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STRUCTURAL STUDIES OF FLASH EVAPORATED a-Ge_2S_3 THIN FILMS NANOLAYERS BY HIGH RESOLUTION X-RAY- AND SYNCHROTRON RADIATION PHOTOELECTRON SPECTROSCOPY

Ge_2S_3-based films have been prepared by flash evaporation of glassy powder and investigated using photoelectron spectroscopy. The SRPS and XPS spectra of a-Ge_2S_3 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_2S_3, photostructural changes, photoelectron spectroscopy.

Introduction

Recently during the investigation of oxysulfide GeS_2-GeO_2 films [1] it has been found that preparation of a-GeS_2 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_x impurities in the structure of GeS_2-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_2S_3 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^{-3} 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+ laser of 35 mW/cm^2 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 $4f_{7/2}$ 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_2S_3-based film [13] a complementary technique, SRPS and ordinary XPS spectroscopy, was used to look for the presence or absence of GeO_x and GeS_x 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_2S_3 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_g-30^0 (Table 1). In an earlier XPS investigation of Ge_2S_3-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 $Ge_{40}S_{60}$ 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 ($3d_{5/2}$) peak of each doublet is considered

Peak number	Core level/ Component	As evaporated sample, peak area, %	Irradiated sample peak area, %	Annealed sample peak, area, %
	Ge3d, 615 eV			
peak 1	S_3Ge-GeS_3 and GeS-like	17	13	19
peak 2	$GeS_{4/2}$	33	32	37
peak 3	GeO_x	34	37	30
peak 4	GeO_2	16	18	14
	Ge3d, 1486 eV			
peak 1	$Ge_{4/4}$	-	2	-
peak 2	S_3Ge-GeS_3 and GeS-like	25	22	29
peak 3	$GeS_{4/2}$	43	46	45
peak 4	GeO_x	30	30	14
peak 5	GeO_2	2	-	12

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_2 on top reduces and GeO_x increases in deeper layers which is confirmed by the XPS peak signal from 3 nm (Table 2). In previous literature for $Ge_{25}Ga_{10}S_{65}$ glasses studied by XPS and XAS, a similar situation can be found [18]. XPS data showed that $Ge_{4/4}$ 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 $Ge_{4/4}$ s.u. after illumination [19]. As already stated on the basis of our previous investigations, $Ge_{4/4}$ 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 deper layers of flash evaporated samples from the same nominal glass composition (Table 2).

In [20] the composition of the thermally deposited film based on $Ge_{40}S_{60}$ glass was determined as $Ge_{46}S_{54}$ 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_2S_3 films on the surface and subsurface as $GeS_2 \times Ge_{1-x}S_x \times GeO_2 \times GeO_y$ (x<0.6, y<2). The ratio $GeS_2 \times Ge_{1-x}S_x / GeO_2 \times GeO_y$ (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_2S_3-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).

Table 3

Individual components determined from curve fitting of Ge 3d spectra of bulk glass $Ge_{40}S_{60}$ surface and their contribution (Area, %). The main ($3d_{5/2}$) peak of each doublet is considered

	Ge3d,1486 eV	Area, %
peak 1	$Ge_{4/4}$	-
peak 2	$S_3Ge\text{-}GeS_3$ and GeS-like	24
peak 3	$GeS_{4/2}$	74
peak 4	GeO_x	-
peak 5	GeO_2	2

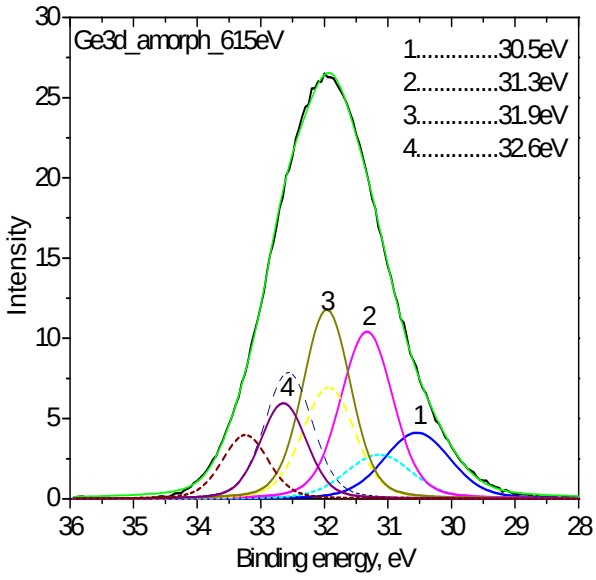

Fig. 1. SRPS spectra of the flash evaporated Ge_2S_3 films before irradiation, with the fitted peaks.

