

# On the photo-induced shift of the optical gap in amorphous $\text{Ge}_6\text{As}_{43}\text{S}_{35}\text{Se}_{16}$ film

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In virgin  $\text{Ge}_6\text{As}_{43}\text{S}_{35}\text{Se}_{16}$  amorphous film with the optical gap at around 2.06 eV we observed an absence of photo-induced optical gap shift induced by white light illumination. However, we found red shift of the optical gap induced by illumination with over-gap photons with energy 2.254 eV. This red shift is erased by illumination of the darkened state of the film with sub-gap photons, with energy 1.907 eV. It is supposed that simultaneous action of over-gap photons and sub-gap photons, present in white light, is responsible for apparent insensitiveness of the optical gap to illumination using white light.

(Received February 2, 2009; accepted April 23, 2009)

**Keywords:** Amorphous chalcogenide film, Photo-darkening, Photo-bleaching

## 1. Introduction

It is well known that in the most of amorphous chalcogenide films the first response of a virgin film to illumination by a convenient light is bleaching or darkening that is blue or red shift of the optical band gap ( $E_g$ ). However, there are some exceptions; for example in  $\text{Ge}_{40}\text{S}_{60}$  amorphous film practically no response to the illumination was observed [1]. This fact was explained assuming: (i) Efficiency of photo-induced changes in interactions involving p-lone pair states excitation is reduced because the top of valence band in Ge-rich Ge-S amorphous films is affected by regular Ge-Ge bonds [2]. In addition, (ii) the network of  $\text{Ge}_{40}\text{S}_{60}$  amorphous film is very rigid (the average coordination number  $\text{CN} = 2.8$ ) making any photo-induced changes of the atom position difficult [1]. Very low or practically absent photo-induced gap shift was observed also in  $\text{As}_x\text{Ge}_{40-x}\text{S}_{60}$  amorphous films for the chemical composition where approximately  $30 \leq x \leq 37$ , [3,4]. In this case, the density of Ge-Ge bonds is assumed to be rather small because of well pronounced tendency of Ge atoms to be coordinated as much as possible by a chalcogen atom, see for instance Refs. [5,6]. It means that the assumption (i), see above, does not need to be considered in this case. Similarly the assumption (ii) above is not applicable for explanation of an absence of photo-induced gap shift because for  $\text{As}_x\text{Ge}_{40-x}\text{S}_{60}$  film for  $30 \leq x \leq 37$  it is valid:  $2.5 \geq \text{CN}(x) \geq 2.435$  ( $\text{CN}(x) = (4x + 4(40-x) + 120)/100$  assuming  $\text{CN}(\text{As}) = 3$ ,  $\text{CN}(\text{Ge}) = 4$  and  $\text{CN}(\text{S}) = 2$ ). It means that the network of  $\text{As}_x\text{Ge}_{40-x}\text{S}_{60}$  films considered belongs to stressed rigid networks [6], in fact to weakly stressed rigid networks which, however, allow propagation of light induced structural changes [7]. Ston et al. [4] tentatively suggested that addition of Ge

into the As-S films ...”can eliminate or even alter the character of photo-induced changes of optical parameters”.

Continuing in the study of physical properties of Ge-As-S-Se amorphous films [8-16], we report our observation of photo-induced changes of the optical gap in virgin  $\text{Ge}_6\text{As}_{43}\text{S}_{35}\text{Se}_{16}$  amorphous film. We show that depending on the way of illumination the optical gap of the film seems to be insensitive to illumination, case of illumination by “white light”(whl) or the red shift of the gap is observed if monochromatic light is used for illumination with wavelength  $\lambda = 550$  nm (the photon energy  $\hbar\omega_p = 2.254$  eV). The red shift of the gap can be erased by subsequent illumination of the film by the light with wavelength  $\lambda = 650$  nm ( $\hbar\omega_p = 1.907$  eV).

## 2. Experimental

The thin films deposited onto microscopic slides were prepared in the way recently described [15]. The actual chemical composition was determined by electron microprobe X-ray analysis (Jeol JSM 5500 LV) within the precision  $\pm 1.5$  at%. Optical transmission in the region of short wavelength absorption edge (SWAE) was measured using a Perkin Elmer Lambda 12 spectrophotometer. The virgin (as-prepared) samples (v) were illuminated from the film side by: (a) white light (whl) using a Hund FLQ 150W light source equipped with light guide (light intensity on sample surface  $\approx 13$  mW/cm<sup>2</sup>), (b) monochromatic light with the wavelength  $\lambda = 550$  nm (light intensity on sample surface  $\approx 105$  mW/cm<sup>2</sup>) and (c) monochromatic light with  $\lambda = 650$  nm (light intensity on sample surface  $\approx 95$  mW/cm<sup>2</sup>). Illumination by the white light was performed for up to 120 minutes and

