JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 10, October 2007, p. 3108 - 3114

Giant photo- and thermo-induced effects in chalcogenides

E. VATEVA
G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

The irreversible photo- and thermo-induced changes in optical parameters and volume of binary and ternary Ge-As-S(Se) films are reviewed and compared with the respective reversible changes in glasses and films. The reached giant values of the studied changes in thin films from a new Ge_2S_3-AsS_3 system are discussed and recommended for applications.

(Received July 3, 2007; accepted October 1, 2007)

Keywords: Chalcogenide thin films, Photo- and thermo-induced effects, Optical properties, Volume changes

1. Introduction

The giant photo-induced effects in chalcogenide glasses and films, and especially the giant photo-expansion, are recently a matter of great interest [1, 2]. A photo-induced (PI) change in the volume or thickness, i.e. a photo-expansion (PE), directly indicates that the structure of the material changes as a result of photo-excitation [3]. The PI red or blue shifts of the absorption edges, the photo-darkening (PD) or photo-bleaching (PB), respectively, are also connected with structural changes, although there is no one-to-one correlation between the two phenomena [1-3]. The high interest in these and other photo-induced phenomena is fostered by the need to clarify the currently debatable mechanism of the changes of volume and optical band gap, as well as by the possible applications utilizing the highest reached, giant, PI effects. For example, micro-lenses for optical fibers and aspherical micro-lenses for semiconductor lasers are produced on the base of the giant PE in annealed As_2S_3 films [1]. The great changes in the optical parameters are also promising for application in holographic recording.

The photo-induced changes are irreversible and reversible. Although the irreversible changes are higher than the reversible ones, which are important for the practical applications of the chalcogenide films, most of the studies and reviews address the reversible changes [3, 1]. In this work however, the attention will be centered on the irreversible photo-induced changes. The key results in binary and ternary Ge-As-chalkogenides are summarized and perspective materials showing giant irreversible changes in film thickness, optical band gap and refractive index are emphasized.

2. Irreversible photo- and thermo-induced changes in binary and ternary Ge-As-chalcogenides

Photo-induced absorption edge shift to longer wavelengths, PD, was established in the 1970s in as-evaporated $As_2S(Se)_3$ films [4]. The recovery after annealing near to the glass transition temperature (T_g) is not complete and reversible shifts are never as high as the irreversible ones. However in certain cases, especially when films were obtained by fast evaporation, absorption edge shift to shorter wavelengths, PB, was also observed [3]. The evaporation of chalcogenide compositions containing Ge is usually accomplished at high-temperature non-equilibrium conditions. The as-evaporated Ge-based chalcogenide films show PB as well, which is observed not only at high deposition rates, about 8-10 nm/s, but also at low rates (~1 nm/s) [5]. However, in some studies in ternary Ge-As-S compositions, no photo-induced changes were induced [3]. It was accepted that during illumination the wrong homopolar bonds of the as-evaporated films (formed from a large number of vapour species during the evaporation) are broken and heteropolar bonds are formed, thereby increasing the local stoichiometry. Assuming that the optical gap is minimal at the stoichiometric compositions of the As-based chalcogenides and maximal at the stoichiometric Ge-based ones, the absence of photo-induced effects was explained by mutual compensation of PD and PB in the As-based and Ge-based microregions of the films [3]. Our investigations of films from the system $Ge_xAs(Sb)_{40-x}S(Se)_{60}$ carried out since the 1980s [5-9] have shown that the appearance and magnitude of PB depends substantially on the composition. For example, the magnitude of the PB increases with the increase of the Ge-content, as in the binary Ge-S system [10], but only up to a maximal value at about x=27, regardless that at higher content of Ge the Ge-based microregions should increase further [7]. Clearly, other factors account for the maximal photo-induced changes at this composition. It is worth noting that` PB is also seen in ternary chalcogenide films after annealing at low enough temperatures, although in well annealed films the reversible process is usually PD. Reversible PB was observed by us originally in thin ~90 nm films from the $Ge_xAs_{40-x}S_{60}$ system annealed at 197 ^oC (far below T_g) [5] and will be further discussed.

Published maximal values of the irreversible photo- and thermo-induced darkening and bleaching, defined by the changes of the optical band gap E_g (calculated from the Tauc formula), and the accompanying changes in the refractive index n and thickness d are summarized in Table 1 for some binary and ternary Ge-As-S(Se) materials (data

for compositions with other elements or with two chalcogenes are not included in all tables).

