

Luminescence, Raman and synchrotron XPS study of amorphous Ge₂S₃ based films

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Abstract – Ge₂S₃-based films have been investigated using Raman, photoluminescence and photoemission spectroscopy. For the sake of comparison some of the photoluminescent properties of bulk glasses have been used. The synchrotron photoelectron spectroscopy (SRPES) and XPS spectra of a-Ge₂S₃ films have been measured after the illumination and annealing. The changes in the parameters of the film's core levels induced by near or above band gap light and thermal treatment are discussed in the paper. We consider the possibility that the PL radiation in Ge₂S₃-based films is a surface contaminant effect from native oxidized layer, which might have formed in the air.

I. INTRODUCTION

The discovery of recombination processes in chalcogenide glassy semiconductors (ChGS) [1] has been the catalyst for the further study of photoluminescence (PL) in binary germanium and arsenide chalcogenides for comparing their band gap energy structure in both crystalline and glassy forms [2-5]. Investigations of PL with respect to the types of structural units and in interconnection with other physical properties have been extended to ternary glassy systems and films based on them [3, 6-8]. Optical quality of the ChGS films at, and near the surface is the most important property for practical optical applications [9]. The tendency to thermal dissociation at higher temperature and formation of Ge-rich species on the surface of films [10] during thermal evaporation of Ge-based glasses have been revealed. The information about high refractive index on the surface of a-GeS₂ films to a depth of 10 nm was used for the compensation of spectral changes of different types of IR interference filters with a-GeS₂ high refractive layers [11]. Recently during the investigation of oxysulfide GeS₂-GeO₂ films [12] it has been found that preparation of a-GeS₂ 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. Information about surface contaminants for a-Si films was obtained from the analysis of the high energy PL radiation [13]. This was an effect unrelated to the bulk

states of the material [13]. In [14] we assumed that the visible PL peak at 2.2-2.3 eV might arise from GeO_x impurities in the structure of GeS₂-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 [15]. The mechanism of luminescence in Ge-based amorphous and nanocrystalline materials is still being disputed [16-21]. It is found that large PL signals correlate with good interface properties [22]. Laser illumination and thermal annealing might be employed in order to get high quality ChGS films [23]. Here, we report the observation of room temperature visible PL emission in amorphous films of As₂S₃-Ge₂S₃ alloys before and after laser illumination with near or above band gap light. Bulk glasses were used for the comparison of film PL properties. Surface characterization of Ge₂S₃-based films on the top was carried out with high resolution synchrotron photoelectron spectroscopy (SRPES). Deeper layers up to 3 nm were investigated by ordinary XPS.

II. 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 Raman spectra have been recorded with a DILOR Z-24 triple spectrometer and FT-Raman module of Perkin-Elmer GX spectrometer. The excitation was provided by a green line $\lambda=514.5$ nm ($E=2.41$ eV) from an Ar-ion laser, and near infrared line $\lambda=1064$ nm ($E=1.17$ eV) from a Nd:YAG laser. A projector lamp NL-100 was used for exciting PL spectra of bulk polished glassy samples. IR illumination from the lamp was cut off by a filter based on CuSO₄ water solution. The PL of film samples were excited by cw light from an Ar⁺ laser illumination with near/or above optical gap photon energy 2.41 eV. The irradiation of films was carried out in air at room temperature for ~0.5 h by the same laser with 35 mW/cm² 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 [24].

III. RESULTS AND DISCUSSION

In PL spectra of (Ge₂S₃)_x(As₂S₃)_{1-x} glasses excited by the lamp, broad PL bands well below the band edge (Figure 1) are seen. The values of the optical pseudogap (E₀) for g-Ge₂S₃ and g-As₂S₃ are equal to 2.16 and to 2.4 eV respectively [3,14]. At x=1, the maximum of the PL spectrum is at 1.12 eV. Near the middle gap position of all maxima of the PL spectra of (Ge₂S₃)_x(As₂S₃)_{1-x} glasses (Figure 1) corresponds to the classical E₀/2 rule, and such PL spectra might be explained in terms of the Street-Davis model [25]. Some deviations from this model are discussed in [14,18]. When the mean coordination number of (Ge₂S₃)_x(As₂S₃)_{1-x} glasses is below the value

