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## STRUCTURAL STUDIES OF FLASH EVAPORATED a-Ge<sub>2</sub>S<sub>3</sub> THIN FILMS NANOLAYERS BY HIGH RESOLUTION X-RAY- AND SYNCHROTRON RADIATION PHOTOELECTRON SPECTROSCOPY

Ge<sub>2</sub>S<sub>3</sub>-based films have been prepared by flash evaporation of glassy powder and investigated using photoelectron spectroscopy. The SRPS and XPS spectra of a-Ge<sub>2</sub>S<sub>3</sub> have been considered after the illumination and annealing of films. The changes in the parameters of the film's core level peaks induced by near or above band gap illumination and thermal treatment have been measured as well. The influence of the oxidation of Ge containing species on the top of the films on their structural changes is discussed in detail.

**Keywords:** chalcogenide glass, Ge<sub>2</sub>S<sub>3</sub>, photostructural changes, photoelectron spectroscopy.

### Introduction

Recently during the investigation of oxysulfide GeS<sub>2</sub>-GeO<sub>2</sub> films [1] it has been found that preparation of a-GeS<sub>2</sub> film by magnetron sputtering is accompanied by the formation of a thin layer at the top of the film, but with lower index of refraction in a layer 20 nm thick. In [2] we assumed that the visible PL peak at 2.2-2.3eV might arise from GeO<sub>x</sub> impurities in the structure of GeS<sub>2</sub>-based glasses. In such glasses the main peak in PL spectra at 1.96 eV was identified with sulfide-dominated dopant sites, while the shoulder at 2.02 eV was attributed to oxide-dominated sites [3]. The mechanism of luminescence in Ge-based amorphous and nanocrystalline materials is still being disputed [4-9]. It is found that large PL signals correlate with good interface properties [10]. Laser illumination and thermal annealing might be employed in order to get high quality chalcogenide glassy (ChG) films [11]. Here, we report the surface characterization of Ge<sub>2</sub>S<sub>3</sub> films on the few top nanolayers. It was carried out with high resolution synchrotron radiation photoelectron

spectroscopy (SRPS). Deeper layers up to 3 nm were investigated by ordinary X-ray photoelectron spectroscopy (XPS).

### Materials and methods

The mixture was synthesized in evacuated (~10<sup>-3</sup> Pa) quartz ampoules by step-wise gradual heating up to 1223 K in a rocking furnace. At the end of the process each ampoule was quenched to room temperature. Films were obtained by flash evaporation of glassy powder onto c-Si substrate with an Al interlayer. The irradiation of films was carried out in air at room temperature for ~0.5 h by an Ar<sup>+</sup> laser of 35 mW/cm<sup>2</sup> intensity. Photoemission measurements were performed at the Materials Science Beamline of the Elettra Synchrotron light source (Trieste, Italy). The spectrometer was calibrated with the Au 4f<sub>7/2</sub> photoemission line at 84.0 eV from an evaporated gold film. The S 3d, Ge 3d, C 1s and O 1s core level peaks were fitted using a Voigt function with subtraction of a Shirley type background to yield peak position and intensity. Other details of measurements were

the same as described in our previous article [12].

### Results and discussion

In order to examine the vibrational modes on the surface of Ge<sub>2</sub>S<sub>3</sub>-based film [13] a complementary technique, SRPS and ordinary XPS spectroscopy, was used to look for the presence or absence of GeO<sub>x</sub> and GeS<sub>x</sub> species. SRPS and XPS analysis has been performed on the as-deposited, illuminated and annealed films. The study was carried out on the Ge 3d, S 2p, O 1s and C 1s core peaks in Ge<sub>2</sub>S<sub>3</sub> glass and evaporated thin films. The values of the binding energies which were found for different germanium sulfide and oxide compounds [14-22] were used as

reference energies during SRPS and XPS analysis. The surface and subsurface composition and their structural assignment obtained from the fitting procedure similar to those [12] shown in Fig. 1 and Fig. 2 are presented in Tables 2 and 3, respectively. The C 1s signal was associated mainly with the surface and near-surface region. Carbon is partially removed from the surface and near surface during the annealing process in high vacuum at temperature T<sub>g</sub>-30<sup>0</sup> (Table 1). In an earlier XPS investigation of Ge<sub>2</sub>S<sub>3</sub>-based films [16] the carbon contamination (an atomic percentage of about 15-20 %) has always been determined but was not taken [16] into account during the consideration of surface composition.

