Coherent Light Photo-modification, Mass Transport Effect, and Surface Relief Formation in $\text{As}_x\text{S}_{100-x}$ Nanolayers: Absorption Edge, XPS, and Raman Spectroscopy Combined with Profilometry Study

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Abstract

$\text{As}_x\text{S}_{100-x}$ ($x = 40, 45, 50$) thin films top surface nanolayers affected by green (532 nm) diode laser illumination have been studied by high-resolution X-ray photoelectron spectroscopy, Raman spectroscopy, optical spectroscopy, and surface profilometry. It is shown that the composition of obtained films depends not only on the composition of the source material but as well on the composition of the vapor during the evaporation process. Near-bandgap laser light decreases both $\text{As}–\text{As}$ and $\text{S}–\text{S}$ homopolar bonds in films, obtained from thermal evaporation of the $\text{As}_{40}\text{S}_{60}$ and $\text{As}_{50}\text{S}_{50}$ glasses. Although $\text{As}_{45}\text{S}_{55}$ composition demonstrates increasing of $\text{As}–\text{As}$ bonds despite to the partial disappearance of $\text{S}–\text{S}$ bonds, for explanation of this phenomenon Raman investigations has also been performed. It is shown that $\text{As}_3\text{S}_3$ structural units (s.u.) responsible for the observed effect. Laser light induced surface topology of the $\text{As}_{45}\text{S}_{55}$ film has been recorded by 2D profilometer.

Keywords: As-S nanolayers, Photoinduced changes, XPS, Raman spectroscopy, Core level, Valence band, Mass transport, Chalcogenide thin films

Background

The research of chalcogenide glassy (ChG) materials formed a general understanding of electronic phenomena in disordered structures [1, 2]. The numerous investigations of their fundamental physical and chemical properties have been already performed [3–6]. Unique structural, electronic, and optical properties determined their various applications. The high infrared (IR) transparency of fibers on the basis of the ChG allows transmitting high-power IR light. The large refractive indices and third-order optical nonlinearities of the chalcogenide glasses make them the best candidates for the photonic devices for ultrafast all-optical switching and data processing [7].

Various applications have been proposed on the basis of the light sensitivity of non-crystalline chalcogenides, especially in amorphous thin film form [8–10]. Thus, photosensitivity is the main feature of chalcogenide glasses for phase-change memory, direct waveguides, and grating patterning.

The high-quality optical elements are required for the development of all-optical signal processing systems. Possibility of high-level integration of these elements in optical chips implies improved fabrication technology in order to achieve low optical losses at the near surface layers and the high level of laser damage threshold at femtosecond laser pulses. Also the large IR transparency or high optical nonlinearity of amorphous As–S binary systems make them a prospective optical media for the future ultrafast photonic systems. Our previous Raman studies of non-crystalline As–S binary system reveal the
differences between the structures of As$_4$S$_3$ films and bulk glass at nano-scale dimension [11]. The analysis shows that it is caused mainly by the phase separation, i.e., contribution of As$_3$S$_4$ cage-like molecules in the vapor during As$_2$S$_3$ thermal evaporation. In the further studies of the structure of amorphous As$_2$S$_3$ glasses and films using photon-energy-dependent Raman spectroscopy, the effect of laser-induced transformation of As$_3$S$_4$ molecules was observed [12]. Therefore, the As$_3$S$_4$ molecules can be classified as light absorption centers in As$_2$S$_3$ structure and leading to increasing the optical losses of an optical media.

The structure and properties of As$_{4x}S_{55}$ glassy material and thin film were investigated earlier [13, 14]. Using macro FT-Raman spectroscopy, energy-dependent micro-Raman spectroscopy and first principle calculations established that the light-induced structural transformations in As$_{4x}S_{55}$ glass take place mainly from alterations of As$_3$S$_4$ molecules in glass network. An impact of near-bandgap laser illumination transforms $\alpha(\beta)$-As$_3$S$_4$ molecules to pararealgar-like p-As$_3$S$_4$ [13]. The extended X-Ray absorption fine structure (EXAFS) study of photoinduced structural changes in amorphous As$_x$S$_{1-x}$ thin films showed that effect of the near-bandgap light illumination to the evaporated a-As$_{45}S_{55}$ and a-As$_{50}S_{50}$ films results in more disordered state and photostructural transformations are related to changes in the amorphous As-S network [14].

