



## **An Insight into the photoinduced phenomena in ternary Ge-Sb-Se sputtered thin films**

T. Halenkovič, M. Kotrla, J. Gutwirth, V. Nazabal, P. Nemec

### **► To cite this version:**

T. Halenkovič, M. Kotrla, J. Gutwirth, V. Nazabal, P. Nemec. An Insight into the photoinduced phenomena in ternary Ge-Sb-Se sputtered thin films. *Photonics research*, 2022, 10 (9), pp.2261-2266. <10.1364/PRJ.460552>. <hal-03798863>

**HAL Id: hal-03798863**

**<https://hal.science/hal-03798863v1>**

Submitted on 23 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# An insight into the photoinduced phenomena in ternary Ge-Sb-Se sputtered thin films

TOMÁŠ HALENKOVIČ,<sup>1,\*</sup> MAGDALÉNA KOTRLA,<sup>1</sup> JAN GUTWIRTH,<sup>1</sup> VIRGINIE NAZABAL<sup>2,1</sup> AND PETR NĚMEC<sup>1,\*</sup>

<sup>1</sup>Department of Graphic Arts and Photophysics, University of Pardubice, Pardubice, Czech Republic

<sup>2</sup>Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

\*tomas.halenkovic@upce.cz

\*petr.nemec@upce.cz

**Abstract:** The kinetics of photoinduced changes, namely photobleaching and photodarkening in sputtered ternary Ge<sub>29</sub>Sb<sub>8</sub>Se<sub>63</sub> thin films was studied. Study of time evolution of absorption coefficient  $\Delta\alpha(t)$  upon room-temperature near-bandgap irradiation revealed several types of photoinduced effects. The as-deposited films exhibited a fast photodarkening followed by dominative photobleaching process. Annealed thin films were found to undergo photodarkening only. Local structure studied by Raman scattering spectroscopy showed significant structural changes upon thermal annealing which are presumably responsible for a transition from the photobleaching observed in as-deposited and reversible photodarkening in annealed thin films. Moreover, transient photodarkening process was observed in both as-deposited as well as in annealed thin films. An influence of the initial film thickness and laser optical intensity onto the kinetics of photoinduced changes is discussed.

© 2021 Optica Publishing Group under the terms of the [Optica Publishing Group Open Access Publishing Agreement](#)

## 1. Introduction

Photostructural changes in amorphous chalcogenide thin films and chalcogenide glasses have been extensively studied for many decades [1]. Chemical bond rearrangement induced by the light excitation having the energy near the bandgap of these materials leads to the modifications of amorphous matrix resulting in changes of optical properties [2]. These are referred to a photodarkening (PD) and a photobleaching (PB) depending on a sign of a change [3]. The magnitude of PD and PB is related to the composition and the structure of chalcogenide materials. While in the binary arsenic-based chalcogenides only PD occurs, both germanium-based binaries [4, 5] and ternaries show rather complex behavior with a sign of the change being a product of a competitive processes of PD and PB [6, 7].

The PD of exposed annealed films of As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>Se<sub>3</sub> which may be partially recovered by the consequent annealing was reported as early as in 1970s by De Neufville *et al.* [1]. It is considered that the as-deposited amorphous chalcogenide thin films possess the irreversible photoinduced changes while the annealed films and melt-quenched glasses undergo the reversible ones [8]. Recently, the waveguide inscription using femtosecond lasers (ultrafast laser inscription, ULI) attracted the attention of some researchers [9, 10]. This process includes the nonlinear absorption of sub-bandgap light resulting in changes in refractive index. Results on ULI in Ge-Sb-S glasses by means of structural study suggest that the driving forces of PD during the ULI in chalcogenide glasses are of the same origin as the photostructural changes due to the near-bandgap continuous-wave laser irradiation [10]. A better comprehension of the processes and variables involved in photoinduced phenomena may play an important role for potential applications, optimization and tailoring properties of these materials in field of photonic integrated circuits, holographic gratings and waveguide inscription [11].

The aim of this paper is to provide a study of photoinduced changes in Ge-Sb-Se chalcogenide thin films which are of particular interest in the field of photonic integrated circuits for their potential application in non-linear optics [12] and optical sensors in mid-infrared domain [13, 14]. The nominal composition of  $\text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65}$  was chosen based on our previous work related to photosensitivity study on this system [15]. It combines favorable optical properties and expected photosensitivity. Relatively high optical bandgap energy causes the orange color of thin films within range of thicknesses under study which in combination with low surface reflectivity allows an easy detection of photoinduced changes. The insight in the photoinduced changes provided in this paper summarizes up to date available references and tries to recognize the challenges in understanding the general principles of these phenomena. The influence of a thickness and the laser optical intensity onto the kinetics of these processes is discussed.

