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DEPTH PROFILING OF THE NEAR-SURFACE LAYER FOR $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ THIN FILMS

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Depth profiles of the near-surface region and chemical composition for amorphous films deposited from $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ bulk glasses and their changes resulting from six months ageing under ambient conditions have been studied by the methods of Auger electron spectroscopy and X-ray photoelectron spectroscopy. It has been shown that there is a surface layer of about 30 nm thickness enriched with oxygen, germanium, and selenium atoms and depleted of arsenic atoms. It has been found that in the process of natural ageing in the near-surface layer of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film the decrease in the relative concentration of germanium and arsenic is observed, with the simultaneous increase in the concentration of selenium and oxygen associated with the formation of As_2O_3 and GeO_2 , oxide compounds resulting in a loosening of the surface layer.

INTRODUCTION

Chalcogenide vitreous semiconductors in the bulk, film, and fiber form find new applications and are promising for development of passive and active components for opto- and nanoelectronics due to memory effects, nonlinear and other properties observed in these materials. The composition under investigation was selected from the Ge-As-Se family as a result of long-term studies of physical, chemical, optical, and electro-physical properties of glasses and films by different authors, including us (see, e.g., [1–5]). Over the past five years, much attention was focused on a comprehensive study of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ glasses and films. Specific properties of this material have made possible a variety of devices, including non-linear integrated optical devices based on planar waveguides [6–10]. Since in going to nanoscale objects the influence of surface effects become significant, the studies of the surface properties and processes that occur on the surface are of a great importance. Thus, the motivation of these studies was the necessity of a deeper understanding of the relationship between structure and properties, aimed to improving the performances of new devices, their life time, the search for new applications and technological methods.

EXPERIMENTAL

The chemical composition of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films in the near-surface region and its changes

during ageing under ambient conditions have been studied by the methods of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The experiments on surface analysis of thin films were carried out in ultrahigh vacuum of about 10^{-8} Pa with the help of PHI-590 scanning Auger microscope integrated with PHI ESCA spectrometer combining measurements of Auger spectra and X-ray photoelectron spectra. Auger spectra were recorded at primary electron beam energy of 5 KeV, the value of beam current up to 2×10^{-6} A/cm² and energy resolution of the analyzer of ~0.4%. Depth profiles were obtained with Ar ion sputtering at ion energy of ~2 KeV. For excitation of photoelectrons, AlK_α ($h\nu = 1486.6$ eV) X-ray source was used with energy width of 0.85 eV. Resolution of the energy peaks in XPS spectra was of 0.5 eV.

Thin films of 120 nm thickness for the studies of the chemical composition of near-surface region were deposited onto unheated silicon substrates by thermal flash evaporation of bulk $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ glass from the effusion cells in vacuum at a pressure of 10^{-3} Pa and source temperature ~ 800 K. The distance between the source and the effusion cell was about 30 cm. Film deposition rate was about (6.0 ± 0.1) nm/s. The starting bulk glasses were prepared by the conventional method of melting of the relevant mixture of high-purity (5N) As, Se, and Ge com-

ponents in pumped and sealed quartz ampoules with the subsequent quenching of the melt.

RESULTS AND DISCUSSION

Fig. 1 shows depth profiles of the relative changes in concentration of selenium, germanium, arsenic (*a*) and oxygen and carbon (*b*) atoms in the near-surface region of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film.

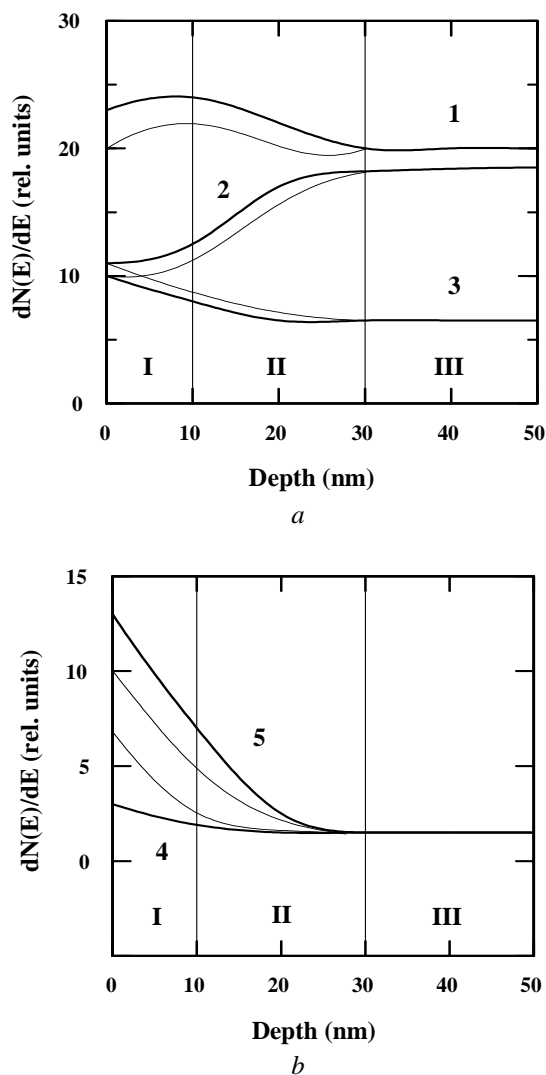


Fig. 1. Depth profiles of chemical elements at the surface of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film *a* – Ge (curve 1), As (curve 2), Se (curve 3); *b* – C (curve 4), O (curve 5). Dashed lines show depth profiles of the elements for the films after the half year ageing under ambient conditions