Raman spectroscopy of As-rich As$_{50}S_{50}$ thin films revealed pararealgar structure of $\chi$-As$_4$S$_4$, $\beta$-As$_4$S$_4$ molecules, clusters of amorphous arsenic, S$_2$As-AsS$_2$ and As$_4$S$_5$ structural units (s.u.), some part of $\alpha$-As$_4$S$_4$, As$_4$S$_3$ molecules, and As$_5$S$_4$ pyramids [15].

The aim of the present work is a complex structural investigation of thin film surface nanolayers prepared from As$_{40}S_{60}$, As$_{45}S_{55}$, and As$_{50}S_{50}$ chalcogenide glasses using X-ray photoelectron (XPS) and Raman spectroscopy, near-bandgap laser light’s influence on structural and compositional changes, and their electronic structure. In addition, the changes of surface morphology induced by laser light illumination were investigated using surface profilometry method.

**Methods**

High-quality optical glasses were used as the source materials for sample deposition in order to avoid the contamination in the volume of the films. The bulk As$_x$S$_{100-x}$ ($x = 40, 45, 50$) samples were prepared by conventional melt-quenching route in evacuated quartz ampoules from a mixture of high purity 99.999% As and S precursors. Nanolayers were prepared by thermal vacuum evaporation of appropriate bulk glass powders onto silicon and glass substrates. The thicknesses of obtained films were $\sim$0.7 µm. Green diode laser operating at $\lambda = 532$ nm wavelength (photon energy of $\sim$2.4 eV) with power $p = 25$ mW was used to investigate the influence of the near-bandgap light irradiation on the samples of As$_{40}S_{60}$, As$_{45}S_{55}$ and As$_{50}S_{50}$ ($E_g \sim$2.4 eV) nanolayers. Optical irradiation was carried out with 280 mW/cm$^2$ intensity at ambient conditions. Laser intensity was chosen based on our previous studies of As–S glasses by means of Raman spectroscopy, mentioned above. To determine exposition of the laser illumination following experiments was done. The absorption edge of the As$_x$S$_{100-x}$ ($x = 40, 45, 50$) thin films and its shift under in situ illumination by green laser light was investigated using millisecond CCD spectrometer ThorLabs CCS200. Sample illumination with in situ optical spectra recording were done until saturation of the shift of the absorption edge.

Photoemission experiments were conducted by using Al K-α anode ($E = 1486$ eV) as a source of X-ray. Spectra were recorded using hemispherical energy analyzer series Phoibos 100. An As 3d and S 2p core levels and valence bands (VB) were measured at normal emission geometry. Apart from this, the C 1s and O 1s core level spectra were recorded in order to normalize the positions of all spectra to a position of the graphitic peak (at 284.5 eV) [16]. C 1s core level spectra were fitted by C–C and C–O components only, and this agrees with the O–C components founded in O 1s core level spectra. Due to that C 1s and O 1s core levels would not be included in the further consideration. The CASA XPS program was used to fit core level spectra. For core level fitting, the Voigt profile components were used and Shirley background was subtracted.

Raman spectra were measured with using Renishaw system 1000 Raman spectrometer, equipped with a CCD detector. The diode laser operating at 785 nm was used as the excitation source. The measurements were made in micro-Raman configuration with using back-scattering geometry. In order to avoid stimulated by this laser photoinduced changes in the structure of the samples, the output power of the excitation source was limited by optical filters [17].

**Results**

**Absorption Edges of As$_x$S$_{100-x}$ Films Under External Influence**

Optical spectra of absorption edges of the As$_{40}S_{60}$, As$_{45}S_{55}$, and As$_{50}S_{50}$ films are shown in Fig. 1. As can be seen, the absorption edge of As$_{40}S_{60}$ sample shifts towards longer wavelengths when film exposed to green laser light illumination ($\lambda = 532$ nm) with photon energy of $\sim$2.4 eV, which is very close to $E_g$ of As$_{40}S_{60}$ material (Fig. 1, left). Typical red shift of the absorption edge of As–S films during the near bandgap illumination was observed earlier [5, 18]. After 45 min of laser illumination of As$_{40}S_{60}$ film, the shift becomes less and at exposure time of $\sim$150 min, the changes almost disappeared.
A similar phenomenon was observed for the absorption edge of illuminated As_{50S50} film (Fig. 1, right). However, the results of the same investigation of As_{45S55} film demonstrate the opposite effect. For this composition, the blue shift of the absorption edge is observed under the green laser illumination and 90 min was enough to reach the saturation. The structural interpretation of this phenomenon will be provided in the next paragraph using the XPS analysis and Raman spectroscopy data.