## 2. Methods

A sputtering target ( $\phi = 50$  mm) of  $\text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65}$  chalcogenide glass was synthesized by melt-quenching technique described elsewhere [16]. Thin films with thicknesses  $d$  of 350, 500, and 650 nm were deposited by rf-sputtering (13.56 MHz) at  $5 \times 10^{-3}$  mbar working pressure of argon onto well-cleaned microscope slides (soda-lime float glass, substrate length of 76 mm). The variance in the thickness was estimated to be  $< 6\%$  within the substrate length. Selected thicknesses were found to be optimal for our experiments as the penetration depth of a pump laser described below is  $\sim 700$  and  $\sim 1800$  nm for as-deposited and annealed films, respectively.

Composition of thin films was verified by energy-dispersive X-ray spectroscopy (EDS) joint with scanning electron microscope (JEOL IT-300, JEOL Ltd., Japan). X-ray diffraction (XRD) patterns were collected within the range of  $2\theta$  from  $10^\circ$  to  $80^\circ$  with a step of  $0.02^\circ$  (Cu K- $\alpha$ , Rigaku, Japan). Thickness of thin films and its initial optical properties, specifically refractive index  $n$  and the optical bandgap energy  $E_g$ , were determined from variable angle spectroscopic ellipsometry (VASE, J. A. Woollam, USA).

Annealing of samples was performed at temperature of  $250^\circ\text{C}$  (*i.e.* glass transition temperature of bulk  $T_g - 50^\circ\text{C}$ ) for 2 hours (heating rate of  $2^\circ\text{C} \cdot \text{min}^{-1}$ , cooling rate of  $1^\circ\text{C} \cdot \text{min}^{-1}$ ) under argon atmosphere.

Kinetics of photoinduced changes of both as-deposited and annealed samples at the room temperature was studied by means of *in situ* transmittance measurements captured by fiber-coupled high-resolution spectrometer (OceanInsight, USA). Samples were placed in a hermetically sealed cell equipped with quartz windows filled with pure argon gas and irradiated by near-bandgap light coming from 589 nm (2.1 eV) continuous-wave DPSS laser source (Shanghai Laser & Optics Century co., Ltd., China) for 180 minutes. The experimental setup for *in situ* kinetics measurements is depicted in Fig. 1(a). In order to retain the athermal nature of photoinduced changes low to moderate laser optical intensities, specifically  $3.0 \pm 0.5$ ,  $19.0 \pm 2.5$ ,  $50.0 \pm 3.0$  and  $125 \pm 5.0$   $\text{mW} \cdot \text{cm}^{-2}$  were used.

The changes were expressed as the time evolution of absorption coefficient  $\Delta\alpha(t)$  calculated as  $\Delta\alpha(t) = \ln[T_0 \cdot T(t)^{-1}] \cdot d^{-1}$ , where  $T_0$  is the initial transmittance,  $T(t)$  is the transmittance at elapsed time  $t$ . Selected value of the initial transmittance at irradiation wavelength was  $\approx 18\%$ , corresponding to the region of exponential absorption edge (Urbach edge, at initial value of absorption coefficient  $\alpha$  in order of  $\sim 10^4 \text{ cm}^{-1}$ ). It is worth to note that the small changes in the thickness are expected during the irradiation (such as photoinduced volume change in  $\text{As}_2\text{S}_3$  chalcogenide glass [17]); however, this effect does not affect the value of  $\Delta\alpha$  significantly. Changes in the reflectance during the irradiation were also neglected.

The magnitude of absorption edge shift by means of a change of  $E_g$  succeeding the irradiation was determined directly from transmittance measurements using WVASE32 software (J. A. Woollam, USA). It should be emphasized that the evaluation of absolute values of  $E_g$  and its changes was not the target of this work and so the precision of the estimation using this approach is rather coarse with expected accuracy about  $\pm 0.02$  eV.

### 100 3. Results and Discussion

#### 101 3.1. Optical properties of thin films

102 Chemical composition of vitreous target was found to be  $\text{Ge}_{24}\text{Sb}_{11}\text{Se}_{66}$  ( $\pm 1$  at. %). In agreement  
 103 with a previous work on this system [16], the slight changes in stoichiometry during the  
 104 sputtering process were observed as the composition of thin films was  $\text{Ge}_{29}\text{Sb}_8\text{Se}_{63}$  ( $\pm 1$  at. %).  
 105 Optical bandgap energy  $E_g$  of as-deposited thin films was  $1.87 \pm 0.02$  eV and the refractive index  
 106  $n$  at 1 550 nm is  $2.55 \pm 0.01$  as determined by VASE using Cody-Lorentz oscillator model. An  
 107 annealing treatment caused bleaching of thin films resulting in optical bandgap energy increase  
 108 to  $1.96 \pm 0.02$  eV accompanied with slight refractive index decrease down to  $2.54 \pm 0.01$ . Both  
 109 as-deposited as well as annealed ones were found to be amorphous according the XRD  
 110 measurements.