Table 1

**Composition (atomic percentages) obtained by SRPS (615 eV) and ordinary XPS (1486.6 eV) analysis for the different elements of amorphous films obtained by flash evaporated Ge<sub>40</sub>S<sub>60</sub> glass powder**

	Energy, eV	Ge, %	S, %	C, %	O, %	Ge/S
As deposited	615	20	15	52	13	1.33
Irradiated	615	19	14	54	13	1.35
Annealed	615	32	25	25	18	1.29
As deposited	1486,6	17	17	40	26	1.0
Irradiated	1486,6	14	14	41	31	1.0
Annealed	1486,6	23	24	24	29	0.95

Table 2

**Individual components determined from curve fitting of Ge 3d spectra as evaporated and irradiated film (Fig. 1-2) and their contribution (area, %). The main (3d<sub>5/2</sub>) peak of each doublet is considered**

Peak number	Core level/ Component	As evaporated sample, peak area, %	Irradiated sample peak area, %	Annealed sample peak, area, %
<u>Ge3d, 615 eV</u>				
peak 1	S <sub>3</sub> Ge-GeS <sub>3</sub> and GeS-like	17	13	19
peak 2	GeS <sub>4/2</sub>	33	32	37
peak 3	GeO <sub>x</sub>	34	37	30
peak 4	GeO <sub>2</sub>	16	18	14
<u>Ge3d, 1486 eV</u>				
peak 1	Ge <sub>4/4</sub>	-	2	-
peak 2	S <sub>3</sub> Ge-GeS <sub>3</sub> and GeS-like	25	22	29
peak 3	GeS <sub>4/2</sub>	43	46	45
peak 4	GeO <sub>x</sub>	30	30	14
peak 5	GeO <sub>2</sub>	2	-	12

Table 3

**Individual components determined from curve fitting of Ge 3d spectra of bulk glass Ge<sub>40</sub>S<sub>60</sub> surface and their contribution (Area, %). The main (3d<sub>5/2</sub>) peak of each doublet is considered**

	<u>Ge3d,1486 eV</u>	Area, %
peak 1	Ge <sub>4/4</sub>	-
peak 2	S <sub>3</sub> Ge-GeS <sub>3</sub> and GeS-like	24
peak 3	GeS <sub>4/2</sub>	74
peak 4	GeO <sub>x</sub>	-
peak 5	GeO <sub>2</sub>	2

It can be noted as well, that in Auger spectra of ternary ChGS film during long term aging, the tail of carbon and oxygen signals extended up to 30 nm in depth [17], but 10-20 nm are below the detection limit in the Auger profile [12]. In our case laser illumination of a thin film in air leads to changes of Ge/S ratio on the surface due to the increasing carbonization of the sample surface and the laser stimulated losses of Ge and S (Table 1). Also illumination with energy above the bandgap results in the breakdown of Ge-S bonds and creation of new Ge-O bonds in the irradiated area on the top of the film (Table 2). The analysis of SRPS of Ge 3d spectra has shown that after illumination and annealing the concentration of GeO<sub>2</sub> on top reduces and GeO<sub>x</sub> increases in deeper layers which is confirmed by the XPS peak signal from 3 nm (Table 2). In previous literature for Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub> glasses studied by XPS and XAS, a similar situation can be found [18]. XPS data showed that Ge<sub>4/4</sub> exists in small quantities in the deeper layers of the illuminated zone and might be connected with the fact that part of the germanium oxides decompose into Ge<sub>4/4</sub> s.u. after illumination [19]. As already stated on the basis of our previous investigations, Ge<sub>4/4</sub> s.u. were found in the illuminated zone too, during measurement of Raman spectra which confirmed the XPS spectrum assignment (Table 2). It is known that evaporation of Ge-based glasses is often a non-congruent vaporization process which can lead to off-stoichiometry films [10].

In the last case, the ratio Ge/S =0.85 which is slightly lower in comparison with the Ge/S ratio on the top and deeper layers of flash evaporated samples from the same nominal glass composition (Table 2).