The determined particular exposure times sufficient to saturate the changes of the absorption edges of As_{40S60} (t_{exp.} = 150 min), As_{45S55} (t_{exp.} = 90 min), and As_{50S50} (t_{exp.} = 150 min) films were used for further experiments.

**XPS Spectroscopy and Valence Band Spectra of As_{x}S_{100-x} (x = 40, 45, 50) Film Surfaces**

X-ray photoelectron spectroscopy can be a useful technique to investigate the surface (i.e., few topmost layers) of the materials at short-range order scale and to determine the structural units which form the investigated material. This method was successfully used to characterize the top surface nanolayer structure of the amorphous materials [19–21]. The results of XPS investigation of As_{x}S_{100-x} (x = 40, 45, 50) thin film surface nanolayers are summarized in Fig. 2. As can be seen, all S 2p core level spectra can be fitted by two components. The energy position of component 1 (and their spin-orbit split 1') allows assigning them to S–As$_2$ s.u. [22, 23]. It is expected that this component is a characteristic s.u. in crystalline As$_2$S$_3$ and is a main component for both stoichiometric, As$_{40}$S$_{60}$, and As-rich As–S glasses and films. The component 2 (and 2') can be assigned to S-rich S–SAs s.u., and it is in a good agreement with our earlier investigations and theoretical estimations [19]. The As 3d core level spectra of As$_{40}$S$_{60}$ nanolayers (both as-deposited and illuminated by green laser light) are fitted using three components: arsenic bonded to three sulfur atoms As–S$_3$ (1, 1'), arsenic bonded to two sulfur, and one arsenic atoms As–S$_2$As (2, 2') and finally, arsenic bonded to one sulfur and two arsenic atoms As–SAs$_2$ (3, 3'). These assignments are based on our previous study [19] and are in excellent agreement with the published data [16, 24]. It should be noted that for the best fit of the As 3d core level spectra of As$_{50}$S$_{50}$ nanolayers, the fourth component is needed. The position of this component allows to interpret it as arsenic bonded to three arsenic atoms [16]. All peak component parameters are listed in Table 1.

The valence band spectra of as-deposited and illuminated by laser As$_{x}$S$_{100-x}$ (x = 40, 45, 50) thin film surface nanolayers were also measured and shown in Fig. 2. The general view of these spectra for all As–S compositions is similar and correlates well with the valence band spectra of As$_{40}$S$_{60}$ films [25, 26]. For a better understanding of the structural changes caused by laser light illumination, differential VB spectra were constructed (Fig. 3, bottom part).

**Raman Spectroscopy of As$_{40}$S$_{60}$, As$_{45}$S$_{55}$, and As$_{50}$S$_{50}$ Glasses and Films**

Results of XPS measurements give a possibility to analyze the structure of investigated materials at micro-level (short-range order) and to determine structural units which form the substance. For a better understanding of the nature of processes and stimulated structural changes, it is necessary to investigate the structure of the samples at the extended scale range (i.e., medium range order) in order to determine the macrostructure of materials. The cage-like molecules, rings, chain-like and bigger clusters in the structure of the As–S glasses and films can clearly be detected and identified from the Raman spectra [27]. Also, the photon energy-dependent micro-Raman spectroscopy can successfully be used for monitoring the photoinduced molecular transformations [7, 12]. Therefore, this technique was used for complex investigation of the structure and induced transformations in As$_{40}$S$_{60}$, As$_{45}$S$_{55}$, and As$_{50}$S$_{50}$ films.

