Some thermally and optically induced changes of optical properties of amorphous As$_{38}$S$_{62}$ films

L. TICHÝ
Joint Laboratory of Solid State Chemistry of Czechoslovak Academy of Sciences and Institute of Chemical Technology, Pardubice, 532 10 Pardubice, Czechoslovakia

H. TICHÁ, K. HANDLÍŘ
Institute of Chemical Technology, Pardubice, 532 10 Pardubice, Czechoslovakia

The exposure (in air) of As$_{38}$S$_{62}$ amorphous film was found to be accompanied (i) by significant structural changes in the film matrix (an increase of As–S bond density as indicated by IR spectroscopy), and (ii) by darkening of the film. No indications of photo-oxidation have been found. Exposure and subsequent annealing of the well-annealed film are accompanied by reversible changes of the As–S bond density, as indicated by the results of differential infrared spectroscopy. The dispersion of the refractive index of the virgin, annealed and exposed films can be described using the Wemple–DiDomenico (W–D) single-oscillator formula. Annealing- and exposure-induced changes of the parameters of the W–D formula follow the changes of both the optical gap and the As–S bond density.

1. Introduction

The optical properties of amorphous As$_x$S$_{1-x}$ films are of considerable interest, especially with respect to the existence and nature of reversible photodarkening (PD) (see e.g. [1] and references cited there). Among the mechanisms discussed as responsible for the process of reversible PD, an increase of As–As bond density due to the illumination of the well-annealed film was proposed [2]. The reaction

$$2[\text{As–S}] \underset{\text{bleaching}}{\overset{\text{darkening}}{\rightleftharpoons}} [\text{As–As}] + [\text{S–S}] \qquad (1)$$
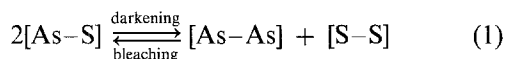
illustrates possible changes in the bond statistics of the darkened or bleached system [2]. According to Equation 1, the process of reversible PD could be associated with a decrease of the density of As–S bonds, and the bleaching of the darkened film with an increase of the density of As–S bonds. The first aim of this paper is to examine whether in using differential infrared (DIR) spectroscopy the corresponding photo-induced changes could be detected in IR vibrational spectra of As$_{38}$S$_{62}$ film. The other aim of the paper is to determine whether the As$_{38}$S$_{62}$ film is sensitive to photo-oxidation if the exposure of the film is made at ambient air pressure. The reason for such an examination follows from the fact that in some papers [3–5] it was found that the photo-oxidation of the surface of As–S films can start during the light exposure of the film. Finally, the changes of the refraction index induced by annealing and exposure are also briefly described.

2. Experimental procedure

Thin amorphous films were prepared from As$_2$S$_3$ bulk by vacuum evaporation ($p \sim 10^{-4}$ Pa, rate of evaporation $\sim 1 \, \text{nm sec}^{-1}$) on to microscope slides and silicon wafer substrates. According to the results of microprobe X-ray analysis the composition of the films was approximately As$_{38}$S$_{62}$. Optical transmittance measurements were made using a UV–visible spectrophotometer (Specord, Carl Zeiss Jena, DDR) in the short-wavelength edge region, and a Perkin Elmer 684 spectrophotometer connected on-line with a Data Station 3600, in the IR region. Exposure of the films was made using a halogen lamp, without an IR filter and at ambient air pressure. The energy of incident light was $\sim 400 \, \text{mW cm}^{-2}$. Differential infrared spectra (DIR) were made in such a way that measured spectra were transformed into absorbance–frequency coordinates and subtracted, after which results were transformed back into transmission–frequency coordinates. All DIR spectra are marked by symbols J-K to indicate the placement of the K film in the reference beam and the J film in the sample beam of the spectrophotometer.

