

SOME PECULARITIES OF PHOTO-INDUCED CHANGES OF THE OPTICAL GAP IN AMORPHOUS $\text{Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ FILMS

M. Štábl, L. Tichý*

Joint Laboratory of Solid State Chemistry of Institute of Macromolecular Chemistry,
Academy of Sciences of Czech Republic and University of Pardubice,
532 10 Pardubice, Czech Republic

Thin amorphous films of $\text{Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ were prepared by thermal evaporation. It is suggested that the film network is composed by various entities of which molecular-like entities of dimorphite (As_4S_3) were unambiguously identified using Raman spectroscopy. Photo-induced changes of the short wavelength optical absorption edge were studied. The reversible photo-darkening (the red shift of the optical gap) was observed after the second cycle of annealing-illumination of the film. The magnitude of the true reversible darkening was found only around -80 meV at room temperature. Also partial photo-bleaching was observed.

(Received April 23, 2003; accepted May 8, 2003)

Keywords: Amorphous Ge-As-S thin film, Photo-induced gap changes

1. Introduction

In 1986 reversible photo-darkening (a red shift of the short wavelength optical absorption edge, SWE) around 125 meV at room temperature was reported in some Ge-As-S bulk glasses with the formal sulfur under-stoichiometry ($\text{Ge}_{20}\text{As}_{20}\text{S}_{60}$, $\text{Ge}_{20}\text{As}_{25}\text{S}_{55}$, $\text{Ge}_{20}\text{As}_{30}\text{S}_{50}$) and with the average coordination number ($\langle\text{CN}\rangle$) close to 2.7 [1]. Subsequently, in series of papers [2-14] various photo-induced phenomena of Ge-As-S amorphous films were studied. In most of cases the irreversible photo-induced changes of various properties were studied. Photo-induced bleaching, the blue shift of the optical gap (E_g) was found up to 60-80 meV in the vicinity of the 2D-3D topological transition ($\langle\text{CN}\rangle\sim 2.7$) suggested by Ke. Tanaka [15]. Consequently, observed light induced changes were ascribed [12] to ...”the percolation two-to-three dimensional transition or to a chemical transition with the nano-scale arrangement”, see also [16]. The irreversible photo-induced changes in some Ge-As-S amorphous (a) films are rather complicated process. For example in a- $\text{Ge}_{40-x}\text{As}_x\text{S}_{60}$ films for $x < 30-35$ the photo-bleaching of as-prepared (virgin) films is observed, while for $x > 30-35$ the photo-darkening is observed [13,14]. The darkening of some $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ bulk glasses induced by γ -irradiation was studied in e.g. [8], and photo-darkening instead of usually observed photo-bleaching was observed in some annealed a-Ge-As-S films illuminated by the light with the wavelength (λ): $\lambda = 488$ nm [10].

In this communication we report our first experimental results related to photo-induced changes of E_g in both virgin (v) and annealed (a) a- $\text{Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ films. Attention is given also to a role of the excitation light on photo-induced changes of SWE or E_g .

* Corresponding author: ladislav.tichy@upce.cz

2. Experimental

Amorphous $\text{Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ films were prepared by thermal evaporation (Balzers BAE 250T system, $p \sim 10^{-4}$ Pa, rate of evaporation 3 nm/s) of bulk with the nominal chemical composition $\text{Ge}_{20}\text{As}_{30}\text{S}_{50}$. The films with thickness (d) between 580-620 nm were deposited at normal incidence onto microscope glass substrate and silicon wafer convenient for far infrared measurements (IR). The chemical composition of films prepared was determined by electron microprobe X-ray analysis Jeol $\text{Ge}_{13.29}\text{As}_{35.655}\text{S}_{51.055}$ with an average precision $\pm 1.5\%$ in atomic fraction of elements. As-prepared (v) films and films annealed (a) for 2 hours in the dry argon at $T = 220\text{ }^\circ\text{C}$ were used for optical properties measurements. Before and after measurements the samples were held in dark desiccator.

The optical properties were measured using a Perkin Elmer Lambda 12 spectrophotometer and using an FTIR Thermo Nicolet Nexus spectrophotometer. The Raman spectra of some films (v, a) were measured using an FTIR spectrophotometer IFS 55 (Bruker Germany) provided with an FRA 106 Raman module in back-scattering geometry using a Nd:YAG laser beam (90 meV, 1064 nm) as the excitation light. The number of scans was 1000, the resolution was 2 cm^{-1} . The photo-darkening or photo-bleaching is measured as a shift of SWE at some convenient transmission, e.g. 10 % or as the energy corresponding to the absorption coefficient (α): $\alpha = 10^3\text{ cm}^{-1}$. Alternatively, as a measure of photo-darkening or photo-bleaching the changes of the values of E_g are used. In this communication we use E_g calculated using the classical Tauc's formula [17] as a measure of darkening or bleaching of studied films. Some constraints related to possible role of the penetration depth of the excitation light are mentioned in discussion. The values of absorption coefficient were calculated from Rel. (4-32) [18]. The transmission range below 20 % was used to determine α values. Measured values of reflectance (R): $R = 0.16$ were used for calculating of α values.

