

J. Bůžek¹, K. Pálka^{1,2}, I. Voynarovych¹, M. Vlček², *Photo- and thermally induced changes in As-S-Se chalcogenide thin films*

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Abstract

In this paper compositional dependence of glass transition temperature T_g and optical properties such as optical transmission T , refractive index n , short wavelength absorption edge position and consequently optical band gap E_g^{opt} of thin films in $As_{35}S_{65-x}Se_x$ system is studied. Changes of studied optical properties induced by either exposition to polychromatic light or annealing are also studied together with *in-situ* kinetics measurement. It was found that exposure by polychromatic light induces more significant changes in optical properties as a result of more significant internal structural changes which were confirmed by Raman spectroscopy.

Introduction

Chalcogenide glasses are inorganic amorphous semiconductors containing in their structure at least one of the chalcogens except for oxygen. To form the glassy matrix, chalcogens are usually mixed with more electropositive elements of groups 15, 14 and 13 of the periodic table. The elements most commonly occurring in chalcogenide glasses are As and Ge.

Chalcogenide glasses possess unique properties in comparison with oxide glasses and also the techniques used for their preparation are fully different. The typical properties by which chalcogenide glasses differ from oxide glasses are namely their high optical transparency in the IR region of the electromagnetic spectrum and significantly higher refractive index values. They also possess much lower rigidity which results in their disposition to structural changes by exposition to suitable radiation or by annealing. These structural changes cause changes of their physical and chemical properties.

In this paper we study compositional dependence of photo- and thermally induced structural changes and consequent changes in optical properties of chalcogenide glass thin films in non-stoichiometric system $As_{35}S_{65-x}Se_x$. We also study the kinetics of these phenomena.

Experimental

Bulk samples of chalcogenide glasses (ChG) from the system $As_{35}S_{65-x}Se_x$ ($x=0$; 16.25; 32.5; 48.75 and 65) were synthesized by commonly used melt-quenching technique from high purity elements [1]. Values of glass transition temperature (T_g) were measured using DTA (Netzsch DTA 404 PC). Weight of the bulk sample was ~50 mg, heating rate 10 K.min⁻¹ and empty corundum crucible was used as reference sample.

Thin films (TFs) were deposited on substrates (silicate microscope slides) using vacuum thermal evaporation under pressure $\sim 10^{-4}$ Pa (Tesla UP 858). Deposition rate and thickness were monitored in situ during the deposition process using quartz crystal microbalance. Deposition rate was ~ 1 nm.s⁻¹ and thickness of deposited films was ~ 1000 nm.

Optical parameters (extinction coefficient α , refractive index n) and thickness (d) of the films were calculated using Swanepoel's method [2]. For the purpose of Swanepoel's calculations, transmission spectra were measured in spectral range 300 – 3000 nm (Shimadzu UV-3600). From the same spectra the optical band gaps (E_g^{opt}) were calculated by Tauc's method [3]. Further optical parameters such as the dispersion energy (E_d) and single oscillator energy (E_0) were calculated by Wemple-DiDomenico model [4].

Exposure to polychromatic light of halogen lamp was carried out with power on the sample ~ 1200 W.m⁻² in Ar atmosphere in order to prevent eventual photo-oxidation of exposed TFs. IR short pass filter (absorption edge ~ 750 nm) was used to prevent samples from heating. *In-situ* kinetics of light induced optical transmission (T) changes were measured using diode array spectrometer (StellarNet EPP2000). Samples were exposed until saturation i.e. position of short-wavelength absorption edge (SAE) of given TF no longer changed with prolonged exposure.

As-prepared thin films were annealed in Ar atmosphere at temperatures 20 °C below T_g of given glass composition. Kinetics of thermo-induced optical transmission T changes

were measured *in-situ* using diode array spectrometer (StellarNet EPP2000). Samples were annealed until saturation (position of SAE no longer changed with prolonged annealing).

The structural changes induced by exposure and annealing were studied using Raman spectroscopy. Measurements were carried out on Fourier infrared spectrometer FT-IR BRUKER IFS 55 with Raman module FRA 106. Nd:YAG laser with wavelength 1064 nm was used as excitation source.

Results and Discussion

Synthesized bulk samples in $As_{35}S_{65-x}Se_x$ compositional line were amorphous and their measured T_g values are plotted in Fig 1. Values of T_g decrease with increasing Se content. Similar trends are observed in data published by [5, 6 and 7] for stoichiometric composition containing 5 % more As. The decrease of T_g values with increasing Se content can be explained by As-chalcogen bond strength. As-Se bond is weaker than As-S bond [8] and thus the structural matrix of the glass is less rigid as the As-S bonds are replaced by As-Se bonds.

