Influence of annealing on the optical properties, structure, photosensitivity and chemical stability of $As_{30}S_{70}$ spin-coated thin films

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Abstract

Chalcogenide glass (ChG) thin films prepared by solution based deposition technique offer important advantages over vacuum deposited films, which are useful for many applications especially in infrared optics. Their fabrication, which comprises dissolving the ChG in volatile organic solvent and then depositing thin film by spin coating the solution, is simpler and significantly cheaper. However, contaminants from the solvent are incorporated. The residual organic content in the films is significantly reduced by appropriate thermal treatment. This work reports the influence of specific annealing conditions and UV light exposure on the structure, opto-physical and chemical properties of $As_{30}S_{70}$ spin-coated ChG films. The results show increase in refractive index with increasing annealing temperature, whereas the thickness and optical bandgap decrease. The UV exposed regions of the samples exhibit positive etching in amine based solvents. The HS-LEIS spectroscopy is used to determine the elemental concentration profile of annealed thin film, which shows almost stable As/S ratio with composition close to that of the source bulk glass. Thus UV light induced structural changes and the mechanism of selective etching are proposed.

Keywords: Chalcogenide glasses, Spin-coating, Thermal treatment, Photo-induced changes, Wet-etching, HS-LEIS

Introduction

Chalcogenide glasses (ChG) are promising materials for the fabrication of high index infrared (IR) optical elements such as planar waveguides, lenses, diffractive optical elements, etc. [1–6]. The thin amorphous films of ChG for such applications are usually deposited by conventional vacuum deposition techniques such as thermal deposition, sputtering or laser deposition [1, 2, 7]. These methods require expensive equipment due to the requirement of high vacuum. The vacuum deposited ChG thin films are often photosensitive due to the presence of localized defects in high concentration such as the homopolar bonds, dangling bonds, etc. in their structure [8–10]. Consequently, simpler and cheaper chemical deposition methods are gaining attention, where bulk ChG is dissolved in an appropriate solvent. The solid films are formed when the solution is deposited on a substrate by spin-coating or dip-coating [11–15]. The spiral bar-coating method has proved to be especially suitable for the mass production of ChG thin films [16]. The solution deposited thin films are more photo-stable with the structure similar to that of the source bulk glasses [14, 17]. However, the as-prepared films are also known for the contamination with solvent molecules as a residue or chemically bonded within the glass matrix, which influences their thickness, chemical stability and optical parameters [12].

The post-deposition annealing is expected to reduce the organic residual content. Therefore, in this work, the thin spin-coated films of binary $As_{30}S_{70}$ glass composition were annealed at various temperatures up to 120 °C. The results are reported about the influence of thermal treatment and the UV irradiation on the thickness, optical parameters, structure, organic molecules content and chemical stability of solution deposited thin films. The optical parameters of spin-coated films were compared

with the optical parameters of thin films deposited by thermal vacuum evaporation. Based on experimental findings the mechanism of photo-induced changes of spin-coated $As_{30}S_{70}$ films was proposed. The elemental concentration profile within the thickness of well-annealed thin film was determined by HS-LEIS spectroscope.

Experiment

The source bulk $As_{30}S_{70}$ chalcogenide glass (ChG) was prepared by standard melt-quenching method. High purity (5N) elements were loaded into a cleaned quartz ampule in calculated amounts. The ampule was evacuated ($\sim 10^{-3}$ Pa) and sealed. The reagents were melted in a rocking tube furnace at 800 °C for 48 hours. Subsequently the ampule with melted glass was quenched in cold water. Bulk glass was powdered in agate bowl and dissolved in n-butylamine (BA) solvent with concentration of 0,1 g of glass powder per 1 ml of BA. The glass solution was pipetted and deposited onto rotating soda-lime glass substrates and spin-coated (spin-coater Best Tools SC110-B) in ambient atmosphere at 4000 rpm for 30 s to yield thin films of optical quality. Immediately after the deposition the films were stabilized by annealing (soft baking) at 60 °C on a hot plate (hereafter referred as as-prepared thin film). The thickness of as-prepared spin-coated samples was ~260 nm. Baked samples were stored in dry, dark environment.

For comparison of optical parameters, the thin films were also deposited by thermal vacuum evaporation technique (device UP-858, Tesla corp.). The films were prepared in conventional manner from source ChG bulk glass by evaporation from a molybdenum boat with the evaporation rate of 1-2 $nm.s^{-1}$ at a pressure of $\sim 10^{-3}$ Pa ($\sim 10^{-5}$ Torr), and deposited onto soda-lime glass substrates. The resulting film's final thickness was ~1000 nm. The thickness of vacuum deposited thin films and evaporation rate were measured using quartz crystal microbalance.

