

CHANGES IN THE ELECTRONIC STRUCTURE OF Ge-As-S THIN FILMS AFTER ILLUMINATION

V. Pamukchieva, E. Skordeva^{*}, D. Arsova, M.-F. Guimon^a, D. Gonbeau^a

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

^aLaboratoire de Chimie Théorique et Physicochimie Moleculaire, UMR CNRS 5624, 2 Avenue du Président Angot, 64053 Pau Cedex 09, France

The electronic structure of Ge-As-S glasses and films has been studied by means of X-ray photoelectron spectroscopy (XPS). Several compositions from two lines ($\text{Ge}_2\text{S}_3 - \text{As}_2\text{S}_3$ and $\text{Ge}_y\text{As}_y\text{S}_{100-2y}$) of the glass-forming region were investigated. The study was carried on the Ge3p, As3d and S2p core peaks in glasses and evaporated from them thin films. Spectra were recorded before and after illumination and/or annealing of the films. Differences between the relative chemical shift of the core peaks connected with changes initiated by illumination and/or annealing are checked and discussed.

(Received April 12, 2005; accepted after revision May 26, 2005)

Keywords: X-ray photoelectron spectroscopy, Core level peaks, Photoinduced changes

1. Introduction

The behaviour of the amorphous chalcogenides to change their structure under appropriate irradiation is well known [1, 2]. Among them, those belonging to the Ge-As-S system are of great interest because of the large glass-forming region and of their possibility to undergo considerable photostructural changes. Our previous studies on films from the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ system have also shown their sensibility to various irradiations [3, 4 and references herein]. The obtained Raman and IR spectra have given information about photoinduced bond rearrangements (short range order transformations). X-ray diffraction studies showed the appearance of photoinduced changes in the medium range order. It was considered useful to check if light and thermal treatment can induce changes in the electronic structure of the Ge-As-S films.

X-ray photoelectron spectroscopy (XPS) is one of the powerful tools for investigating the electronic structure, for identifying local environments of atoms and electronic transfer processes. This technique is also appropriate to study thin films, providing a ~5-nm-depth analysis. Recently, it has been successfully used in a study on the photostructural changes and their electronic origin in chalcogenide materials [5-7].

In the present work the electronic structure of Ge-As-S glasses and films was investigated using XPS. The spectra were taken before and after illumination of unannealed and annealed films. The changes in the parameters of the film's core levels peaks induced by bandgap illumination and thermal treatment were discussed.

2. Experimental

The investigated compositions belong to two lines of the glass-forming region, namely the $\text{Ge}_2\text{S}_3 - \text{As}_2\text{S}_3$ (or $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$) line and the $\text{Ge}_y\text{As}_y\text{S}_{100-2y}$ one. The glasses were prepared by direct synthesis from appropriate amount of the elements with 5N purity using a standard method. Thin films (~ 1.5 μm) were thermally evaporated in a vacuum of ~ 10^{-3} Pa onto SiO_2 -glass substrates. The

^{*} Corresponding author: skordeva@issp.bas.bg

deposition rate was $\sim 80\text{-}100 \text{ \AA/s}$. Bandgap illumination (from a HBO 500 Mercury lamp) was used in order to obtain photoinduced structural changes. The samples were illuminated in air without cut-off filters. The highest temperature measured on the sample surface was 60°C after 2 hours of illumination. For the present investigation the time of illumination of the samples was 45 min. and the intensity was 10 mW/cm^2 .

The films were annealed in an Ar atmosphere at temperatures of $T_g\text{-}30^\circ$ (where T_g is the glass transition temperature). The annealing duration was 1 hour. After that the ampoule with the samples was carried out from the furnace in order to quench the material quickly.