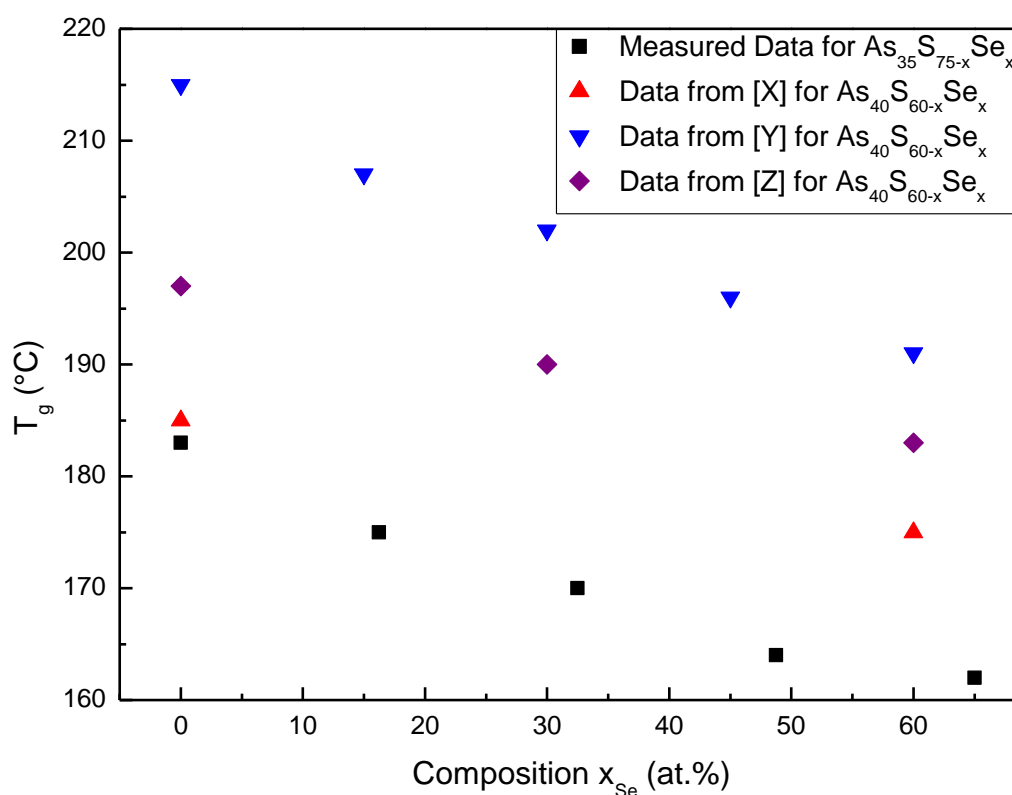


Fig 1: Measured glass transition temperatures (T_g) and data from [5, 6 and 7].

As-prepared thin films

Optical transmission spectra of thin films prepared from synthesized bulk samples were used to determine their optical parameters. At first optical band gap (E_g^{opt}) were determined from extrapolation of $\sqrt{\alpha h\nu} = f(h\nu)$ to the zero value of $h\nu$ (Fig 2). The values of E_g^{opt} plotted in Fig 3(A) monotonously decrease with increasing Se content due to more metallic character of the Se atoms compared to S which leads to narrower band gap. These data are in good correlation with data found in [5, 8 and 9] for stoichiometric compositional line $As_{40}S_{60-x}Se_x$. Our calculated values are $\sim 0,5$ eV higher due to lower As content.

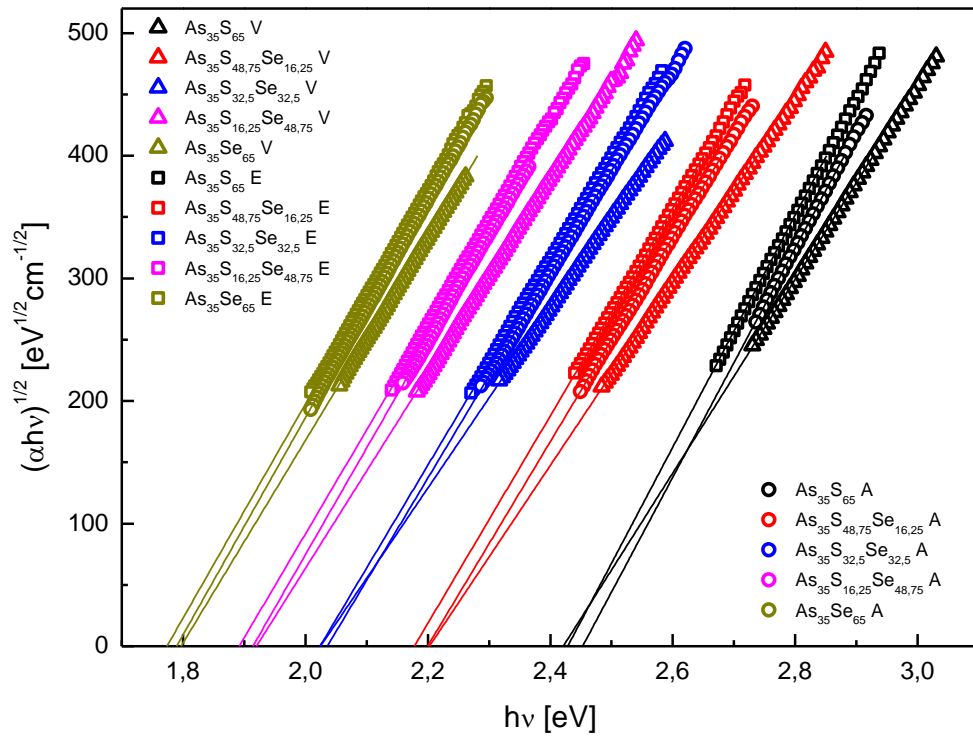


Fig 2: Graphical representation of E_g^{opt} calculation using Tauc's method. V=as-prepared, E=exposed, A=annealed.