The irreversible PD in *binary As-chalcogenides* defined by the decrease of E_g is not high; for example in As_2S_3 the value of $\Delta E_g/E_g$ is -1.5% [11]. As can be seen in Table 1, the PD is accompanied with an increase of the refractive index n of about 4% and a photo-contraction (PC) of about 1-2% [1, 11].

In the *binary Ge-chalcogenides* the irreversible PB is higher than 3%, reaches 8% in GeS_2 and is accompanied by 5.5% photo-expansion [11].

After annealing at temperatures near T_g all irreversible *thermo-induced changes* of the band gap in binary chalcogenides are in the direction of the photo-induced ones. In the As-chalcogenides the thermo-darkening (TD) is about 1-2% [12, 11] (accompanied by a thermo-contraction [1, 11]), while in the Ge-chalcogenides the thermo-bleaching (TB) reaches 17% [10, 11] (accompanied by a low thermo-contraction in GeS_2 [11]). According to Ref. 10, in the Ge-S system the thermo-induced changes in n and E_g agree qualitatively with the Moss' rule ($E_g n^4 \approx$ const).

In the *ternary compositions* from the $Ge_xAs_{40-x}S_{60}$ system the photo- and thermo-induced bleaching appears when the Ge content exceeds 4 at. %. After optimizing the evaporation conditions the PB reached 8% (attended with PE ~6%) and TB reached 18% [11, 14, 15], thereby showing an increase over the values obtained in the initial studies [7-9]. The decrease of n at PB and TB was around 0.1. However, the PI changes can be improved not only by increasing the deposition rate. Their maximal values depend also on the intensity of illumination, energy of photons and illumination time (as well as on sample thickness and temperature). With optimization of the illumination conditions PB of about 10% was reached in 640 nm thin $Ge_{27}As_{13}S_{60}$ films (after 3h illumination with white light, and excluding the influence of oxygen and temperature variations with nitrogen flow around the sample surface) [12].

Table 1. Irreversible photo- and thermo-induced changes in binary and ternary Ge-As-chalcogenides.

Substance	d nm	Δd/d (%)	Δn	Δn/n (%)	E_g (eV)	ΔE_g (meV)	$\Delta E_g/E_g$ (%)	ΔE_g^{th} (meV)	$\Delta E_g^{th}/E_g$ (%)	Δn^{th}
As_2S_3 [1,4]		-1	+0.10	+3.9		-	-			
$Ge_{22}As_{18}S_{60}$ $Ge_{25}As_{15}S_{60}$ [6]	1000				2.23			+195	+8.8	-0.05 -0.1
$Ge_{25}As_{15}S_{60}$ $Ge_{27}As_{13}S_{60}$ [7,8,9]			-0.06	-2.6	2.18	+80	+3.7 	 +240	 +11 +14.5	
$Ge_{36}S_{64}$ $Ge_{32}S_{68}$ [10] GeS_2 [11]		 +5.5			2.21 2.79	 +85	 +3 +8	+370	+16.7 +17	-0.13
As_2S_3 [11] [12]	 1000	-1.8	 +0.08		 2.40		-1.5	 -20	-1.7 -0.8	
$Ge_xAs_{40-x}S_{60}$ [13]			-0.1							
$Ge_{27}As_{13}S_{60}$ $Ge_{14}As_{27}S_{59}$[12]	640 655				2.13 2.10	+270 +70	+10.3 +3.3	+370 +230	+17 +11	
$Ge_{27}As_{13}S_{60}$ [11, 14,15]	~ 1500	+6 +5.5					+8 +7		+15 +18	
$Ge_{32}As_5S_{63}$ [15] $Ge_{30.8}As_{5.7}S_{61.5}$ [16]	1500 1300 970 640 630	+6.5 +5.4 +11 **+11**	 -0.14 **-0.21**	 -6.3 **-9.5**	2.1 2.25 2.2 2.25 	+350 +400 **+560** **+610** **+610**	+16.7 +18 +25.5 +27 	+450 +500 **+580** 	+21 +22.7 +25.8 	