Samples of as-prepared thin ChG films were annealed at 60, 70, 80, 90, 100, 110 and 120 °C for 60 minutes on an annealing table (Conbrio, Czech Republic) in argon atmosphere or in vacuum oven (Vacucell 22, BMT Medical Technology) with residual pressure 0,3 bar (samples hereafter referred as annealed at low residual pressure – LRP)

The as-prepared and annealed thin films were analyzed by energy dispersion x-ray microanalysis method using scanning electron microscope (LYRA 3, Tescan) equipped with EDS analyzer Aztec X-Max 20 (Oxford Instruments) at 5 kV acceleration voltage.

To examine the effect of irradiation on spin-coated as-prepared and annealed thin films the samples were exposed to UV lamp light (365 nm, 156 $mW.cm^{-2}$) in argon atmosphere for 60 minutes.

The transmission spectra of as-prepared, annealed and irradiated thin films were measured using optical spectrometer (Shimadzu UV3600) in the spectral region 190-2500 nm. The measurements were always performed on three samples prepared with the same treatment and on the same position of each film to avoid the influence of thickness variation. The thicknesses and refractive index values of spin-coated and thermally vacuum deposited as-prepared and annealed thin films were determined using the fitting procedure described in [16, 18] based on Wemple-DiDomenico's equation [19] and the model presented by Swanepoel [20]. The parameters of thin films deposited by both techniques and were obtained from transparent region of measured transmission spectra by fitting modeled transmission spectrum (Swanepoel´s model) using refractive index dispersion expressed by Wemple-DiDomenico's equation. The optical bandgap values were calculated using Tauc's method for semiconductors [21]. The error bars for the presented averaged values indicate standard deviation.

The etching kinetics of as-prepared, annealed and exposed thin films were studied by the procedure presented in [22]. Thin film samples were etched in solution of BA in aprotic solvent at 25°C. The etching curves were evaluated from the first interference maxima and the first minima of measured transmission spectra.

The structure of source bulk glass and spin-coated thin films was determined using FT-IR spectrometer IFS55 with Raman module FRA106 (Bruker) utilizing excitation by Nd:YAG laser (1064 nm). The Raman spectra were measured with laser beam intensity of 50 mW (2 cm^{-1} resolution,

200 scans). They were normalized by the intensity of the most intense band in the spectrum, i.e. $AsS_{3/2}$ pyramidal unit band at 334 cm^{-1}.

The As-S depth concentration profile of $As_{30}S_{70}$ thin film annealed at 120 °C in argon atmosphere was recorded using high sensitivity-low energy ion scattering (HS-LEIS) spectrometer (Qtac 100) with $^4He^+$ probe beam (3000 eV, measured area 750x750 μm), and $^{36}Ar^+$ sputtering beam (2000 eV, sputtered area 1500x1500 μm).

Results and Discussion

The transmission spectra of as-prepared and annealed spin-coated $As_{30}S_{70}$ chalcogenide thin films were evaluated according to the procedure described in [18]. It provides the thickness, spectral dependence of refractive index and optical bandgap of the thin films. The thickness values were normalized to the thicknesses of the as-prepared (i.e. pre-annealed) thin film in order to eliminate the minor variation of spin-coating conditions (Fig. 1). As described previously in [11–14], the as-prepared spin-coated As-S ChG thin films contain molecules of residual solvent and alkyl ammonium arsenic sulfide (AAAS) salts, which were already formed in glass solution during dissolution of source chalcogenide bulk glass. These compounds decompose subsequently during annealing, and leave the volume of annealed film, which then decreases its thickness [12].

Figure 1 demonstrates that the thermal treatment has significant influence on the thickness of spin-coated ChG thin film. The first sudden decrease of film's thickness occurs during annealing between 60-70 °C, when the annealing temperature is very close to the boiling point of pure BA solvent (78 °C [23]). Thus the observed thickness loss can be attributed to the release of unreacted (chemically not bonded) occluded organic solvent molecules from the volume of the annealed material. In the temperature region between 70-100 °C the thickness decrease is less pronounced, which is most probably caused by the decomposition of AAAS salts [12] connected with the further polymerization of structure. The thin films annealed in argon atmosphere above 100 °C are considered stabilized because no further thickness decrease was observed. On the contrary, the thin films annealed at low residual pressure (LRP) exhibited another large thickness loss at temperatures above 100 °C. Chern and Lauks [12] observed low molecular weight As-S fragments in vapor phase, which left annealed spin-coated As-S thin films at temperatures above 100 °C. They assumed that during annealing in vacuum at temperatures close to the glass transition temperature (T_g) for $As_{30}S_{70}$ T_g = 132 °C [2]) the low molecular glass fragments evaporate from the top layers of spin-coated film. The observed thickness decrease can be also explained by the release of additional residual molecules supported by LRP at temperature close to the T_g of annealed material. Probably both suggested mechanisms contribute to the observed thinning of $As_{30}S_{70}$ thin films when annealed at LRP above 100 °C.

