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On the reversible photo-darkening in amorphous $Ge_5As_{41}S_{15}Se_{39}$ film

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Reversible photo-darkening was observed in $Ge_5As_{41}S_{15}Se_{39}$ amorphous film. The kinetics of the red shift of the optical gap follows stretched exponential for illumination by over-gap photons and for illumination by white light. For illumination by "near gap" sub-gap light the kinetics of the red shift of the gap follows single exponential. Far infrared transmission spectra indicate an increase in the film network disorder induced upon illumination by over-gap photons, while very weak structural changes were observed induced by illumination using "near gap" sub-gap photons. Different states excited by over-gap photons and by "near gap" sub-gap photons are suggested to be responsible for differences observed in photo-darkening.

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1. Introduction

Amorphous films from Ge-As-S-Se system were studied as possible candidates for rewritable supermicrofishe [1,2], for holographic gratings, for photo-induced channel waveguides [3,4] and for optical switching devices [5]. Photo-darkening in Ge-As-S-Se amorphous films was studied for example in Ref. [6]. Recently some new results related to photo and thermally induced changes in Ge-As-S-Se amorphous films were published [7,8]. In Ref. [8] the irreversible photo-induced changes were examined in some Ge-As-S-Se films prepared by co-evaporation from GeS_2 and AsSe bulks, while in Ref. [7] reversible photo-induced changes of the optical gap (E_g) and refractive index (n) in well annealed films $Ge_xAs_2S_{1.5}Se_{1.5}$, ($0 < x < 5$), prepared by thermal evaporation of corresponding bulks were studied. A maximum in magnitude of reversible photo-darkening measured as a red shift of the gap ($dE = E_g$(annealed) – E_g(illuminated) = 181meV) was found around $x = 1.66$ that is in $Ge_{24.92}As_{30}S_{22..52}Se_{22.52}$ amorphous film. For the same chemical composition also the maximum in magnitude of photo-induced shift in refractive index (dn = n(illuminated) – a(annealed) = 0.166) was observed.

In this communication we report some results related to reversible photo-darkening of amorphous film $Ge_5As_{41}S_{15}Se_{39}$ prepared by co-evaporation from GeS_2 and AsSe bulks. Preliminary measurements of reversible photo-darkening induced by white light illumination (halogen lamp) in various amorphous films prepared by co-evaporation of GeS_2 and AsSe bulks [8] indicate that the composition $Ge_5As_{41}S_{15}Se_{39}$ is the most sensitive one.

2. Experimental

The thin films, deposited onto microscopic slides and also onto silicon wafers convenient for far infrared spectroscopy, were prepared in the way recently described, Ref [7]. The actual chemical composition was determined by electron microprobe X-ray analysis (Jeol JSM 5500 LV). The optical properties were measured using a Perkin Elemer Lambda 12 spectrophotometer and using an FTIR Thermo Nicolet Nexus spectrophotometer. The virgin as-prepared samples (v) were annealed for 2 hours in the dry argon at the temperature T = 250 °C. The annealed samples (a) were illuminated from the film side by: (i) white light (whl) using a Hund FLQ 150 W light source equipped with light guide (light intensity on sample surface ≈ 260 mW/cm^2), (ii) monochromatic light with the wavelength λ = 660 nm (light intensity on sample surface ≈ 41 mW/cm^2) and (iii) monochromatic light with λ = 523 nm (light intensity on sample surface ≈ 6 mW/cm^2). The setup used for a sample protection against oxidation was described in Ref.[9]. As a measure of photo-darkening we used the optical gap values calculated from Tauc`s formula $(\alpha\hbar\omega)^{1/2} = B^{1/2}(\alpha\hbar\omega - E_g)$, where $B^{1/2}$ the slope of Tauc`s edge reflects a sample disorder [10]. The absorption coefficient (α) is given by relation $\alpha = (1/d)\ln\{[(1-R)^2 - ((1-R)^4 + 4R^2T^2)^{1/2}]/2T\}$, where d is the sample thickness, T is the transmission and R is the reflectivity. The transmission range below 30% was used to determine α values, while R = 0.21 was taken to be invariant to the illumination.