111 As shown in Fig. 1(b) the prolonged irradiation caused the change of an opposite sign,  
 112 *i.e.* PB in as-deposited films and PD in annealed ones, reasonably of a highest magnitude when  
 113 the laser optical intensity of  $125 \text{ mW} \cdot \text{cm}^{-2}$  was used. It should be noted that even after three  
 114 hours of irradiation the photoinduced change is not fully saturated and so for the measurements  
 115 at lower laser optical intensities the irradiation time was conserved.

116 The highest magnitude of PB by means of an increase in  $E_g$  about  $0.04 \pm 0.02$  eV was found  
 117 in the sample with the thickness of  $\sim 350$  nm. On the other hand, the highest measure of PD,  
 118 specifically the decrease in  $E_g$  by  $0.05 \pm 0.02$  eV, was found in sample with thickness of  $\sim 650$   
 119 nm at above mentioned conditions.

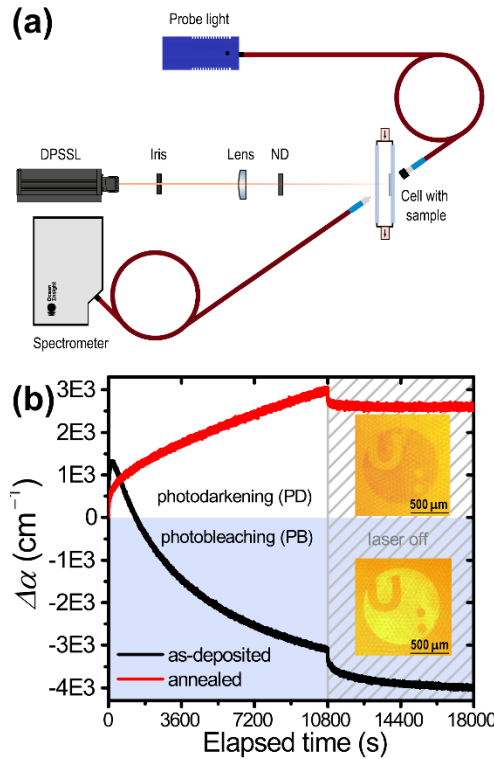


Fig. 1. (a) Experimental setup for irradiation setup for *in situ* measurements. A pump beam from DPSSL laser is aimed onto the sample through the plano-convex lens and its desired optical intensity is adjusted by the neutral density filter(s) (ND). (b) A typical time evolution of absorption coefficient  $\Delta\alpha(t)$  for as-deposited film (black) and annealed film (red) upon room-

temperature irradiation at laser optical intensity of  $125 \text{ mW} \cdot \text{cm}^{-2}$ ; shaded region represents the data acquisition after the laser is switched off; inserts with photodarkened (top) and photobleached (bottom) University of Pardubice logo using 1 mm diameter negative stencil (colors are illustrational only without profiling).

### 3.2 Millisecond kinetics of photoinduced changes

Study of time evolution of absorption coefficient  $\Delta\alpha(t)$  revealed several types of photoinduced effects. First, as-deposited films exhibit fast PD which is entirely dominated by PB in long-term. Such behavior has already been observed in some as-deposited selenide films *e.g.* in evaporated  $\text{GeSe}_2$  [18] and  $\text{Ge-As-Se}$  [7], pulsed laser deposited  $\text{Ge-Sb-Se}$  [19] or in cosputtered  $\text{Ga-Sb-Se}$  [20]. Moreover, only PD takes places during the irradiation of annealed films. Finally, transitory change, specifically transient PD (TPD), was observed in both as-deposited as well as in annealed thin films.

As seen in Fig. 2 (top panel), PB in as-deposited thin films is strongly thickness dependent having the magnitude of a process indirectly proportional to the thickness. It is worthy to note that the PB effect in the film with thickness of  $\sim 350 \text{ nm}$  (violet curve) is closest to being saturated when irradiated by  $125 \text{ mW} \cdot \text{cm}^{-2}$  laser optical intensity. Presumably, the observed PB effect upon prolonged near-bandgap irradiation is of a similar origin as the bleaching upon thermal annealing. Such change is coming from a mutual polymerization of defective entities resulting in ordered structures *via* homo- to heteropolar bond conversion [1]. The excitation generates the charged radiation defects followed by recombination-induced bond rearrangements due to the diffusion of atoms [21]. Although the photoexcited states have not yet been proven experimentally [22], their existence leading to an increased short- and medium-range order [23] is generally accepted explanation of irreversible changes in different properties including absorption edge shift. Other stabilization mechanisms, such as void collapsing [22], evaporation of volatile entities, and the photo-enhanced oxidation [24] may contribute to these changes. As the experiments performed in frame of this work were carried out in a pure argon atmosphere, we do not expect the last mentioned has an important contribution to observed effects.

