

PHOTOINDUCED CHANGES IN THE VALENCE BAND STATES OF $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ THIN FILMS

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Valence band states of $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glasses and amorphous films are obtained by means of X-ray photoelectron spectroscopy. Differences between the broad bands in the spectra, connected with differences in the composition as well as with structural changes initiated by illumination and/or annealing are identified and discussed.

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1. Introduction

Photostructural changes (PSC) induced in chalcogenide amorphous materials are still a subject of great interest, because of the emerging possibilities for their applications. The PSC's are connected with changes of the structure and related properties under irradiation and/or annealing. They are considered as reversible or irreversible. The study of multinary compounds presents great possibilities for the understanding of the PSC mechanism, since they contain various structural units and elements with different electronic structures. Our studies on films and glasses from the Ge-As-S system have shown peculiarities in their properties, due to the differences in composition as well as to the different sensitivities to various irradiation [1, 2 and references herein]. Raman and IR spectra have given information about photoinduced transformations in the short range order, while X-ray diffraction studies showed photoinduced changes in the medium range order of the structure.

EXAFS and XPS studies could provide information on the electronic origin of the PSC, and have been recently used for binary chalcogenides [3,4]. That is why we considered it useful to check if light and thermal treatment can induce transformations in the electronic structure of Ge-As-S films. In order to complete our knowledge on the PSC in $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films, we used X-ray photoelectron spectroscopy (XPS) to investigate electronic states in the valence band of these glasses and films with various values of x .

2. Experimental details

Glassy $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ samples were prepared by direct synthesis from elements of 5N purity in evacuated (10^{-3} Pa) quartz ampoules heated to 950 °C for 24 hours. The melts were quenched in air. Thermally evaporated films with a thickness about 1.5 μm were prepared from the ground up glasses,

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with a deposition rate of 80-100 Ås⁻¹ in a vacuum of about 10⁻³ Pa.

The thin films were illuminated with a HBO 500 Mercury (and in several special cases a Xenophot HLX) lamp, in an air flow without cut-off filters. The highest temperature measured on the sample surface was about 60 °C after 2 hours illumination. The time of illumination of the samples was 45 min, and the intensity was about 10 mWcm⁻². Annealing of the films was performed in an atmosphere of N₂ at $T \approx T_g - 30$ °C for 1 hour.

The XPS analyses were performed with a Surface Sciences Instruments spectrometer (model 301), using focused (diameter = 300 or 600 μm) monochromatised Al-Kα radiation (1486.6 eV). The residual pressure inside the analysis chamber was about 5 × 10⁻⁸ Pa. The spectrometer was calibrated by the photoemission lines of Au (Au 4f7/2 = 83.9 eV, with reference to the Fermi level) and Cu (Cu 2p3/2 = 625.5 eV). For the Au 4f7/2 line, the Full Width at Half Maximum (FWHM) was 0.86 eV under the recording conditions. The peaks were recorded with a pass energy of 50 eV. The spectra were taken before and after illumination of un-annealed and annealed films.

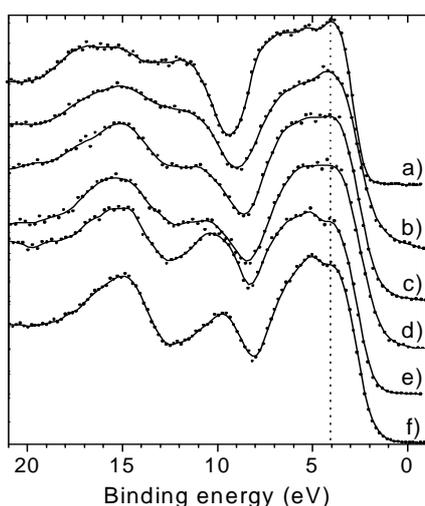


Fig. 1. The valence band spectra of Ge_xAs_{40-x}S₆₀ glasses: a) x=0; b) x=5; c) x=15; d) x=20; e) x=27 and f) x=40.

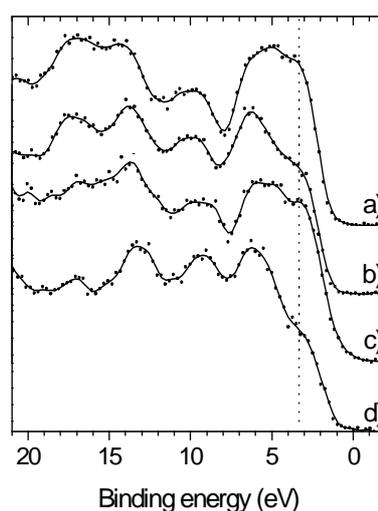


Fig. 2. The valence band spectra of Ge₂₇As₁₃S₆₀ films: a) before illumination; b) illuminated; c) annealed; d) illuminated after annealing.

The XPS measurements showed well expressed changes in the spectra of the valence bands (VB) of the studied compositions after illumination and/or annealing of the films, as well as in the core level energy of the constituent elements. The latter will be discussed in a future paper.