Up to 2005, the Ge-As-S compositions from the line Ge_2S_3-As_2S_3 ($Ge_xAs_{40-x}S_{60}$) had shown the highest irreversible photo- and thermo-induced changes. In the Ge-S films protected against photo-oxidation the PB and TB were explained mainly with increase of the heteropolar Ge-S bond density [10]. In the $Ge_xAs_{40-x}S_{60}$ films (according to Ref. 12) the energy induced ordering of the virgin films proceeds predominantly in the Ge-S part of the network. These changes consist of improving the short-range order (SRO) by increasing mainly the GeS_2-entities and the medium range order (MRO) by increasing the degree of polymerization. The higher sensitivity of $Ge_{27}As_{13}S_{60}$ films from the $Ge_xAs_{40-x}S_{60}$ system was connected [12] with the higher density of reconstructed GeS_2-entities in view of the higher density of Ge-S bonds. As mentioned above, at compositions with x>27 the sensitivity falls irrespectively of the higher Ge-S bond density, which confirms the supposition of the existence of other factors important for the maximum in the

compositional dependences of the parameters of this system [7-9, 14]. The overall highest values of irreversible changes in this system has been related to the fact that a system composed of one non-stoichiometric and one stoichiometric component is more disordered than systems with stoichiometric components only, which allows for more reconstructions (the maximal values appear in compositions where MRO changes ensure larger free volumes, which facilitate these reconstructions).

Recently, a *new system, Ge_2S_3-AsS_3*, has been studied [9, 15, 16] in which even higher photo- and thermo-induced changes have been found. In the most sensitive films from this system, evaporated from the $Ge_{32}As_5S_{63}$ glass, the PB was ~17% and the PE was 6.5% [15]. Initially, films with thickness ~1.5 μm were illuminated with 500 W high pressure Hg lamp for 45 min only. The TB was also high, 21% [15]. It can be noted that the mean coordination number of the used glass composition was Z=2.69. The Z-value of the films from this glass is slightly lower (~1%) because of a decrease in Ge at the expense mainly of the As content. Films from another glass with a similar composition, $Ge_{30.8}As_{5.7}S_{61.5}$, have shown almost the same changes (18% PB, 5.4% PE and 6.3% decrease of n) (Table 1). The parameters of the films from this glass have been studied [16] in dependence on the thickness and the decrease was from 1.3 μm to 630 nm. The purpose of this study was to optimize the penetration depth in the films of the light filtered only by IR cut-off filter; moreover in this study the time of illumination was increased to 180 min to reach a nearly saturated value of the photo-induced effects. Thereby, *giant* photo-induced changes in the optical band gap have been established: increase of about 600 meV in 640 nm thin films (27%), as well as in 630 nm films. The PE was also the giant one, 11%, and the decrease in *n* was ~0.2. To our knowledge, in the Ge_2S_3-AsS_3 we have obtained the highest up to now photo-induced changes of the optical parameters and film thickness. The irreversible TB was also the highest, but in films thinner than 1 μm it does not exceed the irreversible PB (i.e., the high value of E_g reached after illumination of a fresh film, slightly decreases after annealing). This is not typical for other binary and ternary chalcogenide films annealed to temperatures near T_g (Table 1). It would be interesting to further clarify the different behaviours observed in this new system.

3. Reversible photo-induced changes

It is well known that in the *binary As-chalcogenides* the reversible photo-darkening is not very high (Table 2) and the band gap decrease is usually 1–2% [19, 20, 22, 11], similarly to the irreversible PD. Substantial decrease of the band gap (ΔE_g = -190 meV) has been seen in the non-stoichiometric As_3Se_2 only [17]. As well the accompanying refractive-index increase was not high [19].

Table 2. Reversible photo-induced changes in binary Ge- or As-chalcogenides.

Substance	d (μm)	Δd (μm)	Δd/d (%)	n	Δn	Δn/n (%)	E_g (eV)	ΔE_g (meV)	$\Delta E_g/E_g$ (%)
As_2Se_3 As Se As_3Se_2[17,3]								-60 -145 -190	
As_2Se_3 [23] [2]	0.5	0.008	+0.7 +1.6						
As_2S_3 [18,1] [19, 20] [23]			+0.4 +0.7	2.6	+0.02 +0.03	+0.8 +1.2	2.4	-30	-1.25
As_2S_3 [22]	50	**+2.5**	**+5**				2.4	-40	-1.7
As_2S_3 [11] [12]	1-2 1		+1.8					 -70	-1.2
$Ge_{30}Se_{70}$ $Ge_{33}S_{67}$ [21]								-60 -84	
GeS_2 [23]			+0.5						
GeS_2 [11]	1-2								-5.5

In the *binary Ge-chalcogenides,* $\Delta E_g/E_g$ is higher than in the As-chalcogenides (Table 2) and PD reaches 5.5% [11].