For the XPS analysis a SSI 301 spectrometer with focused (diameter of the irradiated area $600 \mu\text{m}$) monochromatic Al-K α radiation (1486.6 eV) was used. The residual pressure inside the analysis chamber was ca. $5 \times 10^{-8} \text{ Pa}$. The spectrometer was calibrated by using the photoemission lines of Au (Au $4f_{7/2} = 83.9 \text{ eV}$, with reference to the Fermi level) and Cu (Cu $2p_{3/2} = 932.5 \text{ eV}$); for the Au $4f_{7/2}$ line, the Full Width at Half Maximum (FWHM) was 0.86 eV under the recording conditions. The peaks were recorded with constant pass energy of 50 eV . Neutralisation of the film's surface charge was performed using a low energy flood gun. In order to avoid the surface charge on the films the latter were additionally covered with a fine nickel grid. The binding energy scale was calibrated using the C1s line (284.6 eV) from the carbon contamination (an atomic percentage of about 15-20 % has always been determined). Quantification was performed on the basis of Scofield's relative sensitivity factors [8]. The XPS signals were analysed by means of a peak synthesis program in which a non-linear background is assumed [9] and the fitting peaks of the experimental curve are defined by a combination of Gaussian (80%) and Lorentzian (20%) distributions. It must be noted that a minimum number of doublets was always used in order to fit the experimental curves.

3. Results

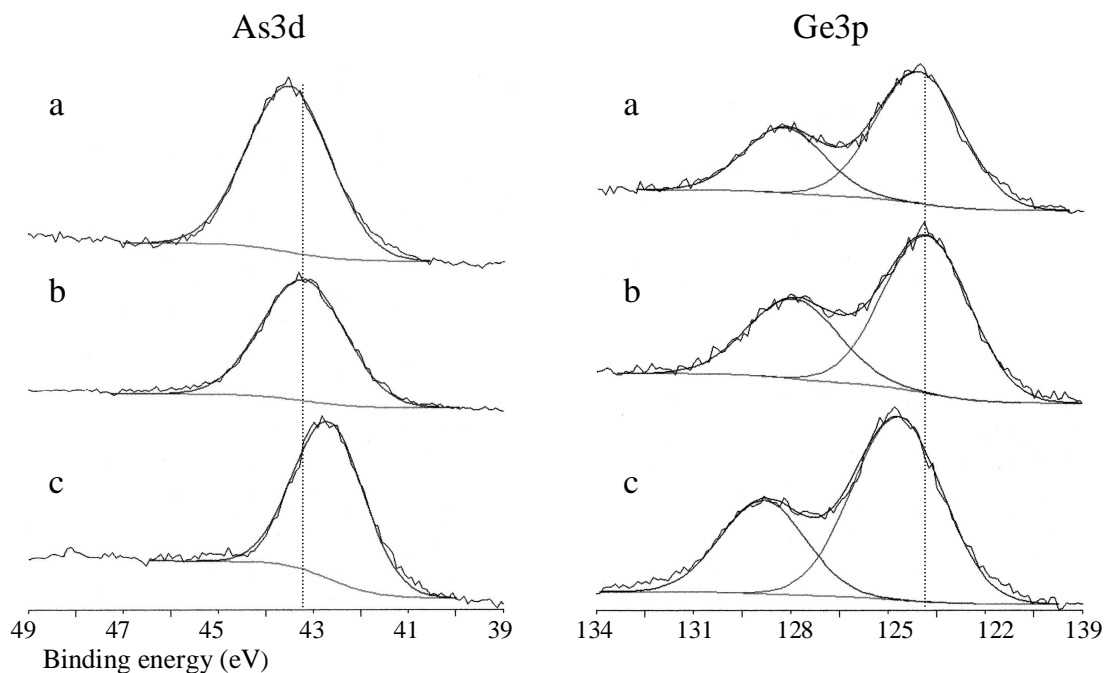


Fig. 1. XPS core peaks (As 3d and Ge3p) for the $\text{Ge}_{20}\text{As}_{20}\text{S}_{60}$ composition: a-fractured glass; b-film before treatment; c-film illuminated.

$\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ (with $x = 5, 15, 20$ and 27) and $\text{Ge}_y\text{As}_y\text{S}_{100-2y}$ (with $y = 15.39, 20$ and 25) were studied as well as several reference compounds (As_2S_3 (a), GeS_2 and Ge_2S_3 glasses). The Ge3p, As3d

and S2p core peaks were the main object of interest. For several compositions the Ge3d and As3p core peaks have also been registered and the same evolutions have been observed.