Discrete values of refractive index calculated using Swanepoel's method were fitted by function (1) by Wemple and DiDomenico [4] using Origin 8.0 software:

$$n^2(\nu) - 1 = \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad (1),$$

where n is refractive index, E_d is the dispersion energy, E_0 is single oscillator energy and $h\nu$ is photon energy. Calculated values of refractive indices are plotted in Fig 3B together with lines fitted using equation (1). Obtained parameters of equation (1) for studied compositions are

given in Tab 2. The values of refractive index increase with increasing selenium content which is in good agreement with [8, 10].

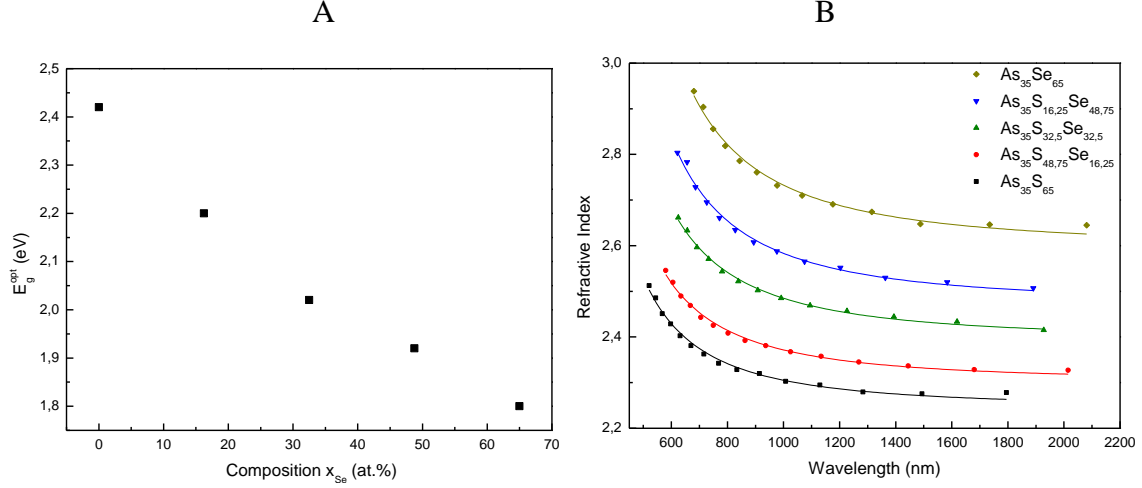


Fig 3: Compositional dependence of E_g^{opt} (A) and spectral dependence of refractive index (B) for as-prepared thin films in $As_{35}S_{65-x}Se_x$ system.

	$As_{35}S_{65}$			$As_{35}S_{48.75}Se_{16.25}$			$As_{35}S_{32.5}Se_{32.5}$			$As_{35}S_{16.25}Se_{48.75}$			$As_{35}Se_{65}$		
	V	E	A	V	E	A	V	E	A	V	E	A	V	E	A
E_g^{opt} [eV]	2.42	2.43	2.45	2.20	2.18	2.20	2.02	2.02	2.04	1.92	1.89	1.91	1.80	1.77	1.79
E_0 [eV]	4.94	4.59	4.64	4.68	4.31	4.37	4.24	4.04	4.09	3.94	3.76	3.75	3.70	3.59	3.58
E_d [eV]	19.96	20.27	20.63	20.12	20.83	21.05	20.09	20.91	21.42	20.17	20.44	21.11	21.26	21.31	21.79
E_0/E_g^{opt}	2.04	1.89	1.89	2.13	1.98	1.99	2.10	2.00	2.00	2.05	1.99	1.96	2.06	2.03	2.00

Tab 1: Values of E_g^{opt} , E_0 , E_d and E_0/E_g^{opt} for studied compositions. V=as-prepared, E=exposed, A=annealed.

Values of E_0 for as-prepared thin films presented in Tab 1 indicate that with increasing content of Se, the value of E_0 decreases. In case of E_d the trend is opposite and values of E_d increase with increasing Se content. Calculated values of E_0 and E_d for composition $As_{35}S_{65}$ are close to those observed by Petkov and Ewen [11]. The decrease of E_0 and increase of E_d with increasing selenium content is in agreement with findings presented by Wemple and DiDomenico [4]. We also observed the correspondence between E_0 and E_g expressed as $E_0 \approx 1.9E_g^{opt}$ (see Tab 2) published by Tanaka [12] but the ratio according to our measurements is generally closer to 2 as published by Kamal in [13].