The reversible thickness changes in the binary Ge-chalcogenides are usually about +0.5% [23]. PE with such value, obtained in As-chalcogenides by band gap illumination, is accepted as a conventional, intrinsic photo-expansion [1, 18]. Using sub-band-gap illumination ($h\nu \approx 0.8\ E_g$) reversible PE of about 5% has been induced in As_2S_3 [22], which is referred as *giant*. In As_2S_3 and in As_2Se_3 films, exposed to white or blue-violet light [11, 2],

PE higher than 0.5% but lower than 2% has been obtained (Table 2). As mentioned before, the magnitude of the effects at a given temperature and thickness depends not only on the photon-energy, but also on light intensity and exposure. In this regard it can be notice, that the giant reversible PE with sub-band-gap illumination was obtained with intensity 10^3-10^4 W/cm^2 (while in the other cases, substantially lower intensities were used).

It is also interesting to compare the irreversible effects with the reversible photo-induced effects in the ternary Ge-As-chalcogenides (Table 3). In the $Ge_{27}As_{13}S_{60}$ and $Ge_{14}As_{27}S_{59}$ films PD is about 7 and 8%, respectively [12]. In the latter films ΔE_g is -190 meV, as in the non-stoichiometric As_3Se_2. But recently, the highest values are ΔE_g = -220 meV, named as *giant*. They are reached firstly in ~600 nm films from $Ge_{16}As_{26}S_{58}$ [24] and also in ~1.5 μm $Ge_{32}As_5S_{63}$ films (from the new Ge_2S_3-AsS_3 system) [15]. So, PD ~ 9% is reached in suitable Ge-As-S films, which is higher than the known reversible and irreversible PD in the stoichiometric binary As-chalcogenides. But it is substantially lower than the irreversible effects (PB and TB), which reach 27% (Table 1).

Table 3. Reversible photo-induced changes in ternary Ge-As-chalcogenides.

Substance	d (μm)	Δd (μm)	Δd/d (%)	n	Δn	Δn/n (%)	E_g (eV)	ΔE_g (meV)	$\Delta E_g/E_g$ (%)
$Ge_{20}As_{20}S_{60}$ $Ge_{20}As_{25}S_{55}$ [21]	20							-125 -125	
$Ge_{22}As_{18}S_{60}$ $Ge_{25}As_{15}S_{60}$ [6]	1			2.25 2.15	+0.02 +0.05	+0.9 +2.3			
$Ge_{27}As_{13}S_{60}$ [14] [11]	1-2		-1.5 -2.5						-2.5 -3.5
$Ge_{27}As_{13}S_{60}$ $Ge_{14}As_{27}S_{59}$ [12]	0.64 0.66						2.45 2.33	-170 -190	-6.9 -8.2
$Ge_{16}As_{26}S_{58}$ [24]	0.58-0.66			2.25	+0.06	+2.7	2.35	**-220**	-9.3
$Ge_{32}As_5S_{63}$ [15]	1.5						2.57	**-220**	**-8.5**
$Ge_{30.8}As_{5.7}S_{63.5}$ [16]	0.97						2.7	-210	-7.8

The reversible volume changes in ternary chalcogenides do not exceed the obtained in As_2S_3. It is interesting to note that instead PE, a photo-contraction of ~2% has been observed in some films from the $Ge_{27}As_{13}S_{60}$ glass (Table 3). However, in the new system, a PE has been seen after annealing [25].

4. Discussion

As previously mentioned, there is no one-to-one correspondence between the reversible photo-induced changes in the optical band gap and in the volume, which is adopted on the basis of their time evolution [1, 23, 2]. The differences in their effective reaction times and dispersion parameters lead to the suggestion, that the origins of the PD and PE are different [2]. In our investigations of the new ternary chalcogenide system Ge_2S_3-AsS_3 we have also supposed that there is no one-to-one correspondence between the irreversible changes of band gap and volume [25]. The giant irreversible increase in band gap (PB) is indeed accompanied with giant volume increase (PE), but the further irreversible band gap increase after annealing (TB) is accompanied with volume *decrease* (TC). Only in the thinnest films (~600 nm), the changes after annealing have the same course – the decrease in the volume is accompanied with a low decrease of the previously increased by illumination band gap. Usually, if the fresh films are only annealed, the thermo-bleaching is not accompanied with thermo-expansion. Thereby, the course of the irreversible changes of the optical band gap and the volume are not always in correspondence.