3. Results and discussion

In Fig. 1 are summarized some IR spectra (left-hand side) and some DIR spectra (right-hand side) of As$_{38}$S$_{62}$ amorphous films. The virgin film of As$_2$S$_3$ contains condensed clusters with compositions varying from arsenic-rich As$_{2n}$S$_{2n}$ to sulphur-rich As$_{2n}$S$_{4n+2}$ [6]. Arsenic-rich clusters with $n = 2$ are most probably responsible for the form of the IR spectra of virgin As$_2$S$_3$ films [7, 8]. Due to the annealing, arsenic-rich and sulphur-rich clusters interact and the density of (As$_2$S$_3$)$_n$ clusters is increased. Hence the IR spectra of annealed films (Curve 2) resemble those of bulk As$_2$S$_3$. DIR spectra (Curve 2–1) clearly manifest a remarkable increase of transmission in the region of 375 cm^{-1} (main IR feature of As$_4$S$_4$) and an increase of absorption in the region of 310 cm^{-1} (main IR feature of amorphous As$_2$S$_3$). The exposure of the

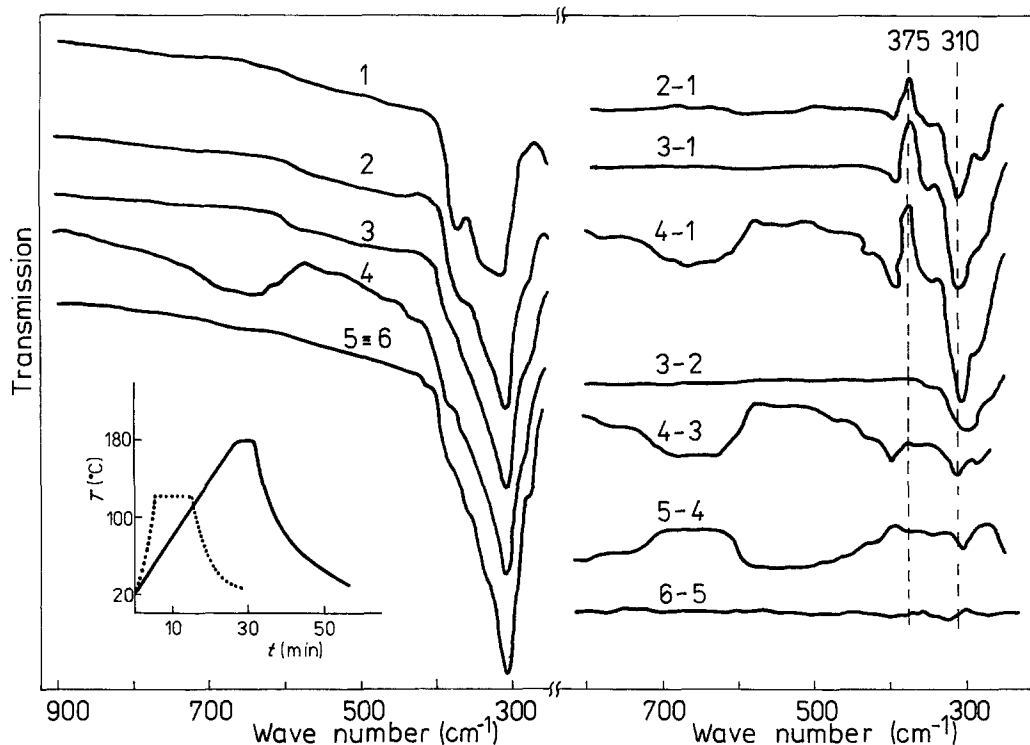*Figure 1* Left-hand side: infrared transmission spectra of amorphous $As_{38}S_{62}$ films. (1) Virgin, (2) annealed (thermal cycle — see full curve in inset), (3) Sample 2 after exposure ($t \sim$ 60 min), (4) Sample 3 after simultaneous exposure and annealing (thermal cycle — see dotted curve in inset), (5) Sample 4 after annealing (thermal cycle — see full curve in inset), (6) Sample 5 after exposure. Right-hand side: differential infrared spectra of studied films. By symbols $J-K$ is indicated the placement of film K in the reference beam and film J in sample beam. Inset: thermal cycles (in T against t).

annealed film leads to a further increase of the density of $(As_2S_3)_n$ clusters, as is clear from the shape of the DIR spectra (Curves 3–1 and 3–2). Although the exposure of the film was made for 60 min in air we did not find any indications of photo-oxidation of the film since, in the case of the existence of a sufficient density of As–O bonds, the corresponding absorption bands should be observable (in the IR spectral region) at 800 to 815 cm^{-1} if crystalline or in the region around 620 cm^{-1} if amorphous As_2O_3 is formed [9, 10].