The composition and contents of organic molecules in spin-coated thin films were determined by EDS. The results indicate the As-S content of all studied samples as $As_{29}S_{71}$, which is close to the composition of synthetized $As_{30}S_{70}$ bulk glass within the EDS measurement error. The organic content N_{rel} was determined using the ratio of nitrogen contents of the annealed film and the as-prepared (or pre-annealed) thin film (Fig. 2). The BA molecule contains only one nitrogen atom and there is no other source of nitrogen in the studied thin film samples. Thus nitrogen content should yield the concentration of the residual organic molecules within the glass matrix. The EDS results confirm decreasing content of organic molecules with increasing annealing temperature, which is in good agreement with previously stated explanation of annealing induced thickness decrease. Moreover, the N_{rel} dependence on the annealing temperature (Fig. 2) exhibits very similar trends as the thickness curves presented in Fig. 1. However, a significant difference is found in more pronounced thickness decrease of thin films annealed at LRP at temperatures above 100 °C (compared with the N_{rel} decrease), which supports the LRP induced loss of organic residual molecules and low evaporation of molecular fragments.
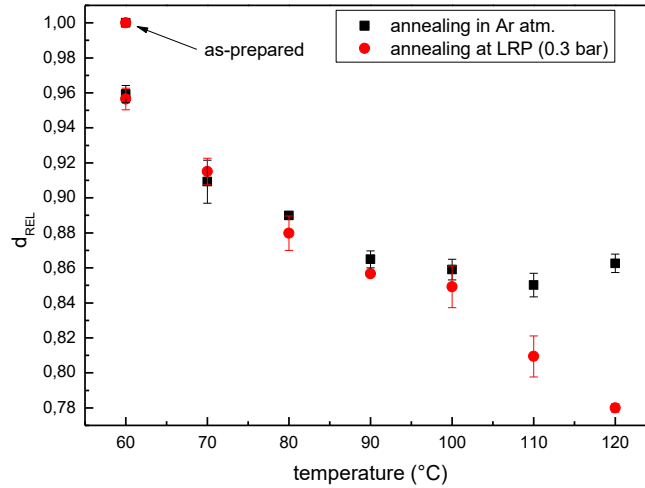
Fig. 1. The dependence of normalized thicknesses (normalized to the thicknesses of as-prepared thin films before annealing ~260 nm) of As$_{30}$S$_{70}$ thin films on annealing temperatures (60 minutes annealing, argon atmosphere and low residual pressure – LRP).
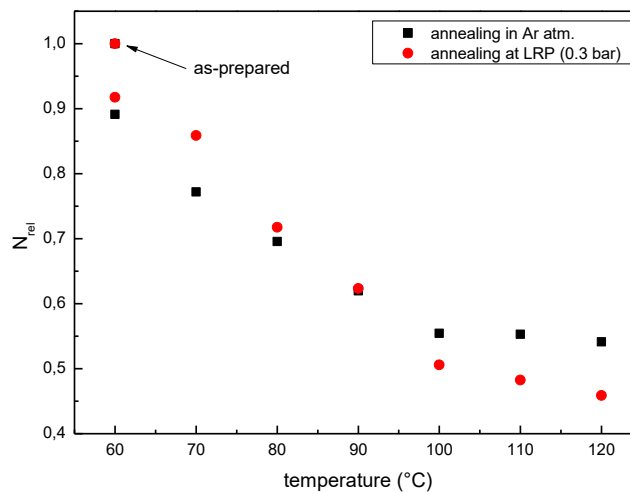

Fig. 2. The dependence of relative nitrogen content N$_{rel}$ (atomic ratio of nitrogen atomic content in measured annealed and as-prepared thin film) of As$_{30}$S$_{70}$ thin films on annealing temperatures (argon atmosphere and low residual pressure – LRP).

The optical parameters of studied samples were calculated from measured transmission spectra. The dependence of refractive index n_D (λ = 589 nm) on annealing temperature is presented in Figure 3. It increases with increasing annealing temperature for both annealing conditions (argon atmosphere and LRP). The corresponding values for the two annealing methods are almost identical within the whole temperature range, and saturate at ~110 °C with n_D = 2,31. Thus annealing atmosphere has no significant influence on a film's refractive index. Its value for thermally vacuum deposited thin film with the same thermal treatment (annealing at 60 °C for 20 minutes followed by annealing at 110 °C for 60 minutes in argon atmosphere) yielded n_D = 2,42. That is, the refractive index of thermally stabilized spin-coated As$_{30}$S$_{70}$ thin films is significantly lower than that of thermally vacuum deposited thin films of the same composition. This difference can be explained by the presence of low refractive index BA organic molecules in the film matrix. As the annealing temperature increases, the