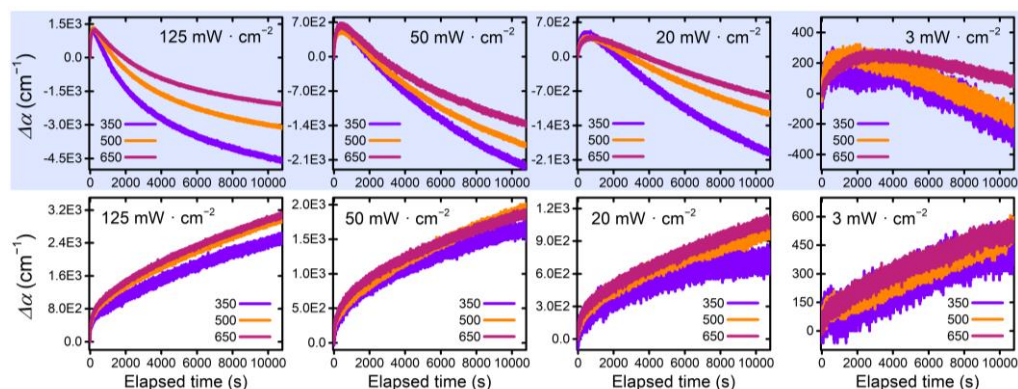


Fig. 2. Time evolution of absorption coefficient  $\Delta\alpha(t)$  of as-deposited (top panel) and annealed (bottom panel)  $\text{Ge-Sb-Se}$  thin films upon room-temperature irradiation depending on thicknesses at different laser optical intensities varying from 3 to  $125 \text{ mW} \cdot \text{cm}^{-2}$ . (This figure should not be reduced).

In contrast with PB observed in as-deposited thin films, the PD in annealed thin films as seen in Fig. 2 (bottom panel) is proportionally dependent on the thickness and is a universal process observed in annealed chalcogenide glasses and thin films – *i.e.* reversible photodarkening effect – which may be recovered by thermal annealing. The mechanism of reversible changes is not yet known as no subtle structural changes have yet been experimentally determined. They are likely the result of a similar elemental process as the

irreversible ones, *i.e.* recombination-induced bond rearrangements and atom motions [3]. Presumably, the reversible photodarkening is coming from the valence band broadening resulting in the red-shift [22].

The origin of fast PD in as-deposited films is not yet fully understood. Sati and Jain [6] proposed that it originates in homo- to heteropolar bond conversion at deformed sites such as Se–Se dimers at the  $[\text{GeSe}_{4/2}]$  or Sb–Sb bonds caused by Sb–Sb–Se in defective  $[\text{SbSe}_{3/2}]$  pyramidal units, present in evaporated Ge–Sb–Se thin films, and is simply a competitive process to slow PB which becomes dominant in long-term. Relative to time, the magnitude of PB is rather small compared to PD.

Besides being thickness dependent, fast PD and slow PB in as-deposited and reversible PD in annealed Ge–Sb–Se thin films are strongly dependent on laser optical intensity as depicted in Fig. 3(a) and (b) respectively. The time evolution of fast PD shows a saturation at  $125 \text{ mW} \cdot \text{cm}^{-2}$  within  $\sim 245 \text{ s}$  and clearly delays with a decreasing intensity. Similar observation was reported for evaporated Ge–As–Se films by Khan *et al.* [25]. The process of fast PD becomes completely dominated by slow PB process.

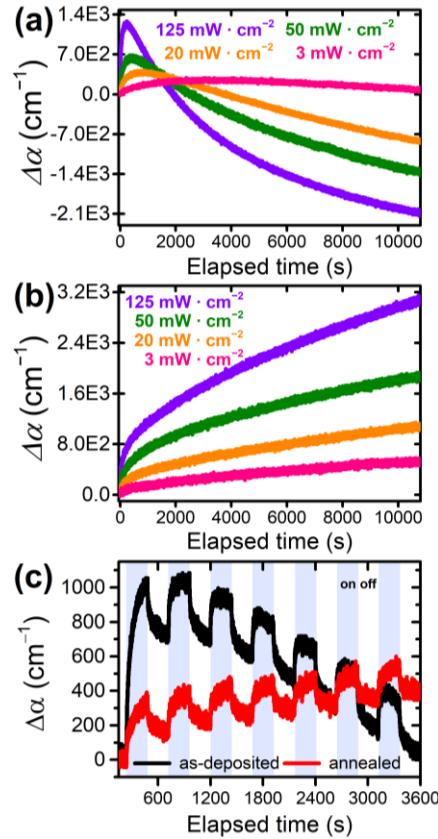


Fig. 3. (a) Time evolution of absorption coefficient  $\Delta\alpha(t)$  of as-deposited and (b) annealed Ge–Sb–Se thin films with thickness of  $\sim 650 \text{ nm}$  depending on the laser optical intensity. (c) On/off cycles (240 s) experiment with as-deposited (black line) and annealed (red line) Ge–Sb–Se thin films with the same thickness using laser optical intensity of  $50 \text{ mW} \cdot \text{cm}^{-2}$ . The shaded area corresponds to the cycle when the laser is switched on.

