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OPTICAL COATINGS BASED ON NON-CRYSTALLINE FILMS WITH TRANSITION SUBSTRATE-FILM LAYERS: SIMS AND AUGER PROFILES

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The results of studies by the SIMS and Auger spectroscopy methods of element distribution in a-As_2S_3 and a-GeS_2 films prepared by vacuum evaporation on Si substrates are presented. In a-GeS_2 films the extended transition region with dimensions of ~ 30 nm has been observed. The intensity of interference maximum of such slightly inhomogeneous thin films on glassy substrate is higher than the maximum of transmission level of the free glassy substrate.

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1. Introduction

The problem of widening the range of film-forming materials is important for the science of film materials and optics of thin-film coatings [1,2]. The development of effective processing methods and those of film condensation combines its practical and scientific aspects [3-5]. A number of works [6-13] devoted to structural and optical studies of a-As_2S_3 films shows evidence of the difference of structural and optical characteristics of the films from those in the bulk glass. The formation of non-equilibrium phases depends first of all on the mechanism of condensation. The non-crystalline state is formed by supercooling the liquid or vapour phases if the condensation is effected according to the mechanism vapour – liquid – solid phase or vapour – solid (amorphous) phase [14].

The characteristics of formation of condensate structure depends first of all on the number of growth centres, and in the general case this is determined by the degree of supersaturation and supercooling of vapour phase [8-12]. The structure and composition of arsenic trisulphide deposited films is genetically connected with the vapour phase composition. With increasing the evaporator temperature above 773 K the homogeneity of vapour phase is destroyed and it becomes rich in arsenic [8,9]. X-ray diffraction studies [12] and results of structural interpretation of vibrational spectra [6,17] testify the availability of As_4S_4 "molecules", a not polymerized sulphur and arsenic in As_2S_3 as-deposited films. The availability of free arsenic in as-deposited films leads to their oxidation [11]. It is important to stress that annealing and laser radiation of a-As_2S_3 as-deposited films is accompanied by the change in their refraction index and thickness [13, 18].

The analysis data of new oxide materials films demonstrate that at the interface of a high-refractive non-crystalline film-substrate are present inhomogeneities of composition and refractive index respectively, [18,19]. Structural data of the melts for many chalcogenide glassy semiconductors (ChGS) testify to the fact that these materials when melted dissociate and the structure of melts at temperatures lower than evaporation temperature does not correspond to that of the initial glass [20]. It means that the preparation of films based on ChGS needs solving the

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problem of fractionation, change in the composition and structure over the profile of the film that leads to its optical inhomogeneity and differences in physical properties from the bulk glass. In this article are presented the results on the profile of element distribution in As_2S_3 and GeS_2 films prepared by flash vacuum evaporation.

2. Methods

To study SIMS profiles of films of wide-band non-crystalline semiconductors the set-up CAMECA IMS 4F (France) was used. To neutralize the charging of the surface of dielectric samples an electronic gun was used. To identify chemical elements by Auger – spectroscopy method at EC-2401 (Russia) spectrometer the factor of relative sensitivity for pure elements was used and concomitant factors which influence the accuracy of methods while analyzing semiconductor materials enumerated in [21] were taken into account. Among the most important of them are the thermal decomposition under the action of electronic and ionic beams, electron- and ion-stimulated diffusion, electrical charging of the sample, additional generation of Auger-electrons of Si and metal under the action of the ionic probe. To remove the charging of film samples over its periphery indium contacts providing for a reliable shunt were applied. The films for studies were prepared by flash vacuum and routine evaporation from a tantalum “boat”. The average deposition rate made up 20 A/s. A low-ohmic Si was used as the substrate. The thickness of natural oxide onto Si (~3 nm) was estimated by ellipsometric method. While evaporating a-As_2S_3 films the evaporator temperature made up 770 K, and depositing a-GeS_2 ones it was 1170 K. Transmission of films deposited on glassy substrate was measured on spectrophotometer SF-46.