The Raman spectra of source As$_{40}$S$_{60}$, As$_{45}$S$_{55}$, and As$_{50}$S$_{50}$ glasses and corresponding As–S thin films are
shown in Fig. 4. As can be seen, the Raman spectra of g-As₄₀S₆₀ demonstrate a broad band with the maximum at 340 cm⁻¹ and shoulders at 310 and 380 cm⁻¹. The main band centered at 340 cm⁻¹ is a characteristic band of symmetric As–S vibrations in AsS₃ pyramids. The shoulders at 310 and ~380 cm⁻¹ are connected with the asymmetric As–S vibrations in AsS₃ pyramids and As–S–As vibrations of “water-like” molecule, respectively. The Raman band at 130 cm⁻¹ can be connected with deformational vibrations of –As–S–As– and –S–As–S– structures. In addition to these bands, the very weak features at 143, 165, 186, 220, 230, and 360 cm⁻¹, connected with homopolar As–As bonds and realgar As₄S₄ inclusions, and small intensive band at 490 cm⁻¹ associated with S–S bonds are detectable in the Raman spectra of As₄₀S₆₀ glass. In contrast with the Raman spectra of stoichiometric glass, the broad band in the region of As–S valence vibrations (~300–400 cm⁻¹) in the Raman spectra...
of corresponding As$_{40}$S$_{60}$ films clearly show the double-peak structure. The simultaneous increases in intensities of 360 cm$^{-1}$ Raman band and bands in the region of molecular and As–As valence band vibrations (100–300 cm$^{-1}$) can indicate the increasing of the concentration of cage-like As$_4$S$_4$ molecules in As$_{40}$S$_{60}$ films in comparison with those found in the structure of corresponding target glass. As can be seen from intensities of 490 cm$^{-1}$ bands (Fig. 4, curve 1), the concentration of homopolar S–S bonds in the structure of As$_{40}$S$_{60}$ films is larger than in As$_{40}$S$_{60}$ glass. At the same time, the new band at ~270 cm$^{-1}$ is detected in the Raman spectra of As$_{40}$S$_{60}$ films. This band is assigned to the vibrations in As-rich As$_4$S$_3$ cage-like molecules [28].

### Table 1 Binding energies (BE, ±0.1 eV) and full width at half maximum (FWHM) (±0.05 eV) data of individual components determined from curve fitting of S 2p and As 3d XPS spectra of as-deposited and illuminated by green ($\lambda = 532$ nm) laser As$_{40}$S$_{60}$, As$_{45}$S$_{55}$, and As$_{50}$S$_{50}$ nanolayers

| Core level/component | As$_{40}$S$_{60}$ | As$_{45}$S$_{55}$ | As$_{50}$S$_{50}$ |
|---------------------|------------------|------------------|------------------|
|                     | As received      | Illuminated      | As received      | Illuminated      | As received      | Illuminated      |
|                     | BE FWHM         | BE FWHM         | BE FWHM         | BE FWHM         | BE FWHM         | BE FWHM         |
| S 2p:               |                 |                 |                 |                 |                 |                 |
| S–As$_2$            | 162.1 1.2       | 162.1 1.2       | 162.1 1.1       | 162.1 1.1       | 162.1 1.1       | 162.1 1.1       |
| S–SA$_5$            | 163.2 1.3       | 163.2 1.1       | 163.3 1.3       | 163.2 0.9       | 163.1 1.1       | 163.1 1.3       |
| As 3d:              |                 |                 |                 |                 |                 |                 |
| As–S$_3$            | 43.0 1.3        | 43.0 1.3        | 42.9 1.2        | 42.9 1.5        | 42.9 1.3        |
| As–S$_2$As          | 42.5 1.2        | 42.4 1.2        | 42.5 1.2        | 42.5 1.0        | 42.5 1.3        |
| As–SA$_5$           | 42.0 1.3        | 42.0 1.3        | 42.1 1.2        | 42.0 1.5        | 42.0 1.3        |
| As–As$_3$           | – –             | – –             | – –             | – –             | – –             |

Fig. 3 Valence band spectra of as-deposited (black line) and illuminated by green ($\lambda = 532$ nm) laser light (green line) As$_{40}$S$_{60}$, As$_{45}$S$_{55}$, and As$_{50}$S$_{50}$ thin film nanolayers (top part). Differential (illuminated minus as received) original (blue spiked lines) and smoothed (red thick lines) spectra (bottom part).