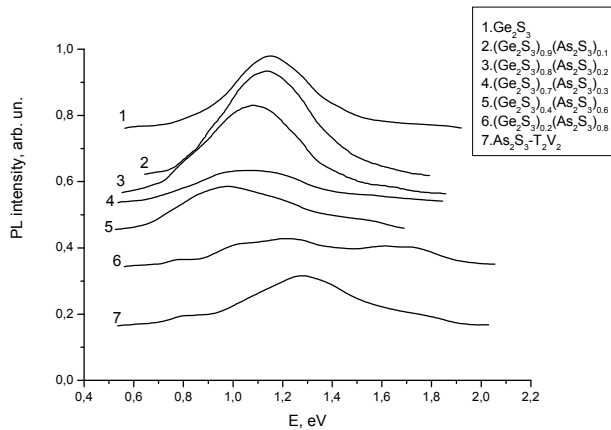


Figure 1. PL spectra of (Ge₂S₃)_x(As₂S₃)_{1-x} glasses measured at nitrogen temperature (composition is shown on insert of Fig. 1)

of z=2.67, the intensity of the PL spectrum for x=0.2 decreased and the half width increased (Figure 1). For this composition, the PL spectrum is very similar to the PL spectrum of freshly thermally deposited a-As₂S₃ films [26]. The concentration of As₄S₄ molecules (235 cm⁻¹) for a-As₂S₃ film and for bulk (Ge₂S₃)_x(As₂S₃)_{1-x} glass have maxima near x=0.3 [27]. During excitation of PL spectra of natural realgar (E_g=2.5-2.6 eV) by laser beams with different energies at 2.38 and 2.6 eV, a low energy PL band was found with peak near 0.9 and 1.7 eV peak of the higher energy correspondingly [5]. Exciting PL spectra of ternary glasses (Figure 1) by the lamp with a wide band energy distribution leads to the appearance in PL spectra for samples at x=0 and x=0.2 of two shoulders near 0.9 and 1.7 eV in same position as peaks in the PL

spectrum of natural realgar, which were registered by different lasers line excitation [5].

Table 1. The relation between the composition of film samples and mean coordination number

(Ge ₂ S ₃) _x (As ₂ S ₃) _{1-x} Ge _x As _{40-x} S ₆₀	Z	d/nm
(Ge ₂ S ₃) _{0.3} (As ₂ S ₃) _{0.7} Ge ₁₂ As ₂₈ S ₆₀	2.52	400
(Ge ₂ S ₃) _{0.5} (As ₂ S ₃) _{0.5} Ge ₂₀ As ₂₀ S ₆₀	2.6	500
(Ge ₂ S ₃) _{0.7} (As ₂ S ₃) _{0.3} Ge ₂₈ As ₁₂ S ₆₀	2.68	750
(Ge ₂ S ₃) _{0.9} (As ₂ S ₃) _{0.1} Ge ₃₆ As ₄ S ₆₀	2.78	450