To shed light on the origin of the two phenomena the main suppositions for the *irreversible PB* in Ge-S films (protected against photo-oxidation [10]) should be recalled. Upon illumination with nearly-gap light, the excitation of electrons from p-LP states changes the p-LP interactions and the disordered frozen-in as-deposited state relaxes to an energetically more stable state. The voided network polymerized, thereby increasing the regular heteropolar Ge-S bonds and decreasing wrong homopolar and frozen-in broken bonds, which increases the band gap [10]. If the density ρ of the new entities in the chemically more ordered structure is lower or their arrangement is looser, decrease of n and increase of d (a PE) can be expected.

The *irreversible TB* at annealing is due to network ordering too, which is similar to the ordering caused by illumination (illumination may also cause disordering because of the dual action of light, which will be discussed latter). In particular, the thermal excitation of electrons from the p-LP states of the valence band leads to a more ordered state. At annealing of virgin Ge-As-S films, where the increase in order is mainly in the Ge-S part of the

network [12], the heteropolar bonds will increase, while homopolar wrong bonds decrease as in the Ge-S films [10], which leads to a band gap increase, i.e. to TB. However, the TB was not accompanied by TE in our experiments and only the PB was accompanied by giant irreversible PE. The question then arises whether, and to what degree, the latter can be regarded as intrinsic phenomenon related to the appearance of new entities and arrangements.

In Ge-S films the formation of Ge-S bonds at annealing was confirmed by ESR experiments [26]. The X-ray diffraction studies of the first sharp diffraction peak (FSDP) in these films have shown not only a reduction of disorder in the short range but also a decrease of interlayer distance after annealing. A volume decrease after annealing can be expected in Ge-S films similarly to that in Ge-As-S films [11, 14], where TC was established by the optical transmission studies. An interlayer decrease after illumination of Ge-S virgin films was also assumed [26]. Our X-ray diffraction studies have suggested, that in $Ge_xAs_{40-x}S_{60}$ films [11] the interlayer distance (determined from the position of the FSDP) slightly decreases or is nearly the same after illumination. However, the changes in the shape of the peak were more expressed, which has lead to the conclusion that high increase of interlayer distances may exist at a few places governing a total expansion. This would be consistent with an irreversible intrinsic PE, but can hardly explain the giant values of the PE in the thin Ge_2S_3-AsS_3 films.

The reasons for the appearance of *reversible photo-expansion* in binary As-chalcogenides were discussed in many papers [23, 1, 2]. It was accepted [1, 23] that in As_2S_3 flakes with thickness ~50 μm the obtained with focused light (2 eV) prominent volume expansion with height ~2 μm occurs because the intrinsic isotropic volume expansion (supposed to be ~ 0.5%) is seemingly amplified by a geometric factor. This factor is related to a transfer of the intrinsic expansion to an expansion at free surfaces due to the photo-induced fluidity (the fluidity is accepted to be sufficient at intensity $>10^2 W/cm^2$). The geometric factor is L/r, where L is sample thickness or penetration depth, and r is the light spot radius. In thin films the role of this factor decreases. In As_2Se_3 and As_2S_3 films the expansion is ~1.7% [2, 11] even though the intensity was less than $10^{-1} W/cm^2$. It is reasonable to accept that the value of the intrinsic expansion differs in various materials.

Although there is no one-to-one correlation between the parameters of PD and PE, the photo-induced band gap and volume changes are related to each other as supposed in Ref. 1. The PD in As_2S_3 is connected with bond changes, for instance with twisting [1], which increase a kind of structural disorder producing interlayer stresses. They lead to an *interlayer relaxation*, which in As_2S_3 can induce a microscopic expansion, creating *condition to further processes of PD*. For the photo-expansion, the role of electrical charging effects were also considered: [2]. In the ternary chalcogenides the reversible volume changes are not always similar to that of the binary chalcogenides (tables 3 and 2). In the As-reach films from the Ge_2S_3-As_2S_3 system a PC usually exists, similar to the pointed in Ref. 1 exceptional PC in the $Ge_{10}As_{40}Se_{50}$ glass seen in early studies [18]. In the more complicated structures of the ternary chalcogenides (where the main structural units are As-pyramids and Ge-tetrahedra) the relaxation processes would not necessarily provoke volume increase. Such PI increase usually appears in the poor of As compositions from the new Ge_2S_3-AsS_3 system; in composition where the As-content is only ~5 at. % a reversible PE of about 2 % has been seen [25].