Raman spectroscopy was used to investigate the structure of studied bulk samples and as-prepared TFs (Fig 4). In the Raman spectrum of $\text{As}_{35}\text{S}_{65}$ bulk glass the dominant band around 345 cm^{-1} is assigned to the vibrations of pyramidal units $\text{AsS}_{3/2}$ [14]. While replacing S with Se in studied samples this band decreases and at the same time band at 225 cm^{-1} , which is assigned to $\text{AsSe}_{3/2}$ units, starts to increase in intensity. This finding is in agreement with other authors [15, 16, 17]. In Raman spectra for sulfur rich compositions ($\text{As}_{35}\text{S}_{65}$ and $\text{As}_{35}\text{S}_{48.75}\text{Se}_{16.25}$) further presents the weak band at 495 cm^{-1} which can be assigned to S–S chain vibrations [18]. The maximum of the band at 225 cm^{-1} observed in the Raman spectra of $\text{As}_{35}\text{Se}_{65}$ is shifted to higher wave numbers with decreasing Se content and is shifted up to 250 cm^{-1} in Raman spectra of $\text{As}_{35}\text{S}_{48.75}\text{Se}_{16.25}$ glass. This shift can be explained by the fact that glasses from this system can create mixed pyramidal units AsS_2Se and AsSSe_2 [19, 20]. Since S atoms are lighter than Se atoms the shift of the peak maximum to the higher values is in agreement with substitution of Se atom with S atoms in $\text{AsSe}_{3/2}$ pyramidal units. According to [21] vibrations of mixed pyramidal units AsS_2Se and AsSSe_2 can be assigned to the bands at 257 and 241 cm^{-1} respectively.

The Raman spectra for as-prepared TF (Fig 4) contain more bands than corresponding bulk spectra. This is caused by the evaporation process in which vapours of the glass are cooled very rapidly, thus creating more different structural units. The most intensive bands in Raman spectra of $\text{As}_{35}\text{S}_{65}$ and $\text{As}_{35}\text{S}_{48.75}\text{Se}_{16.26}$ samples are at 345 cm^{-1} (corresponding to $\text{AsS}_{3/2}$ pyramids) and 360 cm^{-1} which is according to [18] assigned to the vibrations of As_4S_4 clusters. These clusters also have vibrations corresponding to the band at 222 cm^{-1} [22]. The band at 495 cm^{-1} is visible even for composition $\text{As}_{35}\text{S}_{32.5}\text{Se}_{32.5}$ of as-prepared TF in contrary to bulk samples which is caused by the rapid cooling during evaporation process where energetically less suitable clusters are forced to form. With increasing selenium content the band around 225 cm^{-1} becomes dominant in the Raman spectra. This band is divided into 3 smaller bands which is again caused by creation of mixed structural pyramids AsS_2Se and AsSSe_2 [21]. Similar shift of Raman bands was observed for mixed structural units in Ge-S-Se based glasses [23].

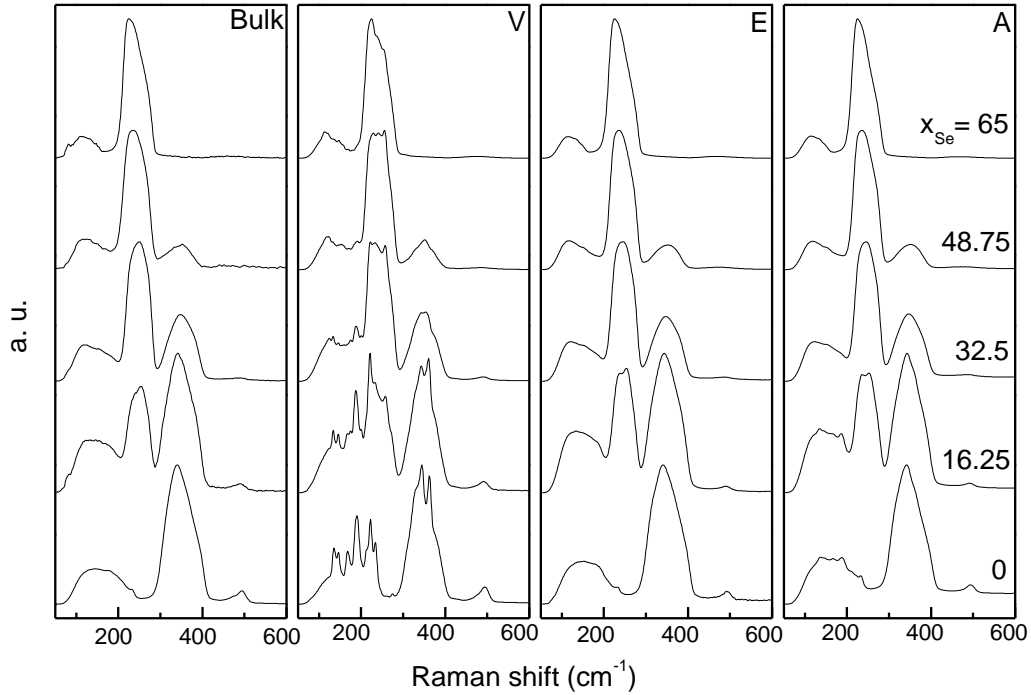


Fig 4: Raman spectra of studied glasses from system $As_{35}S_{65-x}Se_x$. $V=as\text{-prepared}$, $E=exposed$, $A=annealed$.