Transitory changes by means of transient PD (TPD) were easily noticed by on/off experiments found in Fig. 3(c). TPD has already been observed by various authors [7, 19, 26–29] and may be related to a phenomenon termed as an ‘optical stopping effect’ by Matsuda *et al.* back in 1970s [30]. Ganjoo *et al.* [27] observed TPD in annealed evaporated amorphous

selenium a-Se and As<sub>2</sub>Se<sub>3</sub> of ~ 500 nm thickness when irradiated by Ar ion laser ( $\lambda = 514$  nm, optical intensity of  $80 \text{ mW} \cdot \text{cm}^{-2}$ ). An apparent rise in the transmittance after switching the laser off ( $\lambda = 488$  and  $660$  nm,  $150 \text{ mW} \cdot \text{cm}^{-2}$ ) was also reported for  $1 \mu\text{m}$  thick as-deposited GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> evaporated films by Yan *et al.* [28]. Similar behavior was found in sputtered as-deposited Ge-As-Se thin films at different intensities when exposed to  $655$  nm laser diode [29]. Additionally, the magnitude of TPD among the references herein seems to be affected by the optical intensity and the metastable PD or PD depending on composition. The structural origin of TPD is yet to be understood. *In situ* EXAFS experiments on amorphous selenium indicate that it may be associated to a chalcogen coordination number increase upon irradiation [22, 31].

Finally, the results on millisecond kinetics of photoinduced changes in as-deposited and annealed Ge-Sb-Se thin films suggest that they are of a very same origin as in Ge-As-Se system [29]. Even though the sign and the magnitude of a change may differ with a composition and the structure [5, 7, 15], the TPD and reversible PD in annealed thin films seem to be a universal feature of photoinduced changes in amorphous chalcogenides.

### 3.3 Structural changes upon annealing and the irradiation

Changes in local structure upon thermal annealing and irradiation were investigated using Raman scattering spectroscopy measurements. As depicted in Fig. 4, the Raman spectra of Ge-Sb-Se thin films are *prima facie* dominated by the band peaking at  $\sim 199 \text{ cm}^{-1}$ , which corresponds to  $A_1$  symmetric stretching vibrations of heteropolar Ge-Se bonds in a corner-sharing [GeSe<sub>4/2</sub>] tetrahedra. The companion mode  $A'_1$  assigned to edge-sharing tetrahedral units is located at  $\sim 214 \text{ cm}^{-1}$ , [32]. Overlapping  $E_1$  mode of [SbSe<sub>3/2</sub>] pyramidal units around  $\sim 191 \text{ cm}^{-1}$  may contribute to the Raman intensity of  $A_1$  mode [33]. Peak around  $\sim 174 \text{ cm}^{-1}$  is considered to be coming from Ge-Ge homopolar bonds in ethane-like [Ge<sub>2</sub>Se<sub>6/2</sub>] units [34]. Vibrational modes of Sb-Sb in [Se<sub>2</sub>Sb-SbSe<sub>2</sub>] found at  $\sim 160 \text{ cm}^{-1}$  probably contribute to this peak [35].

In order to justify changes in the structure, Raman spectra were deconvoluted using 8 Gaussian peaks. Besides five peaks mentioned above, the rotational modes in selenium polymeric chains ( $\sim 140 \text{ cm}^{-1}$ , [35]) and bending vibrational modes of Se-Se at the outrigger ( $135\text{--}145 \text{ cm}^{-1}$ , [36]) are altogether represented by Gaussian peak centered at  $\sim 134 \text{ cm}^{-1}$ .  $A_1$  vibrational mode of Se<sub>n</sub> chains in amorphous selenium found at  $\sim 235 \text{ cm}^{-1}$ , stretching vibrational modes of Se-Se bonds at the outrigger ( $\sim 245 \text{ cm}^{-1}$ ),  $A_1$  vibrational modes of Se-Se dimers and short Se<sub>n</sub> chains in corner-linked [GeSe<sub>4/2</sub>], ( $\sim 260\text{--}265 \text{ cm}^{-1}$ , [35]), and Ge-Ge homopolar bonds' vibrations coming from [Ge-Ge<sub>m</sub>Se<sub>4-m</sub> ( $m = 1, 2, 3, 4$ )], found  $\sim 270 \text{ cm}^{-1}$  [34] are collectively represented by Gaussian at  $\sim 262 \text{ cm}^{-1}$ . Finally,  $F_1$  asymmetric vibrational modes of GeSe<sub>4</sub> tetrahedrons are found at  $\sim 300 \text{ cm}^{-1}$ , [32].

Upon thermal annealing an apparent change in the ratio between  $A_1$  (green) and  $A'_1$  (blue) peaks occurred. Simultaneous decrease in the intensity of a peak centered at  $\sim 134 \text{ cm}^{-1}$  (red) and  $\sim 262 \text{ cm}^{-1}$  (orange) indicates the consumption of selenium atoms as a consequence of increased local order. Other noticeable changes occurred around  $\sim 174 \text{ cm}^{-1}$  peak. These changes may be due to a decrease of Ge-Ge homopolar bonds in ethane-like [Ge<sub>2</sub>Se<sub>6/2</sub>] units. Changes in intensity of surrounding peaks upon thermal annealing are low and difficult to justify.