The absence of any significant increase of absorption in the above-mentioned spectral regions leads us to the conclusion that, within the detectivity of IR spectroscopy, the films studied are more stable to photo-oxidation in comparison e.g. with Ge–S films [11]. Only after exposure to air made in the thermal cycle shown in the inset of Fig. 1 (dotted curve) have we found a broad absorption band around 650 cm^{-1} (see Fig. 1, Curve 4), indicating with most probability the photo-oxidation of the film surface. It is remarkable that the DIR spectra (Curve 4–3, right-hand side of Fig. 1) do not show a decrease of absorption in the vicinity of 310 cm^{-1}. This can be explained by the fact that (i) the still existing As–As bonds — as wrong bonds — are mainly photo-oxidized, or (ii) in the course of annealing the density of As–S bonds increases but these bonds are photo-oxidized during the exposure. Annealing of photo-oxidized film (in a vacuum) leads to the disappearance of the broad band around 650 cm^{-1} due to the evaporation of As_2O_3, as is evident from Curve 5 (left-hand side of Fig. 1). This is a well-known process of light-enhanced vaporiz-

ation (described e.g. in [12]). We have also observed a decrease of thickness of the film from $d \sim$ 1.3 μm in films after Procedures 1 to 4 to $d \sim$ 1.2 μm in films after Procedure 5.

In Fig. 2 the behaviour of the short-wavelength edge of the studied film is shown in the course of the same procedures of annealing and exposure which have been used for a study of the changes of IR spectra in our experiments. The changes of position of the short-wavelength edge and of IR spectra are compared in Table I. Two facts are remarkable: (i) the short-wavelength edges of the photo-oxidized and deoxidized films are very close ($\Delta E \sim$ 10 meV) and the changes in chemical composition induced by partial photo-oxidation and following deoxidation of the film do not influence the photodarkening (see changes of the short-wavelength edge in the process 5 → 6), (ii) exposure of annealed film (film in State 2) leads to a darkening (as usually observed) accompanied by an increase of the absorption around 310 cm^{-1} which indicates rather an increase in the density of As–S bonds. This seems to be in contradiction with a recent proposal in the literature [2], i.e. that the exposure of annealed $As_{40}S_{60}$ film leads to an increase of As–As bonds which should be accompanied rather by a decrease in the density of As–S bonds (see Equation 1). However, our film in State 2 was probably not in a well-annealed state and thus it is not possible to accurately compare these results with those referred to [2].

In order to make such a comparison we have annealed a virgin film for 240 min at $T \sim$ 170° C in a vacuum of $p \sim$ 10^{-3} Pa, then we have measured the
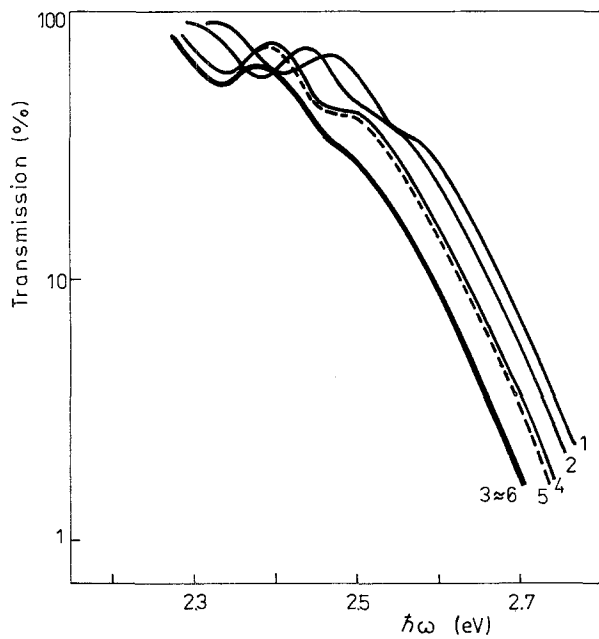
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Figure 2 Optical transmission spectra in the region of the short-wavelength edge of $As_{38}S_{62}$ films. (1) Virgin, (2) annealed (thermal cycle — see full curve in inset of Fig. 1), (3) Sample 2 after exposure, (4) Sample 3 after simultaneous exposure and annealing (thermal cycle — see dotted curve in inset of Fig. 1), (5) Sample 4 after annealing (for thermal cycle see Sample 2), (6) Sample 5 after exposure. Approximate edge shifts as follows: (1 → 2) −20 meV, (2 → 3) −75 meV, (3 → 4) +45 meV, (4 → 5) −10 meV, (5 → 6) −35 meV.