The samples (virgin and annealed films) were illuminated by white light (whl) using a Hund FLQ 150M light source equipped with light guide and using monochromatic light sources (a band width of 20 nm) with the wavelength (λ , [nm])/photon energy (E_{ph} , [eV]): 417/2.973; 442/2.805; 493/2.515; 532/2.371; 660/1.878. In all cases we used for illumination special sample holder, see Fig. 1 in [19]. The construction of this sample holder allowed to protect the sample surface against photo-oxidation and also allowed to minimize light induced overheating of the sample by a continuous flow of dry nitrogen around the sample surface. For the monochromatic light the incident photon flux was measured before and after each illumination sequence with a Laser Check (Coherent, USA) accurately placed at the sample (film) position. The series of blind tests confirmed that we always measured and illuminated identical part of the sample. The fluctuation of the incident photon flux during a long time of illumination (up to 16 hours in some cases) was $\pm 5\%$. For readers convenience in Fig. 1, lower part typical spectral dependencies of the transmission of the virgin (full curve) and annealed (dashed curve) films are shown. Full vertical line indicates the position of E_g for annealed film, dashed vertical lines indicate the λ values used for the sample illumination. In upper part of Fig. 1 the spectral distribution of the used whl source is shown.

It is well known that gap and over-gap photons are mainly responsible for photo-darkening, while below-gap photons could stimulate backward process, that is the photo-bleaching of a darkened state. Hence cross-dashed area indicates strongly absorbed over-gap part of the light, while hatched area indicates below-gap part of the light. The films were illuminated from the front side of the film, except explicitly mentioned cases where the illumination was done also from the back side of the film.

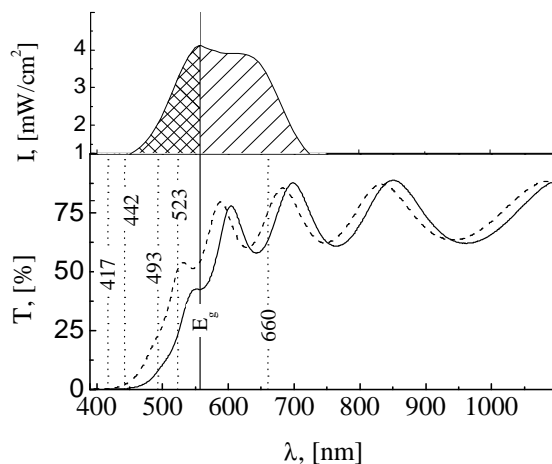


Fig. 1. Upper part - the spectral distribution of the white light source. Crosshatched area - over-gap photons region, hatched area - below gap photons region. Lower part - the spectral dependence of the transmission of studied $\text{a-Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ film. The full curve - virgin film, the dashed curve - annealed film. The full vertical line indicates the position of the gap for annealed film. The dashed vertical lines and the numbers indicate the wavelength (in [nm]) of the monochromatic light used for illumination.

3. Results

The most typical features observed in Raman spectra of the virgin (v) and annealed (a) films, see Fig. 2 are: (i) a broad major band in the spectral region $300\text{-}450\text{ cm}^{-1}$, (ii) a sharp band at around 273 cm^{-1} and (iii) the series of smaller bands at about 180 , and in the region $200\text{-}250\text{ cm}^{-1}$. The most evident differences seen in Raman spectra of the samples examined are: (i) a narrowing of the major band ($300\text{-}450\text{ cm}^{-1}$) after annealing, and (ii) some decrease in the intensity of the sharp band at about 273 cm^{-1} after annealing.

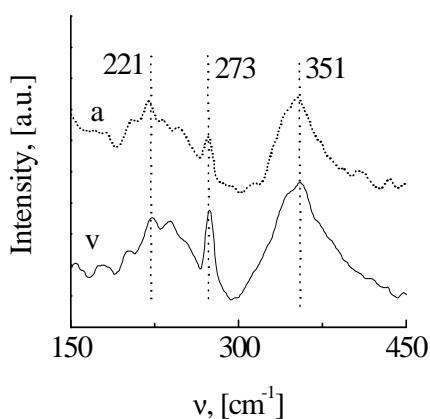


Fig. 2. Raman spectrum in arbitrary units of intensity for virgin (v) and annealed (a) films. For the readers convenience some features are marked by the numbers indicating relevant Raman frequency in $[\text{cm}^{-1}]$.