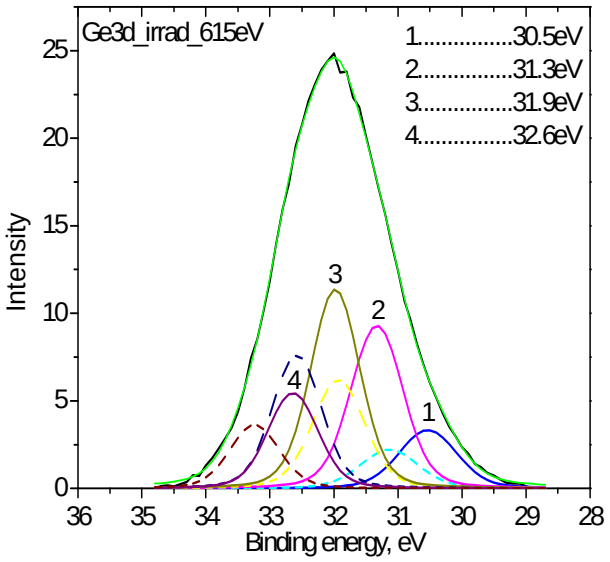

Fig. 2. SRPS spectra of the flash evaporated Ge_2S_3 films after irradiation, with the fitted peaks.

Conclusion

We suggested that oxidation of Ge containing species on the top and subsurface layers of Ge_2S_3-based films have a leading role in radiative recombination process from the surface of films. The changes of surface stoichiometry of amorphous Ge_2S_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 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.

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СТРУКТУРНІ ДОСЛІДЖЕННЯ ТОНКОПЛІВКОВИХ НАНОШАРІВ a-Ge_2S_3 МЕТОДОМ РЕНТГЕНІВСЬКОЇ ФОТОЕЛЕКТРОННОЇ СПЕКТРОСКОПІЇ ТА ФОТОЕЛЕКТРОННОЇ СПЕКТРОСКОПІЇ З ВИКОРИСТАННЯМ СИНХРОТРОННОГО ВИПРОМІНЮВАННЯ

Плівки Ge_2S_3 були виготовлені методом дискретного термічного випаровування порошку і досліджувалися методом фотоелектронної спектроскопії. Досліджені СФС і РФС спектри опромінених лазером та відпалених плівок Ge_2S_3. Також проаналізовані зміни параметрів фотоелектронних спектрів плівок, індуковані лазерним опроміненням з енергією, близькою до ширини забороненої зони, і термічним відпалом. Обговорюється вплив окислення Ge у при поверхневих шарах на структурні зміни у плівці.

Ключові слова: халькогенідне скло, Ge_2S_3, фотоструктурні зміни, фотоелектронна спектроскопія.

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СТРУКТУРНЫЕ ИССЛЕДОВАНИЯ ТОНКОПЛЕНОЧНЫХ НАНОСЛОЕВ a-Ge_2S_3 МЕТОДОМ РЕНТГЕНОВСКОЙ ФОТОЭЛЕКТРОННОЙ СПЕКТРОСКОПИИ И ФОТОЭЛЕКТРОННОЙ СПЕКТРОСКОПИИ С ИСПОЛЬЗОВАНИЕМ СИНХРОТРОННОГО ИЗЛУЧЕНИЯ

Пленки Ge_2S_3 изготавливались методом дискретного термического испарения порошка и исследовались методами фотоэлектронной спектроскопии. Получены СФС и РФС спектры облученных лазером и термически отожженных пленок Ge_2S_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, Ge_2S_3, фотоструктурные изменения, фотоэлектронная спектроскопия.