Fig. 1 shows as an example the As 3d and Ge 3p spectra obtained for the $\text{Ge}_{20}\text{As}_{20}\text{S}_{60}$ glass and for the evaporated from this glass film – before and after its illumination.

Table 1. Binding energies, eV, and peak's width (FWHM), eV, of As, Ge and S calculated from the core level XPS spectra (for the p-peaks data the two spin orbit components are reported).

	Element el. level	Fractured glass	Film, before treatment	Film, illuminated	Film, annealed	Film, illumin. after anneal.
x=5	As 3d	43.4 (1.8)	43.1 (1.5)	43.1 (1.5)	42.8 (1.5)	43 (1.5)
	Ge 3p	123.9-128.3 (3.3) (2.6)	123.4-127.5 (2.5) (2.7)	123.8-128.0 (2.8) (3.2)	123.5-127.6 (3) (3.2)	124.0-128.3 (3.2) (2.6)
	S 2p	162.4-163.6 (1.7) (1.8)	162.0-163.2 (1.3) (1.2)	162.0-163.2 (1.4) (1.3)	161.9-163.1 (1.3) (1.2)	161.8-163.1 (1.0) (0.9)
x=15	As 3d	43.5 (1.8)	43.1 (1.8)	43.0 (1.7)	42.9 (1.8)	43.1 (1.5)
	Ge 3p	124.0-128.2 (3.1) (2.7)	123.7-127.8 (2.9) (2.9)	124.2-128.5 (3.4) (3.2)	123.6-127.8 (3.1) (3.3)	124.3-128.6 (3.8) (2.8)
	S 2p	162.5-163.7 (1.4) (1.4)	162.2-163.4 (1.2) (1.3)	162.0-163.2 (1.4) (1.4)	162.0-163.3 (1.3) (1.3)	162.2-163.5 (1.4) (1.3)
x=27	As 3d	43.1 (1.7)	42.9 (1.9)	43.3 (1.5)	42.6 (1.8)	42.9 (1.7)
	Ge 3p	124.0-128.2 (2.6) (2.9)	123.5-127.6 (2.9) (3)	124.5-128.7 (3.2) (3)	123.8-128.0 (3.4) (3.4)	124.4-128.6 (3.2) (2.8)
	S 2p	162.6-163.8 (1.1) (1.1)	162.2-163.4 (1.1) (1.1)	162.2-163.5 (1.2) (1.2)	162.1-163.3 (1.3) (1.3)	162.0-163.2 (1.4) (1.4)
x=y=20	As 3d	43.6 (2)	43.3 (2)	42.7 (1.8)	42.4 (2.2)	42.5 (2.4)
	Ge 3p	124.2-128.3 (3.1) (2.9)	123.9-128.0 (3.2) (3.3)	124.8-128.9 (3.3) (3.1)	124.2-128.4 (3.6) (3.4)	124.5-128.6 (3.9) (4.0)
	S 2p	162.7-163.9 (1.6) (1.6)	162.4;163.6 (1.3) (1.3)	161.9-163.1 (1.5) (1.5)	161.7-163.0 (2.2) (2.2)	161.6-162.8 (2.8) (2.2)
y=25	As 3d	42.8 (2.6)	42.4 (2.1)	42.3 (2.0)	41.7 (1.8)	42.3 (1.6)
	Ge 3p	123.9-128.0 (3.4) (3.5)	123.3-127.4 (3.4) (3.4)	124.7-128.7 (3.4) (3.4)	124.4-128.5 (3.2) (3.2)	124.5-128.7 (3.0) (3.2)
	S 2p	162.4-163.6 (2.0) (1.8)	162.0-163.2 (1.4) (1.5)	161.8-163.1 (1.8) (1.7)	161.7-163.2 (2.0) (2.2)	161.8-163.2 (1.8) (1.7)
y=15.39	As 3d	43.7 (1.6)	43.3 (1.6)	42.9-44.8 (1.6) (2.0)	43.0 (1.8)	42.9 (1.6)
	Ge 3p	124.1-128.3 (2.8) (3.1)	123.7-127.9 (2.8) (3.0)	124.8-128.9 (3.1) (3.1)	123.8-128.0 (3.4) (3.7)	124.9-129.0 (3.0) (3.2)
	S 2p	162.7-163.8 (1.7) (1.8)	162.3-163.5 (1.5) (1.5)	162.0-163.3 (1.8) (1.7)	161.9-163.1 (1.7) (1.7)	161.9-163.1 (1.6) (1.4)

