Comparative study of electron- and photo-induced structural transformations on the surface of $\text{As}_{35}\text{S}_{65}$ amorphous thin films

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Abstract

Change of electronic structure and chemical composition on the surface of freshly prepared $\text{As}_{35}\text{S}_{65}$ thin films caused by electron- and light irradiation have been studied by high-resolution X-ray photoelectron spectroscopy. The mechanisms of the induced transformations are compared. It is shown that light irradiation causes redistribution of chemical bonds without change in chemical composition. The products of such light-induced structural transformations were also identified by Raman spectroscopy in the volume of thin films. Electron irradiation changes chemical composition of the surface by creating an As-enriched layer due to the formation of As–O bonds. Anomalous increase of the ~10 eV band associated with non-bonding As 4s electrons was observed after light- and low dose e-beam irradiation.

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1. Introduction

Photo- and electron lithography [1–4] are two of the most promising applications of thin films of chalcogenide glasses (ChG), which are non-oxide vitreous compounds of chalcogen atoms (S, Se or Te) with elements of IVA and VA groups of Periodic Table (Ge, As, Bi, P, etc.). Photo-induced effects in ChG have been widely studied by different authors [5–7], being explained within photodarkening, photo-induced volume change, photo-induced defect creation and photorelaxation mechanisms. However, the mechanism of the photo-induced effects and, especially, the kinetics of photostuctural changes are still the exciting topics in the physics of disordered solids. At the same time, lithography applications of high-energy electrons, such as from a scanning electron microscope (SEM), have been reported to be based on a thermal expansion through the thickness of films [8], as well as increasing the refractive index of the glass [9]. Several authors have offered also such explanations as electron trapping within the film causing electrostatic repulsion between layers [8,10] and homopolar bonds breaking, akin to that proposed for explaining photo-induced effects [8]. We utilized earlier the electron-induced change in ChG to fabricate by wet etching parallel nanolines 80 to 250 nm in height, 27 nm in widths and separated only by 7 nm [4]. Such fine motives can be obtained by electron beam irradiation of $\text{As}_{35}\text{S}_{65}$ thin films due to the amorphous nature of their structure and small size of structural building blocks. Chalcogenide layers of this composition have been effectively used also for direct laser writing of complex patterns with hexagonal air holes [11]. However, the atomic and electronic origin of the induced structural transformations, as well as the role of surface oxidation, if any, remains unclear. The aim of this paper is to compare the mechanisms of photo- and electron-induced structural effects of the surface layers in thin ChG film using high-resolution X-ray photoelectron spectroscopy (XPS). Additionally, we have compared these photo-induced structural changes in the very top part of ChG film with
those deeper into the film thickness as characterized by Raman spectroscopy.

2. Experimental details

Thin films (400 nm) of As$_{35}$S$_{65}$ composition were evaporated onto microscope glass slides that had 5 nm of chromium previously deposited to make a conducting substrate. These samples were stored in the dark with minimal exposure to indirect lighting during patterning and etching. Since one goal was to mimic conditions and doses used in electron beam lithography (EBL), extremely high doses were required. Typical EBL utilizes a spot size of 1 nm with ~4 fC doses, equating to doses of 5 C/cm$^2$. In order to accommodate the larger X-ray probe required for XPS (1–2 mm$^2$), large spot sizes with larger currents were used to approach this dose. The dose I was applied on a Philips XL 30 E-SEM at 30 kV with 3 nA probe current exposing a sample of size 0.7 cm$^2$ for 1260 s (5 $\times$ 10$^{-6}$ C/cm$^2$). The higher dose II was applied on a JEOL 733 Microprobe at 30 kV with 0.3 $\mu$A probe current exposing a sample of 8 $\times$ 10$^{-3}$ cm$^2$ for 240 s (9 $\times$ 10$^{-3}$ C/cm$^2$). Both above samples were exposed to the air for the very short time necessary to move them from electron microscope to XPS chamber. The calculation of these doses are provided to present a comparison, but do not constitute precise quantified data since the exact areas of exposure on the sample is approximated, along with the measurement of the absorbed current through the sample. One more sample of size 0.7 cm$^2$ was exposed for 360 s to the dose $\sim$7 $\times$ 10$^{-4}$ C/cm$^2$ (dose III) on a JEOL 6400 SEM at 30 kV with 1.4 $\mu$A probe current. However, this sample after electron irradiation was exposed to the air for longer time ($\sim$24 h) and can be used only for estimation of influence of oxygen on the electron-induced transformations in As$_{35}$S$_{65}$ thin film. To compare the mechanisms of light- and electron-induced effect the same As$_{35}$S$_{65}$ thin film samples were irradiated by halogen lamp (P $\sim$ 15 mW/cm$^2$) to saturation of photo-induced effects.