Exposure

Photo-induced changes in optical properties and structure were studied under the exposure to polychromatic light, which provided exposure in the whole volume of TF, due to its variety of wavelengths and thus variety of penetration depths. Photo-darkening (PD) effect was observed in samples of all studied compositions. PD resulted in the red shift of SAE and increase in refractive index of studied samples (Fig 5). Values of E_g^{opt} exhibit only insignificant shift on the verge of the method preciseness (Tab 1).

Values of refractive index for the wavelength of Nd:YAG laser (1064 nm) of as-prepared and exposed TF together with annealed TF are given in Fig 5. Compositional dependences of n in Fig 5 give evidence that S rich samples ($x_{Se} = 0 - 32.5\%$) exhibit more significant increase in refractive index ($\Delta n \sim 0.1$) in comparison to Se rich samples ($x_{Se} = 48.75 - 65\%$; $\Delta n \sim 0.05$). Calculated values of E_0 and E_d for exposed samples of composition $As_{35}S_{65}$ are 4.59 ± 0.05 eV and 20.27 ± 0.29 eV respectively (for other compositions and treatments see Tab 1). Our results for $As_{35}S_{65}$ exposed TF are similar to those presented by Petkov et al. [11] ($E_0 = 4.65$ eV; $E_d = 21.61$ eV) but in our study we broadened the range of studied compositions by replacing S with Se in the glassy matrix.

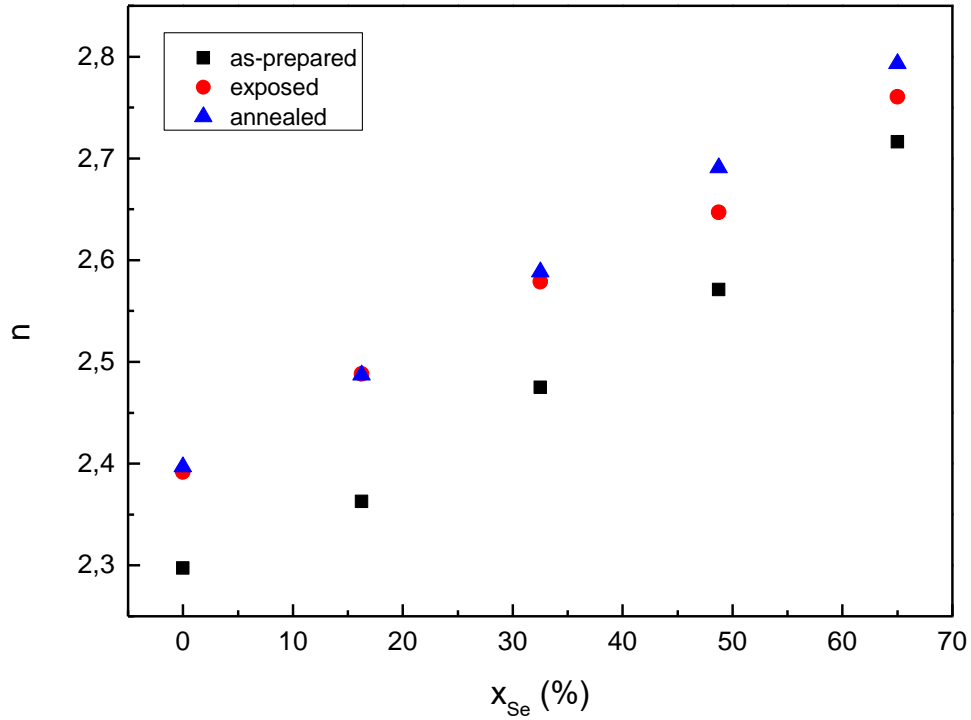


Fig 5: Compositional dependences of refractive index (at 1064 nm) of the studied TF in system $As_{35}S_{65-x}Se_x$.

In-situ exposure kinetics of PD were studied. The shift of SAE was observed in dependence on the time of exposure, particularly the wavelength where transmittance (T) reached 10% ($\Delta\lambda^{T=10\%}$) was used to characterize the position of SAE in time. Typical behaviour of PD kinetics is given in Fig 6. Measured data were fitted using equation:

$$\Delta\lambda_t^{T=10\%} = \frac{\Delta\lambda_{lim}^{T=10\%} \cdot t^q}{k^q + t^q} \quad (2),$$

where $\Delta\lambda^{T=10\%}$ stands for wavelength corresponding to 10% transmittance at time t , $\Delta\lambda_{lim}^{T=10\%}$ is limit value of SAE shift, k represents the reciprocal rate of PD (time t (s) when $\Delta\lambda^{T=10\%} = \Delta\lambda_{lim}^{T=10\%} / 2$) and q is cooperativity coefficient [24]. The fit of the obtained data is shown in Fig 6.