The valence band spectra (intensity in arbitrary units vs. binding energy) of four representative Ge_xAs_{40-x}S₆₀ glasses are shown in Fig. 1. The spectra of two reference glasses (As₂S₃ and Ge₂S₃) are also included. The spectrum of Ge₅As₃₅S₆₀ glass is rather similar to that of As₂S₃. With increasing Ge-content, the shape of the spectra gradually approaches that of the Ge₂S₃. The spectra of the untreated as well as of the annealed thin films are similar to those of the parent glasses. Changes after illumination are observed mainly in the broad band on the low binding energy side of the spectra, for all studied compositions. The most significant changes in the VB spectra of the Ge_xAs_{40-x}S₆₀ thin films are observed for the Ge₂₇As₁₃S₆₀ composition (Fig. 2).

4. Discussion

It is known that the lack of major differences between the VB spectra of the crystal and an amorphous film with the same composition may be due to the rather small deviations in the short

range order caused by amorphization [5]. The similarity between the obtained VB spectra of the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ glasses and the films evaporated from them (Figs. 1e, 2a) confirm that no great changes occur in the electronic structure of the investigated samples when the degree of disorder increases from a glass to an evaporated film.

The interpretation of the VB experimental data is based on that for previously obtained results for Ge_2S_3 , GeS_2 and As_2S_3 glasses [6-9]. The VB spectra of the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ (located on the Ge_2S_3 - As_2S_3 line) exhibit three broad bands in the 0 - 20 eV range:

(i) a broad band at 1-8 eV which can be associated with ionization involving mainly sulfur lone pairs (at about 3.5 eV) and Ge-S (As-S) bonds (at about 6 eV)

(ii) a band in the intermediate range (9-11eV), which corresponds to ionization characteristic of the 4s orbitals of Ge (As) atoms (with a lower binding energy for the 4s orbitals of Ge atoms than for As atoms)

(iii) structures at about 14 and 17 eV, which are probably due to ionization of the 3s orbitals of S atoms.

For the compositions with small amounts of Ge, the shapes of VB spectra are close to that of As_2S_3 , while for $x > 20$ they approach the VB spectra shape of Ge_2S_3 . This is an evidence for a gradual transformation of the glass structure from dominant As_2S_3 -structural units to dominant GeS_2 ones, with increasing Ge content. The similarity in the spectra between the glasses and the annealed films over the whole measured range (Figs. 1e and 2c) confirm that the degree of structural ordering of the glass and the annealed film is about the same. The main difference in the VB spectra of the glass and the evaporated film (Figs. 1e and 2a) is observed in the bands at about 14 and 17 eV.

After irradiation of the films, a large difference in the shapes and relative intensities of the broad band on the low binding energy side (~ 3.5 and 6 eV) is observed. The relative intensities of the bands at 14 and 17 eV are also changed (Fig. 2). Thus, it is evident that after illumination of the films, some photostructural changes occur and manifest themselves in the VB spectra. It should be noted that PSCs are less pronounced in the annealed films. This effect is in agreement with the fact that reversible photostructural changes are smaller than the irreversible ones.

There could be several reasons for the PSC. For the studied $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films, greater changes in the VB spectra were obtained for higher Ge-content compositions. Thus, the observed changes are probably due mainly to the presence of the Ge-containing structural units. The differences in the shape on the low binding energy side could be interpreted in terms of changes in the relative proportions of S and Ge atoms at the surface. A similar suggestion has been advanced previously [10]. Certain changes in the composition during the thermal evaporation, as well as the possibility of the surfaces of the films absorbing oxygen from the ambient atmosphere, could also affect the shape of the VB spectra. It has been suggested previously that oxygen plays a substantial role in the irreversible photostructural changes [11, 12]. Our XPS measurements of the core levels of the same films show an increase of the amount of oxygen after illumination. The oxygen is found to be located around the Ge atoms. XPS studies of $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films and ESCA spectra of illuminated $\text{Ge}_{30}\text{S}_{70}$ films also suggested a photo-oxidation of Ge atoms at the surface [13, 14]. Our previous IR spectra [15], as well as the Fourier IR spectra of the films, studied with those obtained by XPS, have not shown any bands due to As-O or Ge-O bonds. This discrepancy is due to the fact that the XPS is sensitive to the depth of the films, over about 30 Å. The oxygen diffusion and the formation of the Ge-O bonds probably occur in the same surface region. It should be noted that oxidation is not the only reason for the photoinduced changes of the film structures [16]. However, it seems to be the cause of the difference in the absolute values of the irreversible and reversible PSC.

Our previous Raman and IR investigations on $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films have shown that the photoinduced changes in their properties could be attributed to reconnection and reorientation of the bonds in the amorphous matrix [1,2]. Thus, bond rearrangements are still supposed to give the main contribution to the reversible PSC and to take part in the irreversible one. In the investigated $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films, the oxidation of a part of the Ge atoms gives the possibility for the sulfur atoms to form new S-As or S-S bonds. This may be the reason for the changes observed in the higher binding energy range of the valence band, where ionization of 3s orbitals of S atoms occurs. Indeed, we have obtained similar structures for oxysulfide films, and have interpreted these structures as the signatures of S-S

bands [17].

5. Conclusions

The valence band spectra of $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films are sensitive to heat and irradiation treatment, but it is better to use XPS with other experimental techniques. The obtained photoinduced changes in the valence band states are complex. The previously proved bond reorientation affects the PSC, and a low influence of the oxidation of the surface is also supposed. A new investigation using oxygen-free illumination is now being made.

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