In [20] the composition of the thermally deposited film based on Ge<sub>40</sub>S<sub>60</sub> glass was determined as Ge<sub>46</sub>S<sub>54</sub> and did not matches well with that of the bulk glass. During fitting of SRPS and XPS of C 1s core level spectra (not shown here) there is no indication about formation Ge-C bonds (binding energy 284.3 eV [21]). Only C-S and/or C-O bonds were found at 286 eV. That is why we consider the structural composition of Ge<sub>2</sub>S<sub>3</sub> films on the

surface and subsurface as GeS<sub>2</sub>×Ge<sub>1-x</sub>S<sub>x</sub>×GeO<sub>2</sub>×GeO<sub>y</sub> (x<0.6, y<2). The ratio GeS<sub>2</sub>×Ge<sub>1-x</sub>S<sub>x</sub>/GeO<sub>2</sub>×GeO<sub>y</sub> (see data in Table 2) on the surface of films before illumination is near 1 and drastically differs from those represented by a bulk sample with polished surface (Table 3). We suggested that oxidation Ge plays an important role in radiative recombination processes from the surface of Ge<sub>2</sub>S<sub>3</sub>-based films. The results obtained are the evidence that annealing removed GeS-rich species from both the top and bottom surfaces. Annealing did not change the composition and local coordination of the films (Table 2) to those in bulk glass (Table 3).

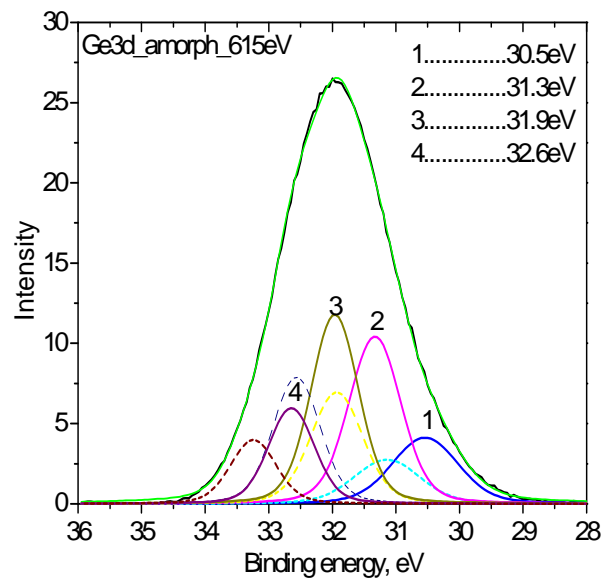


Fig. 1. SRPS spectra of the flash evaporated Ge<sub>2</sub>S<sub>3</sub> films before irradiation, with the fitted peaks.

## Conclusion

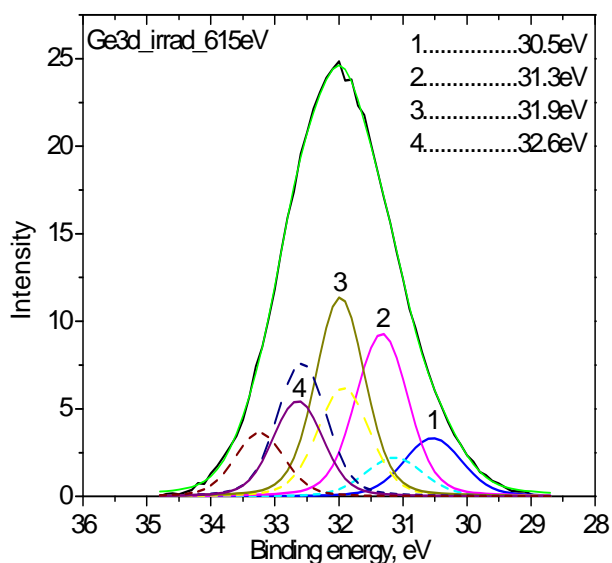


Fig. 2. SRPS spectra of the flash evaporated  $\text{Ge}_2\text{S}_3$  films after irradiation, with the fitted peaks.

We suggested that oxidation of Ge containing species on the top and subsurface layers of  $\text{Ge}_2\text{S}_3$ -based films have a leading role in radiative recombination process from the surface of films. The changes of surface stoichiometry of amorphous  $\text{Ge}_2\text{S}_3$  films exposed to air are found to be mainly due to germanium oxidization and carbonization of the surface and subsurface layers. The laser illumination of thin films in air leads to changes of Ge/S ratio on the surface and subsurface due increasing carbonization on top and oxidation, carbonization of the sample subsurface surface layers and the laser stimulated losses of Ge and S. Annealing removed  $\text{GeS}_x$ -rich species and partially carbon from both the top and bottom surfaces, but did not move the surface toward the composition and local coordination of bulk glass.