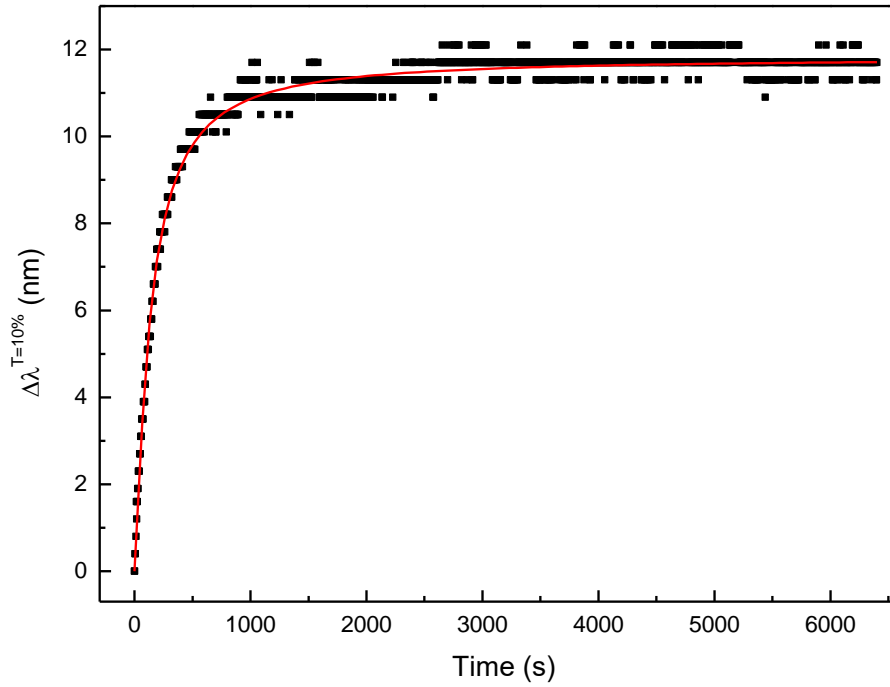


Fig 6: *In-situ* kinetics of PD induced by polychromatic light in composition $As_{35}S_{32.5}Se_{32.5}$.
The red line is fitted using equation (2).

The measured *in-situ* kinetics of PD for all studied compositions were fitted using equation (2) and composition dependences of obtained values of parameters $\Delta\lambda_{lim}^{T=10\%}$ and k are given in Fig 7. The most significant photo-induced shifts of SAE were observed in case of TFs of binary compositions $As_{35}S_{65}$ and $As_{35}Se_{65}$. On the contrary the smallest shift of SAE was observed for composition $As_{35}S_{32.5}Se_{32.5}$. The rates of the photo-induced shift of SAE expressed as rate coefficient k gives evidence that the shift of SAE is significantly faster in glasses of compositions containing Se in comparison with pure sulfur based glass of $As_{35}S_{65}$ composition.

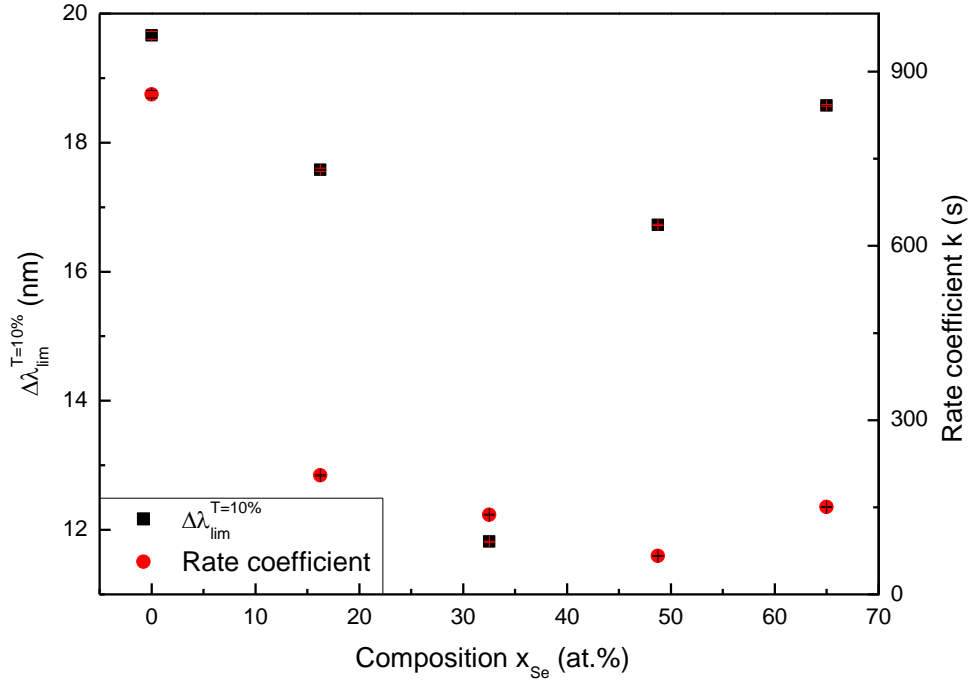


Fig 7: Compositional dependence of calculated values of maximal SAE shift $\Delta\lambda_{lim}^{T=10\%}$ and rate coefficient k from equation (2) for polychromatic light exposure of the thin film.