3. Results and their discussion

In Fig. 1 SIMS-profile of a-As_2S_3 film evaporated by the flash thermal evaporation onto SiO_2 natural oxide sublayer (~ 4 nm) at the evaporator temperature T = 670 K is presented.

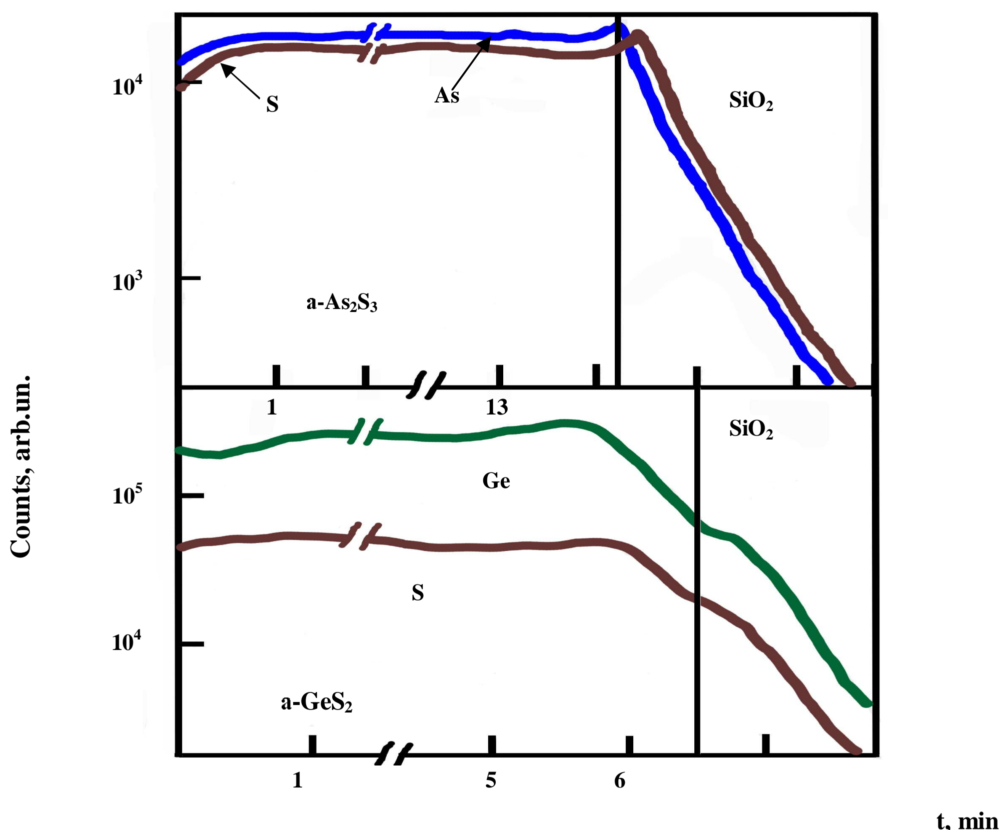

Fig. 1. SIMS profiles of a-As_2S_3 and a-GeS_2 films.

The analysis of SIMS-profile of films based on c-As_2S_3 low-coordinated glass shows that the distribution of As and S over the thickness of the film deposited onto Si substrate with SiO_2 sublayer of 3 nm thickness bears a uniform character (Fig. 1). The change in the composition is observed only in the transition film-SiO_2 sublayer region (d_l<3.0 nm) and does not exceed the resolution ability over the depth (3.0 nm) of Cameca IMSF device used for studies. That is, the transition region in a-As_2S_3 evaporated onto Si substrate with SiO_2 sublayer is practically absent.