## REFERENCES

1. Maurel C., Cardinal T., Vinatier P., Petit L., Richardson K., Carlie N., Guillen F., Lahaye M., Couzi M., Adamietz F., Rodriguez V., Lagugné-Labarthe F., Nazabal V., Royon A., Canioni L. Preparation and characterization of germanium oxysulfide glassy films for optics. // *Materials Research Bulletin*. - 2008. – Vol. 43. - P. 1179-1187.
2. Mitsa V., Holomb R., Lovas G., Ivanda M., Rudyko G., Gule E., Fekeshgazi I. Room temperature visible luminescence in wide band gap chalcogenide glasses // *MIPRO Proceedings of the 35th Intern. Conf.* – 2012.- P. 21-22.
3. Liu X., Naftaly M., Iha A. Spectroscopic evidence for oxide dopant sites in  $\text{GeS}_2$ - based glasses using visible photoluminescence from  $\text{Pr}^{3+}$  probe ions // *Journ. of Luminescence*. - 2002. - Vol.96. - P. 227-238.
4. Nakanishi T., Tomii Y., Hachiya K. Temperature dependence of the photoinduced fatigue-recovery phenomena of photoluminescence under prolonged irradiation in  $\text{GeS}_2$  chalcogenide glass // *J. Non-Cryst. Sol.* - 2008. - Vol.354. - P. 1627-1632.
5. Martin D., Volodin V., Rinnert H., Vergnat M. Anomalous temperature dependence of photoluminescence in  $\text{GeO}_x$  films and  $\text{GeO}_x/\text{SiO}_2$  nanostructure // *Pis'ma v ZhTF*. - 2012. - 95. - P. 472-476.
6. Tanaka K. Excitation-energy-dependent photoluminescence in glassy As-S and crystalline  $\text{As}_2\text{S}_3$  // *Phys. Stat. Sol. B*. - 2013. - Vol. 1-6. - DOI 10.1002/pssb.201248519.
7. Mingfa Peng, Yang Li, Jing Gao, Duo Zhang, Zheng Jiang, Xuhui Sun. Electronic Structure and Photoluminescence Origin of Single-Crystalline Germanium Oxide Nanowires with

- Green Light Emission // *J. Phys. Chem. C*. - 2011. - Vol.115. - P. 11420–11426.
8. Ko S., Shieh J., Yang M.C., Lu T.C., Kuo H.C., Wang S.C. Phase transformation and optical characteristics of porous germanium thin films // *Thin Sol. Films*. - 2008. - Vol. 516. - P. 2934-2938.
  9. Sun K.W., Sue S.H., Liu C.W. Visible luminescence from Ge quantum dots // *Physica E*. - 2005.- Vol.28.- P. 525-530.
  10. Characterization of Semiconductor Heterostructures and Nanostructures / Ed. Carlo Lamberti. - P.B. “Elsevier”, 2008.
  11. Wang R.-P., Rode A., Madden S., Luther-Davies B. Physical aging of arsenic trisulfide thick films and bulk materials // *J. American Ceramic Soc.* – 2007. - Vol.90. - P. 1269-1271.
  12. Kondrat O., Popovych N., Holomb R., Mitsa V., Lyamayev V., Tsud N., Cháb V., Matolín V., Prince K.C. Synchrotron radiation photoelectron spectroscopy studies of self-organization in  $As_{40}Se_{60}$  nanolayers stored under ambient conditions and after laser irradiation // *J. Non-Cryst. Sol.* – 2012. -Vol. 358. - P. 2910–2916.
  13. Gamulin O., Ivanda M., Mitsa V., Balarin M., Kosovic M. Monitoring structural phase transition of  $(Ge_2S_3)_x(As_2S_3)_{1-x}$  chalcogenide glass with Raman spectroscopy // *J. Molecular Struct.* - 2011. - Vol.993. - P. 264–268.
  14. Hiromichi Takebe, Hiroki Maeda, Kenji Morinaga. Compositional variation in the structure of Ge-S glasses // *J. Non-Cryst.Sol.* – 2001. - Vol.291. - P. 14-24.
  15. Holomb R., Johansson P., Mitsa V., Rosola I. Local structure of technologically modified g- $GeS_2$ : resonant Raman and absorption edge spectroscopy combined with ab initio calculations // *Phil. Mag.* – 2005. - Vol. 85. - P. 2947-2960.
  16. Pamukchieva V., Skordeva E., Arsova D., Guimona M.-F., Gonbeau D. Changes in the electronic structure of Ge-As-S thin films after illumination // *J. Optoelectr. and Adv. Mat.* – 2005. - Vol. 7. - P. 1265–1270.
  17. Shchurova T.N., Savchenko N.D., Popovic K.O., Baran N.Yu. Depth profiling of the near-surface layer for  $Ge_{33}As_{12}Se_{55}$  thin films // *Chemistry, physics and technology of surface (Ukraine)*. – 2010. - Vol.1. - P. 343–347.
  18. Lisboa-Filhoa P.N., Mastelarob V.R., Schreiner W.H., Messaddeq S.H., Siu Lib M., Messaddeq Y., Hammerc P., Ribeiroc S.J.L., Parentd P., Laffond C. Photo-induced effects in  $Ge_{25}Ga_{10}S_{65}$  glasses studied by XPS and XAS // *Sol. St. Ionics*. – 2005. - Vol.176. - P. 1403–1409.
  19. Broqvist P., Binder J.F., Pasquarello A. Formation of substoichiometric  $GeO_x$  at the Ge– $HfO_2$  interface // *Appl. Phys. Lett.* – 2010.- Vol.97. - P. 202908-202911.
  20. Mitkova M., Kovalskiy A., Jain H., Sakaguchi Y. Effect of photo-oxidation on the photodiffusion of silver in germanium chalcogenide glasses // *J. Optoel. and Adv. Mat.* – 2009. - Vol. 11, No. 12. - P. 1899–1906.
  21. Hua C.Q., Zhenga W.T., Zhenga B., Lia J.J., Jina Z.S., Baia X.M., Tiana H.W., Jianga Q., Wanga X.Y., Zhuh J.Q., Mengb S.H., Heb X.D., Han J.C. Chemical bonding of a- $Ge_{1-x}C_x:H$  films grown by RF reactive sputtering // *Vacuum*. – 2004. - Vol.77. - P. 63–68.
  22. Mirabella F., Johnson R.L., Ghijsen J. Photoemission investigations of manganese thin films deposited on  $GeS(001)$  surfaces // *Surf. Sci.* - Vol. 506. - P. 172–182.