BA content decreases (Fig. 2), resulting in higher compactness of studied thin films and the observed increase of refractive index.
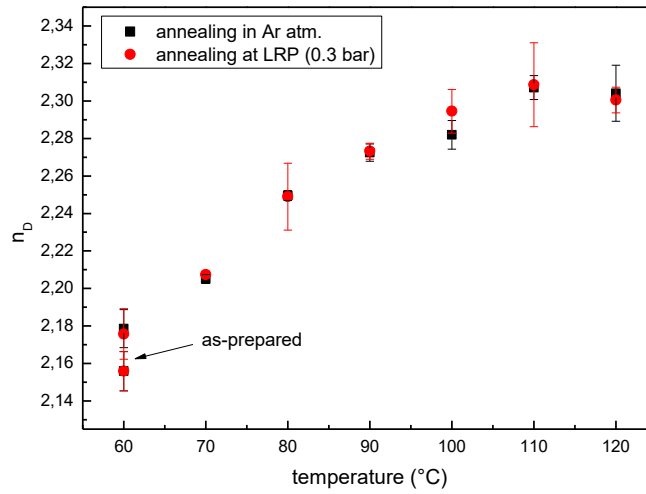

Fig. 3. The dependence of refractive index n_D (λ = 589 nm) on the annealing temperature of $As_{30}S_{70}$ thin films (60 minutes annealing, argon atmosphere and low residual pressure – LRP).

The dependence of optical bandgap (E_g^{opt}) on annealing temperature is presented in Figure 4. Similar to the refractive index, the E_g^{opt} is almost identical for both annealing methods. The E_g^{opt} results exhibit two significant step-like drops at 60 °C and at 100-110 °C. The first decrease at 60 °C is attributed to the intensive loss of free (chemically non-bonded) residual solvent molecules. The second decrease at 100-110 °C is attributed to the complete decomposition of AAAS salts and expected distinctly higher release of organic residuals due to the relaxation of glass structure during annealing close to the T_g of material (for $As_{30}S_{70}$ T_g = 132 °C [2]). Optical bandgap values now stabilize at 2,24 eV (for thermally vacuum evaporated thin films with the same thermal treatment it is 2,55 eV). The temperature corresponding to the second decrease of both annealing methods differs by 10 °C but this effect can be explained by the influence of LRP during annealing, which helps remove decomposed AAAS salt residues and thus the E_g^{opt} stabilization is completed at 10 °C lower than during annealing in argon atmosphere.
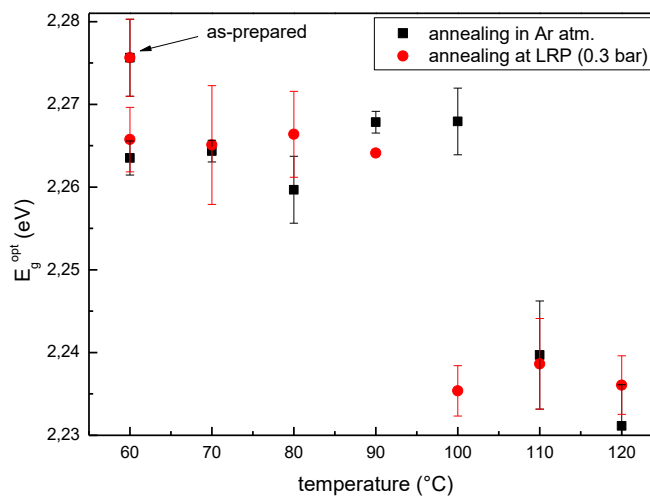

Fig. 4. The dependence of optical bandgap (E_g^{opt}) on annealing temperatures of $As_{30}S_{70}$ thin films (60 minutes annealing, argon atmosphere and low residual pressure – LRP).

The structure of source bulk glass, and as-prepared and annealed (in argon atmosphere and at LRP) thin spin-coated thin films of $As_{30}S_{70}$ was determined by Raman spectroscopy (Figure 5-A, B). The strong band at 344 cm^{-1} confirms that the basic structural unit of studied ChG composition is trigonal pyramid $AsS_{3/2}$ [24–26]. In addition, the structure comprises of S_8 rings represents by the bands at 151, 218 and 475 cm^{-1} [25, 27, 28] and S-S chains by the band at 495 cm^{-1} [25, 28, 29]). In the spectra of spin-coated thin films there is also a strong band at 369 cm^{-1} which can be assigned to the vibrations of arsenic rich realgar-like As_4S_4 structural units [18, 26, 30], and a new weak band at 415 cm^{-1} which belongs to the vibrations of AAAS salts [14, 17]. The bands at 2800-3000 cm^{-1} prove that the deposited thin films contain also residual BA solvent molecules [14].