illumination by monochromatic light was performed for 60 minutes ( $\lambda = 550$  nm) and 120 minutes ( $\lambda = 650$  nm) i.e. up to saturated state. The setup used for a sample protection against oxidation was described in [1]. As a measure of photo-induced changes of the optical properties we used the optical gap values calculated from Tauc's formula  $(K\hbar\omega)^{1/2} = B^{1/2}(K\hbar\omega - E_g)$ , where  $B^{1/2}$  the slope of Tauc's edge reflects a sample disorder [17]. The absorption coefficient ( $K$ ) is given by relation  $K = (1/d)\ln\{[(1-R)^2 - ((1-R)^4 + 4R^2T^2)^{1/2}]/2T\}$ , where  $d$  is the sample thickness,  $T$  is the transmission and  $R$  is the reflectivity [18]. The transmission range below 30% was used to determine  $K$  values and  $R = 0.17$  was taken to be invariant to the illumination and wavelength in the narrow region of SWAE. The values of refractive index ( $n$ ) were determined using Swanepoel method [19]. Using Wemple-DiDomenico model (WDM) [20] the values of  $d$ ,  $n_{\hbar\omega \rightarrow 0}$ , effective oscillator energy ( $E_0$ ) and dispersion energy ( $E_d$ ) were estimated.

### 3. Results

In Fig.1, typical transmission spectra for virgin sample ( $v$ ), for virgin sample illuminated by white light ( $v \rightarrow whl$ ) and for virgin sample illuminated by monochromatic light,  $\lambda = 550$  nm ( $v \rightarrow i,550$ ) are shown.

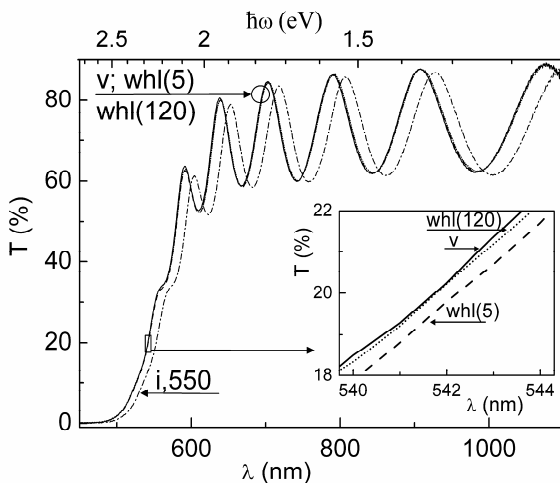


Fig. 1. Spectral dependencies of the transmission of the virgin sample ( $v$ ) and the sample illuminated by white light ( $whl$ ), and by monochromatic light with  $\lambda = 550$  nm ( $i,550$ ), dash-dotted curve. The parentheses indicate time of illumination in minutes. Inset illustrates subtle changes at around  $0.002$  eV induced by  $whl$  illumination.

As evident from Fig 1, the optical gap is practically not affected by illumination with  $whl$  whereas the monochromatic light induced the red shift of SWAE. In the inset a part of spectral dependence of the optical transmission is displayed for illustration of changes induced by  $whl$  illumination. The changes observed are around  $0.002$  eV and are taken to be negligible.

In Fig. 2, the spectral distribution of  $whl$  source used for illumination together with the typical transmission spectrum of virgin sample ( $v$ ) is shown.

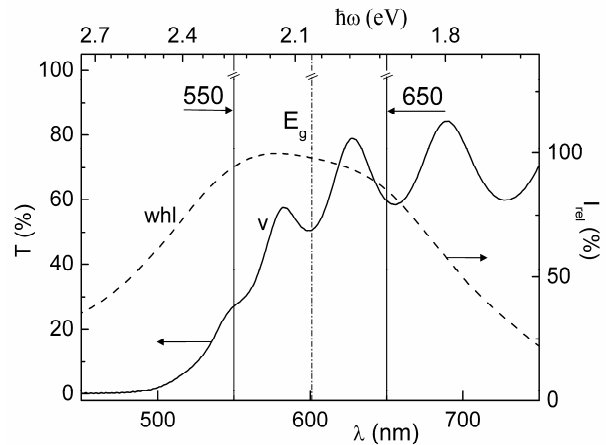


Fig. 2. Spectral distribution of the white light source used ( $whl$ ), dashed curve, and spectral dependence of the optical transmission for virgin sample ( $v$ ), full curve. For explanation of the vertical lines see text.