Could one accept similar mechanisms about the *irreversible volume changes*? The following facts pertain to this question.

Firstly, studies of the new system have shown [16] that *decrease of the film thickness* leads to increase of the irreversible volume and band gap changes (Table 1). Presumably, because the illumination was in air ambient, these increased PE and PB are related to the increased influence of the changes in the near-surface regions, possibly connected with photo-oxidation. Secondly, in films thinner than 1μm the values of ΔE_g after annealing are lower than that after illumination (*TB is lower than PB*). However, in films protected against photo-oxidation [10, 12] the PB is lower than TB, both in Ge-S films as well as in $Ge_xAs_{40-x}S_{60}$ 640 nm thin films (Table 1). The usually higher TB than PB was explained by taking into account that in the case of thermal treating the whole matrix of the film is excited and the as-deposited network relaxes very effectively into the ordered state [10]. In this state, according to Raman and IR spectra [12], short range ordering (with mainly reconstructed tetrahedral entities in Ge-As-S films) and medium range ordering (polymerization due to formation of more edge shared tetrahedra) is attained. As mentioned before the PB is also accepted as a response to such increase in both SRO and MRO. However, it has been also proposed [12] that the PB is lower than the TB due to the *dual action of the light* – the process of reversible photo-darkening could accompany the process of irreversible bleaching during illumination. If the PD may induce a microscopic expansion as noted above (as for As_2S_3 [1]), it would follow that the irreversible PE is connected with the PD-process. This explanation is appropriate when the penetration depth of the light is high enough and the phenomena take place preferentially in the volume. In films thinner than 1μm, processes near to the surface may dominate; however, in the more disordered near-surface region the structural changes leading to red shift of the absorption edge (PD) would be less effective. If the irreversible PE is related only to the PD, the irreversible PE must also decrease. This supposition is obviously not acceptable because the PE is high in films with thicknesses reduced down to about 600 nm (Table 1).

In *thicker than 1μm* $Ge_xAs_{40-x}S_{60}$ films not protected against oxygen influence [11, 14, 15] the PB is lower than the TB. The XPS experiments on such films have shown the presence of Ge-O bonds in the near surface region and their increase at illumination in air ambient [27]. However the PB, similarly to that at illumination in inert atmosphere, is lower than the TB most likely because of the prevalence of the volume processes (data for PE in

inert atmosphere are not available). Moreover, in the films from the new Ge_2S_3-AsS_3 system, according to some preliminary results [28], the PB at illumination in vacuum slightly decreases, while the accompanying PE substantially decreases and in some case has not been detected.

In films *thinner than 1μm* the processes in the near surface region may have a dominant role, especially in the new Ge-As-S system with relatively low As content. According to Ref. 29 the As-S films are more stable to oxidation at 300 K than the Ge-S films. The ternary $Ge_xAs_{40-x}S_{60}$ glasses are chemically more durable in air than that from Ge_2S_3 [13]. The exposure of Ge-S films in air leads to photo-oxidation indicated by the appearance of IR peaks assigned to Ge-O bonds and GeO_2 entities [26, 29]. However, it was pointed out that *not only the photo-oxidation leads to PB* [26, 29] and the increases of the Ge-S bonds due to short and medium range ordering should be taken into account. According to the DIR spectra, during illumination in air a tendency for ordering and increase of the fundamental vibrations assigned to Ge-S bonds exists, however in the near-surface regions these bonds are simultaneously photo-oxidized [29]. The existence of GeO_2 at the surface layers is confirmed also by ESCA spectra (of Ge3d) in Ge-S films [26]. It can be assumed that the products of oxidation at illumination of the fresh films are with lower density ρ, thereby explaining the decrease of n and the PE, which accompanied the PB. With decreasing of d of Ge_2S_3-AsS_3 films from 1.5 μm to 630 nm the processes of *surface oxidation can lead to the increase towards the giant irreversible PI changes* of E_g, n and d. (The high values of the irreversible PB are not substantially decreased by the light induced local disorder connected with the Ge-O bonds increase, as well as with the disorder connected with bond changes, which in thermally ordered films lead to PD). Further studies of the structural changes, for example with DIR and Raman studies, should clarify the details of the origin of the giant effects found in the Ge-reach compositions, which are interesting for applications.