Fig. 4 Raman spectra of As$_{40}$S$_{60}$ (1), As$_{45}$S$_{55}$ (2), and As$_{50}$S$_{50}$ (3) target glasses (dotted line) and corresponding thin films (solid line).
The Raman spectra of As\textsubscript{50}S\textsubscript{50} and As\textsubscript{50}S\textsubscript{50} glasses are very similar (Fig. 4, curves 2 and 3). The main contributions in the Raman spectra of both glasses originate from As\textsubscript{4}S\textsubscript{4} cage-like molecules. Weak band at 270 cm\textsuperscript{-1} characteristic of As\textsubscript{4}S\textsubscript{3} molecules was detected, and no S–S bonds (490 cm\textsuperscript{-1} Raman mode) were found for both glass compositions. The difference in the Raman spectra of As\textsubscript{45}S\textsubscript{55} and As\textsubscript{50}S\textsubscript{50} glasses is connected with redistribution of 340 and 360 cm\textsuperscript{-1} band intensities only. In contrast with the glasses, the Raman spectra of As\textsubscript{45}S\textsubscript{55} and As\textsubscript{50}S\textsubscript{50} thin films are different. The main differences are connected with the intensity of Raman band at 270 and 360 cm\textsuperscript{-1}. These bands are more intensive in the Raman spectra of As\textsubscript{45}S\textsubscript{55} films indicating the drastic separations of cage-like As\textsubscript{4}S\textsubscript{3} and As\textsubscript{4}S\textsubscript{4} molecules from pyramidal network. Also, the very weak band at ~490 cm\textsuperscript{-1} (S–S bonds) is detected in the Raman spectra of both As\textsubscript{45}S\textsubscript{55} and As\textsubscript{50}S\textsubscript{50} films.

**Discussion**

**Atomic Stoichiometry of As–S films**

From the core level spectra of As\textsubscript{x}S\textsubscript{100-x} \((x = 40, 45, 50)\) thin film surface nanolayers which are shown in Fig. 3, the atomic concentrations and As to S ratios of as-deposited and illuminated by green laser light samples were calculated. The appropriate values are given in Table 2.

As it can be seen, the thermal evaporation of the bulk chalcogenide glass of As\textsubscript{40}S\textsubscript{60} composition causes the As\textsubscript{42.9}S\textsubscript{57.1} composition of deposited thin film. Laser light illumination with near-bandgap photon energy leads to further slight arsenic enrichment. More As-rich thin film in comparisons with target composition is obtained when the As\textsubscript{45}S\textsubscript{55} glass is evaporated (see Table 2). Further arsenic content increment from 48.9% in the as-deposited sample to 51.0% in the sample illuminated by a green laser light during 90 min takes place. Correspondingly, the appropriate As to S ratio is changed from 0.96 to 1.04. Unexpectedly, the thermal evaporation of As\textsubscript{50}S\textsubscript{50} glass leads to deposition of thin film with the As/S ratio which is less than for the bulk glass (As\textsubscript{45.4}S\textsubscript{54.6} composition) (Table 2). The laser treatment of this sample causes small arsenic enrichment, but the ratio between As and S remains far from the appropriate value in the bulk glass.

Such deviations of the thin film stoichiometry from the bulk glasses and further changes to them under the external (laser) influence with photon energy close to the band gap of investigated materials can be understood and explained from a detailed component analysis [29, 30].

**Component Analysis of As\textsubscript{x}S\textsubscript{100-x} \((x = 40, 45, 50)\) Thin Films Under External Influence**

As mentioned above, the fit of core level spectra of all films (before and after treatment) demonstrates the presence of structural units with homopolar bonds (see Fig. 2). Because of sulfur is twofold coordinated and arsenic is threefold coordinated in As–S system, the As\textsubscript{40}S\textsubscript{60} composition should demonstrate the water-like S–As\textsubscript{2} and pyramidal As–S\textsubscript{3} components only in their S 2p and As 3d core level spectra, respectively. However, the homopolar As–As bonds were detected in the As 3d core level spectra of all As\textsubscript{x}S\textsubscript{100-x} \((x = 40, 45, 50)\) nanolayers which is expected from As-enrichment \((x > 40\text{ at.}\%\) As) of their top surface. In accordance with this for the As\textsubscript{40}S\textsubscript{60} composition, it was found of 5.7% s.u. which are assigned to arsenic bonded to two sulfur and one arsenic atoms, and of 4.1% s.u. which mean the presence of the arsenic