The vertical lines indicate the wavelength of monochromatic light used for illumination and the dashed line indicates the position of the optical gap of virgin sample. It is clear that for illumination we used over-gap photons ( $\hbar\omega_p = 2.254$  eV,  $\lambda = 550$  nm) and sub-gap photons ( $\hbar\omega_p = 1.907$  eV,  $\lambda = 650$  nm). In Fig.3 spectral dependencies of absorption coefficient are shown in  $(K\hbar\omega)^{1/2}$  versus  $\hbar\omega$  coordinates for virgin film, for virgin film illuminated by over-gap photons ( $v \rightarrow i,550$ ) and for subsequent illumination of this film state by sub-gap photons ( $i,550 \rightarrow i,650$ ).

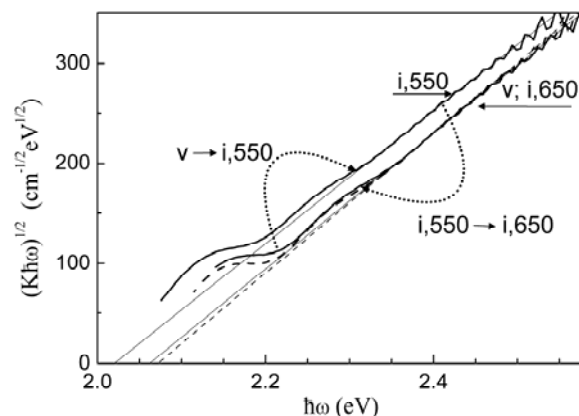


Fig. 3. Spectral dependencies of the absorption coefficient  $(K\hbar\omega)^{1/2}$  for virgin film ( $v$ ), for film illuminated by the light with  $\lambda = 550$  nm, ( $v \rightarrow i,550$ ) - darkening and for subsequent illumination of the darkened state by light with  $\lambda = 650$  nm, ( $i,550 \rightarrow i,650$ ) - bleaching, respectively.

Table 1 summarizes relevant optical parameters of studied films. From our results it is evident that illumination by over gap photons induced the red shift of the gap by about 42 meV, while illumination by sub-gap photons practically erased the red shift and the gap reached the original value: 2.06<sub>2</sub> eV. The values of the parameters of Wemple-DiDomenico model and refractive index values for  $\hbar\omega \rightarrow \infty$ , are also shown in Table 1.

Table 1\*. The state of the film with corresponding illumination process, the optical gap ( $E_g$ , [eV]), the slope of SWAE ( $B^{1/2}$ , [ $\text{cm}^{-1/2}\text{eV}^{-1/2}$ ]), the single effective oscillator energy ( $E_0$ , [eV]), dispersion energy ( $E_d$ , [eV]) and the refractive index ( $n_{\hbar\omega \rightarrow 0}$ ), respectively.

Film state	$E_g$	$B^{1/2}$	$E_0$	$E_d$	$n_{\hbar\omega \rightarrow 0}$
v, v $\rightarrow$ whl	2.06 <sub>2</sub>	680	4.3 <sub>2</sub>	19. <sub>0</sub>	2.3 <sub>2</sub>
v $\rightarrow$ i,550	2.02 <sub>0</sub>	665	4.2 <sub>0</sub>	18. <sub>2</sub>	2.3 <sub>1</sub>
i,550 $\rightarrow$ i,650	2.06 <sub>2</sub>	695	4.3 <sub>0</sub>	18. <sub>9</sub>	2.3 <sub>2</sub>

\* We note that the penetration depth of the light ( $d_{\text{pnt}}$ ) for case v  $\rightarrow$  i,550 varied from 1200 nm to 850 nm while in the case i,550  $\rightarrow$  i,650 it was found in the region 850 nm  $<$   $d_{\text{pnt}}$   $<$  6000 nm, that is in both cases the penetration depth of the light was comparable or higher than the sample thickness  $d \approx 1200$  nm.

Observed changes in  $B^{1/2}$ ,  $E_0$ ,  $E_d$  and  $n_{\hbar\omega \rightarrow 0}$  are too small to be used for a quantitative discussion however these are in a harmony with photo-induced changes in the optical gap.