In these depth profiles we can separate three regions of chemical elements. For germanium and arsenic chemical elements in the regions I and II, complex depth distribution is observed, when the concentrations of the other observed elements,

namely, selenium, oxygen and carbon, decreases with depth up to 30 nm. At greater depth (region III) chemical composition remains the same both for the as-deposited and for the aged films. As it is seen from Fig. 1 (dotted lines), the behaviour of depth distribution of chemical elements in as-deposited films does not change after storage for six months in the laboratory. However, as a result of natural ageing in the near-surface layer of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film, the decrease in germanium, arsenic, and carbon concentration is observed, while the relative concentration of selenium and oxygen increases.

Fig. 2 shows Se, As, and Ge 3d XPS spectra for $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films. Comparing the spectra for as-deposited film (*a*) and half year aged film (*b*), we can see that the spectra show additional peaks corresponding to the formation of oxide compounds, such as As_2O_3 and GeO_2 , and the peaks corresponding to different chemical bonds manifest themselves indicating a process of self-organization of film structure under ambient conditions.

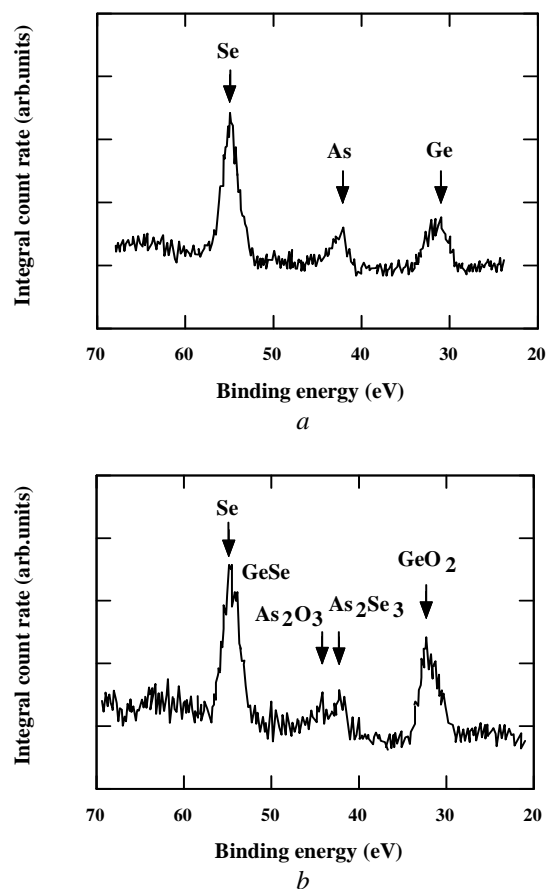


Fig. 2. 3d XPS spectra of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film: *a* – as-deposited; *b* – after half year ageing

These peaks are shown on enlarged scale in Fig. 3 *a–c*, for each of the $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film components, namely selenium (*a*), arsenic (*b*) and germanium (*c*), near the $3d$ states. The possible chemical bounds responsible for the features seen in Fig. 3 are collected in the Table, compiled from the data of published handbooks and electronic directories of "XPS International Inc." and "Perking-Elmer Corporation" companies, U.S. Lawrence Berkeley National Laboratory [11–14] and databases collected in the review [15].