The Raman spectra of thin films annealed in argon atmosphere (Figure 5-A) show that thermal treatment has also strong influence on the structure of films. In particular, thermal treatment induces polymerization. The intensities of S_8 (151, 218 and 475 cm^{-1}) and As_4S_4 (369 cm^{-1}) bands decrease and the intensity of $AsS_{3/2}$ (344 cm^{-1}) band proportionally increases with increasing annealing temperature. Observed structural polymerization is accompanied by the decomposition of AAAS salts (415 cm^{-1} band decreases) and release of organic residuals (2800-3000 cm^{-1} bands decrease). Generally, the structure of annealed thin films shifts towards the structure of source bulk glass. The same observed structural changes occur in thin films annealed at LRP (Figure 5-B). Unfortunately, high intensity fluorescence band (appearing in the spectra of thin films annealed above 110 °C) interferes with the Raman bands and makes the spectra difficult to evaluate.
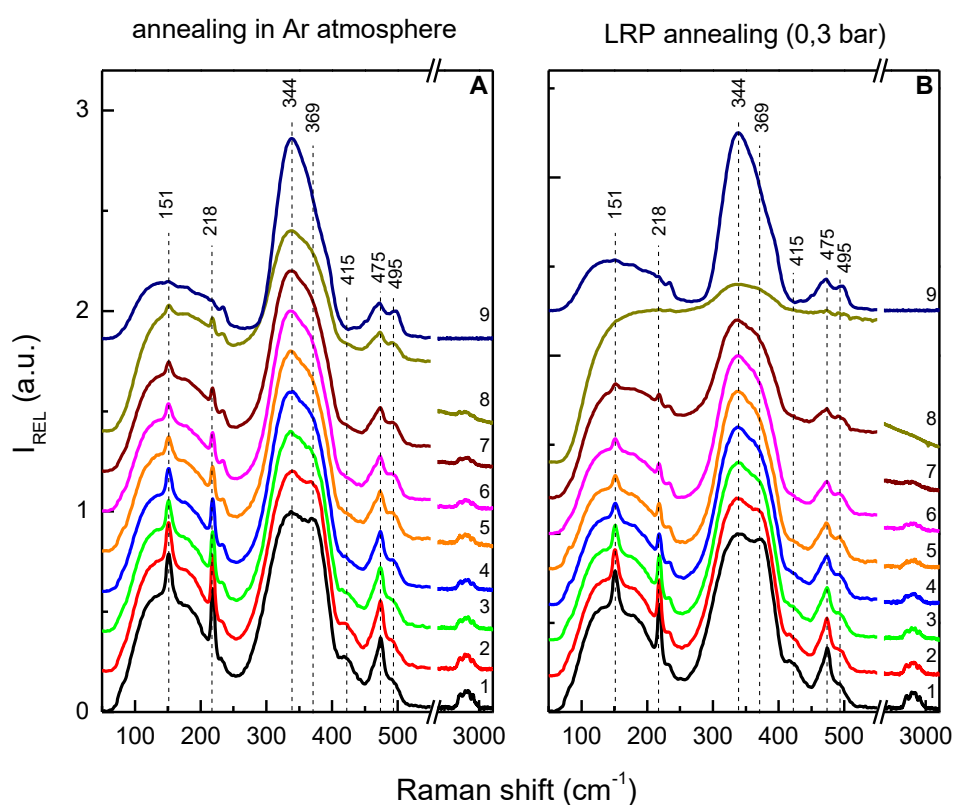

Fig. 5. Raman spectra of $As_{30}S_{70}$ thin films annealed in argon atmosphere (A) and at low residual pressure – LRP (B). 1: as-prepared; 2: annealed at 60 °C; 3: annealed at 70 °C; 4: annealed at 80 °C; 5: annealed at 90 °C; 6: annealed at 100 °C; 7: annealed at 110 °C; 8: annealed at 120 °C; 9: source bulk glass.