The calculated from the spectra binding energies (BE) and the peak's width (FWHM) of each of the elements in the respective compositions are presented in Table 1. The letters "x" and "y" in the Table are the indices in the formulae for the parent glass compositions.

Table 2 shows the quantitative data in terms of atomic percentages for all the elements analysed (the total sum has been considered without carbon). The oxygen is absorbed on the film's surface and it is not supposed to be present in the bulk of the films. It should be mentioned that the method allows only a surface investigation (~5 nm in the film thickness). That is why our transmission far-IR Fourier spectra had not detected Ge-O neither As-O, nor S-O bonds, the films thickness being ~1.5 μm .

Table 2. Quantitative data (atomic percentages) for the different elements of the samples analysed. The values are given in the order: Ge (%) / As (%) / S (%) / O (%).

	Fractured glass	Film, before treatment	Film, illuminated	Film, annealed	Film, illumin. after annealing
x=5	5 / 33 / 57 / 5	2 / 36 / 56 / 6	2 / 32 / 53 / 13	2 / 27 / 42 / 29	3 / 12 / 25 / 60
x=15	15 / 24 / 56 / 5	11 / 21 / 42 / 26	14 / 16 / 31 / 39	11 / 16 / 34 / 39	14 / 11 / 26 / 49
x=27	24 / 12 / 59 / 5	18 / 13 / 42 / 27	21 / 9 / 26 / 44	22 / 6 / 26 / 46	23 / 4 / 14 / 59
x=y=20	22 / 18 / 53 / 7	18 / 18 / 40 / 24	27 / 6 / 11 / 56	30 / 3 / 9 / 58	32 / 2 / 5 / 61
y=25	26 / 16 / 44 / 14	26 / 17 / 40 / 17	26 / 5 / 9 / 60	30 / 2 / 4 / 64	31 / 1 / 2 / 66
y=15.39	19 / 15 / 62 / 4	14 / 19 / 57 / 10	23 / 10 / 7 / 60	13 / 14 / 42 / 31	25 / 5 / 8 / 64

4. Discussion

The variety of the investigated compositions implies the supposition that many different structural units (s.u.) could be involved to form the film's matrices in different cases. According to the literature, they might be As_2S_3 , As_4S_4 , GeS_2 and GeS , as well as Ge-S ethane-like units. The mentioned units are expected to be interconnected through the S-atoms. Bonds of the Ge-As type are not expected to exist [10, 11]. The spectra of our Ge 3p peaks in the $\text{Ge}_x\text{As}_y\text{S}_{100-2y}$ system exhibited preferentially the values of Ge^{4+} state: the maximum of the $3p_{3/2}$ component was around 123.5-124.5eV while the Ge^{2+} peak position is around 122 eV. In the Ge-S system the increase of the Ge-amount leads to spectra whose peak shifts to approximately 1.2 eV depending on the valences of the Ge-ions predominance (Ge^{4+} for GeS_2 or coexistence of Ge^{4+} and Ge^{2+} for GeS) [13]. It is probable that in our ternary systems the coexistence of Ge-based with As-based s.u. excludes the possibility of a significant amount of GeS particles. This conclusion has been previously drawn taking into account the vibrational spectra of amorphous $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ [3]. Thus, we suppose that the main Ge-S structural units in the investigated films are the GeS_2 ones and Ge^{4+} predominates. The expected homopolar bonds that will be mentioned below arise mainly from Ge ethane-like s.u. and from As_4S_4 ones as well as from undercoordinated s.u. (e.g. like GeS_{2-x}).