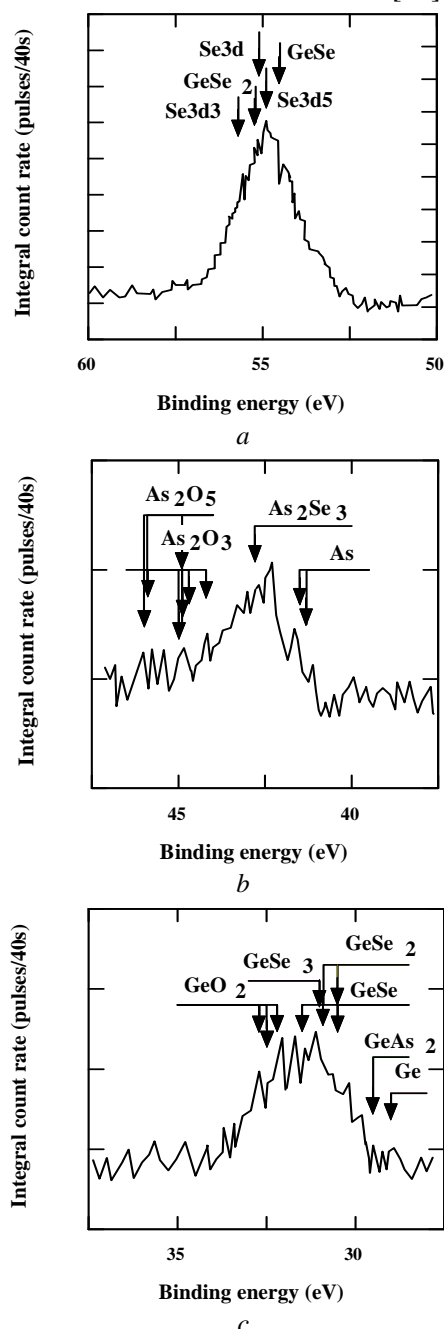


Fig. 3. XPS spectra for $3d$ Se (*a*), As (*b*), and Ge (*c*) in $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film

Table. Energy of the chemical bounds, possible between the components of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ glass and oxygen

Energy (eV)	Chemical bound
Se	
54.5	GeSe
54.9; 55.1; 55.7	Se
55.2	GeSe ₂
As	
41.3; 41.5	As
42.8	As ₂ Se ₃
44.2; 44.9; 45.0	As ₂ O ₃
44.9; 45.9; 46.0	As ₂ O ₅
Ge	
29.0; 29.1	Ge
29.5; 29.6	GeAs ₂
30.5; 31.5	GeSe
30.5; 30.9	GeSe ₂
31.0	GeSe ₃
32.2; 32.5; 32.7; 33.2	GeO ₂

The studies of the microstructure for $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films in transmission electron microscope have shown that the diffraction pattern of the films is typical of amorphous materials, and the structure of the films consists of 30–40 nm size areas of dense phase separated by the areas with lower density. From these studies we can assume that the areas of a denser phase present self-limited ordered clusters, which are surrounded by the channels of molecular dimensions. In these channels it is possible to find different type of inclusions and over stoichiometric atoms, which do not form chemical bonds with the clusters.

Considering the data of Auger-electron spectroscopy and X-ray photoelectron spectroscopy, we can assume that the surface layer is formed as follows. Germanium, arsenic, and selenium atoms which do not interact with clusters diffusing to the surface, where some of them, interacting with O_2 or H_2O molecules, form As_2O_3 and GeO_2 natural oxide compounds, and form GeSe, GeSe₂, GeSe₃, and, possibly, GeAs₂ chemical bonds. Volatile As_2O_3 compound leaves the surface for the atmosphere, resulting in a depletion of the surface layer of arsenic atoms.

Recent research of Wang R. with co-authors [8] concerning the effects of thermal processing on the surface oxidation of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films obtained by ultrafast laser deposition confirms the value of possible

penetration depth for oxygen obtained in our studies and the presence of germanium and arsenic oxides both at the surface of as-deposited films and under the next film processing despite all precautionary measures to protect the films from the environment attack.

CONCLUSIONS

Analysis of Auger spectra of the surface for $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ amorphous films and depth profiles of chemical elements has shown that there is a surface layer of 30 nm thickness enriched with oxygen, germanium, and selenium atoms and depleted of arsenic atoms. It has been found that in the process of natural ageing in the near-surface layer of $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ film the decrease in the relative concentration of germanium and arsenic is observed, with the simultaneous increase in the concentration of selenium and oxygen, associated with the formation of As_2O_3 and GeO_2 , oxide compounds resulting in loosening of the surface layer.

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**Визначення профілів розподілу елементів
по глибині приповерхневого шару
тонких плівок $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$**

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Методами Оже-електронної спектроскопії і рентгенівської фотоелектронної спектроскопії досліджувалися профілі розподілу елементів по глибині приповерхневого шару і хімічний склад аморфних плівок напилених зі стекол $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$, а також їх зміна при природному старінні протягом півроку. Показано, що існує поверхневий шар товщиною до 30 нм, збагачений атомами кисню, германію та селену і збіднений атомами арсену. У процесі природного старіння в приповерхневому шарі плівки $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ спостерігається зниження відносної концентрації германію та арсену при одночасному збільшенні концентрації селену та кисню, що пов'язано з утворенням оксидних сполук As_2O_3 і GeO_2 , внаслідок чого відбувається розпушення поверхневого шару.

**Определение профилей распределения элементов
по толщине приповерхностного слоя
тонких пленок $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$**

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Методами Оже-електронної спектроскопії і рентгеновської фотоелектронної спектроскопії досліджувалися профілі розподілу елементів по товщині приповерхностного шару і хімічний склад аморфних плівок, напилених із стекол $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$, а також їх зміна при природному старінні в течение півроку. Показано, що існує поверхневий шар товщиною до 30 нм, збагачений атомами кисню, германію та селену і збіднений атомами арсену. У процесі природного старіння в приповерхневому шарі плівки $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ спостерігається зниження відносної концентрації германію та арсену при одночасному збільшенні концентрації селену та кисню, що пов'язано з утворенням оксидних сполук As_2O_3 і GeO_2 , внаслідок чого відбувається розпушення поверхневого шару.