the high temperature region (Fig. 2), and the transition itself becomes sharper.

During the study of $As_2S_3$-SbSI system glasses by using methods of X-ray diffraction and Raman spectroscopy their nanoheterogeneous structure was established [6-8]. It has been shown that their matrix is formed only by binary structural groups with heteropolar bonds ($AsS_3$, $SbS_3$, $SbI_3$, $AsI_3$) and also contains molecular fragments with homopolar As-As and S-S bonds. The presence of several types of structural groups in the glass matrix leads to the interaction and deformation in it, then, as a result, to the considerable nonequivalence of distances and binding forces between atoms. During the heating process the structural lattice lability grows even more, and there exists the possibility of breaking and switching of chemical bonds in these binary structural groups within the range "glassforming temperature – crystallization temperature". This process is accompained by the diffusion of Sb and I atoms. As a result, the triple chain of $SbS_{2/2}I$ groups that are typical for crystalline SbSI are formed.

The same mechanism of formation of nanocrystals SbSI in the amorphous matrix is proposed for the films $(As_2S_3)_{100-x}(SbSI)_x$. The growth of film transmission in the precrystallization region confirms the idea that formation of structural chain groups $SbS_{2/2}I$ is accompanied by diffusion of antimony and iodine atoms. And this, in its turn, is accompanied by a decrease of their amount in the amorphous matrix on the basis of arsenic sulphide. But the absorption edge of $As_2S_3$ is in the shorter wavelength range of the spectrum than the absorption edge of films $(As_2S_3)_{100-x}(SbSI)_x$ (Fig. 3).

Research of isothermal crystallization of films $(As_2S_3)_{100-x}(SbSI)_x$ confirms the assumptions about the chain nature of crystalline inclusions in the amorphous matrix. The study of isothermal crystallization processes was conducted at different temperatures, which were chosen for each composition considering the results of thermographic studies of these materials. For example,

Fig. 4 shows the dependence of transmission changes with time during isothermal crystallization ($T_a$=396 K) of thin film $(As_2S_3)_{20}(SbSI)_{80}$. It is seen that transmission change, and, accordingly, the change of crystalline phase fraction does not take part immediately, but with a certain delay $\tau_0$. It is obvious that the process of formation of crystalline nuclei occurs at this stage. The value $\tau_0$ depends on the chemical composition of films and their annealing temperature. For example, for the case shown in Fig. 4, $\tau_0$ = 500 s. With the growing of $T_a$ value $\tau_0$ decreases.

The kinetics of crystallization process is described by the empirical dependence of Kolmogorov-Avrami[10], which determines the change of crystalline phase fraction $X$ from time $t$:

$$X(t)=1-\exp(-Kt^n).$$

Here, $K$ is a constant of the process speed (depends on $T$), $n$ - reaction index (shows the mechanism of the process). For one-, two - and three-dimensional growth, value $n$ is in the range of 1-2, 2-3 and 3-4, respectively.

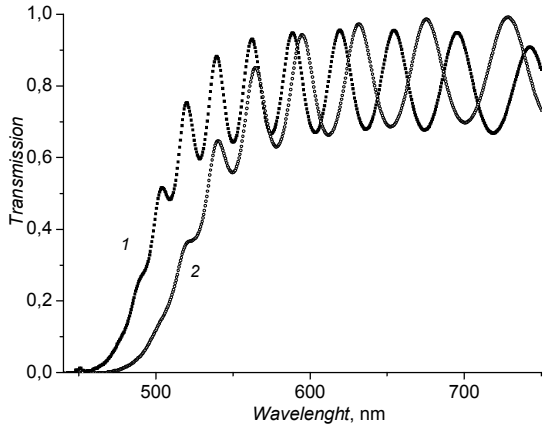


**Fig. 3.** Transmission spectra of $As_2S_3$(1) and $(As_2S_3)_{47}(SbSI)_{53}$ (2) films.

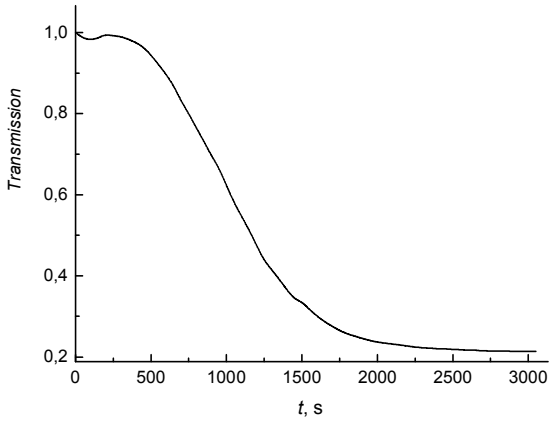


**Fig. 4.** Dependence of transmission on the time at isothermal crystallization ($T_a$=396 K) of $(As_2S_3)_{20}(SbSI)_{80}$ amorphous film

Calculations of the value $n$ for the films under current study were performed by the procedure described in [11]. They showed that at the initial stage of crystallization process ($t < \tau_0$) $n$=0.6-0.8. This testifies to the growth of crystalline nuclei until they reach the critical size. At the next stage of the process, $n$=1.6-1.8. The growth of one-dimensional crystals SbSI takes place. The obtained non-integer values of $n$ indicate that the crystallization process is accompanied by nonstationary diffusion processes.

## 4. Conclusions

The crystallization of amorphous $(As_2S_3)_{100-x}(SbSI)_x$ films is accompanied by a sharp decrease in transmission. The transition temperature from amorphous into crystalline state depends on the composition of films and their heating rate. With the $q$ increasing and $x$ decreasing, the temperature interval $\Delta T$ of films transition into crystalline state is shifted into the region of higher temperatures. With the antimony sulphoiodide concentration in the composition of $(As_2S_3)_{100-x}(SbSI)_x$ films decreasing, the value of $\Delta T$ increases (from 5-10 K for films with $x$=80-90 up to 20-30 K for films with $x$=53-55), while relative transmission change of films decreases.

The phase strucrure arising in the matrix of amorphous films during crystallization corresponds to the structure of crystalline antimony sulphoiodide. Formation of chain nanocrystals SbSI and their growth is accompanied by an nonstationary diffusion processes.

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