In addition, as mentioned above, *PB appears instead PD* after annealing at temperatures far below T_g in 90 nm thin films. Recently, we have shown [25] that PB appears after low-temperature annealing also in 900 nm films from the Ge_2S_3-AsS_3 system. And what is more remarkable, the transition from reversible PB to reversible PD appears at the higher temperatures of annealing, the thinner the films are. In ~100 nm thin films such transition cannot be seen and at annealing up to temperatures ~T_g only TB is found. It seems that the surface disorder in the thinnest films does not allow the disordering process leading to PD. Also in oblique deposited GeS_2 layers [30] PD has not been seen after annealing and it could be accepted that this is not due to insufficiently annealing but to the type of disorder of the columnar structure. Besides, reversible PB has been seen before in some Ge-S films (probably with low thickness) [29]. Therefore, in nanometer sized films PD is not always observed and in well-annealed films the PD is not the only one photo-induced change in the band gap.

Finally, the compositional dependences of the irreversible and reversible photo- and thermo-induced changes from the mentioned Ge-As-S systems have shown [9,15] maximal values at coordination where high free volumes can be expected at a threshold from a nearly layered to a more cross-linked three dimensional structure [31]. To answer the question why the PI irreversible and reversible changes are the highest in the new Ge_2S_3-AsS_3 system, another fact could be noted. In the Ge-rich glasses from this system, the differential scanning calorimetric scans reveal two glass transitions (usually in the first DSC run). Bimodal T_gs are also observed for other chalcogen-rich compositions [32]. It can be supposed that the character of the most sensitive compositions is intrinsically heterogeneous. It is possible that energy could induce easily changes or decomposition into Ge-S and As-S phases, which would influence the studied effects. According to Ref. 33 compositions that actually do work in devices are alloys, which suggest a possibility of existence of different phases. Nano-phase separations or vice versa can be the driving forces behind the greater structural changes during photo – or thermo-induced disordering or ordering of the network state.

Recently, the first steps for recording of holographic gratings in $Ge_{30.8}As_{5.7}S_{63.5}$ films have been done [25] and the realizations of recordings in ~95 nm thin films has been accepted as promising. To clarify the possibilities for applications of the giant photo-induced changes in films from the Ge_2S_3-AsS_3 system, further studies must be done for optimizing the first optical recording attempts [25]. The use of the giant irreversible PE for micro-lenses seems also promising.

5. Conclusions

Comparison of the parameters of the photo- and thermo-induced changes in some binary and ternary Ge-As-chalcogenides (Table 1-3) shows that the highest irreversible changes are found in a relatively new system studied by us [9,15,16]. Ge-rich compositions from the Ge_2S_3-AsS_3 system (with a mean coordination number ~2.7) have irreversible photo-bleaching, which is "giant" for about 600 nm thin films and is accompanied by giant photo-expansion. The PB does not disappear with decreasing the thickness of the film down to ~90 nm. Giant reversible photo-darkening exist also in ~1.5 μm films, which decreases with thickness reduction and disappears and converts to PB in ~90 nm thin films. The higher PI changes in the new system (as compared to other Ge-As-chalcogenides) clearly prompt further studies of their origin and are quite promising for practical applications.

Acknowledgments

The author acknowledges her long-term collaborators whose efforts contribute substantially to the results reviewed in the paper. The helpful discussions and suggestions from Dr. D. Arsova are especially appreciated.

References

[1] K. Tanaka, A. Saitoh, N. Terakado, J. Optoelectron. Adv. Mater. **8**, 2058 (2006) and Ref. therein.

[2] K. Shimakawa, Y. Ikeda, J. Optoelectron. Adv. Mater. **8,** 2097 (2006).

[3] A. V. Kolobov, K. Tanaka in Handbook of Advanced Electronic and Photonic Materials and Devices, **5**, Ed. H. S. Nalwa, Acad. Press, 2001, p.47; K. Shimakawa, A. V. Kolobov, S. R. Elliott, Advances in Physics **44**, 475 (1995) and Ref. therein.

[4] J. P. De Neufville, S. C. Moss, S. R. Ovshinsky, J. Non-Cryst. Solids **13**, 191 (1973/74); M. Kasai, H. Nakatsui, Y. Hadjimoto, J. Appl. Phys. **45**, 3209 (1974).