3. Results and discussion

For readers convenience in Fig. 1 the spectral distribution of whl source used for illumination (upper part) together with the typical transmission spectrum of virgin (v), annealed (a) and darkened (λ = 660 nm) $Ge_5As_{41}S_{15}Se_{39}$ film are shown. The results of photo-darkening experiments are summarised in Fig. 2 in the gap shift ($dE_g = E_{g,(t)} - E_{g,a}$) versus time of illumination co-

ordinates. Full and dotted curves are the best fits using the relation:

$$dE_g(t) = dE_{g,\infty}(1 - \exp[-(kt)^{\beta}]), \quad (1)$$

where $dE_{g,\infty} = E_g(t\rightarrow\infty) - E_{g,a}$, k is the formal rate constant of the overall process, t is the time of illumination and β is so called stretching parameter.

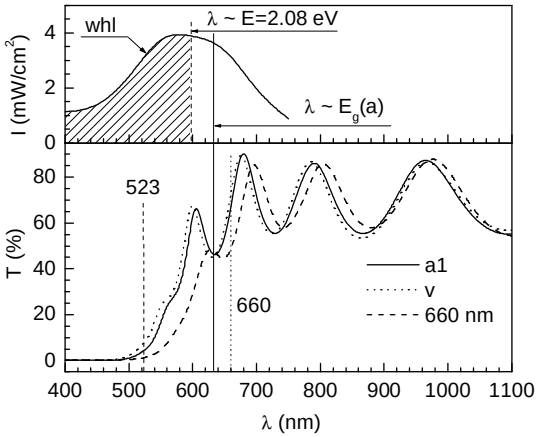


Fig. 1. Upper part - the spectral distribution of the white light source. Dashed area indicates the region of over-gap photons where photons energy exceeds the bond enthalpy of As-As bonds. The vertical line indicates the wavelengths corresponding to the gap of annealed film ($E_{g,a}$ = 1.96$_5$ eV, full line). Lower-part - typical spectral dependence of transmission for virgin (v), annealed (a1) and darkened (λ(darkening)= 660 nm) film. The vertical lines indicate the excitation light where λ = 523 nm (dashed line) and λ = 660 nm (dotted line), respectively.

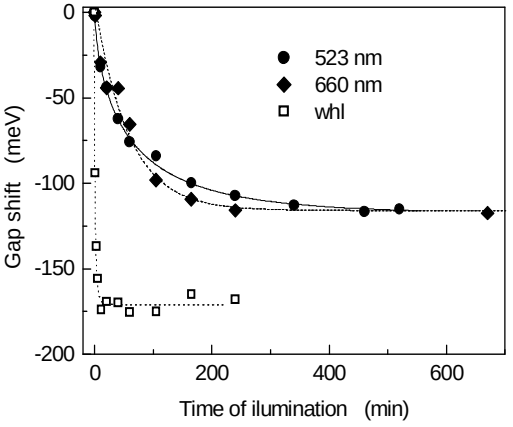


Fig. 2. The kinetics of the red shift of the gap induced by illumination using whl, over-gap photons (λ=523 nm) and "near gap" sub - gap photons (λ=660 nm), respectively. The symbols - experimental values, the curves - fits using Rel. 1. For the fitting parameters, see Table 1.

In the Table 1 are summarised some conditions of illumination together with the parameters of the fits.

Table 1. Wavelength (λ)/photons energy ($\hbar\omega_{Ph}$) of light used for illumination, the light intensity on the sample surface (I), the penetration depth of the light (d_{pnt}), the saturated photo-induced gap shift ($dE_{g,\infty}$), the formal rate constant (k) and the stretching exponent (β).The sample thickness ≈ 770 nm.

λ,[nm], $\hbar\omega_{Ph}$,[eV]	I,[mW/cm^2]	d_{pnt}, [μm]	$dE_{g,\infty}$, [meV]	k,[min^{-1}]	β
660, 1.878	≈41	≈7	116	0.019	1
523, 2.371	≈6	≈0.3	118	0.016	0.65
Whl	≈260	?	171	0.833, 0.487*	0.65, 1*

* Overall fits for single exponential, the numbers marked by asterisk, (whl), and for stretched exponential seem to be comparable, however, while for the stretched exponential the condition $dE_g(kt=1) = 0.632$ is practically fulfilled ($dE_g(t=1.2) = 0.60$), for the single exponential $dE_g(t=2.05) = 0.45$ this condition is not satisfied. Hence, in this case we shall prefer the fit using the stretched exponential form.