| Element/Core level/Component | As\textsubscript{40}S\textsubscript{60} | As\textsubscript{45}S\textsubscript{55} | As\textsubscript{50}S\textsubscript{50} |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| As, %                       | 42.9                        | 43.0                        | 48.9                        |
| S, %                        | 57.1                        | 57.0                        | 51.1                        |
| As/S                        | 0.75 (0.67)                 | 0.75                        | 0.96 (0.82)                 |
| S 2p:                       |                             |                             |                             |
| S–As\textsubscript{2}, %    | 84.8                        | 90.4                        | 93.0                        |
| S–SAs, %                    | 15.2                        | 9.6                         | 7.0                         |
| As 3d:                      |                             |                             |                             |
| As–S\textsubscript{3}, %    | 90.2                        | 92.1                        | 44.5                        |
| As–SAs\textsubscript{2}, %  | 5.7                         | 4.1                         | 43.8                        |
| As–SAs\textsubscript{2}, %  | 4.1                         | 3.8                         | 6.6                         |
| As–As\textsubscript{3}, %   | –                           | –                           | 5.1                         |
bonded to one sulfur and two arsenic atoms (peaks 2, 2’ and 3, 3’, respectively). The contributions of these two As-rich components are much significant in As 3d core level spectra of As₄S₅ film surface (see Table 2). Moreover, the fourth component, As–As₃ is appeared with 5.1% contribution, which is reasonable for calculated composition (AsS₄₋₁, AsS₄,9). Finally, the thin film obtained by thermal evaporation of the As₅₀S₅₀ target glass contains 35.6% of As–S₂As s.u. and 6.9% of As–SAs₂ s.u. apart from the pyramidal one.

Despite to arsenic enrichment of all three as-deposited As-S samples in comparison with the stoichiometric composition, the S 2p core level spectra contain a component with the homopolar S–S bond (Fig. 2). There is a strong correlation between the As to S ratio of as-deposited samples and the percentage of S–SAs s.u. in the appropriate S 2p core levels. However, the further exploration of the existence of S–S bonds in As-rich structures is needed.

The properties and micro structure of vapor-deposited films depend on the deposition methods and conditions. Therefore, the resulting film structure can be different from the structure of the corresponding bulk glasses as established earlier [31]. The As–As bond formation in the as-deposited As₄S₃ film was detected with using X-ray diffraction technique. On the basis of the arsenic enrichment of the film and detected by mass spectroscopy fragmentation into S₂ and As₅S₄ during the evaporation of the bulk As₂S₃ glass, the formation of a sheet-like open structure of the film is supposed [31]. Also, it is pointed out that the As–As bonds may be incorporated as S₂As–AsS₂ units, as in As₃S₄ molecules as determined using extended X-ray absorption edge fine structure and Raman and IR spectroscopy. Apart from this, the dominance of As₂S₄ and sulfur molecules in as-deposited films were shown by neutron diffraction study [31]. The mass spectrometry study shows the presence of S₂ and different AsS particles in the gas phase of As–S system [32]. Therefore, the presence of S–S s.u. (S 2p spectra) in the structure of all As–S films and the appearance of As–S₂As s.u. in the As 3d core level spectra of even stoichiometric As₄₀S₆₀ composition can be understood. Moreover, apart from the composition of the target glass, the type of molecules in vapor plays a significant role in the formation of the film composition and structure. This way, the differences in compositions of the films and corresponding source materials can be explained. Additional support of mentioned As-enrichments of top surface As–S nanolayers can be confirmed by Raman spectroscopy. In particular, the biggest arsenic enrichment is found for As–S film deposited from As₄₅S₅₅ glass where the most significant contribution of As-rich As₄S₃ molecules is detected (Fig. 4, curve 2).

Near-bandgap laser light illumination of As₂S₁₀₀₋ₓ (x = 40, 45, 50) samples causes decreasing of the contribution of components with the homopolar S–S bonds in all the samples (Table 2). This phenomenon was observed in our previous investigations [19] and was explained by the processes of the structural ordering under the laser light illumination. In addition, the decreasing of components with homopolar As–As bonds in the structure of As₄₀S₆₀ and As₅₀S₅₀ nanolayers under the near-bandgap laser light illumination was observed (Fig. 2, Table 2). This is in accordance with the results of our in situ under-bandgap laser light illumination of As₂S₃ nanolayers [19]. The decreasing of concentration of homopolar As–As bonds in the structure of As₄₀S₆₀ and As₅₀S₅₀ films under laser illumination correlates well with the partial disappearance of the S–S bonds and creation of new As–S bonds.

However, the different behavior in compositional and structural changes under laser illumination was observed for As₄₅S₅₅ films. In contrast with As₄₀S₆₀ and As₅₀S₅₀ nanolayers, the increasing of concentration of components with As–As bonds was detected in As₄₅S₅₅ films as a result of the near-bandgap laser light illumination (Fig. 2, Table 2). Similar increasing was also detected in As₂S₃ nanolayers when over-bandgap laser light illumination was applied [19]. This effect was explained by atomic movement of As from deeper to top layers under the laser treatment, leading to As-enrichment of the sample surface. Such movement appears due to a creation of electric field gradient which is driving force on dipoles and charged defects resulting in mass transport.