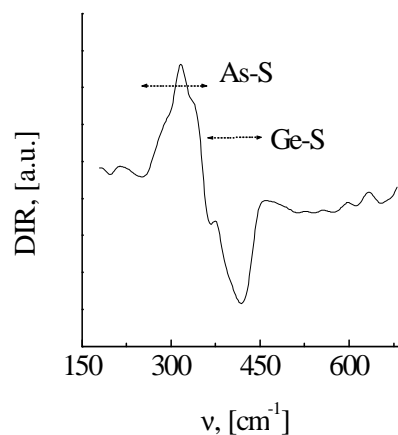


Fig. 3. Differential infrared spectrum (DIR) in arbitrary units for annealed versus virgin film. The spectral regions of the most intensive infrared response for Ge-S and As-S based network are marked by horizontal arrows.

In Fig. 3 the differential infrared spectra are shown for annealed versus virgin film. It is evident that after annealing the absorption increases in the high frequency region ($360\text{--}450\text{ cm}^{-1}$) while simultaneously the absorption decreases in the lower frequency region ($250\text{--}360\text{ cm}^{-1}$) of the feature observed. For readers convenience the approximate spectral regions of the most intensive IR activity of a As-S network and a Ge-S network, see e.g. [20-22] are marked by horizontal lines.

In Fig. 4 the most typical results of the shift of the optical gap (dE_g) induced by illumination of the virgin $a\text{-Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ films are shown. Here $dE_g = E_{g,i} - E_{g,v}$, the symbol i stands for illumination. For both the over-gap photons ($\lambda = 417\text{ nm}$) and whl the shift of the gap is qualitatively similar. Within rather short time of illumination (7 min for whl and 15 min for $\lambda = 417\text{ nm}$) the gap increases from $E_{g,v} = 2.07 \pm 0.007\text{ eV}$ by about 37 meV, while after further illumination the gap decreases back by about 25 meV (whl) or 20 meV ($\lambda = 417\text{ nm}$). Moreover, if practically saturated state reached by whl illumination is further illuminated by the light with $\lambda = 523\text{ nm}$ the bleaching by about 40 meV is observed, see open triangles in Fig. 4. This apparently surprising response of the virgin film on illumination indicates rather complicated origin of photo-induced process.

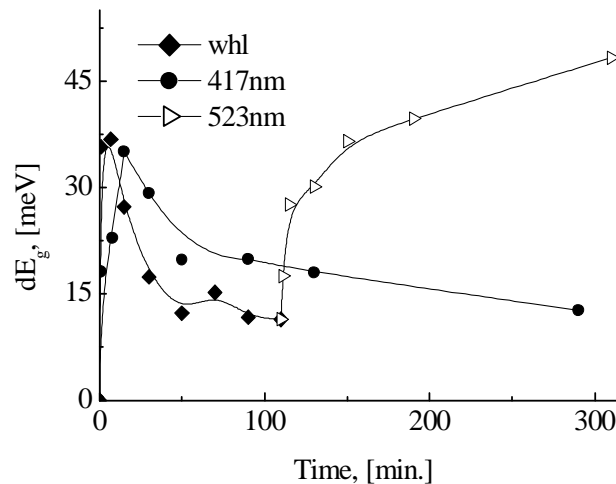


Fig. 4. The $dE_g(t)$ shift induced by illumination of the virgin $a\text{-Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ film. The full symbols indicate $dE_g(t)$ for illumination by the white light (whl) and by the monochromatic light ($\lambda = 417\text{ nm}$), respectively. The open symbols indicate the bleaching induced by monochromatic light ($\lambda = 523\text{ nm}$) of the film in saturated state reached by illumination with monochromatic light $\lambda = 417\text{ nm}$. The curves are only guide for the eye.

For well annealed films illuminated by whl or by over-gap photons the darkening is always observed, see Fig. 5. Considerable differences in the magnitude of darkening measured as $dE_g = E_{g,i} - E_{g,a}$ (the symbol a stands for annealed film) are evident: (i) Darkening induced by photons with the energy close to the gap ($\lambda = 523\text{ nm}$) proceeds slowly, while darkening induced by over-gap photons ($\lambda = 442\text{ nm}$) is rather quick process and reached values of $dE_g \cong -200\text{ meV}$ is one of the biggest dE_g values induced by illumination of an amorphous chalcogenide film at room temperature. (ii) The magnitude of darkening induced by whl illumination is smaller in comparison with darkening induced by over-gap photons. (iii) The film in advance darkened by over-gap photons ($\lambda = 442\text{ nm}$) could be partially bleached by illumination using over-gap photons with energy, however, smaller ($\lambda = 493\text{ nm}$). (iv) The illumination by over-gap photons, $\lambda = 417\text{ nm}$ shows considerable role of the light penetration depth on the overall magnitude of photo-darkening. In the part I, see Fig. 5, the $dE_g(t)$ dependence reflects darkening induced by illumination from the front side of the film. Part II in