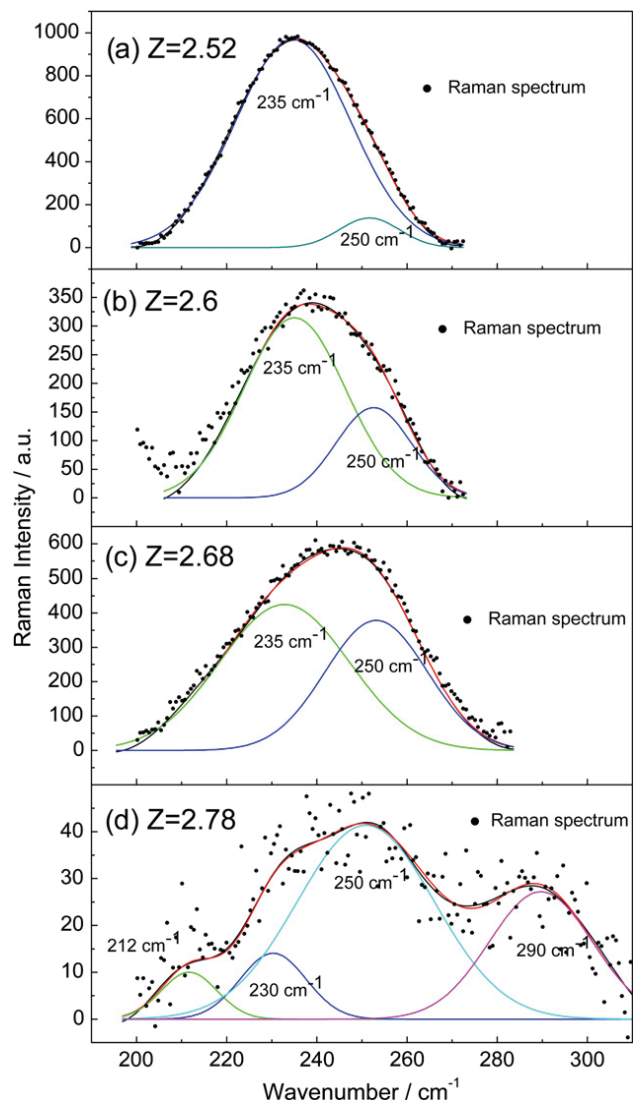


Figure 2. Raman spectra of (Ge₂S₃)_x(As₂S₃)_{1-x} films, E_{ex}=2.41 eV: (a)- x=0.3; (b)-x=0.5; 3-(c)- 0.7; (d)- x=0.9

In the process of room temperature measurement PL spectrum of bulk g-As₂S₃ with realgar-type As₄S₄ molecular inclusions, while the low intensity PL band peaking at 1.7 eV has been also found [14]. We expect

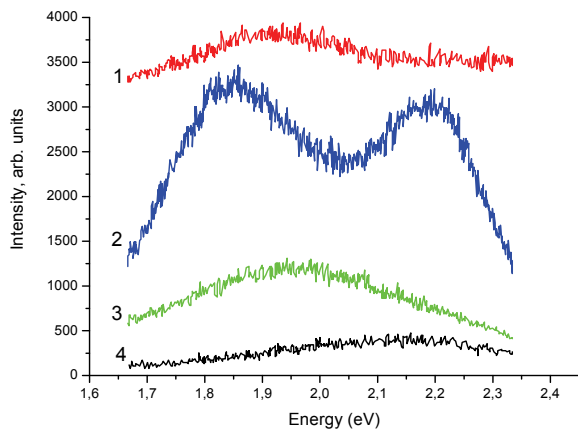


Figure 3. Room temperature PL spectra of $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ films, $E_{\text{ex}}=2.41$ eV: 1- $x=0.9$; 2- $x=0.7$; 3- $x=0.5$; 4- $x=0.3$

that a similar band could appear at room temperature in the PL spectrum of $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ film samples (Table 1) at $x=0.3, 0.5$ in which Raman spectra we registered intense vibration of $p\text{-As}_4\text{S}_4$ molecules (235 cm^{-1}) (Figure 2). However the film sample at $x=0.3$ gives in the PL spectrum a low intensity wide band PL signal whose maximum is centered at 2.15 eV (Figure 3). For thicknesses of the films from 400 to 500 nm at $x=0.5$ (Table 1) the intensity of this band slightly increased and its maximum is red shifted to 1.95 eV . Further increasing the Ge content ($x=0.7$) and thickness of the film to 750 nm (Table 1) leads to the appearance in the PL spectrum of two well separated bands near 1.85 and 2.2 eV (Figure 3, curve 2). When the composition of ternary films is approaching Ge_2S_3 and the thickness of the film decreases to 450 nm ($x=0.9$) the maximum of PL spectrum is seen near 1.95 eV and there is a shoulder near 2.2 eV (Figure 3, curve 1). The decrease of intensity of PL light and Raman signal (Figure 2) in the last case might be connected with a decrease of the penetration depth of the exciting laser beam at 2.41 eV (from the absorption coefficient, $1/\alpha=100\text{ nm}$) due to narrowing of the $g\text{-Ge}_2\text{S}_3$ optical band gap ($E_g=2.16\text{ eV}$). We note that for As_2S_3 based ternary films ($E_g=2.4\text{ eV}$) the value $1/\alpha$ is a few times more than for $g\text{-Ge}_2\text{S}_3$. If we take together the known data about luminescent properties of binary bulk Ge-S glasses and films in the region $1.9\text{-}2.5\text{ eV}$, we might find common PL emission characteristics of the species in other Ge-containing materials. For example, in Ge-doped silica gel glasses was observed room temperature red PL emission with peaks at 1.89 and 2.12 eV for 514.5 nm of an Ar^+ laser excitation [28]. Green PL ($2.1\text{-}2.5\text{ eV}$) of GeO_2 was reported in nc-Ge or Ge nanocrystals embedded in GeO_x ($0 < x < 2$) thin films [29]. In general, depending on the excitation wavelength the PL energy in GeO_x shows variations. Usually a blue PL band ($2.8\text{-}3.1\text{ eV}$) is observed when the PL is excited in the near UV [19], and when the excitation wavelength is longer than the blue wavelengths, the other PL bands (i. e. $1.6\text{-}1.9\text{ eV}$, $2.1\text{-}2.3\text{ eV}$, bands) are observed [28].