The larger magnitude of laser-induced changes in As–S system was found for As-rich compositions with As₄S₄ inclusions [7]. It should be noted here that XPS spectroscopy reveals the most As-enriched composition of As–S film prepared from As₄₅S₅₅ glass among studied As₂S₁₀₀₋ₓ (x = 40, 45, 50) films. Moreover, the significant As enrichment of the As₄₅S₅₅ sample was confirmed by Raman spectroscopy (Fig. 4, curve 2) where the 270 cm⁻¹ Raman band characteristic of As₄S₃ molecules show maximal intensity. In this manner, the specific behavior and the structural rearrangement of the As₄₅S₅₅ nanolayers are conditioned by a considerable number of As-rich s.u., particularly As₄S₃. This can stimulate laser-induced mass transport effect resulting in further arsenic enrichment of the sample surface.

Valence Band Spectra of As–S films
In general, the valence band can be determined as the highest range of electron energies which can be occupied at absolute zero temperature [33]. According to Mott and Devis model, the valence band of amorphous materials contains the states formed by defect centers [34]. For the As–S system, the top of the VB is formed
by lone-pair 3p electrons of sulfur (at ~3 eV), as 4p and S 3p levels (bonding electrons) are situated at ~5 and ~7 eV, respectively. Next energy band is located lower than 10 eV and formed by the S 3s and As 4s electrons. These data were confirmed by DFT electronic structure calculations of As- and S-centered s.u. [19].

A qualitative comparison of the VB spectra of As$_x$S$_3$ nanolayers investigated in situ [19] with the VB spectra of As$_x$S$_{100-x}$ ($x$ = 40, 45, 50) films show the differences connected with the presence of additional states at energies ranged from ~1.7 to 0.6 eV (Fig. 3). According to the calculated data, the formation of homopolar As–As bonds leads to the appearance of the energy levels in the band gap of the As–S structures [35, 36]. The concentration of As–As bonds in As$_x$S$_{100-x}$ ($x$ = 40, 45, 50) films was found to increase in order: As$_{40}$S$_{60}$, As$_{50}$S$_{50}$, and As$_{45}$S$_{55}$ (Table 2). Taking into account, the changes of the concentrations of s.u. with homopolar As–As bonds induced by laser treatment (decreasing for As$_{40}$S$_{60}$, As$_{50}$S$_{50}$ composition and increasing for As$_{45}$S$_{55}$ structure) (Table 2) and intensities of electronic states in the VB spectra of As–S films (from ~1.7 to 0.6 eV) (Fig. 3) can be assumed that they are formed by structural units with As–As bonds.

The main changes in the electronic structure of As–S samples induced by laser light illumination can be selected (highlighted regions in Fig. 3). The changes in these regions (denoted as A, B, and C) can clearly be seen from the differential valence band spectra (Fig. 3. bottom). The right highlighted region (A) in the differential VB spectra of As$_x$S$_{100-x}$ ($x$ = 40, 45, 50) films points out to the changes of the states in the band gap of the structures. Middle highlighted region (B) indicates that the band gap decreases in the As–S samples of the As$_{40}$S$_{60}$ and As$_{50}$S$_{50}$ compositions and increases in the As$_{45}$S$_{55}$ structure under the near-bandgap laser light illumination. It should be noted that these results correlate with the shift of absorption edge measurements. And finally, left marked region (C) demonstrates common decreasing of the concentration of S–S homopolar bonds in all As–S films under laser treatment (see Figs. 2 and 3, Table 2).

**Profilometry Analysis of Laser Induced Relief Formation in As$_x$S$_{100-x}$ ($x$ = 40, 45, 50) Films**

As it was mentioned above, the increasing of the components with the As–As bonds under the near-bandgap laser light illumination takes place due to a creation of electric field gradient resulting in mass transport. In order to examine of this effect, the additional experiments were performed. The as-deposited films of all three compositions were illuminated by green laser light through the copper mesh with grating period of 60 μm during time sufficient for saturation of shift of absorption edge, measured previously (see previous chapter). Then, the surface of irradiated As–S samples was examined by AMBIOS XP-1 type profilometer with 10 nm vertical resolution (stylus tip radius—2.5 μm). For the profilometer measurements, a 0.5 mg load was applied. This load was small enough to make the accurate profiling without destroying the surface morphology. Results are shown in Fig. 5.