The composition, structure and properties of films mainly depend on the degree of substance decomposition into components at the transition from solid phase to vapour [15]. The process of forming binary As_2S_3 films is connected with evaporation conditions of the bulk glass which within the range of temperatures of 495-584 K is defined by reactions [10]:

$$As_2S_3 \leftrightarrow 2/n\ As_nS_n + ½\, S_2\ .$$

When quenching the components of As_2S_3 vapour phase in supercooled helium vapours the most intensive is As_4S_4 component among the number of As_nS_m clusters (n,m=1-10) observed in the mass-spectrum [10].

The increase in the deposition rate up to 100 Å/s is reached with increasing the evaporator temperature and leads to the enrichment of a-As_2S_3 films in arsenic [8]. That is why in the present article the deposition rate of a-As_2S_3 was kept 20 Å/s, and the evaporator temperature was put at 770 K. It is considered that the increase in the evaporator temperature leads to the increase in the degree of dissociation of the melt in the evaporator and the increase in the fraction of the uncombined sulphur and arsenic, and the decrease in the fraction of many-atomic clusters in vapour phase. The uncombined sulphur as the lightest component of chalcogenide glass vapour phase is pumped by the pumping system [8].

The conclusion about homogeneity of the composition of a-As_2S_3 films across the thickness correlates with the data [8] about homogeneity of vapour phase at vacuum evaporation of c-As_2S_3 glass at the evaporator temperatures of 670-770 K.

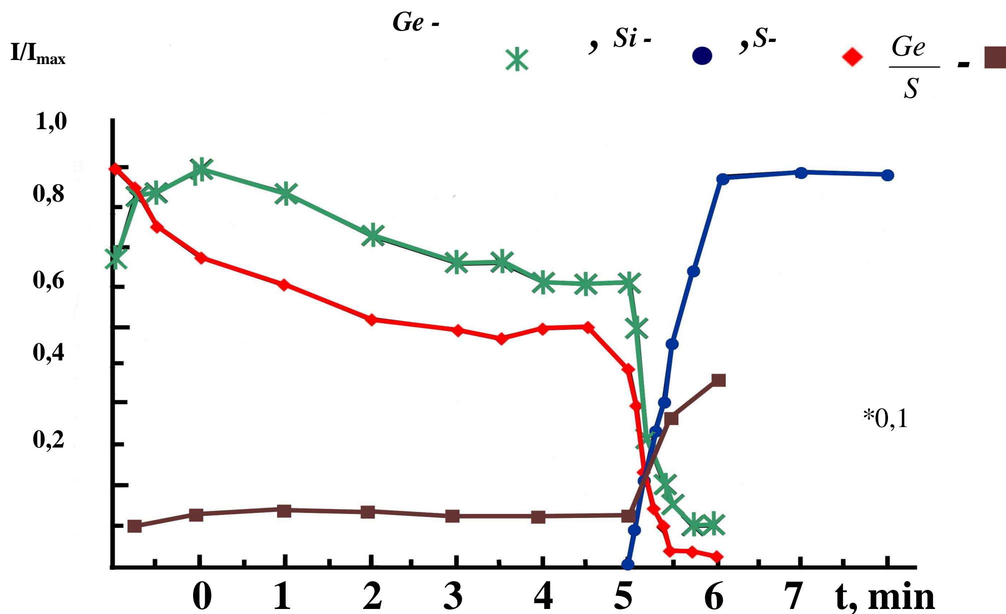

Fig. 2. Auger profile of a-GeS_2 film prepared by direct evaporation of piece of glass from tantalum boat.

In Fig. 2 Auger-profile of a-GeS_2 film prepared by routine and in Fig.3 – by flash vacuum evaporation is presented. As it is seen from Figs.2 the routine thermal evaporation from boat leads to big losses of a volatile component due to dissociative evaporation of g-GeS_2 As to the data of mass-spectroscopic analysis at the thermal evaporation of g-GeS_2 a volatile sulphur prevails at the initial stage in vapour at T=1100 K [16]. At high evaporator temperatures (T~1000 K), at the initial evaporation stage of films a volatile component of strongly dissociative materials is prevailing in vapour phase and pumped by the pumping system of the vacuum device [8]. While going to vacuum evaporation the ratio of Ge/S becomes to some extent equal (Fig. 3). The distribution of Ge, S elements on SIMS-profile of a-GeS_2 film on Si substrate prepared by vacuum evaporation proves the change of the composition in the transition region of films based on g-GeS_2 (Fig. 4).