Photostructural changes by means of Raman scattering spectroscopy have already been described by several authors. The bond breaking mechanism upon the irradiation followed by bond rearrangement and/or crystallization of structural sites are usually connected with changes in optical properties (*i.e.* shift of the absorption edge and the refractive index changes upon irradiation) [4, 7, 37]. Noteworthy, even in highly photosensitive composition of As<sub>2</sub>S<sub>3</sub>, the fully saturated PD process results in only up to 1 % of nearest neighbors bonds' alteration at available atomic sites [2]. As only low to moderate laser optical intensities were used in the



present study negligible changes in Raman spectra were observed and do not allow a fine analysis of the mechanisms involved.

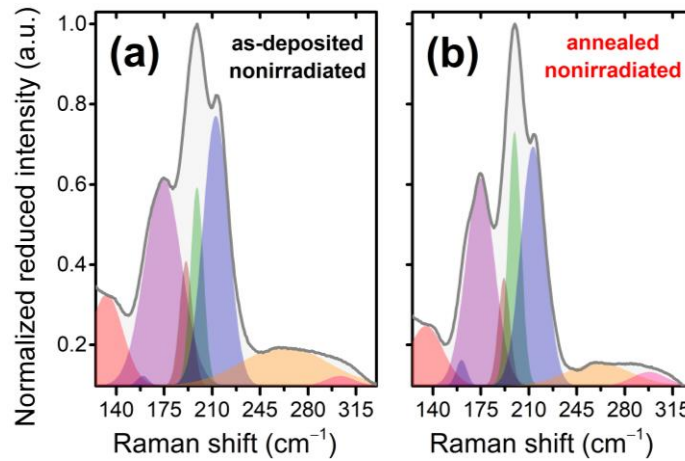


Fig. 4. (a) Normalized reduced intensity of Raman spectra of nonirradiated as-deposited, and (b) nonirradiated annealed Ge-Sb-S thin films.

It can be assumed that above mentioned structural changes upon thermal annealing are responsible for a transition from the PB observed in as-deposited and reversible PD in annealed Ge-Sb-Se thin films respectively. In addition, although the experiments were carried out under the pure argon atmosphere the photo-enhanced oxidation should be not completely ruled out from the contribution to the photoinduced changes as the concentration of germanium is  $\sim 29$  at. % [38].

#### 4. Conclusions

Comprehensive study of photosensitivity in amorphous  $\text{Ge}_{29}\text{Sb}_8\text{Se}_{63}$  thin films by means of time evolution of the absorption coefficient  $\Delta\alpha(t)$  revealed several types of photoinduced effects in these materials. Fast PD followed by slow dominative PB process is present in as-deposited films while only PD takes places during prolonged irradiation of annealed films. The structural changes upon thermal annealing seem to be responsible for a transition from the PB observed in as-deposited and reversible PD in annealed thin films. Transient PD (TPD) was observed in both as-deposited as well as in annealed thin films and, together with a PD in annealed films, seems to be a universal feature of photoinduced changes in amorphous chalcogenides. The processes behind metastable PD and PB in the as-deposited films as well as TPD, which seem to be associated with transitory photoexcited states, remain to be better understood. Furthermore, the throughout study of surface and thickness changes upon the irradiation and annealing as well as long-term stability at normal room conditions in similar systems are also of interest. Such investigations may lead towards the implementation of these materials and photonic processes in them in the design and engineering of photonic integrated circuits by means of tailoring and optimization of optical properties and inscription of tree-dimensional structures (*e.g.* waveguides, holographic gratings and diffractive optics elements).

#### Funding

Czech Science Foundation (project No. 22-05179S). Ministry of Education, Youth and Sports of the Czech Republic (project No. LM2018103).

#### Disclosures



The authors declare that they have no competing financial interests.