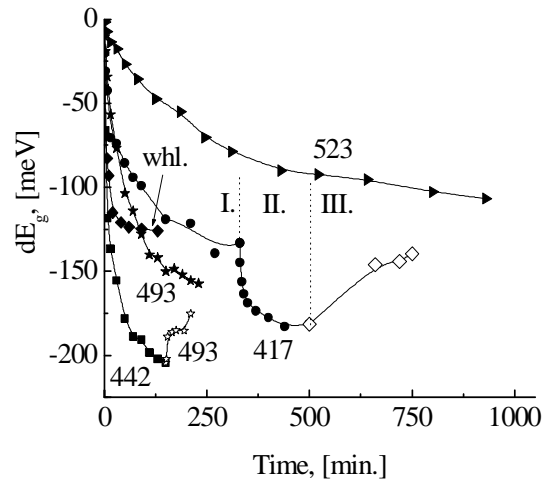


Fig. 5. The $dE_g(t)$ dependence - darkening (full symbols) induced by illumination of annealed films using the monochromatic light with various wavelengths [nm], see the numbers in the figure. The open symbols stand for photo-induced bleaching by whl or by the light with $\lambda = 493$ nm. The curves are only guide for the eye.

Fig. 5 indicates an increase of overall photo-darkening if the film is subsequently illuminated from the substrate side. If the film in the state II is illuminated (from the front side of the film) by whl filtered by another $\text{a-Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ film, the bleaching is observed and the overall dE_g value approaches dE_g value reached by whl illumination only, see Fig. 5, part III.

Darkening of the well annealed film induced by over-gap photons is not completely reversible. After annealing of the film in the saturated darkened state ($\lambda = 493$ nm) the first well annealed state of the film can not be reached even after annealing in following sequence: annealing at 220°C for 2 hours and subsequent annealing at 235°C for 3 hours. After next annealing at 250°C the optical properties of the film degraded due to appearance of some turbidity and film peeling. In fact, true reversible darkening is observed between the second annealed state ($T = 220^\circ\text{C}$, 2 hours) and illumination of this state, see Fig. 6. The magnitude of this darkening is around 80 meV only.

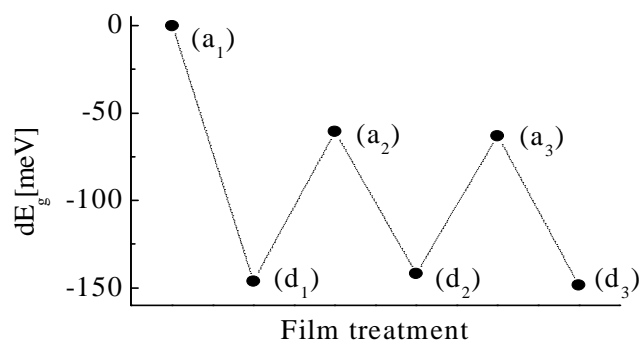


Fig. 6. The schematic illustration of the dE_g shift after annealing and subsequent illumination by the light with $\lambda = 493$ nm. The sequence of the treatment: (a1)-well annealed film \rightarrow (d1) the first darkening \rightarrow (a2) the second annealed state \rightarrow (d2) the second darkened state \rightarrow (a3) the third annealed state \rightarrow (d4) the fourth darkened state. The true reversibility is observed after darkening of the (a2) state.

For readers convenience some conditions of the sample illumination and the magnitude of the red shift of SWE or the gap (dE_g) are summarized in Table 1.

Table 1. MS „Some peculiarities of photo-induced changes of the optical gap in amorphous $\text{Ge}_{13.3}\text{As}_{35.7}\text{S}_{51}$ films”, by M.Štábl and L.Tichý

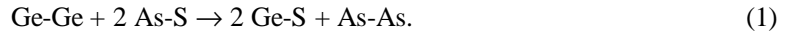
Photon energy, [eV] / wavelength, [nm]	Photon flux on the sample surface [photons/cm ²]	dE_g [meV]	α [cm ⁻¹]	d_{pd} [nm]
1.878 / 660	$1.34 \cdot 10^{18}$	0	~140	~71428
2.371 / 523	$3.45 \cdot 10^{16}$	-106	~3600	~2778
2.515 / 493	$7.82 \cdot 10^{16}$	-155	~18 000	~555
2.805 / 442	$2.67 \cdot 10^{17}$	-205	> 50 000	< 200
2.974 / 417	$1.27 \cdot 10^{17}$	-180	> 50 000	< 200
whl	* $\approx 200 \text{ mW/cm}^2$	-137		

$E_{g,v} = 2.07 \pm 0.007 \text{ eV}$, $E_{g,a} = 2.243 \pm 0.005 \text{ eV}$. * Incident light energy only.