#### 4. Discussion

We suppose that insensitivity of our sample to whl illumination is only apparent. Over-gap photons induced red shift of the gap, sub-gap photons completely erased this red shift and hence whl where significant portion of both over-gap and sub-gap photons is present, see Fig. 2, can hardly induce shift of the gap. The fact that sub-gap photons bleach in advance darkened sample is known, see e.g. [21,22]. From the phenomenological point of view, the process of darkening induced by over-gap photons and bleaching induced by sub-gap photons can be described within the “three level system” [21, 22] where from the ground state represented by energy  $E_{\text{Gr}}$  an electron is excited to an excited state with energy  $E_{\text{Ex}}$  and it is valid:  $E_{\text{Ex}} - E_{\text{Gr}} \geq E_g$ . The excited state is a transient state and by non-radiative recombination from  $E_{\text{Ex}}$  new quasi-stable state  $E_{\text{Qs}}$  is reached and it is valid:  $E_{\text{Gr}} < E_{\text{Qs}} < E_{\text{Ex}}$ . Since  $E_{\text{Qs}} < E_g$  the  $E_{\text{Qs}}$  state can be excited by sub-gap photons and via excited transient state and subsequent recombination the ground state is recovered. Hence bleaching is observed since the density of quasi-stable state  $E_{\text{Qs}}$  is reduced and, at the same time, sub-gap photons can not excite effectively the ground state because  $E_{\text{Ex}} - E_{\text{Gr}} \geq E_g$ .

Following our recent communication [16] in studied sample we can expect existence of at least 5 different

bonds. For simplicity we assume that Ge atoms are preferably coordinated by a chalcogen atoms, see e.g. [6] and we neglect formation of Ge-As bonds [23]. We also neglect formation of S-S, Se-Se and S-Se bonds, because the probability of their formation is considered to be small since our sample is chalcogen pure and e.g. in hundred atoms sample the number of bonding electrons of “cations” (Ge+As) = 153 exceeds the number of bonding electrons of “anions” (S+Se) = 102. For two simplest bonding arrangements we estimated the numbers of individual bonds assuming: (1) Formation of strongest Ge-S bonds is preferred. (2) Distribution of bonding electrons of sulphur and selenium atom into covalent bonds with four bonding electrons of germanium atom is statistical one and it is independent on the bond enthalpy. In Table 2 the numbers of individual bonds estimated and corresponding values of the bond enthalpy are summarised.

Table 2. The type of bond, the number of bonds (N.B.) in a hundred atoms sample, case (1) and (2), respectively, and the bond enthalpy ( $H_B$ ) [24].

Bond	N.B. (1)	N.B. (2)	$H_B$ , [eV]
Ge-S	24	16.47	2.71
Ge-Se	0	7.53	2.43
As-S	46	53.53	2.63
As-Se	32	24.47	2.35
As-As	25.5	25.5	2.08

Using over-gap photons ( $\hbar\omega_p = 2.254$  eV) can effectively excite only upper part of valence band formed by p-LP states [2] and from bonding states most probably only As-As bonds and some weaker e.g. strained As-Se bonds can be excited, see Table 2. The energy of sub-gap photons ( $\hbar\omega_p = 1.907$  eV) is lower than  $E_g$  and bond enthalpy of any bond of our sample network. Hence illumination by sub-gap photons can not induce effective darkening while quasi-stable state  $E_{\text{Qs}}$  with energy by about 0.15 eV above the ground state ( $0.15 \approx E_g - 1.907$ ) can be excited by sub-gap photons the process which results into bleaching in advance darkened state.

#### 5. Conclusions

Apparent insensitivity of amorphous Ge<sub>6</sub>As<sub>43</sub>S<sub>35</sub>Se<sub>16</sub> film to illumination by white light has been explained as a result of competitive process of photo-darkening induced by over-gap illumination and simultaneous bleaching induced by sub-gap photons illumination. We assume that similar origin can explain the absence of photo-induced shift of the gap observed in some Ge-As-S amorphous films [3,4]. We note that this is different origin of insensitivity to illumination in comparison with Ge<sub>40</sub>S<sub>60</sub> and Ge<sub>25.4</sub>As<sub>29.4</sub>S<sub>45.2</sub> amorphous films, [1,25] where rather high rigidity of the film network was supposed to be a

major reason for insensitivity of the optical gap to illumination.

### Acknowledgements

M.K. and L.T. acknowledge support from the project AVOZ 40500505, P.K. acknowledges support from the project VZ 00216217501 and J.T. and K.P. acknowledge support from the "Scientific Exchange Program" between Bulgarian Academy of Sciences and Academy of Sciences of the Czech Republic. We are indebted to Dr. Milan Vlček, Joint Laboratory<sup>1</sup>, for electron microprobe X-ray analysis.

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