The XPS spectra were recorded with a Scienta ESCA-300 spectrometer using monochromatic Al $K_{\alpha}$ X-ray (1486.6 eV). The usual analysis area is a spot $\sim$ 3–4 mm long and $\sim$ 250 $\mu$m wide. To decrease that area the appropriate gold mask was used. Data acquisition was restricted electronically to a region smaller than the X-ray illuminated area. For all measurements the angle between the surface and the detector was 90°. The instrument was operated in a mode that yielded a Fermi-level width of 0.4 eV for Ag metal for the core level (CL) spectra and 0.54 eV for valence band (VB). Energy scale was calibrated using the Fermi level of clean Ag.

The XPS data consisted of survey scans over the entire binding energy (BE) range and selected scans over the VB or CL photoelectron peaks of interest. An energy increment of 1.0 eV was used for recording the survey spectra and 0.05 eV for the case of CL spectra. The CL peaks were recorded by sweeping the retarding field and using the constant pass energy of 150 eV, whereas for the VB spectra we used 300 eV pass energy. The reproducibility of the measurements was checked on different regions of the investigated surfaces. The surface charging from photoelectron emission was neutralized using a low energy (<10 eV) electron flood gun. Though effective in minimizing distortions that might arise from differential surface charging on the surfaces, the use of the flood gun resulted in the surfaces attaining a uniform, though net negative potential with respect to earth. The magnitude of this potential depended upon the geometry and conductivity of the surface. The XPS data were calibrated according to impurity carbon 1s line (285.0 eV).

Note that X-irradiation of the As$_{35}$S$_{65}$ thin film within the spectrometer for 400 min did not produce any detectable changes in its XPS spectra. Similar lack of X-ray sensitivity was observed by us earlier for Ge$_{30}$Se$_{70}$ thin films.

Data analysis was conducted with standard ESCA-300 software package. For analyzing the CL spectra, Shirley background was subtracted and a Voigt line-shape was assumed for the peaks [12]. Concentrations of appropriate chemical elements were determined from the areas of CL peaks taking into account appropriate experimentally determined sensitivity coefficients.

Each 3d CL spectrum for As and 2p spectrum for S in our samples consisted of one or more spin orbit doublets (3d$_{3/2}$ and 3d$_{5/2}$ for As; 2p$_{3/2}$ and 2p$_{1/2}$ for S), whose separation and area ratios were fixed and linked using the previously obtained data. The number of doublets within a given peak was determined by an iterative curve fitting process in which a doublet was added only if it significantly improved the goodness of fit of the experimental data to the envelope of the fitted curve. The parameters used to link the S 2p$_{3/2}$ and 2p$_{1/2}$ peaks were: a peak separation of 1.26 eV and an area ratio of 0.525. For As 3d$_{3/2}$ and 3d$_{5/2}$ the parameters were 0.7 eV and 0.7, respectively. These reference values were obtained experimentally for bulk stoichiometric As$_2$S$_3$ using the same Scienta ESCA-300 spectrometer.

The full width at half maximum (FWHM) was assumed to be the same for the peaks within one doublet. However, differences between FWHM values for different doublets of the same CL peak were allowed. The mix between the Gaussian and Lorentzian fractions in the Voigt function was chosen to be the same for all doublets of a given CL. The fitting procedure gave asymmetry values close to zero and Gaussian/Lorentzian mix values close to 0.9 (1.0 is the value for pure Gaussian) for all peaks. With these constraints the uncertainty in the peak position and area of each component was $\pm 0.05$ eV and $\pm 2\%$, respectively.