The most commonly reported PL band from GeO_x is the broad yellowish-green band located between $2.1\text{-}2.3\text{ eV}$ [30]. From the variety of oxygen-deficient defects the theoretical modeling shows that X3Ge-GeX2 ($\text{X}=\text{OH}$, OAH3 , $\text{A}=\text{Ge}$) defect gives only a red/orange PL band at $2.0\text{-}2.1\text{ eV}$ [31]. Oxygen related bands in the PL spectrum of an as-synthesized GeO_x nanowire, which was excited at the O K-edge (536.5 eV), showed during fitting procedure four components at 1.90 , 2.17 , 2.42 , and 2.70 eV . Thermal annealing of the GeO_x nanowire leads to the disappearance of the high energy bands at 2.42 and 2.70 eV and decreasing intensity of PL yield [19]. Taking into account the similarity of GeO_x , Ge-based glasses and films PL spectra (Figure 3) we consider the possibility that the PL radiation in Ge_2S_3 -based films is a surface contaminant effect [13] from native oxidized layer, which might have formed in the air. In order to determine if this hypothesis is correct, we have analyzed a difference plot of Raman spectra of $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ $z=2.78$, excited by IR and Ar-ion lasers (Figure 4) first of all. Due to the different penetration depth of IR and Ar-ion laser illumination into the film, this curve is characteristic of the surface of the film. Comparing both Figure 2 and Figure 3 in the range $200\text{-}300\text{ cm}^{-1}$ shows that the surface is enriched in GeS-like ($212, 230\text{ cm}^{-1}$), ethane-like (250 cm^{-1}) and $\text{Ge}_{4/4}$ (290 cm^{-1}) structural units (s.u). Detailed assignment of the Raman bands for these samples has been done in [27]. In the range $300\text{-}500\text{ cm}^{-1}$ the Raman spectrum $g\text{-Ge}_2\text{S}_3$ has two intense bands near 340 and 410 cm^{-1} [33,34], but the intensity of the last band is lower in comparison with the main band at 340 cm^{-1} . The most prominent band near 410 cm^{-1} in glassy GeO_2 is identified as symmetric stretching mode of bridging oxygen in 6-membered GeO_4 rings [17]. In Raman spectra of suboxide this maximum is shifted to 440 cm^{-1} [17]. So in the difference Raman spectrum (Figure 4) the maximum near 420 cm^{-1} is more reasonably ascribed to the presence of GeO_x species on the surface of the film ($z=2.78$). A new band at 380 cm^{-1} is seen at $x=0.9$ in the difference plot of the $(\text{Ge}_2\text{S}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ film (Figure 2). Similar peculiarities have been noted in the process of Raman investigation of Ge-O-S films [17]. This band was assigned [17] to mixed anion (sulfur and oxygen) germanium tetrahedral sites or phase separation of the glass structure. In order to examine the vibrational modes on the surface of the film at $x=0.9$ a complementary technique, SRPES and ordinary XPS spectroscopy, was used to look for the presence or absence of GeO_x and GeS_x species. SRPES and XPS analysis has been performed on the as-deposited, illuminated and annealed films. The study was carried out on the Ge 3d, As 3d and 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 [19,28,33,37,41] were used as reference energies during SRPES and XPS analysis. The surface and subsurface composition and their structural assignment obtained from the fitting procedure similar to those shown in (Figure 5) are presented in Tables 2 and 3, respectively.