[5] E. Vateva, M. Nikiforova, E. Skordeva, J. Non-Cryst. Solids **77-78**, 1133 (1985).

[6] D. Minkov, E. Vateva, E. Skordeva, D. Arsova, M. Nikiforova, J. Non-Cryst. Solids **90**, 481 (1987).

[7] E. Vateva, E. Skordeva, D. Arsova, Phil. Mag. B **67**, 225 (1993).

[8] E. Vateva, D. Arsova, E. Skordeva, E. Savova, Proc. ISCMP, Varna, Eds. J.M. Marshall, N. Kirov and A. Vavrek, Research Studies Press LTD, Taunton, Somerset, England, 1994, p. 604.

[9] E. Vateva, E. Skordeva. JOAM **4**, 3 (2002).

[10] M. Munzar, L. Tichy, H. Ticha, Curr. Appl. Phys., **2,** 187 (2002).

[11] E. Vateva, D. Arsova, E. Skordeva, V. Pamukchieva, J. Non-Cryst. Sol. **326-327,** 243 (2003).

[12] M. Stabl, L. Tichy, Optical Mater. **27**, 549 (2004).

[13] R. Ston, M. Vlcek, H. Jain, J. Non-Cryst. Solids **326-327**, 220 (2003).

[14] D. Arsova, V. Pamukchieva, E. Vateva, E. Skordeva, J. Mat. Sci.: Mat. Elec. **14**, 835 (2003).

[15] D. Arsova, E. Skordeva, V. Pamukchieva, E. Vateva, J. Optoelectron. Adv. Mater. **7**, 1259 (2005).

[16] F. Yakuphanoglu, D. Arsova, E. Vateva, J. Optoelectron. Adv. Mater. **9**, 334 (2007).

[17] S. B. Gurevich, N. N. Ilyashenko, B. T. Kolomiets, V. M. Lyubin, V. P. Shilo, Proc. 6th Conf. Amorphous and Liquid Semic., Ed. B.T. Kolomiets, Acad. Sci., Leningrad, 1976, p.451.

[18] H. Hamanaka, K. Tanaka, A. Matsuda, S. Iizima, Sol. State Comm. **19**, 499 (1976).

[19] K. Tanaka, Y. Ohtsuka, J. Appl. Phys. **49**, 6132 (1978).

[20] K. Tanaka. J. Non-Cryst. Solids **35-36**, 1023 (1980).

[21] K. Tanaka, T. Nakagawa, A. Odajima, Phil. Mag. B **54**, L3 (1986) and Ref. therein.

[22] H. Hisakuni, K. Tanaka, Appl. Phys. Letters **65**, 2925 (1994).

[23] K. Tanaka, Phys. Rev.B **57**, 5163 (1998) and Ref. therein.

[24] M. Stabl, L. Tichy, Sol. State Sci.**7**, 201 (2005).

[25] D. Arsova, K. Beeva, E. Vateva, V. Pamukchieva, K. Beev, S. Sainov, J. Optoelectron. Adv. Mater. **9**(10), 3115 (2007).

[26] T. Kawaguchi, S. Maruno, K. Masai, J. Non-Cryst. Solids **97-98**, 1219 (1987).

[27] V. Pamukchieva, D. Gonbeau, M.-F. Guimon, E. Skordeva, R. Dedryvere, D. Arsova, Phys. B **371,** 302 (2006).

[28] D. Arsova, unpublished results.

[29] L. Tichy, H. Ticha, K. Handlir, K. Jurek, J. Non-Cryst. Sol. **101**, 223 (1988).

[30] Y. Kuzukawa, A. Ganjoo, K. Shimakawa, J. Non-Cryst. Sol. **227-230**, 715 (1998); A. Ganjoo, N. Yoshida, K. Shimakawa, Recent Res. Devel. Appl. Phys. **2**, 129 (1999).

[31] K. Tanaka, Phys. Rev. B **39**, 1270 (1989).

[32] M. Mitkova, Yu Wang, P. Boolchand, Phys. Rev. Letters **89,** 3848 (1999)

[33] A. V. Kolobov, J. Haines, A. Pradel, M. Ribes, P. Fons, J. Tominaga, J. Optoelectron. Adv. Mater. **8**, 2161 (2006).

Corresponding author: vateva@pronto.phys.bas.bg