It should be noted that the areas underneath the VB curves strongly depends on the oxidation and their parity cannot be used to compare the features of VB spectra. So, the decisive principle of the comparison was the recognition of maximum coincidence of spectral shape at of the low energy side (0–17 eV), which is not influenced by O 2s core level situated close to 22 eV [13]. Sensitivity is a unique parameter for each band in VB spectrum and depends on the cross-section of electron release, influencing the area under the spectrum too.

The Raman spectra were measured by using a Fourier Transformation spectrometer IFS 55 provided with FRA 106 accessory (Bruker, Germany). The Nd:YAG laser ($\lambda$ = 1.064 $\mu$m) with output power 90 mW was used for the excitation of the
Raman spectra. The resolution of the Raman spectrometer was 4 cm\(^{-1}\) at 300 scans.

3. Results

The changes in the shape of As 3\(d\) and S 2\(p\) XPS CL spectra after light- and electron irradiation of As\(_{35}\)S\(_{65}\) thin films are shown in Figs. 1, 2. The detailed analysis of photo- and electron-induced changes of electronic structure as well as control of chemical composition on the surface of the film was made through the appropriate fitting procedure. The example of the fitting for freshly deposited and light-irradiated samples is

Fig. 1. Comparison of As 3\(d\) CL spectra of freshly deposited As\(_{35}\)S\(_{65}\) thin films with the thin film light-irradiated with halogen lamp (a) and the thin films electron-irradiated with dose I (b) and dose II (c).

Fig. 2. Comparison of S 2\(p\) CL spectra of freshly deposited As\(_{35}\)S\(_{65}\) thin films with the thin film light-irradiated with halogen lamp (a) and the thin films electron-irradiated with dose I (b) and dose II (c).
demonstrated in Fig. 3. The quantitative parameters of the fitting and obtained chemical compositions are presented in Table 1.

It is clear from the table that light irradiation at given conditions does not change the chemical composition of the film surface, although electronic irradiation gradually decreases the S/As ratio from 1.92 to 1.54 for HD sample. The latter result is similar to that found for the laser-induced changes on the surface of As$_3$Se$_3$ thin films [14].

Oxygen content on the surface of the freshly prepared, light- and electron-irradiated samples (doses I and II), which were exposed to the air for very short time did not exceed 9 at.%. Only dose III sample, which was exposed to the air for 24 h, had 19 at.% oxygen on the surface. Position of oxygen O 1s CL peak

![Fig. 3. Fitting of As 3d (a,b) and S 2p (c,d) CL spectra for freshly deposited (a, c, respectively) and light-irradiated (b,d) As$_3$S$_6$ thin films.](image)

Table 1
Quantitative parameters of the fitted As 3$d$ and S 2$p$ CL spectra, chemical composition, oxygen content and change of intensity of VB $\sim$ 10 eV band for freshly deposited, light-irradiated and electron-irradiated As$_3$S$_6$ thin films (As and S positions are provided for As 3$d_{5/2}$ and S 2$p_{3/2}$ peaks)

<table>
<thead>
<tr>
<th>Sample</th>
<th>S(I) $\Delta eV$</th>
<th>S(II) $\Delta eV$</th>
<th>S(III) $\Delta eV$</th>
<th>As(I) $\Delta eV$</th>
<th>As(II) $\Delta eV$</th>
<th>As(III) $\Delta eV$</th>
<th>As(IV) $\Delta eV$</th>
<th>O $\Delta eV$</th>
<th>S/As$\Delta$fWHM</th>
<th>Rel. at. (10 eV band)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>161.1/0.81</td>
<td>25</td>
<td>3</td>
<td>41.9/0.68</td>
<td>80</td>
<td>41.5/0.81</td>
<td>-</td>
<td>530.7/1.80</td>
<td>5</td>
<td>1.92</td>
</tr>
<tr>
<td>Dose I</td>
<td>161.1/0.83</td>
<td>21</td>
<td>-</td>
<td>41.9/0.73</td>
<td>85</td>
<td>41.4/0.65</td>
<td>7</td>
<td>530.95/1.85</td>
<td>5</td>
<td>1.83 ↑</td>
</tr>
<tr>
<td>Dose II</td>
<td>161.2/0.84</td>
<td>12</td>
<td>13</td>
<td>42.1/0.76</td>
<td>85</td>
<td>-</td>
<td>-</td>
<td>531.0/1.48</td>
<td>9</td>
<td>1.54 ↓</td>
</tr>
<tr>
<td>light</td>
<td>161.0/0.83</td>
<td>22</td>
<td>-</td>
<td>41.9/0.76</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>530.7/1.90</td>
<td>8</td>
<td>1.92 ↑</td>
</tr>
<tr>
<td>Dose III</td>
<td>161.2/0.83</td>
<td>19</td>
<td>-</td>
<td>41.9/0.73</td>
<td>91</td>
<td>-</td>
<td>-</td>
<td>531.1/2.38</td>
<td>19</td>
<td>1.80 =</td>
</tr>
</tbody>
</table>
is the same for freshly prepared and light-irradiated samples, but shifts into the higher energies for electron-irradiated specimens.