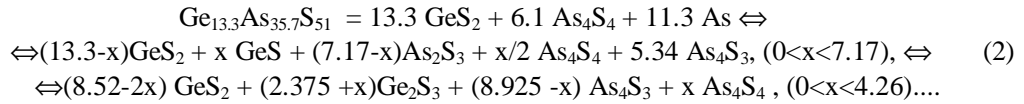
4. Discussion

4.1. Thermally induced changes

The optical gap of virgin films $E_{g,v} = 2.07 \text{ eV}$ increases after annealing by about +173 meV up to the value $E_{g,a} = 2.243 \text{ eV}$. It is well known that virgin a-Ge-S films are bleached after annealing, see e.g. [23], while a-As-S films are rather darkened after annealing, see e.g. [24]. Consequently, observed thermally induced bleaching reflects most probably dominant role of an increase of order in a-Ge-S network of the film on the overall thermally induced changes. This seems to be qualitatively consistent with the results of Raman spectroscopy, Fig. 2, and differential infrared spectroscopy, Fig. 3. Our Raman spectra taken on 600 nm thin films do not allow precise assignment of the feature observed, however, some changes induced by annealing are seen. Most evident is thermally induced decrease in intensity of well pronounced feature at around the 273 cm^{-1} which is typical feature indicating presence of As_4S_3 molecular entities [22, 25, 26]. The series of features in the region of $180\text{-}260 \text{ cm}^{-1}$ could be assigned to the presence of As-As bonds either in As clusters, for example a-As has a broad Raman band in the region $220\text{-}240 \text{ cm}^{-1}$ [27], or in As_4S_4 and As_4S_3 units, see e.g. [20]. Simultaneously, in this region Ge-Ge bonds in tetrahedra with fewer than four S atoms could be responsible for the features around $220\text{-}250 \text{ cm}^{-1}$ [28]. Alternatively, also existence of a-GeS micro-phase [29] can not be excluded, as indicated by the feature at around 221 cm^{-1} . Of interest is thermally induced narrowing of the broad Raman feature in the region $300\text{-}450 \text{ cm}^{-1}$. This broad band most probably arise from superposition of the series of Raman features relevant to As_4S_4 and As_4S_3 units ($340\text{-}370 \text{ cm}^{-1}$), see e.g. [22,25,26] and GeS_4 units, either corner shared tetrahedra ($\sim 340 \text{ cm}^{-1}$) or edge shared tetrahedra ($\sim 370 \text{ cm}^{-1}$), see e.g. [30]. We suppose that observed thermally induced narrowing of this broad band indicates some increase of order of the units mentioned above. Some more insight into origin of thermally induced changes of studied films can be deduced from the results of differential infrared spectroscopy, see Fig. 3. Here it is seen an increase of absorption in the Ge-S stretching region and simultaneous decrease of absorption in the As-S stretching region. Of interest is absorption peak around 423 cm^{-1} which could probably be assigned to bending motion of S atom in $\text{S}_3\text{Ge-S-GeS}_3$ units, see e.g. [31]. This bending motion can also be seen in Raman spectra [31] and indeed some indication of this weak feature (430 cm^{-1}) is seen in Raman spectrum of well annealed film, see Fig. 2. We suppose that thermally induced bleaching can be connected with an increase of order mainly in Ge-S part of a network which could be schematically described by reaction :



In fact, however, the studied films should be taken as a mixture of various entities forming structurally heterogeneous system. For example, the chemical composition of studied films can be expressed as a molecular mixture of various units, neglecting a possibility of formation of GeAs and GeAs₂ entities, in the following way :



4.2. Optically induced changes

Before discussion of our experimental results related to optically induced changes of the SWE or E_g we should clarify the meaning of the dE_g value, which is taken as a measure of photo-darkening or photo-bleaching. From Fig. 5 is evident that dE_g value depends significantly on the penetration depth of the excitation light, see darkening induced by over-gap photons ($\lambda = 417 \text{ nm}$), part I and part II. Consequently, the magnitude of photo-induced change depends also on the number of states which in the measured sample volume are influenced by relevant photons. We define effective penetration depth (dpd) of photons : $\text{dpd} [\text{nm}] = 107 / \alpha [\text{cm}^{-1}]$, where α is the absorption coefficient of the excitation light. For the case where the sample thickness (d) is comparable to dpd or $\text{dpd} > d$ one can assume that the whole illuminated volume of the sample is influenced by absorbed photons and calculated dE_g value reasonably reflects photo-induced shift of the gap. For the case where $\text{dpd} < d$, the calculated dE_g value does not reflect correctly the gap change but it could be taken only as a rough measure of the shift of SWE. For our film thickness $d \approx 600 \text{ nm}$ it means that only for photons with $\alpha < 17\,200 \text{ cm}^{-1}$ we can take dE_g as a measure of the gap shift, while for photons where $\alpha > 17\,200 \text{ cm}^{-1}$ dE_g roughly measures a shift of SWE.