For all the investigated glasses the binding energies of the As3d, Ge3p and S2p core peaks were similar to those obtained for As_2S_3 and GeS_2 [13]. No significant variation in the difference (BE (S2p) - BE (Ge3p)) was observed. This result suggests similar electronic distribution along the Ge-S bonds. As concerning the films, only small variations in the BE compared to those of the glasses were observed (Table 1 and Fig. 1). They are related rather to changes in the condition of samples preparation (degree of disorder) than to real evolution of the chemical environment of atoms. The shifts of all the core level peaks positions presented on Table 1 relative to that for the respective elemental BE (41.7 for As 3d, 164.0-165.2 for S 2p, and 121.2-125.1 for Ge3p [13-15]) are consistent with the covalence of the heteropolar As-S or Ge-S bonds compared to the respective homopolar As-As, S-S and Ge-Ge ones. The degree of disorder can also be verified by the peak positions: the greater difference from the respective elemental BE gives an indication for the increase of the amount of the heteropolar bonds. The prevalence of the heteropolar bonds amount compared to that of the homopolar ones points out on ordering in the amorphous matrix. E.g., the mentioned above shifts of the As3d BE for the glasses are greater than the respective shifts for the films in almost all their states and compositions. (1.1 eV for the glass and 0.7 eV for the film in

$x=25$, $2/1.6$ for $y=15.39$ etc.). This result (see also Fig. 1, curves a and b) proves the common concept that the thin film has a more disordered structure than its parent glass. Some broadening of the peak spectra also supposes the existence of a less homogeneous electronic distribution in the more disordered states of the films. This parameter, however, was almost not changed in the different states of the structure due to the great disorder in the film matrices.

As concerning the photo- and thermally induced structural changes in the studied films, it was not possible to check them for 3 reasons: (i) the fact that the method permits only surface investigations; (ii) the fact that the changes were in the frame of the experimental error; (iii) the role of the oxygen.

The main result from the carried out study is precisely the role of the oxygen. Since the samples were kept and illuminated in air, as could be expected [5, 7], a significant amount of oxygen was found on their surfaces (Table 2). Meantime the Ge3p peak of compositions with high Ge content shifts about 1 eV towards higher BE after illumination (Table 1). Taking into account these shifts, it can be concluded that oxygen surrounds the Ge atoms. ESCA spectra of $\text{Ge}_{30}\text{S}_{70}$ films also suggested that photo-oxidation of Ge atom at the surface layer occurs by the illumination [16]. As has been shown previously, after illumination in air the thickness of the Ge-As-S films increases due to photoinduced structural changes [17]. This increase was related previously to a decrease of the compactness. It was supposed that the surface of the film becomes looser (as becomes its volume) and the absorption of oxygen – more probable. After annealing of the untreated film in an inert atmosphere, however, the film thickness decreases. Nevertheless, the oxygen amount increases, too (Table 2). Obviously, the oxygen has been absorbed after the annealing. It can be supposed that changes on the surface that lead to an increased ability for oxygen absorption have occurred during illumination and annealing. Those changes might be structural transformations, the same as the occurring in the volume ones. More probable, however, is that the leading process is sulphur release. Indeed, great changes were observed in the Ge/S ratio after both illumination and annealing processes. Of course, the calculated amount of both elements on the film surface was approximate and with a relatively great error due to the great oxygen amount. The mentioned ratio, however, increased significantly. E.g. for $\text{Ge}_{27}\text{As}_{13}\text{S}_{60}$ it was about 0.42 for the glass and the untreated film, 0.81 - for the illuminated, 0.85 - for the annealed and 1.64 - for the post-annealing illuminated film. Previous studies have shown that the UV irradiation of amorphous $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ films changes the Vickers hardness and depending on the Ge content a softening or hardening was observed. It was supposed a significant release of sulphur by the treatment [18], which is in agreement with the present XPS results.

It should be remained that the defined amount of the elements is characteristic only for the surface of the films. Nevertheless, surface oxidation significantly affects the photoinduced changes in the electronic structure of the chalcogenide films. As has been recently pointed in XPS studies of As-Se films, oxygen can amplify the changes induced by light [19 and references herein]. It seems very probable that the increase of the film thickness is partially due to oxidation of its surface. E.g. it was shown recently that the photoexpansion of amorphous $\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65}$ after subbandgap illumination existed only if oxygen was present by the illumination process [20].