IR spectrum of the film, and under the same conditions the film was annealed for 60 min once again. In the DIR spectra of these annealed films we did not find any changes (Fig. 3, Curve A2–A1) which may indicate that the film, with respect to the changes detectable by IR spectroscopy, is well stabilized. In the inset of Fig. 3 are shown corresponding changes of the shift of the short-wavelength edge. A well-annealed film was darkened by exposure for 30 min (see Curve E in inset). The DIR spectrum which compares the changes of IR activity due to the exposure of the well-annealed film is shown by Curve E–A2 in Fig. 3. There is evident a

small but detectable increase of transmission in the region of $310\,cm^{-1}$ which could be associated with a decrease of As–S bond density. Annealing of darkened (exposed) film leads to bleaching (Curve A3) and the DIR spectra of these films (A3–E) show an increase of absorption in the region of $310\,cm^{-1}$ which is probably due to an increase in the density of As–S bonds. The process is reversible.

Hence it seems that the process of reversible PD of well-annealed film of $As_{38}S_{62}$ is accompanied by reversible changes in the intensity of IR absorption at $310\,cm^{-1}$. This indicates, as recently found from results of Raman studies [2], that the reversible PD of $As_{38}S_{62}$ film is accompanied by reversible changes in the density of As–S bonds, perhaps according to Equation 1. However, the amount of this change is very small. Compare, for example, the magnitude of the irreversible structural change of IR spectra due to the transition of the film from the virgin to the well-annealed state, accompanied by irreversible darkening ($\Delta E \sim -55$ meV, see Fig. 3), with the magnitude of the reversible structural change around $\sim 310\,cm^{-1}$ of the well-annealed film, accompanied by reversible PD ($\Delta E \sim -40$ meV, see Fig. 3). From this comparison it seems that very subtle reversible changes of the intensity of the fundamental absorption band of $As_{38}S_{62}$ film (Fig. 3, DIR E–A2, A3–E) accompany the process of reversible PD, but these are not the only or dominant origin of this process. Most probably the process of photoinduced changes of the intermolecular interaction can play a role in the process of reversible PD of $As_x S_{1-x}$ ($x \sim 0.4$) films (see e.g. [1]). If, for example, changes of the medium-range order (MRO) are also responsible for reversible PD it would be of interest to study the behaviour of the boson peak in Raman scattering [13]. Changes in the amplitude of the boson peak seem to be much more sensitive to changes of MRO in comparison with the major Raman mode. For example, for bulk $As_2 S_3$ prepared with different cooling rates around the softening temperature, the changes of the amplitude of the major Raman mode are $\sim 3\%$ while the changes of the amplitude of

TABLE I The change of the short-wavelength edge shift (ΔE) and IR spectra of $As_{38}S_{62}$ amorphous film in the course of Procedures 1 to 6