The photo-sensitivity of $As_{40}S_{60}$ spin-coated thin films was previously investigated by Chern et al. [31], who reported their tendency to photo-induced oxidation. In order to avoid photo-oxidation during the exposure the as-prepared and spin-coated $As_{30}S_{70}$ thin films annealed in argon atmosphere were irradiated with UV lamp (365 nm ~ 3,4 eV) in inert argon atmosphere. The exposure wavelength

was chosen with respect to the optical bandgap of $As_{30}S_{70}$ unexposed samples (2,23-2,28 eV). The refractive index of $As_{30}S_{70}$ thin films slightly increased upon UV exposure (Figure 6). However, the optical bandgap and thickness did not change after the exposure; also no photo-bleaching or photo-darkening was observed. The annealing process had no significant influence on the level of UV light-induced optical changes.
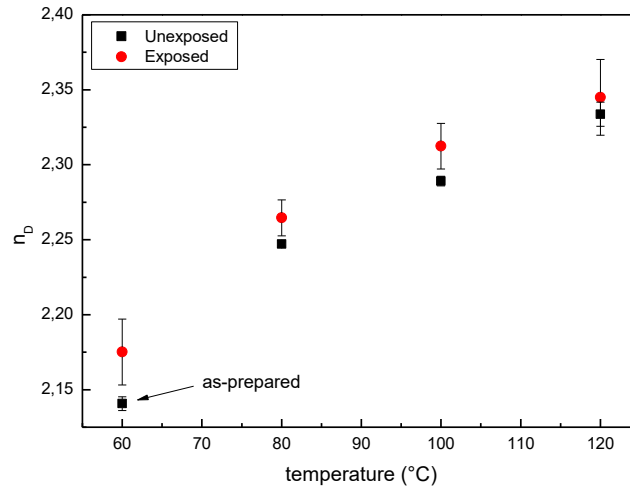

Fig. 6. Dependence of refractive indices of unexposed and exposed spin-coated $As_{30}S_{70}$ thin films on the annealing temperature.

The unexposed and UV light exposed spin-coated thin films were etched in aprotic solvent containing 0,01 vol.% of BA. The etching curves are presented in Fig. 7; the insets show the dependence of transmittance at the wavelength of the first interference maximum in the transmission spectrum on the etching time.

The average etching rates (Figure 8-A) were calculated using the time needed for the complete film dissolution and the thicknesses of etched thin film as obtained from the transmission spectra. The etching rates show that the annealing process considerably increases chemical stability of spin-coated thin films. The etching rates significantly decrease with increasing annealing temperature. For example, the etching rate of the sample annealed at 120 °C is 18 times lower than the etching rate of the as-prepared thin film. The etching curves also indicate that the unexposed samples dissolve slowly at the start of the etching process. This behavior can be explained by the organic residue depleted thin film surface, probably from annealing process.