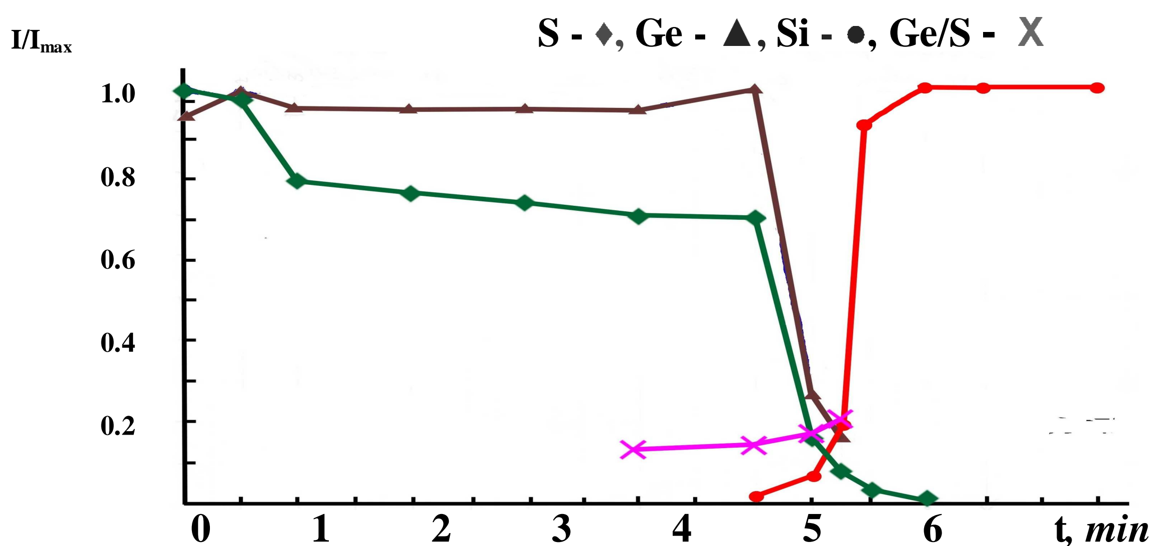

Fig. 3. Auger profile of a-GeS_2 film prepared by flash evaporation of chalcogenide glass powder from tantalum boat.

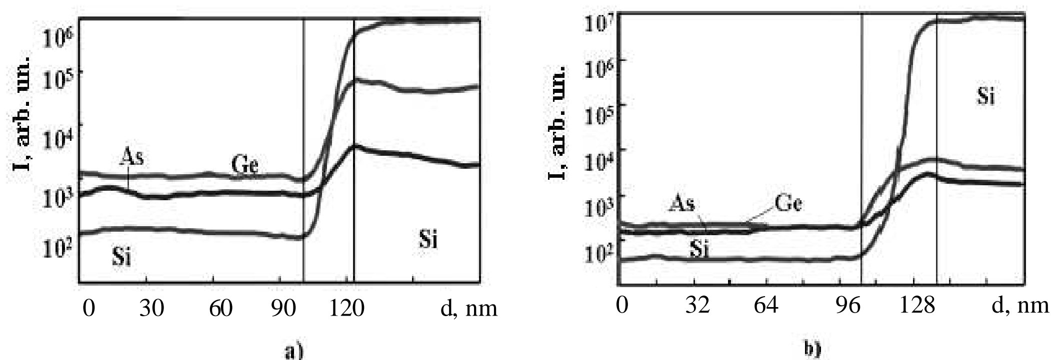

Fig. 4. SIMS profiles of $(GeS_2)_x(As_2S_3)_{1-x}$ films : a) x = 0.3; b) x = 0.7 [23].