Photoinduced changes in the film volume, however, are probably not connected with oxidation but mainly with bond rearrangements. A fact supporting this thesis, is the decrease with the time of the values of the obtained photoinduced changes, checked by various optical and physicochemical properties.

New experiments with illumination in oxygen-free atmosphere on samples from the investigated systems are in process in order to verify the hypotheses drawn above.

5. Conclusion

XPS study of glasses and films from the $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ and $\text{Ge}_y\text{As}_y\text{S}_{100-2y}$ systems has shown that photo- and thermally induced changes can influence the electronic structure of the elements on the surface of the amorphous matrix. Illumination and annealing in air lead to a significant increase of the absorbed oxygen onto the surface. The oxidation is probably due to surface defects related to structure disorder as well as to sulphur release.

Acknowledgments

This work was performed in the frames of a NATO CLG.980343. It was partially supported by the F-1309 Grant of the Bulgarian Ministry of Education and Science.

References

- [1] A. Kolobov, Ka. Tanaka, in Handbook of advanced electronic and photonic materials and devices, ed. Hari Singh Nalwa, Academic press, v. 5, 2001, p. 47.
- [2] V. M. Lyubin, Proc. Intern. Conf. "Amorphous semiconductors'82", Bucharest, Ed. R. Grigorovici, A. Vancu, 1982, p. 19 (in Russian).
- [3] E. Vateva, E. Skordeva, J. Optoelectron. Adv. Mater. **4**, 3 (2002).
- [4] E. Skordeva, in Contributions to Non-Crystalline Semiconductor Physics and to Optoelectronics, Eds. Arthur Buzdugan&Mihai Iovu, Int. Association of Academies of Sciences, Chisinau, 2003, p. 40.
- [5] K. Antoine, J. Li, D. A. Drabold, H. Jain, M. Vlcek, A. C. Miller, J. Non-Cryst. Solids **326&327**, 248 (2003).
- [6] S. Krishnaswami, H. Jain, A. C. Miller, J. Optoelectron. Adv. Mater. **3**, 695 (2001).
- [7] K. Petkov, J. Optoelectron. Adv. Mater. **4**, 611 (2002)
- [8] J. H. Scofield, J. Elect. Spectrosc. **8**, 129 (1976).
- [9] D. A. Shirley, Phys. Rev. B **5**, 4709 (1972).
- [10] R. Andreichin, M. Nikiforova, E. Skordeva, L. Yurukova, R. Grigorovici, R. Manaila, M. Popescu, A. Vancu, J. Non-Cryst. Solids **20**, 101 (1976).
- [11] S. Sen, C. W. Ponader, B. G. Aitken, Phys. Rev. B **64**, 104202 (2001).
- [12] Hiromishi Takebe, Hiroki Maeda, Kenji Morinaga, J. Non-Cryst. Solids **291**, 14 (2001).
- [13] D. Foix, D. Gonbeau, D. Granier, A. Pradel, M. Ribes, Solid State Ionics **154-155**, 161 (2002).
- [14] R. B. Shalvoy, G. B. Fisher, P. J. Stiles, Phys. Rev. B **15**, 1680 (1977)
- [15] Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, 1979.
- [16] K. Hachiya, J. Non-Cryst. Solids, **312-314**, 566 (2002).
- [17] E. Vateva, D. Arsova, E. Skordeva, V. Pamukchieva, J. Non-Cryst. Solids **326&327**, 243 (2003).
- [18] M. Popescu, E. Skordeva, F. Sava, A. Lorinczi, P.-J. Koch, H. Bradaczek, J. Non-Cryst. Solids **227-230**, 719 (1998).
- [19] K. Antoine, H. Jain, J. Li, D. A. Drabold, M. Vlcek, A. C. Miller, J. Non-Cryst. Solids **349**, 162 (2004)
- [20] S. H. Messadeq, V. R. Mastelaro, L. M. Siu, M. Tabackniks, D. Lezal, A. Ramos, Y. Messadeq, Appl. Surf. Sci. **205**, 143 (2003).