The exposure of as-prepared thin film to 365 nm UV light slightly increases a film's chemical stability. The UV exposure of annealed samples increases the etching rates, resulting in positive etching (exposed areas dissolve faster in comparison to the non-exposed areas). The highest etching selectivity (ratio between the etching rates of exposed and unexposed thin films) is achieved for samples annealed at 120 °C when the etching rate of exposed thin films is 1,8 times higher than the etching rate of unexposed sample (Figure 8-B). The observed changes in thin film etching rates are in good agreement with the findings of similar experiment performed on $As_{30}S_{45}Se_{25}$ thin films [18].
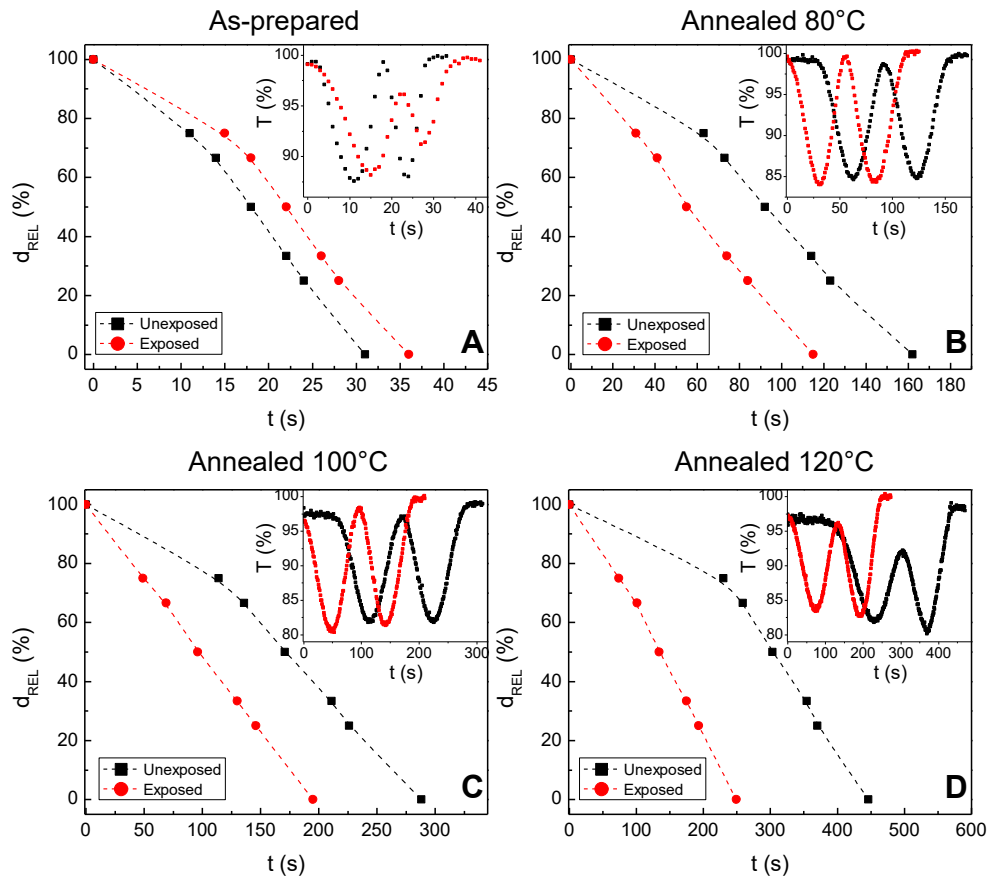
Fig. 7. Etching curves of spin-coated As$_{30}$S$_{70}$ thin films. Insets show the dependence of transmittance related to the wavelength of the first interference maximum in the transmission spectrum on the etching time. A – as-prepared thin film, B – annealed at 80°C, C – annealed at 100°C, D – annealed at 120°C.
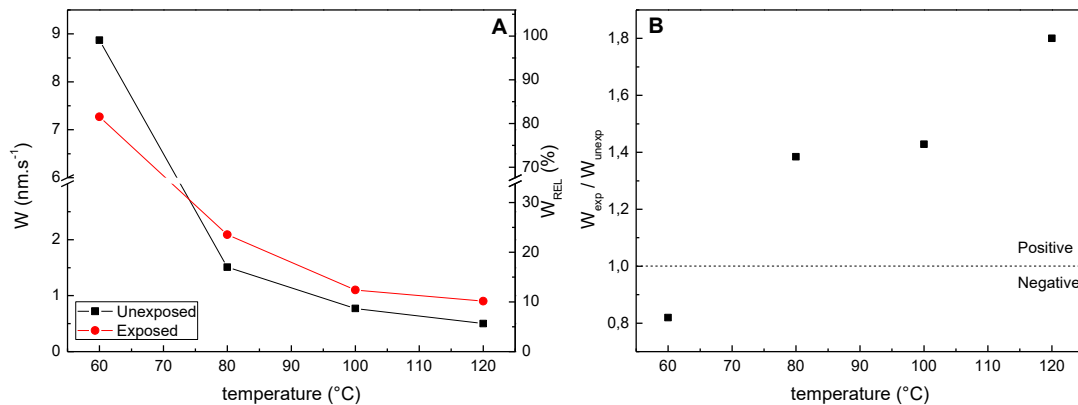

Fig. 8. Dependence of etching rates W and relative etching rates (relative to the etching rate of as-prepared thin film) of As$_{30}$S$_{70}$ spin-coated thin films on the annealing temperature for unexposed and exposed samples (A), and the dependence of etching selectivity (W$_{exp}$/W$_{unexp}$) on the annealing temperature (B). Solid lines are merely to guide the eye.

The effect of UV exposure on the structure of thin film was also studied by Raman spectroscopy (Figure 9). The sharp Raman bands at 184, 268, 370 and 472 cm^{-1} characteristic for vibrations of arsenic

oxide [32] are not observed. So it is reasonable to assume that no significant photo-oxidation occurred during UV light treatment. The exposure of as-prepared thin film induces structural polymerization similar to that due to annealing. The intensities of bands representing S_8 rings (151, 218, 475 cm^{-1}) and As_4S_4 realgar-like structural units (369 cm^{-1}) decrease, whereas the intensity of the band for $AsS_{3/2}$ pyramidal units (344 cm^{-1}) proportionally increases. Together these results indicate higher chemical stability of the exposed vs. pre-exposed, as-prepared sample. The Raman spectra of unexposed and exposed annealed thin films show no difference in band intensities, except a gradual increase of fluorescence background. According to [33, 34] the fluorescence background in Raman spectroscopy occurs mostly due to the presence of impurities or defect sites. We suggest that UV light exposure of $As_{30}S_{70}$ spin-coated thin films creates such defect sites with energy levels inside the energy bandgap allowing partial absorption of excitation laser beam. The presence of defect sites can subsequently decrease chemical stability of thin films resulting in the observed exposure induced increase of etching rates.
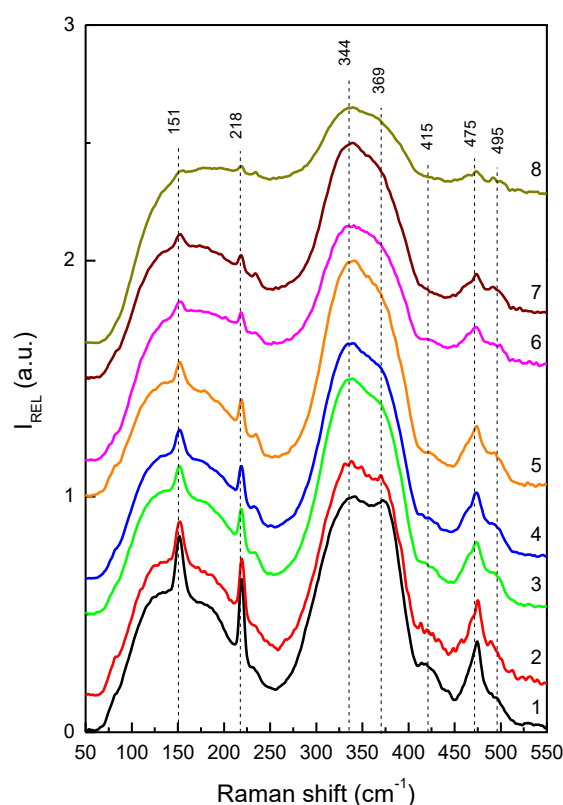