## Data availability

Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

## References

1. J. P. De Neufville, S. C. Moss, and S. R. Ovshinsky, "Photostructural transformations in amorphous As<sub>2</sub>Se<sub>3</sub> and As<sub>2</sub>S<sub>3</sub> films," *Journal of Non-Crystalline Solids* **13**, 191-223 (1974).
2. S. Ducharme, J. Hautala, and P. C. Taylor, "Photodarkening profiles and kinetics in chalcogenide glasses," *Physical Review B* **41**, 12250-12259 (1990).
3. H. Fritzsche, "The origin of reversible and irreversible photostructural changes in chalcogenide glasses," *Philosophical Magazine Part B* **68**, 561-572 (1993).
4. R. R. Kumar, A. R. Barik, E. M. Vinod, M. Bapna, K. S. Sangunni, and K. V. Adarsh, "Crossover from photodarkening to photobleaching in a-GeSe<sub>100-x</sub> thin films," *Opt. Lett.* **38**, 1682-1684 (2013).
5. T. Halenkovič, J. Gutwirth, T. Kuriakose, M. Bouška, M. Chauvet, G. Renversez, P. Němec, and V. Nazabal, "Linear and nonlinear optical properties of co-sputtered Ge-Sb-Se amorphous thin films," *Opt. Lett.* **45**, 1523-1526 (2020).
6. D. C. Sati and H. Jain, "Coexistence of photodarkening and photobleaching in Ge-Sb-Se thin films," *Journal of Non-Crystalline Solids* **478**, 23-28 (2017).
7. P. Khan, H. Jain, and K. V. Adarsh, "Role of Ge:As ratio in controlling the light-induced response of a-GeAs<sub>35-x</sub>Se<sub>65</sub> thin films," *Scientific Reports* **4**, 4029 (2014).
8. G. Pfeiffer, M. A. Paesler, and S. C. Agarwal, "Reversible photodarkening of amorphous arsenic chalcogenides," *Journal of Non-Crystalline Solids* **130**, 111-143 (1991).
9. A. Arriola, S. Gross, M. Ams, T. Gretzinger, D. Le Coq, R. P. Wang, H. Ebendorff-Heidepriem, J. Sanghera, S. Bayya, L. B. Shaw, M. Ireland, P. Tuthill, and M. J. Withford, "Mid-infrared astrophotonics: study of ultrafast laser induced index change in compatible materials," *Opt. Mater. Express* **7**, 698-711 (2017).
10. G. Torun, A. Yadav, K. A. Richardson, and Y. Bellouard, "Ultrafast Laser Direct-Writing of Self-Organized Microstructures in Ge-Sb-S Chalcogenide Glass," *Frontiers in Physics* **10**(2022).
11. A. Zakery and S. R. Elliott, "Optical properties and applications of chalcogenide glasses: a review," *Journal of Non-Crystalline Solids* **330**, 1-12 (2003).
12. E. Delcourt, N. Jebali, L. Bodiou, M. Baillieul, E. Baudet, J. Lemaitre, V. Nazabal, Y. Dumeige, and J. Charrier, "Self-phase modulation and four-wave mixing in a chalcogenide ridge waveguide," *Opt. Mater. Express* **10**, 1440-1450 (2020).
13. M. Baillieul, E. Baudet, K. Michel, J. Moreau, P. Němec, K. Boukerma, F. Colas, J. Charrier, B. Bureau, E. Rinnert, and V. Nazabal, "Toward Chalcogenide Platform Infrared Sensor Dedicated to the In Situ Detection of Aromatic Hydrocarbons in Natural Waters via an Attenuated Total Reflection Spectroscopy Study," *Sensors* **21**, 2449 (2021).
14. V. Mittal, G. Z. Mashanovich, and J. S. Wilkinson, "Perspective on Thin Film Waveguides for on-Chip Mid-Infrared Spectroscopy of Liquid Biochemical Analytes," *Analytical Chemistry* **92**, 10891-10901 (2020).
15. T. Halenkovič, J. Gutwirth, P. Němec, E. Baudet, M. Specht, Y. Gueguen, J.-C. Sangleboeuf, and V. Nazabal, "Amorphous Ge-Sb-Se thin films fabricated by co-sputtering: Properties and photosensitivity," *Journal of the American Ceramic Society* **101**, 2877-2887 (2018).
16. F. Verger, V. Nazabal, F. Colas, P. Němec, C. Cardinaud, E. Baudet, R. Chahal, E. Rinnert, K. Boukerma, I. Peron, S. Deputier, M. Guilloux-Viry, J. P. Guin, H. Lhermite, A. Moreac, C. Compère, and B. Bureau, "RF sputtered amorphous chalcogenide thin films for surface enhanced infrared absorption spectroscopy," *Opt. Mater. Express* **3**, 2112-2131 (2013).
17. K. Tanaka, "Photoexpansion in As<sub>2</sub>S<sub>3</sub> glass," *Physical Review B* **57**, 5163-5167 (1998).
18. A. R. Barik, R. Naik, and K. V. Adarsh, "Unusual observation of fast photodarkening and slow photobleaching in a-GeSe<sub>2</sub> thin film," *Journal of Non-Crystalline Solids* **377**, 179-181 (2013).
19. M. Olivier, R. Boidin, P. Hawlová, P. Němec, and V. Nazabal, "Kinetics of photosensitivity in Ge-Sb-Se thin films," in *2015 International Conference on Photonics, Optics and Laser Technology (PHOTOPTICS)*, (2015), 61-66.
20. T. Halenkovič, J. Gutwirth, M. Bouška, L. Calvez, P. Němec, and V. Nazabal, "Amorphous Ga-Sb-Se thin films fabricated by co-sputtering," *Opt. Lett.* **45**, 29-32 (2020).
21. Y. S. Kaganovskii, H. Genish, and M. Rosenbluh, "Laser Recording in Chalcogenide Glass Films: Driving Forces and Kinetics of the Mass Transfer," *physica status solidi (a)* **217**, 2000523 (2020).
22. K. Tanaka and K. Shimakawa, "Light-Induced Phenomena," in *Amorphous Chalcogenide Semiconductors and Related Materials* (Springer International Publishing, Cham, 2021), pp. 163-226.