The As 3d CL spectra were centered close to 42.0 eV that roughly coincides with the data obtained by other authors for chalcogenide glasses [15]. The eventual difference of the peak positions in comparison with other sources can be explained by the reference used for calibration and resolution of the spectrometer. Fitting of the As 3d CL spectra results into 1, 2 or 3 splitted components (Table 1). For freshly prepared film contains 2 pairs of peaks, with position of As 3d\(_{5/2}\) at 41.9 (major component, \(\sim 80\%\) of all As atoms) and 41.5 eV (\(\sim 20\%\)). Further we will use position of As 3d\(_{5/2}\) peak as characteristic of the component. The position of the 3d\(_{5/2}\) constituent is fixed relative to the 3d\(_{5/2}\) one. The light-irradiated sample has only a single component at 41.9 eV. For the sample electron-irradiated with dose I three-component fitting and for the sample electron-irradiated with dose II two-component fitting are valid. Major constituents for the dose I sample are situated at 41.9 eV (\(\sim 85\%\) at.\%), with two minor at 41.4 (\(\sim 7\%\) at.\%) and 42.2 eV (\(\sim 6\%\) at.\%). The spectrum of the dose II sample contains components at 42.1 (85 at.\%) and 41.3 (15 at.\%) eV.

For the freshly prepared and dose II samples, the S 2p spectra were fitted by 3 doublets, and for all others by 2 pairs only. Position of the major components was within the limits 161.1 ± 0.1 eV for S 2p\(_{3/2}\) peak (we will use BE of this peak to characterize the constituents of the S 2p spectrum), second component was found at 161.8–161.9 eV and third one at 160.3–160.4 eV.

The light- and electron-induced changes of the VB spectra are presented in Fig. 4 together with the structure of a typical XPS VB spectrum for freshly prepared As\(_{35}\)S\(_{65}\) thin film. Positions and FWHM of each of the bands can be slightly changed depending on the composition of the film. On the very top of the VB (\(\sim 2\) eV) we observe the strong line associated with lone-pair 3p electrons of sulfur [16]. The bonding electrons contributing from As 3d and S 2p levels are situated in the region from 3 to 5 eV [16,17]. The region from \(\sim 10\) to \(\sim 17\) eV is the superposition of the contributions from As 4s, S 3s non-bonding orbitals and O 2p bonding electrons [16–18]. Higher energy band at \(\sim 22\) eV belongs to O 2s CL [13]. The origin of the band close to 30 eV still should be determined.

We utilized Raman spectroscopy to find out whether the same structural changes occur by light exposure within the
volume of the film. These results in Fig. 5 show that structural changes are induced in the whole film volume as measurable changes were found in the intensity of individual bands of Raman spectra. Decreasing after exposure of As–As bonds concentration associated with the bands 362 and 120–220 cm\(^{-1}\) [19,20] is the main result of this study.

4. Discussion

The first important data about the difference between the mechanisms of photo- and electron-induced structural transformations in S-enriched As\(_{35}\)S\(_{65}\) thin films can be obtained already from the chemical composition of the surface, presented in the Table 1 as a S/As ratio.