Fig. 9. Raman spectra of unexposed and exposed $As_{30}S_{70}$ spin-coated thin films. 1: as-prepared; 2: as-prepared exposed; 3: annealed at 80 °C; 4: annealed at 80 °C exposed; 5: annealed at 100 °C; 6: annealed at 100 °C exposed; 7: annealed at 120 °C; 8: annealed at 120 °C exposed.

In order to determine the depth profile of As/S concentration ratio within $As_{30}S_{70}$ spin-coated thin film annealed at 120 °C (argon atmosphere) the HS-LEIS spectroscopy was used (Figure 10). The results are presented as the variation of S:As atomic ratio as a function of sputtered depth of the measured film. Clearly, the surface of annealed thin film is arsenic deficient with the composition being $As_{25,1}S_{74,9}$. Then the arsenic content quickly increases and stabilizes at the $As_{29,1}S_{70,9}$ composition, which is in a good agreement with the EDS measurements. The arsenic deficiency of the upmost surface layer is expected in part from the presence of the thin layer of native arsenic oxide [35] which, due to arsenic oxide volatility [36], easily evaporates during HS-LEIS measurement under ultrahigh vacuum. The results suggest that approximately 95% of film's volume has stable As-S concentration close to the original bulk glass value.
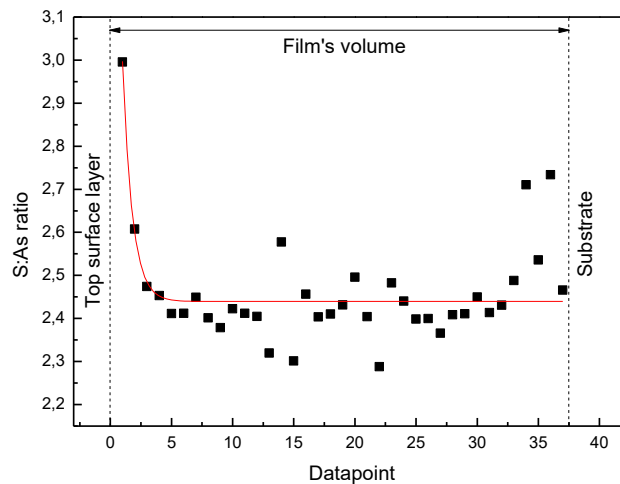
Fig. 10. The S:As atomic ratio depth profile of As$_{30}$S$_{70}$ spin-coated thin film (annealed in argon atmosphere at 120 °C) measured by HS-LEIS spectroscopy. The red curve is drawn to guide the eye.

Conclusion

The experimental results have shown that the thermal treatment has a major impact on the structure and opto-physical properties of As$_{30}$S$_{70}$ spin-coated thin films. With increasing annealing temperature, refractive index increases, whereas thickness and optical bandgap decrease. These changes are accompanied by significant structural polymerization connected with the release of organic residuals from the matrix of spin-coated chalcogenide glass.

The etching profiles and Raman spectra show that as-prepared and annealed As$_{30}$S$_{70}$ spin-coated thin films are photosensitive. The annealing treatment gradually stabilizes deposited films resulting in an increase of their chemical stability. UV light exposure induces structural changes which significantly increase etching rates of exposed samples, opening the possibility for positive wet-etching photoresist applications.

The elemental concentration profile as determined by HS-LEIS spectroscopy demonstrate that As/S ratio is stable almost within the whole volume of spin-coated thin film with the composition close to the source As$_{30}$S$_{70}$ bulk glass.

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