The photostructural changes were studied using Raman spectroscopy (Fig 4). The spectra of exposed TF exhibit significant differences in comparison with spectra of as-prepared TF. There are only three main regions in the exposed TF spectra corresponding to either homopolar bonds vibrations ($100 - 200 \text{ cm}^{-1}$) or pyramidal units ($225 - 241 \text{ cm}^{-1}$ and 345 cm^{-1}). The band at 345 cm^{-1} corresponds to $\text{AsS}_{3/2}$ pyramidal units vibrations as mentioned before. The band with maximum between 225 and 241 cm^{-1} corresponds to $\text{AsSe}_{3/2}$ pyramidal units vibrations together with mixed pyramidal units AsSSe_2 and AsS_2Se . The maximum of this band shifts to lower wave numbers with decreasing S content. This is caused by lower concentration of mixed pyramidal units due to lower amount of S present in the glass. From the shift of the band maximum we can also assume, that S containing pyramidal units are preferred to Se ones. This assumption is supported by the higher energy of As-S bond (260 kJ/mol) in comparison with energy of As-Se bond (230 kJ/mol) [25]. The Raman spectra of exposed TFs resemble the spectra of corresponding bulk glass samples indicating that exposition with polychromatic light allows for structural relaxation of as-prepared TFs. The change of the glass structure is the cause of observed change of properties [10].

Annealing

Thermo-induced changes in structure and optical properties of the samples were measured *in-situ* during the annealing process using modular spectrometer. Samples were annealed for 120 minutes at temperatures 20 °C below T_g of given composition. This time was sufficient for all samples to reach their saturation i.e. optical properties of the samples no longer changed with prolonged annealing. Shifts of SAE, n and E_g^{opt} were calculated using *in-situ* measured transmission spectra. Shifts of SAE (expressed as parameter $\Delta\lambda_{lim}^{T=10\%}$ from equation (2)) induced by annealing for the studied compositions are given in Fig 9. Shifts of SAE induced by annealing were less significant than those induced by polychromatic light exposure in all studied samples. Thermo-induced changes in E_g^{opt} were observed (Tab 1) but the differences are on the verge of the method preciseness.

The value of refractive index of TF of all studied compositions increased after annealing (Fig 5; Tab 1) which is a similar result as for the polychromatic light exposition. $As_{35}S_{65-x}Se_x$ TF samples containing S (i. e. $x = 0 - 48.75$) exhibited significantly larger increase in refractive index ($\Delta n \sim 0.1$) after annealing in comparison with $As_{35}Se_{65}$ TF ($\Delta n \sim 0.075$).

During *in-situ* measurements the position of SAE was determined; particularly the wavelength $\Delta\lambda^{T=10\%}$ was deducted from transmission spectra and studied as a function of annealing time. Obtained time dependencies of $\Delta\lambda^{T=10\%}$ were fitted using function (2). Values of parameters $\Delta\lambda_{lim}^{T=10\%}$ and rate coefficient k are shown in Fig 9. Compositional dependence of the SAE shift measured *ex-situ*, i.e. at laboratory temperature (after annealing and cooling down) had similar trend as in case of *in-situ* measurements but their values were different (compare Fig 10 and 9, respectively). We believe that the higher values of SAE shifts during *in-situ* measurements in comparison with *ex-situ* measurements are caused by the thermal dependence of E_g^{opt} (these values decrease with temperature increase for all compositions). Compositional dependence of the rate coefficient k of the thermo-induced shift of SAE (Fig 9) proves that the shift occurred fastest for composition $As_{35}Se_{65}$. With decreasing content of Se the rate of the SAE shift decreased monotonously up to the composition $As_{35}S_{48.75}Se_{16.25}$ then slightly increased for binary $As_{35}S_{65}$ composition. We assume that this anomaly is caused by higher content of As_4S_4 structural units in as-prepared $As_{35}S_{48.75}Se_{16.25}$ TF in comparison with more Se containing films (see Fig 4). Annealing induced decomposition of As_4S_4 structural units and creation of pyramidal units and/or mixed pyramidal units occurring at a slower rate

but with slightly higher maximal induced change might be the explanation of this phenomenon considering the difference in As_4S_4 and pyramidal units shape (Fig. 4).