Taking into account the etching rate of the films by cesium ions, the depth, the time dependence of the intensity of As and Ge deposited ions was transformed into the depth dependence. Besides, the intensities of As and Ge distribution were normalized to sulphur intensity. With increasing the content of GeS_2 in films the dimensions of a transition region increase from ~ 25 (x=0.3) to 30 (x=0.7) nm. That is 30 times larger than in SiO_2 film prepared by thermal oxidation of silicon [18] and by one order of magnitude larger than the estimates got at the theoretical analysis of the flash vacuum evaporation process [15]. Solving an inverse ellipsometric problem based on multi-

angle ellipsometry data at λ_0=632.8 nm gave the following values of the dimensions of regions and averaged refractive indices different from the central part of the $(GeS_2)_x(As_2S_3)_{1-x}$ films : 1) a near – surface region n_v=2.4–2.6, d_v=2.5–3 nm; 2) the central part of the film n_f=2.05–2.2, d_f= 90–100 nm; 3) a transition region of film – substrate n_p=2.3–2.45, d_p=30–40 nm. [21] The latter is in agreemnet with the dimensions of a transition region obtained on the basis of studying SIMS-profile of films (Fig.1, fig.4) and structural study of these films given in [10]. The refractive indices of the central part of films well agree with the refractive indices of respective bulk glasses [21,22].

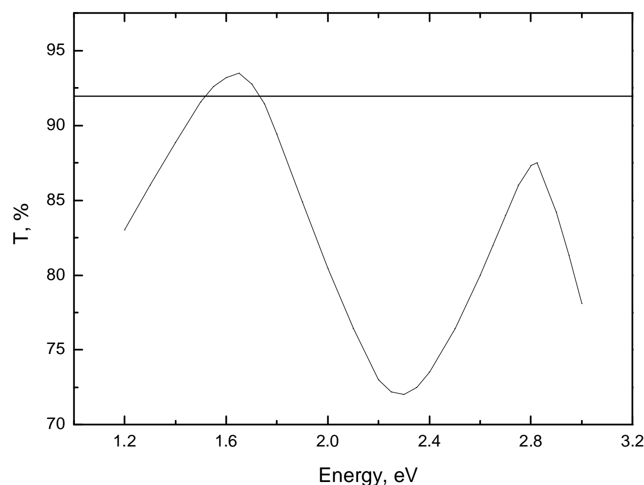

Fig. 5. Fragment of energy dependence of transmittance of a-GeS_2 film (Tauc' band gap, E_o=3.2 eV) on glassy substrate (n=1,51) in non absorbing region (transmittance of free substrate is shown as horizontal line, T= 92 %).

Theoretically has been found that the increase in the intensity of interference maximum of slightly inhomogeneous film on glassy substrate was higher than the maximum of transmittance level of the free glassy substrate [22,23]. It confirmed experimental result of transmissivity of free glassy substrate (n=1.51) with flash evaporated a-GeS_2 film on it in non absorbing region (Fig. 5). The theoretical analysis [23] pointed to a probable physical explanation according to which whether for the change in transmission in interference maxima is due to the appearance of the transition layer enriched in germanium (Fig. 1, Fig. 4) with higher refractive index than in the central part of the film.

4. Conclusions

It has been established by SIMS and Auger-spectroscopy that in a-As_2S_3 film prepared by vacuum evaporation, the transition film-substrate region is practically absent. In case of usual evaporation of germanium disulphide strongly dissociative glass in a-GeS_2 condensated layer from a tantalum 'boat', a non-uniform distribution of germanium and silicon over the film thickness is observed. While going to flash vacuum evaporation the distribution of components becomes even but between the film and substrate the transition region with thickness of ~ 30 nm is present which is enriched in germanium in respect to the central part of the film. The intensity of interference maximum of such slightly inhomogeneous film on glassy substrate is higher than the maximum of transmittance level of the free glassy substrate.

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