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## **СТРУКТУРНІ ДОСЛІДЖЕННЯ ТОНКОПЛІВКОВИХ НАНОШАРІВ $\alpha$ - $\text{Ge}_2\text{S}_3$ МЕТОДОМ РЕНТГЕНІВСЬКОЇ ФОТОЕЛЕКТРОННОЇ СПЕКТРОСКОПІЇ ТА ФОТОЕЛЕКТРОННОЇ СПЕКТРОСКОПІЇ З ВИКОРИСТАННЯМ СИНХРОТРОННОГО ВИПРОМІНЮВАННЯ**

Плівки  $\text{Ge}_2\text{S}_3$  були виготовлені методом дискретного термічного випаровування порошку і досліджувалися методом фотоелектронної спектроскопії. Досліджені СФС і РФС спектри опромінених лазером та відпалених плівок  $\text{Ge}_2\text{S}_3$ . Також проаналізовані зміни параметрів фотоелектронних спектрів плівок, індуковані лазерним опроміненням з енергією, близькою до ширини забороненої зони, і термічним відпалом. Обговорюється вплив окиснення Ge у приповерхневих шарах на структурні зміни у плівці.

**Ключові слова:** халькогенідне скло,  $\text{Ge}_2\text{S}_3$ , фотоструктурні зміни, фотоелектронна спектроскопія.

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## **СТРУКТУРНЫЕ ИССЛЕДОВАНИЯ ТОНКОПЛЕНОЧНЫХ НАНОСЛОЕВ $\alpha$ - $\text{Ge}_2\text{S}_3$ МЕТОДОМ РЕНТГЕНОВСКОЙ ФОТОЭЛЕКТРОННОЙ СПЕКТРОСКОПИИ И ФОТОЭЛЕКТРОННОЙ СПЕКТРОСКОПИИ С ИСПОЛЬЗОВАНИЕМ СИНХРОТРОННОГО ИЗЛУЧЕНИЯ**

Пленки  $\text{Ge}_2\text{S}_3$  изготавливались методом дискретного термического испарения порошка и исследовались методами фотоэлектронной спектроскопии. Получены СФС и РФС спектры облученных лазером и термически отожженных пленок  $\text{Ge}_2\text{S}_3$ . Проанализированы изменения параметров фотоэлектронных спектров пленок, вызванные лазерным облучением с энергией, близкой к ширине запрещенной зоны, и термическим отжигом. Детально обсуждается влияние окисления Ge в приповерхностных слоях на структурные изменения в пленке.

**Ключевые слова:** халькогенидное стекло,  $\text{Ge}_2\text{S}_3$ , фотоструктурные изменения, фотоэлектронная спектроскопия.