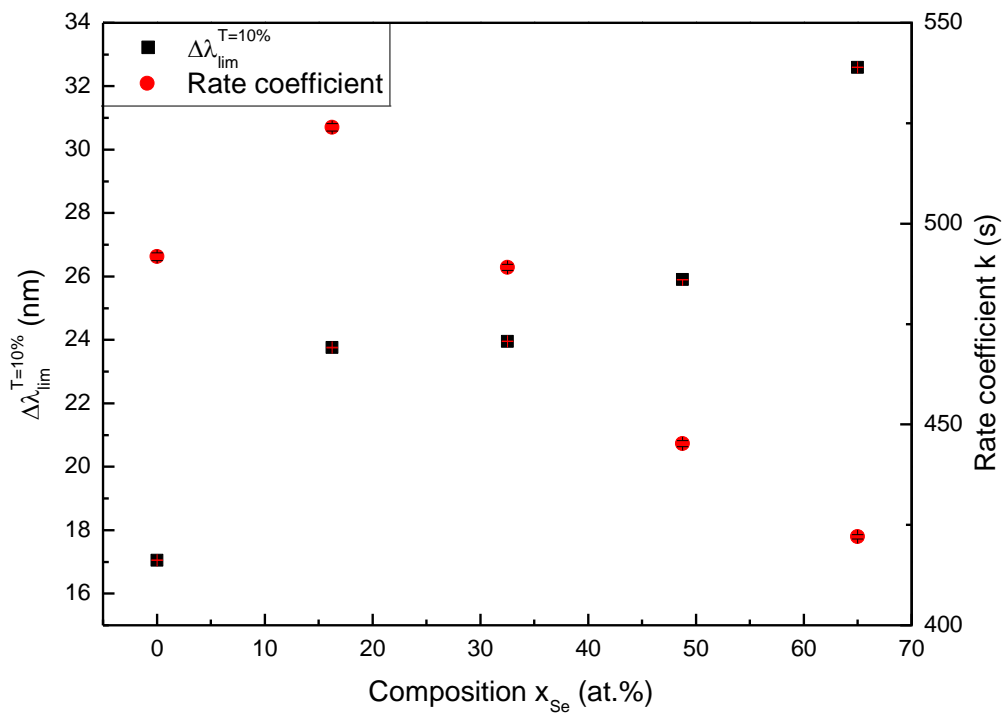


Fig 8: Compositional dependence of calculated values of parameters $\Delta\lambda_{\text{lim}}^{T=10\%}$ and k from equation (2) for annealing kinetics of the $\text{As}_{35}\text{S}_{65-x}\text{Se}_x$ TFs.

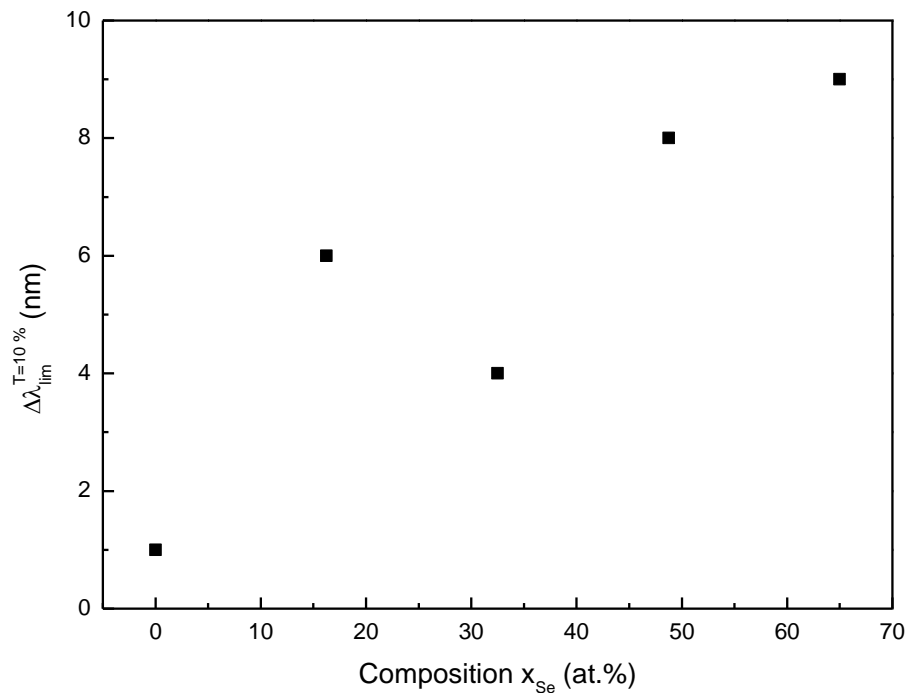


Fig 9: Annealing induced shift of SAE, ex-situ measurement.

The Raman spectra of annealed TFs (Fig 4) contain lower number of bands than corresponding as-prepared TFs. There are only the three main bands corresponding to homopolar bonds ($100 - 200 \text{ cm}^{-1}$) and vibrations of pyramidal units $\text{AsSe}_{3/2}$ and/or $\text{AsS}_{3/2}$ ($225 - 241 \text{ cm}^{-1}$ and 345 cm^{-1} , respectively). The band at 495 cm^{-1} for S-S vibration is visible only in the two most sulfur rich composition spectra. The Raman spectra of annealed TF are very similar to those measured for bulk and exposed TF, thus we conclude that annealing induces similar structural changes as exposition by polychromatic light and both processes lead to structure, that is similar to the structure of bulk sample of the same composition.

Conclusion

It has been found that the refractive index increases and E_g^{opt} decreases with increasing Se content in the $\text{As}_{35}\text{S}_{65-x}\text{Se}_x$ thin films. Annealing and exposition to polychromatic light had similar effect on optical properties and structure of these TFs of all studied compositions, although changes induced by polychromatic light exposure were more significant. The *in-situ* kinetics of SAE changes during annealing and exposure to polychromatic light gave evidence of higher rate of SAE shift while Se is present in the structure of the TF.

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