Table 2.
Composition (atomic percentages) and Ge/S ratio obtained by SRPES (615 eV) and ordinary XPS (1486,6 eV) spectra analysis of amorphous films obtained by flash evaporated Ge₄₀S₆₀ glass powder

	Energy eV _s	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	20	0.95

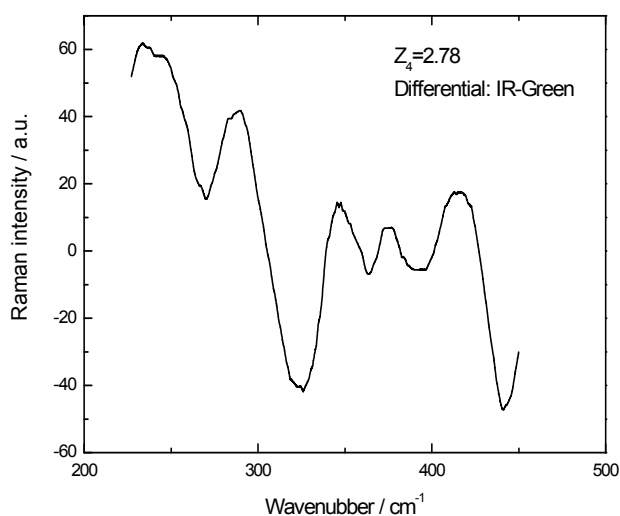


Figure 4. Difference plot between spectra recorded with two different excitation lines: 1.17 and 2.41 eV

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 ultra high vacuum at temperature, less than softening temperature of g-Ge₂S₃ (T_g-30⁰), (Table 2). In an earlier XPS investigation of Ge₂S₃-based films [35] the carbon contamination (an atomic percentage of about 15-20 %) has always been determined but was not taken [35] into account during the consideration of surface composition. 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 [36], 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 2). 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 3). The analysis of SRPES Ge 3d spectra has shown that after illumination and annealing the concentration of GeO₂ on top reduces and GeO_x increases in deeper layers which is confirmed by the XPS peak signal from 3 nm depth (Table 3). In previous literature for Ge₂₅Ga₁₀S₆₅ glasses studied by XPS and XAS, a

similar situation can be found [37]. 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 [38]. As already stated, Ge_{4/4} s.u. were found in the illuminated zone too, during measurement of Raman spectra (Figure 2) which confirmed the XPS spectrum assignment (Table 3). 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 [39] the composition of the thermally deposited film based on Ge₄₀S₆₀ glass was determined as Ge₄₆S₅₄ and did not matches well with that of the bulk glass. In the last case, the ratio Ge/S = 0.85 is slightly lower in comparison with the Ge/S ratio on the top (1.33) and deeper layers (1.0) of flash evaporated samples from the same nominal glass composition (Table 2).

Table 3.

Individual components of Ge 3d spectra determined from curve fitting as evaporated, irradiated and annealed films (Table 1) and their contribution (%) to total peak area. The main (3d_{5/2}) peak of the 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	S3Ge-GeS3 and GeS-like	16	13	-
peak 2	GeS _{4/2}	33	32	19
peak 3	GeO _x	34	37	57
peak 4	GeO ₂	17	18	14
<u>Ge3d, 1486 eV</u>				
peak 1	Ge _{4/4}	-	2	-
peak 2	S ₃ Ge-GeS ₃ and GeS-like	25	22	-
peak 3	GeS _{4/2}	43	46	25
peak 4	GeO _x	30	30	29
peak 5	GeO ₂	2	12	-

Table 4.