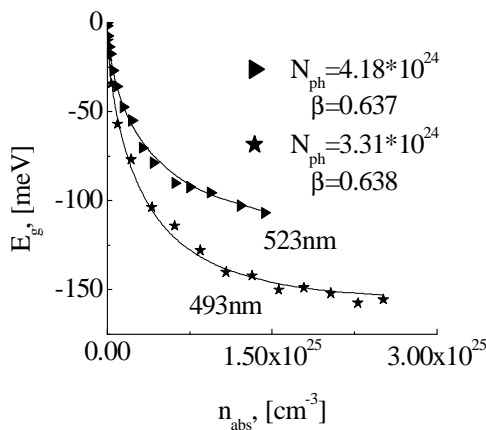


Fig. 7. The $dE_g(t)$ shift – photo - darkening (well annealed film) versus the number of absorbed photons per cm^3 . The numbers [nm] indicate the wavelength used for illumination. The symbols stand for experimental values, the curves are calculated using Rel. 4. N_{ph} is the effective number of photons and β is the stretching parameter.

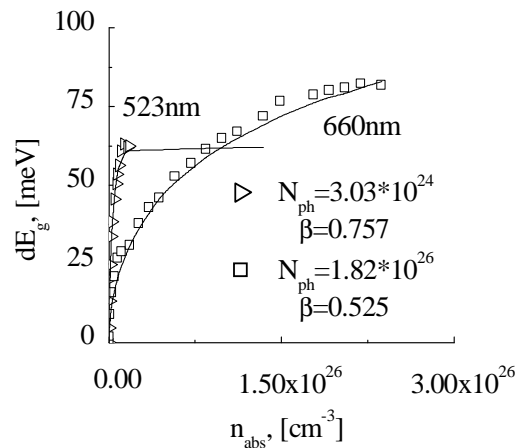


Fig. 8. The $dE_g(t)$ shift - photo-bleaching of the film in advance darkened by $\lambda = 493 \text{ nm}$ versus the number of absorbed photons per cm^3 . The numbers [nm] indicate the wavelength used for illumination. The symbols stand for experimental values, the curves are calculated using Rel. 4. N_{ph} is the effective number of photons and β is the stretching parameter.

Complicated response of virgin film on illumination, see Fig. 4, indicates that there proceed simultaneously more processes: (i) Photo-induced irreversible structural changes in a-Ge-S network which are responsible for bleaching, see e.g. [23]. (ii) Photo-induced irreversible changes in a-As-S network which are responsible for darkening, see e.g. [24]. (iii) Reversible darkening of which presence is clearly indicated by photo-bleaching induced by illumination of the darkened saturated state (whl, Fig. 4) using photons with energy $E_{ph} = 2.371$ eV, ($\lambda = 523$ nm).

Well annealed films are only darkened, see Fig. 5. For a quantitative evaluation of photo-darkening we shall consider only darkening induced by photons with energy $E_{ph} = 2.515$ eV ($\lambda = 493$ nm) and $E_{ph} = 2.371$ eV ($\lambda = 523$ nm) where the condition $dph \geq 1/\alpha$ is fulfilled. In Fig. 7 photo-induced gap changes ($dE_g = E_{g,i} - E_{g,a}$) are shown versus the number of absorbed photons/cm³ (n_{abs}):

$$n_{abs} = n_{ph}(1 - R - T_t)/d, \text{ for } dph > 1/\alpha ; n_{abs} = n_{ph} (1 - R - T_t)\alpha t, \text{ for } dph \approx 1/\alpha, \quad (3)$$

where n_{ph} is the incident photon flux, T_t , αt are the actual transmission and absorption coefficient at a given time (t) of illumination. Full curves in Fig. 7 are calculated using Rel.:

$$dE_g = (E_{g,\infty} - E_{g,a})(1 - \exp[-(n_{abs}/N_{ph})\beta]), \quad (4)$$

where $E_{g,\infty}$ is the gap value for a saturated state, $E_{g,a}$ is the gap for well annealed film, N_{ph} is the effective number of photons and β is the stretching parameter. The difference in dE_g values for identical number of absorbed photons indicates that the process can be spectral sensitive (the photon flux for both the excitation lights is comparable, see Table 1). The darkening induced by photons with $\lambda = 493$ nm can be partly bleached by illumination with below gap photons ($\lambda = 660$ nm) but also using over gap photons ($\lambda = 523$ nm) that is using the photons with energy smaller than photons used for darkening, see Fig. 8, where the full curves are calculated using Rel. (4). Of interest is that the bleaching induced by over-gap photons is rather effect of a quick process ($\beta(\lambda = 523 \text{ nm}) = 0.757 > \beta(\lambda = 660 \text{ nm}) = 0.525$), but the magnitude of bleaching is lower than the magnitude of bleaching induced by below-gap photons. We suppose that this behavior reflects a spectral sensitivity of the process. The excitation light used for darkening ($\lambda = 493$ nm) excites relevant, for darkening susceptible ground states. Below gap light is practically ineffective to excite the ground state and to produce observable darkening (within four hours of illumination, $\lambda = 660$ nm, we did not observe any darkening). Consequently, the below-gap light can only transform a darkened state back to the ground state or to a state similar to the ground state. The over-gap light ($\lambda = 523$ nm) can, however, transform only smaller part of the states darkened in advance by the light with $\lambda = 493$ nm, because this light ($\lambda = 523$ nm) itself is susceptible to produce darkening, see Fig. 5. Hence a dynamical equilibrium between darkening and bleaching (forward and backward processes) limits the magnitude of bleaching induced by over-gap photons ($\lambda = 523$ nm).

Unfortunately, no definitive conclusion can be done from studied photo-darkening process of the well annealed films, because the process is not fully reversible. After annealing of the darkened state, ($dE_g = -150$ meV), see Fig. 6, the film is only partially bleached ($dE_g \approx +80$ meV) and reversible darkening we observed between this second annealed state and subsequent illumination/darkening. This true reversible darkening is around 80 meV only, see Fig. 6.

The complicated response of studied a-Ge_{13.3}As_{35.7}S₅₁ film on illumination we tentatively attribute to complicated film network composed most probably from Ge-S based and As-S based networks with some nano-scale separation in both the cases. Moreover, if in the network As₄S₄ molecular entities are present, see Rel. (3) some irreversibility of the response on the illumination can be associated with photo-induced transformation of the realgar and/or β -As₄S₄ phase to pararealgar [22]. If also photo-induced transformation between both phases (α -phase - dimorphite I and β -phase - dimorphite II, [32,33]) of As₄S₃ exists this one can also assists to some irreversibility of the first photo-induced changes of well annealed a-Ge_{13.3}As_{35.7}S₅₁ film. Following Ref. [34] we suppose that studied film represents the example of a network with several nano-phases. Consequently, we speculate that a two-phase structural model as suggested in Ref. [35] can be relevant to studied films.

5. Conclusion

The photo-induced phenomena in a-Ge_{13.3}As_{35.7}S₅₁ film are complicated. Illumination of the virgin film using over-gap photons leads only to a small overall bleaching. This state of the film can, however, be again bleached by illumination using nearly band-gap photons. This behavior is taken as an indirect indication of simultaneously passing both the irreversible and reversible processes induced by illumination using over-gap photons and white light. Annealing of the virgin films leads to considerable bleaching ($\approx +173$ meV). The first illumination of the well annealed film results into significant darkening by about ≈ -150 meV for over-gap photons ($\lambda = 493$ nm). This darkening, however, is not completely reversible. We observed reversible darkening of the magnitude around -80 meV, only for the second and next illumination-annealing cycles. We speculate that observed photo-induced changes reflects rather complicated network arrangement of studied film which consists most probably from at least two nano-phase separated interpenetrating networks based on a-Ge-S network and a-As-S network.

Acknowledgement

We acknowledge the support from the project GA CR 202/98/K002 and from the project AVOZ 4050913.

We are indebted to Assoc. Prof. Miloslav Vlček (Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice) for Raman spectra measurements and to Dr. M. Vlček from our Laboratory for EDX analysis.