| Procedure no.	Kind and conditions of procedure	ΔE (meV)	Feature in DIR spectra		
			$650\,cm^{-1}$	$375\,cm^{-1}$	$310\,cm^{-1}$
1	Virgin film	−	No	Yes	Yes
2	1 → 2; annealing in vacuum, thermal cycle, see inset of Fig. 1, full curve	20 (darkening)	No	Decrease of intensity	Increase of intensity
3	2 → 3; exposure in air, 60 min	−75 (darkening)	No	No	Increase of intensity
4	3 → 4; simultaneous exposure and annealing, thermal cycle, see inset of Fig. 1, dotted curve	+45 (bleaching)	Yes: appearance of absorption	Increase of intensity	
5	4 → 5; annealing in vacuum, thermal cycle, see inset of Fig. 1, full curve	−10 (darkening)	Removal of absorption	Increase of intensity	
6	5 → 6; exposure in air, 60 min	−35 (darkening)	No	Not identified	
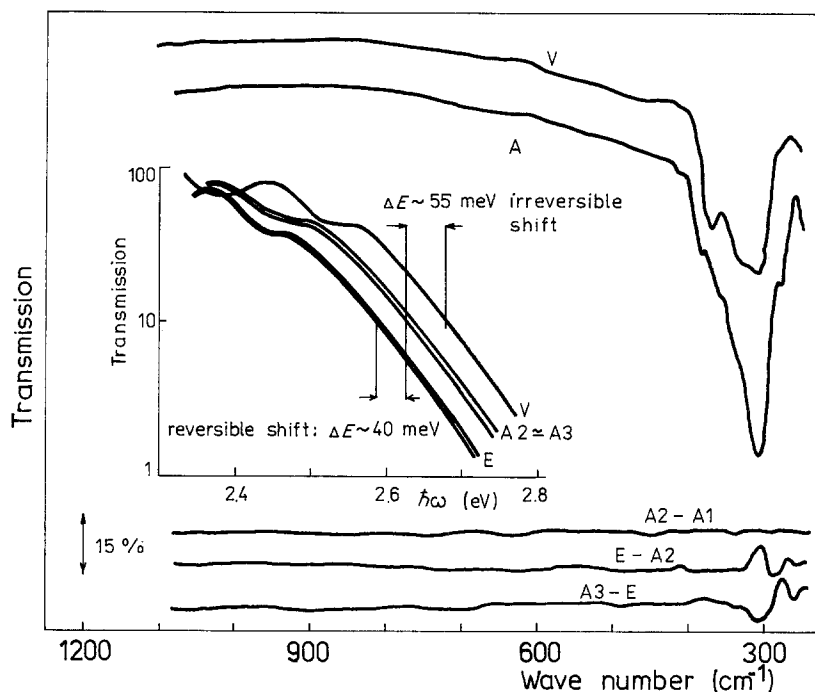
Figure 3 Upper part: infrared transmission spectra of amorphous $As_{38}S_{62}$ films. (V) virgin, (A) annealed ($T \sim 170°C, t = 240$ (and $+60$) min, $p \sim 10^{-3}$ Pa). Inset: optical transmission spectra in the short-wavelength region. (V) virgin, (A2) after annealing ($T \sim 170°C, t = 240 + 60$ min), (E) Sample A2 after exposure, (A3) Sample E after annealing. Lower part: ($A_2 - A_1$) DIR spectrum of Sample A2 against A1, (E–A2) DIR spectrum of Sample E against A2, (A3–E) DIR spectrum of Sample A3 against E.

the boson peak are $\sim 30\%$ [14]. A study of the changes of the boson peak amplitude in connection with the photostructural properties of amorphous films could significantly contribute to an understanding of the nature of the reversible PD of amorphous films.

Finally, we have examined the dispersion of the refractive index (n) of virgin (V), annealed (A) and exposed (E) films. In Fig. 4 are shown typical transmission spectra of virgin and exposed (after annealing) $As_{38}S_{62}$ films. For determination of the spectral dependence of the refractive index we have used the method of envelope curves (as indicated by dashed curves in Fig. 4) (see e.g. [15]). The thickness (t) of the film is given by the relation

$$t = \frac{M\lambda_1\lambda_2}{2n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1} \qquad (2)$$
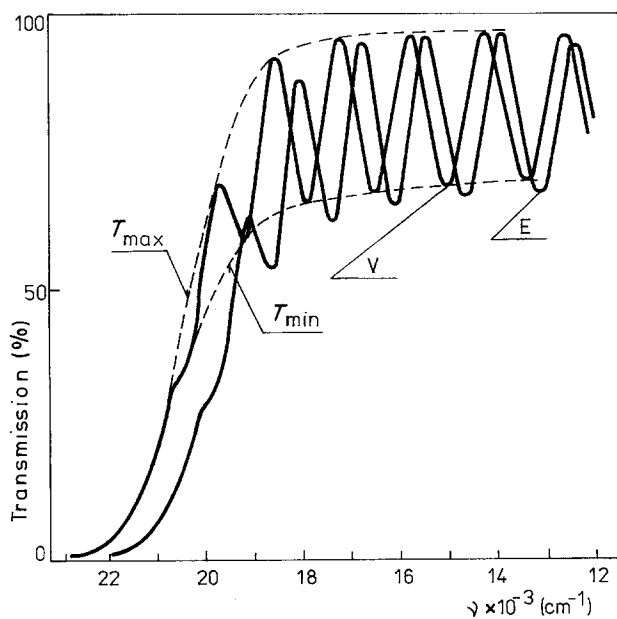

Figure 4 Typical transmission spectra of amorphous $As_{38}S_{62}$ film in the short-wavelength region. (V) Virgin, (E) exposed. The envelope curves for Sample V are shown by dashed curves.

where M is the number of oscillations between two extrema and λ_1, $n(\lambda_1)$, λ_2, and $n(\lambda_2)$ are the wavelengths and corresponding indices of refraction. The refraction index (n) of the film is given by the relation

$$n = [N + (N^2 - n_0^2n_1^2)^{1/2}]^{1/2} \qquad (3)$$

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1 \frac{T_{max}(\lambda) - T_{min}(\lambda)}{T_{min}(\lambda)} \qquad (4)$$

In Equation 4, n_0 is the refraction index of air, n_1 the refraction index of the substrate and $T_{max}(\lambda)$, $T_{min}(\lambda)$ the values of transmission at λ taken from envelope curves (see Fig. 4).