Individual components of Ge 3d spectra determined from curve fitting of bulk glass Ge₄₀S₆₀ surface and their contribution (%) to total peak area. The main (3d_{5/2}) peak of the doublet is considered.

	Ge3d,1486 eV	Area, %
peak 1	Ge _{4/4}	-
peak 2	S ₃ Ge-GeS ₃ and GeS-like	24
peak 3	GeS _{4/2}	74
peak 4	GeO _x	-
peak 5	GeO ₂	2

IV. 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 oxidation 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 layers and the laser stimulated losses of Ge and S. Annealing removed c-GeS-like $\times\text{S}_3\text{Ge-GeS}_3$ species and partially carbon from both the surface and near surface region, but did not move the surface toward the composition and local coordination of bulk glass.

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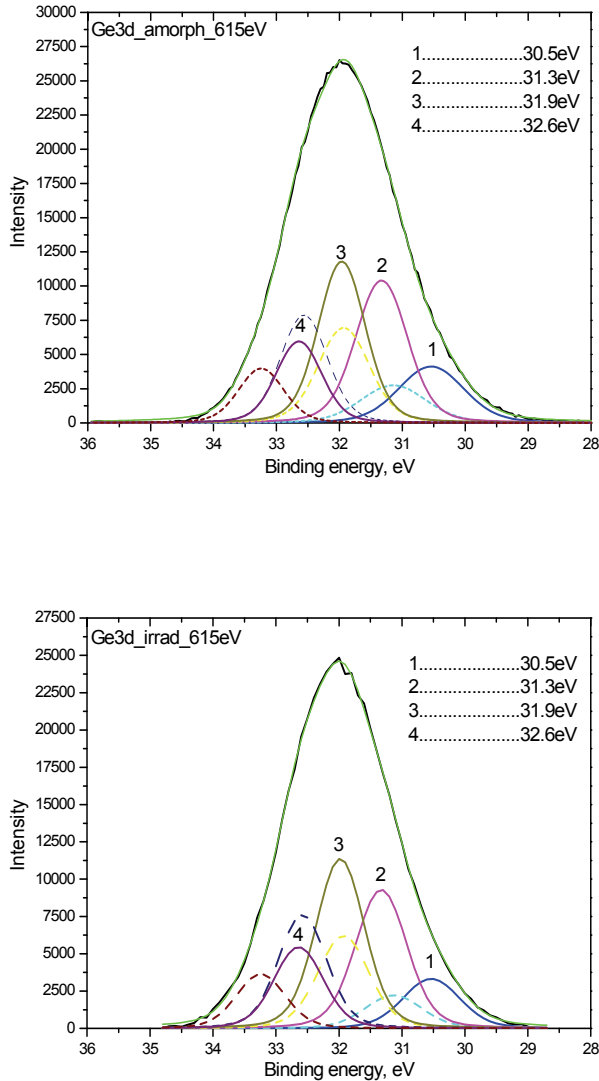


Figure 5. SRPES spectra of the flash evaporated Ge_2S_3 films before and after irradiation, with the fitted peaks

During fitting of SRPES and XPS C 1s core level spectra (not shown here) there is no indication of the Ge-C bonds formation (binding energy 284.3 eV [40]). 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 mixing of structural units: $\text{GeS}_{4/2} \times \text{c-GeS-like} \times \text{S}_3\text{Ge-GeS}_3 \times \text{GeO}_{4/2} \times \text{GeO}_{2/2}$. The ratio $\text{GeS}_{4/2} \times \text{c-GeS-like} \times \text{S}_3\text{Ge-GeS}_3 / \text{GeO}_{4/2} \times \text{GeO}_{2/2}$ (see data in Table 3) on the surface of films before illumination is near 1 and drastically differs from those represented by a bulk sample with polished surface (Table 4). We suggested that Ge oxidation plays an important role in radiative recombination processes from the surface of Ge_2S_3 -based films. The obtained results showed that annealing removed c-GeS-like $\times\text{S}_3\text{Ge-GeS}_3$ species from both the surface and near surface region. Annealing did not change the composition and local coordination of the films (Table 3) to those in bulk glass (Table 4.)

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