The S/As ratio does not change at all after light exposure, testifying that any possible structural changes are of a bond-switching character, without any phase transformations. The position of the oxygen O 1s CL peak is the same after illumination by halogen lamp at the given conditions as in the freshly prepared film (530.7 eV). This means that in these both cases oxygen exists on the surface mostly in the form of uncontrolled impurity complexes, and no oxide species are formed. Analysis of the As 3d and S 2p CL for freshly prepared and light-irradiated samples (Table 1, Figs. 1–3) confirm this conclusion. The present high-resolution results confirm the absence of oxidation on the surface of As\(_{35}\)S\(_{65}\) glass previously indicated by low-resolution XPS data [21]. The photo-induced surface oxidation reported earlier [22,23] occurred under different conditions of irradiation and in samples that had higher arsenic content than the present samples.

The major component of the As 3d spectrum for the freshly prepared film at 41.9 eV (Fig. 3) represents As atoms within pyramidal units As\(_{5}\), the pair with BE for As 3d\(_{5/2}\) at 41.6 eV is probably related to the 3-fold coordinated As linked with 1 As and 2 S atoms. The relatively large value of FWHM for the minor component (0.81 eV) could be explained by structural non-homogeneity of freshly prepared film, where only pyramidal units should have standard low FWHM. Light exposure leads to structural rearrangement and full disappearance of As–As bonds on the surface of S-enriched As\(_{35}\)S\(_{65}\) film. The presence of homopolar As–As bonds in the whole volume of the S-rich thin films was confirmed by Raman bands at 360 cm\(^{-1}\) and at 100–250 cm\(^{-1}\) [19,20]. Thus we can conclude that exposure by halogen lamp light decreases As–As bond concentration within the volume of thin film (Fig. 5). However the process of structural ordering (replacement of “wrong” homopolar As–As and S–S bonds by more stable heteropolar As–S bonds) is most efficient in the top 10 nm surface layer probed by XPS. The light-induced disappearance of As–As bonds is accompanied by the decreasing of S–S concentration (Table 1, component at 161.8 eV associated with S within=As–S–S–As=fragments), full disappearance of 1-fold coordinated S within=As–S–S fragment (component at 160.3 eV) and increase of the major pair related to sulfur within regular=As–S–As=fragments (161.0–161.1 eV). Finally after light exposure of freshly prepared As\(_{35}\)S\(_{65}\) thin films by halogen lamp, the surface of the film contains pyramidal As\(_{5}\) units, some linked by homopolar S–S bonds. FWHM values for all components in As 3d and S 2p spectra of light-irradiated sample are quite low, which suggests an ordering of the structure.

The decreasing S/As ratio from 1.92 to 1.83 for the sample electron-irradiated with dose I can be explained by formation of As–O bonds instead of part of As–As ones on the film surface from the short-time air exposure of the preliminarily irradiated surface. Appearance of these bonds changes the chemical composition of the surface towards the decreasing of sulfur content. The structure of As 3d spectrum for the sample electron-irradiated with dose I (Table 1) shows that the high-energy component at 42.2 eV appears, in addition to components at 41.9 eV and 41.5 eV (41.4 eV for LD sample). New component at higher energies can be associated either with 3-fold coordinated As, which contains at least one As–O, or with increasing of As oxidation number. However, we exclude the relationship of 42.2 eV component with As\(_{2}\)O\(_{3}\) or As\(_{2}\)O\(_{5}\) oxides [24]. Analyzing the O 1s CL position (Table 1) we observed 0.25 eV shift of the peak to higher BE, confirming the interaction of electron-irradiated matrix with oxygen, most probably with formation of arsenic oxysulphide [22]. Radiation-induced oxidation of ChG was previously reported by one of the co-authors (AK) for gamma-irradiated bulk glasses [25]. At the same time, on this stage of the study, we cannot exclude fully
the possibility for the formation of 4-fold coordinated As predicted earlier theoretically by different authors [26,27].

Fitting of S 2p peak of this sample reveals that electron irradiation of the freshly prepared film causes disappearance of 1-fold coordinated S and some decreasing of $^{\text{=As-S-S-As=L}}$-fragments concentration.