We did not find significant changes in the thickness of the films in the course of the process of annealing or exposure. In all cases the thickness of the film was $\sim 1.3 \pm 0.03\,\mu m$ (i.e. within sensitivity of the method used). However, some changes in the dispersion of the index of refraction were found. In Fig. 5 the dispersion of the refraction index in $(n^2 - 1)^{-1}$ against $(\hbar\omega)^2$ coordinates is shown. All the dependences can be well fitted using the Wemple–DiDomenico [16] single-oscillator formula:

$$n^2(\omega) = \frac{E_0E_d}{E_0^2 - (\hbar\omega)^2} \qquad (5)$$

where E_0 is the single-oscillator energy and E_d the dispersion energy. In Table II are summarized calculated values of E_0, E_d and the optical frequency dielectric constant ε_∞ ($= n_{(\omega\to 0)}^2$). For comparison there are also shown corresponding changes of the shift of the short-wavelength edge (ΔE, see Fig. 2). Our values of E_0 are higher than those reported by Tanaka [17] ($E_0 \sim 4.7\,eV$) or in de Neufville et al. [18] ($E_0 \sim 5.2\,eV$). These differences could perhaps be associated with different conditions of preparation of the films (and perhaps also due to subtle differences in chemical composition) in our work and in the work cited.
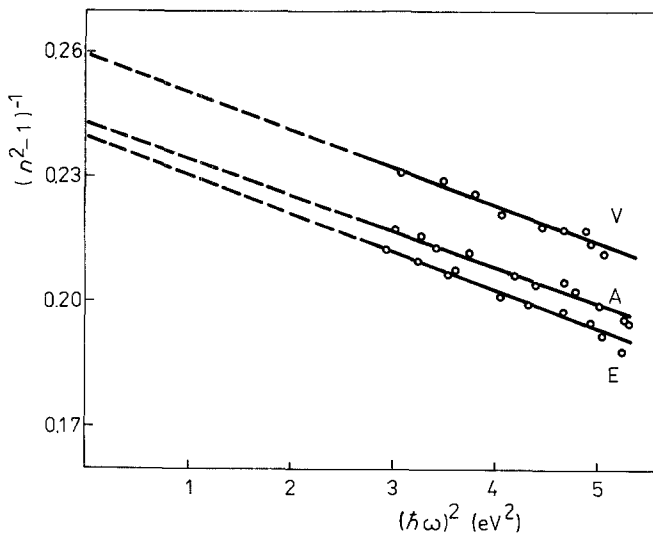
Figure 5 Refractive index dispersion of $As_{38}S_{62}$ amorphous films in $(n^2-1)^{-1}$ against $(\hbar\omega)^2$ coordinates. (V) Virgin, (A) annealed, (E) exposed.

From Table II it follows that due to the annealing or exposure of $As_{38}S_{62}$ film the value of E_0 decreases, while the values of E_d and ε_∞ rather increase. We shall qualitatively discuss these changes. In the As_xS_{100-x} amorphous system it was found that there exists a correspondence between $E_0(x)$ and $E_g^{opt}(x)$ which can be expressed as $E_0 \sim 1.9\,E_g^{opt}$ [17]. Hence, the decrease of E_0 values simply reflects a decrease of the optical gap, i.e. darkening, as we have found. In chalcogenide glasses the value of E_0 can be taken as a mean energy of transition between filled lone-pair p states of the valence band and empty antibonding states [16], while the optical gap could be taken rather as an energy of transition from the vicinity of the top of filled lone-pair p states of the valence band to the vicinity of the bottom of the antibonding states. Hence the qualitative correspondence in the changes of E_0 and E_g^{opt}, or ΔE values, has a reasonable physical meaning.