References

- [1] Ke. Tanaka, T. Nakagawa, A. Odajima, *Phil. Mag.* **B54**, L3-L7 (1986).
- [2] P. Arsova, E. Vateva, M. Nikiforova, E. Skordeva, E. Savova, *Proceedings of the Sixth International School on Physical Problems in Microelectronics, Varna 1989, Singapore* World Scientific, p. 267.
- [3] E. Skordeva, D. Arsova, E. Vateva, L. Petkov, M. Nikiforova, *Proceedings of the International Conference on Non-Crystalline Semiconductors, Uzhgorod* p. 216 (1989).
- [4] E. Vateva, E. Skordeva, D. Arsova, *Phil. Mag.* **B67**, 225 (1993).
- [5] K. Christovova, Z. Dimitrova, E. Skordeva, *Thin Solid Films* **306**, 174 (1997).
- [6] M. Popescu, F. Sava, A. Lorinczi, E. Skordeva, P. J. Koch, H. Bradaczek, *J. Non-Crystalline Solids* **230**, 719 (1998).
- [7] E. Skordeva, T. Christova, M. Tzolov, Z. Dimitrova, *Appl. Phys. A- Mat. Science & Processing* **66**, 103 (1998).
- [8] O. I. Shpotyuk, A. P. Kovalskiy, E. Skordeva, E. Vateva, D. Arsova, R. Ya. Golovchak, M. M. Vakiv, *Physica B* **271**, 242 (1999).
- [9] O. I. Shpotyuk, M. M. Vakiv, A. P. Kovalskiy, E. Skordeva, E. Vateva, D. Arsova, R. Ya. Golovchuk, R. V. Lutsiv, *Glass Physics and Chemistry* **26**, 260 (2000).
- [10] M. Klebanov, V. Lyubin, D. Arsova, E. Vateva, V. Pamukchieva, *Physica B* **301**, 399 (2001).
- [11] A. Kovalskiy, *J. Optoelectron. Adv. Mater.* **3**, 323 (2001).
- [12] E. Vateva, E. Skordeva, *J. Optoelectron. Adv. Mater.* **4**, 3 (2002).
- [13] K. Petkov, B. Dinev, *J. Mater. Sci.* **29**, 468 (1994).
- [14] R. Ston, M. Vlček, H. Jain, *XIIIth International Symposium on Non-Oxide Glasses and New Optical Materials, Extended Abstracts Vol. 1, University of Pardubice (M. Frumar, P. Němec, T. Wágner, B. Frumarová and E. Černošková eds.)* Pardubice, 2002, p. 200.
- [15] Ke. Tanaka, *J. Non-Crystalline Solids* **103**, 149 (1988), *Phys. Rev.* **B 39**, 2270 (1989).
- [16] J. C. Phillips, in *"Rigidity Theory and Applications"*, (M. F. Thorpe and P. M. Duxbury eds.),

- Kluwer Academic/Plenum Publishers, N.Y., 2000, p. 155.
- [17] J. Tauc, R. Grigorovici, A. Vancu, *phys. stat. sol.* **15**, 627 (1966).
- [18] S. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, Engelwood Cliffs, N.J., 1971.
- [19] M. Munzar, L. Tichý, H. Tichá, *Current Appl. Phys.* **2**, 181 (2002).
- [20] M. D. Mikhailov, I. I. Kryzhanowsky, I. M. Petcherizin, *J. Non-Crystalline Solids* **263**, 1 (2000).
- [21] M. Munzar, L. Tichý, *J. Phys. Chem. Solids* **61**, 1647 (2000).
- [22] M. Muniz-Miranda, G. Sbrana, P. Bonazzi, S. Menchetti, G. Pratesi, *Spectrochimica Acta, Part A* **52**, 1391 (1996).
- [23] T. Kawaguchi, S. Maruno, Ke. Tanaka, *J. Appl. Phys.* **73**, 4560 (1993).
- [24] Ke. Tanaka, *J. Non-Crystalline Solids* **35/36**, 1023 (1980).
- [25] B. G. Aitken, C. W. Ponader, *J. Non-Crystalline Solids* **274**, 124 (2000).
- [26] B. H. Christian, R. J. Gillespie, J. F. Sawyer, *Inorg. Chem.* **20**, 3410 (1981).
- [27] J. S. Lannin, *Phys. Rev.* **B 15**, 3864 (1977).
- [28] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, *Phys. Rev.* **B 10**, 5134 (1974).
- [29] P. Boolchand, J. Grothaus, M. Tenhover, M. A. Hazle, R. K. Grasseli, *Phys. Rev.* **B 33**, 5421 (1986).
- [30] K. Jackson, A. Briley, S. Grossman, D. V. Porezag, M. R. Pederson, *Phys. Rev.* **B60**, 14985 (1999).
- [31] G. Lucovsky, *Vibrational Properties of Amorphous Solids in "Physical Properties of Amorphous Materials"* (D. Adler, B. B. Schwartz, M. C. Steele eds.), Institute for Amorphous Materials Studies-Series, Plenum Press, N.Y., 1985.
- [32] H. J. Whitfield, *J. Chem. Soc.* **A10**, 1820 (1970).
- [33] L. S. Franchel, T. Zolotoi, Z. Krist, **138**, 161 (1973).
- [34] S. Mamedov, D. G. Georgiev, Tao Qu, P. Boolchand, in *Proceedings of the conference "Glass and Optical Materials"* American Ceramic Society, Pittsburgh, Pa, October 13-16, 2002.
- [35] Ke. Tanaka, in *"Reviews of Solids State Science"* **4(2&3)**, 641 (1990).