23. L. Tichý, V. Smrčka, H. Tichá, E. Sileckx, and P. Nagels, "On the origin of photo-induced and thermally induced irreversible bleaching of amorphous Ge-Se films," *Philosophical Magazine Letters* **68**, 73-79 (1993).
24. C. A. Spence and S. R. Elliott, "Light-induced oxidation and band-edge shifts in thermally evaporated films of germanium chalcogenide glasses," *Physical Review B* **39**, 5452-5463 (1989).
25. P. Khan, A. R. Barik, E. M. Vinod, K. S. Sangunni, H. Jain, and K. V. Adarsh, "Coexistence of fast photodarkening and slow photobleaching in Ge<sub>19</sub>As<sub>21</sub>Se<sub>60</sub> thin films," *Opt. Express* **20**, 12416-12421 (2012).
26. K. Shimakawa and Y. Ikeda, "Transient responses of photodarkening and photoinduced volume change in amorphous chalcogenide films," *Journal of Optoelectronics and Advanced materials* **8**(2006).
27. A. Ganjoo, K. Shimakawa, K. Kitano, and E. A. Davis, "Transient photodarkening in amorphous chalcogenides," *Journal of Non-Crystalline Solids* **299-302**, 917-923 (2002).
28. Q. Yan, H. Jain, J. Ren, D. Zhao, and G. Chen, "Effect of Photo-Oxidation on Photobleaching of GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> Films," *The Journal of Physical Chemistry C* **115**, 21390-21395 (2011).
29. Z. Zhang, S. Xu, Y. Chen, X. Shen, and R. Wang, "Photo-induced effects in Ge-As-Se films in various states," *Opt. Mater. Express* **10**, 540-548 (2020).
30. A. Matsuda, H. Mizuno, T. Takayama, M. Saito, and M. Kikuchi, "Stopping effect" on guided light in As-S films by a laser beam," *Applied Physics Letters* **24**, 314-315 (1974).
31. A. V. Kolobov, H. Oyanagi, K. Tanaka, and K. Tanaka, "Structural study of amorphous selenium by in situ EXAFS: Observation of photoinduced bond alternation," *Physical Review B* **55**, 726-734 (1997).
32. P. Němec, B. Frumarová, and M. Frumar, "Structure and properties of the pure and Pr<sup>3+</sup>-doped Ge<sub>25</sub>Ga<sub>5</sub>Se<sub>70</sub> and Ge<sub>30</sub>Ga<sub>5</sub>Se<sub>65</sub> glasses," *Journal of Non-Crystalline Solids* **270**, 137-146 (2000).
33. Z. G. Ivanova, E. Cernoskova, V. S. Vassilev, and S. V. Boycheva, "Thermomechanical and structural characterization of GeSe<sub>2</sub>-Sb<sub>2</sub>Se<sub>3</sub>-ZnSe glasses," *Materials Letters* **57**, 1025-1028 (2003).
34. K. Jackson, A. Briley, S. Grossman, D. V. Porezag, and M. R. Pederson, "Raman-active modes of a-GeSe<sub>2</sub> and a-GeS<sub>2</sub>: A first-principles study," *Physical Review B* **60**, R14985-R14989 (1999).
35. M. Olivier, J. C. Tchahame, P. Němec, M. Chauvet, V. Besse, C. Cassagne, G. Boudebs, G. Renversez, R. Boidin, E. Baudet, and V. Nazabal, "Structure, nonlinear properties, and photosensitivity of (GeSe<sub>2</sub>)<sub>100-x</sub>(Sb<sub>2</sub>Se<sub>3</sub>)<sub>x</sub> glasses," *Opt. Mater. Express* **4**, 525-540 (2014).
36. E. Baudet, C. Cardinaud, A. Girard, E. Rinnert, K. Michel, B. Bureau, and V. Nazabal, "Structural analysis of RF sputtered Ge-Sb-Se thin films by Raman and X-ray photoelectron spectroscopies," *Journal of Non-Crystalline Solids* **444**, 64-72 (2016).
37. S. Zhang, Y. Chen, R. Wang, X. Shen, and S. Dai, "Observation of photobleaching in Ge-deficient Ge<sub>16.8</sub>Se<sub>83.2</sub> chalcogenide thin film with prolonged irradiation," *Scientific Reports* **7**, 14585 (2017).
38. L. Tichý, H. Tichá, K. Handlíř, and K. Jurek, "Photoinduced bleaching of Ge<sub>35</sub>S<sub>65</sub> amorphous film," *Journal of Non-Crystalline Solids* **101**, 223-226 (1988).