As can be seen, the laser light illumination does not change the shapes of the surfaces of both As$_{40}$S$_{60}$ and As$_{45}$S$_{55}$ thin films. Thus, it can be concluded that laser illumination was not influenced on morphology of the surface of these samples. However, the different behavior in laser-induced transformations and surface morphology changes was discovered for As$_{45}$S$_{55}$ thin film (see Fig. 5, curve 2). It is clearly seen that under the laser light illumination the “wave-like” relief on the surface of As$_{45}$S$_{55}$ film is formed. The parameters of the induced grating can be seen in the insert of Fig. 5. This relief corresponds to the period of the mash grating.

Taking into account that the As$_{45}$S$_{55}$ composition demonstrates peculiarities and opposite induced phenomena (shift of the absorption edge, stoichiometry and local structure changes, untypical VB shift, and shape changes) in comparison with the As$_{40}$S$_{60}$ and As$_{50}$S$_{50}$ thin films and contains the largest concentration of As$_4$S$_3$ cage-like molecules, it can be concluded that the presence of polar As$_3$S$_3$ molecules (which are sensitive to the electric field generated by the laser) is responsible for observed laser-induced mass transport effect. The drift and re-arrangements of this molecules results in photexpansion of illuminated areas. The observed phenomena can be used for optical grating formation, controlled laser surface modification, laser induced surface activation, etc.

**Fig. 5 Profiles of the surface of As$_{40}$S$_{60}$, As$_{45}$S$_{55}$, and As$_{50}$S$_{50}$ thin films illuminated by green (λ = 532 nm) laser light through the copper grid**
Conclusions
The local and molecular structures of As$_x$S$_{100-x}$ ($x = 40$, $45$, $50$) thin film surfaces and their transformations induced by coherent near-bandgap laser illumination have been investigated using XPS and Raman spectroscopy. The optical properties and induced transformation of surface morphology of As–S nanolayers have been also studied by means of absorption edge spectroscopy and 2D profilometry.

A significant difference in surface stoichiometry between amorphous As–S films and composition of corresponding target glasses was established, and it was found to be related with the peculiarities in molecular constituent of gas phase during the deposition process, indicating that the type of molecules in vapor plays a crucial role in resulting film composition. Near-bandgap laser illumination decreases the concentration of the homopolar S–S bonds in the structure of all As$_x$S$_{100-x}$ ($x = 40$, $45$, $50$) nanolayers. However, the decreasing of the concentration of homopolar As–As bonds upon laser illumination was observed in the structure of As$_{40}$S$_{60}$ and As$_{50}$S$_{50}$ films only. In contrast with As$_{40}$S$_{60}$ and As$_{50}$S$_{50}$ films, the contribution of As–S$_2$As and As–SA$_2$S$_2$ components and appearance of a new As-rich As–As$_3$ s.u. in the structure of As$_{45}$S$_{55}$ thin film during laser illumination were detected. Moreover, this particular film (As$_{45}$S$_{55}$) demonstrates peculiarities in laser-induced shift of the absorption edge, in Raman spectra, and finally, in effect of induced surface morphology transformation.

The results of Raman investigation of As–S films indicate the presence of As-rich As$_5$S$_3$ molecules in the structure of As$_{45}$S$_{55}$ nanolayers in largest concentration among studied samples. Therefore, the As$_5$S$_3$ molecules were found to be responsible for drastic difference in behavior of absorption edge spectra and surface morphology transformation of As$_{45}$S$_{55}$ nanolayers during near-bandgap laser illumination. The presence of these As$_5$S$_3$ structures in the structure of As$_{45}$S$_{55}$ nanolayers results in laser-induced mass transport effect observed for this material and can be useful for optical grating formation and related external nanofabrication technologies.

Abbreviations
BE: Binding energy; ChG: Chalcogenide glass; FWHM: Full width at half maximum; VB: Valence bands; XPS: X-ray photoelectron spectroscopy

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Authors’ Contributions
All authors (O.K, R.H, ACh, VT, MV, and VM) equally contributed in developing the general idea and methodological aspects of performed investigation. O.K, R.H, and VM prepared the source glasses and synthesized As$_x$S$_{100-x}$ thin films of different ($x = 40$, $45$, $50$) compositions. O.K, VT, and ACh performed the XPS, absorption edge spectroscopy, and profilometer measurements to characterize the samples. RH and MV performed the Raman spectroscopy measurements and spectral interpretation. VM carried out the general control of the processing and analysis of the results. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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