The dispersion energy E_d obeys the empirical relation [16]

$$E_d = \beta N_c Z_a N_e \qquad (6)$$

where N_c is the coordination number of the nearest-neighbour cation to the anion, Z_a is the formal chemical valency of the anion, N_e is the total number of valence electrons and $\beta = 0.37 \pm 0.04\,\text{eV}$ in the covalent materials while $\beta = 0.26 \pm 0.03\,\text{eV}$ in the more ionic materials. We assume that in our case the values of Z_a and N_e are given rather by the chemical composition of the film and they are constant, while the values of N_c and β could reflect possible changes in the structure or bonding arrangements of the films. As in the virgin film there is a significant number of As–As bonds (due to the existence of e.g. As_4S_4 entities), while in the course of annealing or exposure (of virgin film) the density of these bonds should decrease (due to the increase of the density of $(As_2S_3)_n$

TABLE II Values of the single-oscillator energy (E_0), dispersion energy (E_d), optical frequency dielectric constant (ε_∞) and short-wavelength edge shift (ΔE)

Film	E_0 (eV)	E_d (eV)	$\varepsilon_\infty\ (=n^2_{(\omega\to 0)})$	ΔE (meV)
Virgin	5.41	20.9	4.8_7	–
Annealed	5.3	21.8	5.1_1	–(20 to 30)
Exposed	5.21	22.1	5.2_6	–75

clusters, see IR and DIR spectra in Fig. 1), we suppose that N_c for virgin film is lower than N_c for annealed or exposed film. Consequently, annealing or exposure of virgin film should be accompanied by an increase in N_c and thus with an increase in E_d. The magnitude of the increase of E_d could however be masked, in our case, by some changes in the value of β. Because an increase in the density of As–S bonds is most probably associated with an increase of ionicity, the value of β could slightly decrease in the course of annealing or exposure of virgin film. The magnitude of the increase of N_c is most probably significant and thus, as we have found, the value of E_d increases in the transition from virgin to annealed or exposed film.

The increase in ε_∞ for annealed and exposed film can be qualitatively discussed with the help of the relation

$$\varepsilon_\infty = 1 + 4\pi N_0 \varrho \bar{N}\bar{\chi}/M \qquad (7)$$

where N_0 is Avogadro's number, ϱ is the density, N is the number of bonds per atom, $\bar{\chi}$ is the average bond susceptibility and M is the average mass. As mentioned above, due to the annealing and exposure of $As_{38}S_{62}$ film there are significant changes of the short-range order — a decrease of As–As bond density and an increase of As–S bond density. The density of the film and the average bond susceptibility are most probably changed and hence, for a conserved chemical composition, the variable quantities in Equation 7 are ϱ and $\bar{\chi}$. The increase of ε_∞ can reflect a decrease of the volume of film and also an increase of the average bond susceptibility (we note that in the $\bar{\chi}$ (x) dependence of the As_xS_{100-x} system a local maximum around $x \sim 40$ was found [19]). However, more precision measurements of the changes of thickness and dimensions of the film induced by annealing and exposure are necessary to distinguish which quantity $(\varrho, \bar{\chi})$ is mainly responsible for an increase of the ε_∞ value.

4. Conclusion
Our results can be briefly summarized as follows.

1. Exposure (in air for $\sim 60\,\text{min}$ and incident energy of light $\sim 400\,\text{mW\,cm}^{-2}$) of virgin amorphous $As_{38}S_{62}$ did not lead to significant photo-oxidation of the film

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and the film is darkened. This indicates a rather higher stability to photo-oxidation of the film in comparison with some Ge–S amorphous films [11].

2. Exposure of a well-annealed film (darkening) and subsequent annealing (bleaching) is a reversible process accompanied by changes of the As–S bond density as indicated by results of differential infrared spectroscopy. This agrees with the recent results of a study of Raman scattering of As_2S_3 film [2]. The magnitude of the reversible change of the intensity of maxima of absorption band at $310 \, \text{cm}^{-1}$ does not exceed 6% (see Fig. 3).

3. The dispersion of the refractive index of virgin, annealed and exposed films can be described using the Wemple–DiDomenico single-oscillator formula. The annealing- and exposure-induced changes of the single-oscillator energy (E_0), dispersion energy (E_d) and optical frequency dielectric constant (ε_∞) follow the changes of the optical gap (E_0^g), an increase of the As–S bond density (E_d) and possible densification and/or increase of the average bond susceptibility due to an increase of the As–S bond density (ε_∞).

Acknowledgement

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