Higher dose electron irradiation (dose II) drastically decreases the S/As ratio from 1.92 to 1.54 forming distinct As-enriched surface layer. The position of O 1s CL shifts on 0.3 eV towards higher BE in comparison with freshly prepared film what could be character for the formation of oxidized layer [22]. We suppose that as a result of electron-induced surface destruction, $\sim 15\%$ of all As atoms are under-coordinated and participate in the development of such oxidized layer. The As 3d component at 41.3 eV with a large FWHM (1.67 eV) is characteristic for low coordinated oxygen-bonded As atoms. The major component at 42.1 eV with FWHM=0.76 eV is related to AsS$_3$ pyramids. A BE shift to higher values (0.2 eV) in comparison with other studied samples is explained by superposition of two factors: 1) some of the S atoms within the pyramids are 1-fold coordinated (defect) of higher electronegativity; 2) presence of neighboring highly electronegative oxygen atoms. Fitting of S 2p spectrum shows presence of $^{\text{=As-S-As=L}}$-fragments (75% of all S atoms, component at 161.2 eV), $^{\text{=As-}}$S2$^{\text{=As=L}}$-fragments (12%, 161.9 eV) and large amount of 1-fold coordinated S (13%, 160.4 eV). The latter component has large FWHM (1.37 eV) probably because of the mentioned neighborhood of highly electronegative oxygen atoms.

Analysis of the VB spectrum for all studied samples (Fig. 4) confirms the above conclusions. Decreasing of concentration of sulfur lp-electrons after light irradiation (~2 eV band) can be associated with disappearance of 1-fold coordinated S defects, which provide electrons on the top of the VB. Oxidation of the samples is clearly seen due to increasing of O 2s band at $\sim 25$ eV as well as the bonding O 2p states at 15–23 eV region [18]. Electron-induced destruction of the surface for the sample irradiated with dose II is also evident from Fig. 4c. However, there are a few features in the VB spectra that cannot be explained on the basis of this data. First of all, the same concentration of sulfur lone-pair electrons for the freshly prepared and dose I samples contradicts the structure of the CL spectra. More precisely, it contradicts the disappearance of 1-fold coordinated S defects after low dose electron irradiation. Another unclear observation is the origin of the peak at $\sim 30$ eV, which is evident for the sample irradiated with dose I and light-irradiated samples but disappears at higher electron doses. Other authors explained this peak by the interaction of S 3s and O 2s electrons [28], but we cannot confirm sulfur oxidation by CL spectra. But the most intriguing observation is the peak at $\sim 10$ eV, which is usually associated with As 4s non-bonding electrons [24]. This band evidently increases (!) after light- and dose I electron beam irradiation. To exclude oxygen-related origin of this band we present data for the sample irradiated with dose III (Table 1, Fig. 4d), which contains $\sim 19$ at.% of oxygen, but intensity $I$ of 10 eV band is the same as in the case of freshly prepared sample. The most probable explanation of the increased intensity of 10 eV band after light- and dose I e-beam exposure could be participation of As 4s electrons in some of the bonding configurations of freshly prepared films, As–As bonds, for example. Unfortunately, we cannot propose the reliable explanation of this anomaly at this time.

5. Conclusions

Comparison of the mechanisms of photo- and electron-induced structural transformations in S-rich As$_{35}$S$_{65}$ ChG thin film reveals that light irradiation from halogen lamp does not change the chemical composition of the surface. However, it causes bond-switching and ordering of the structure, which results in the gradual disappearance of “wrong” homopolar As–As bonds. Similar process proceeds even within the volume of the exposed region but relatively slowly. The diminishing concentration of As–As bonds on the surface is not significantly influenced by oxygen environment during illumination. Low dose electron beam irradiation activates the surface, which contributes to the oxidation of As atoms in “wrong” As–As bonds, thereby decreasing the S concentration in the very top parts of thin ChG film. Electron irradiation with high doses destroys the structure drastically. On subsequent exposure to air, the under-coordinated As atoms react with oxygen and decrease S/As ratio dramatically. Analysis of the VB spectra shows anomalous increase of the $\sim 10$ eV band associated with non-bonding As 4s electrons after light- and low dose e-beam irradiation. It also confirms the destruction of the surface during high-dose electron irradiation.

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References