From Fig. 2 and Table 1 it is clear that the magnitude of photo-darkening depends on the actual conditions of illumination. For illumination by "near gap" sub-gap light (λ = 660 nm) and for illumination by over-gap light (λ = 523 nm) practically the same saturated state was reached, however, the overall kinetics of photo-darkening is different. In the former case (λ = 660 nm) the kinetics of photo-darkening follows the single exponential form, while in the second case the best fit is obtained using stretched exponential. For illumination by whl the magnitude of photo-darkening increased by about 54 meV (up to 171 meV) in a saturated state and the kinetics of the process follows also stretched exponential form. We suppose that differences in kinetics of photo-darkening reflects following facts:

(i) Determination of dE_g for illumination by over gap light (λ = 523 nm) is not fully correct. In this case the penetration depth of over gap photons is estimated close to: $d_{pnt} \leq 1/\alpha \approx 0.3$ μm. It means that from all absorbed photons in the sample, around 63% of photons are absorbed within the thickness close to 0.3 μm while in remaining sample thickness (≈ 0.47 μm) there are absorbed only around 37% of photons. Hence the sample is not homogeneously darkened and our values of absorption coefficient used for E_g determination represent rather some averaged α. Indeed if such sample in the saturated state is illuminated from the back side the darkening proceeds, see also e.g. Ref. [11]. Similar is true also for over-gap photons of whl. However, in this case there is a broad spectrum of other photons (gap and "near gap" sub-gap photons) which can be effectively absorbed in the sample. Practically no changes in magnitude of photo-darkening induced by whl are observed if the sample in the saturated state is illuminated from the substrate side.

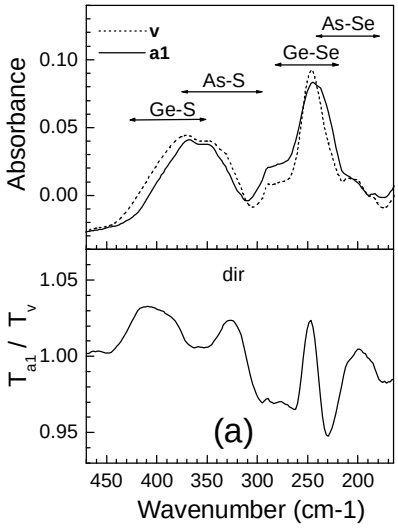
(ii) Contrary to "near gap" sub-gap light (λ = 660 nm, $\hbar\omega_{Ph}$ = 1.878 eV) the over gap photons with energy sufficiently exceeding the gap energy (short wavelength part of whl) and the light with λ = 523 nm, $\hbar\omega_{Ph}$ = 2.371 eV) can excite not only the states from the upper part of valence band but also deeper states can be simultaneously excited. Hence, as the photon energy approaches the bond energy of some bonds forming the film network there is a finite probability that a part of such bonds are broken and e.g. some photolysis can proceed within the penetration depth of relevant over-gap photons.

Consequently it is probable that for illumination by whl or by over-gap photons more processes proceed simultaneously and hence, the stretched exponential fits the data in a better way. In studied Ge_5As_{41} S_{15} Se_{39} thin film we assume existence of at least 5 different bonds. In the Table 2 are summarised the numbers of individual bonds estimated for two bonding arrangements. (1) Formation of strongest Ge-S bonds is preferred and (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.

Table 2. The type of bond, the number of bonds in a hundred atoms sample, case (1) and (2), respectively, and the bond enthalpy [12].

Bond	Number of bonds, (1)	Number of bonds, (2)	Bond enthalpy, [eV]
Ge-S	20	5.555	2.71
Ge-Se	0	14.444	2.43
As-S	10	24.445	2.63
As-Se	78	63.555	2.35
As-As	17.5	17.5	2.08

From the Table 2 it is evident that considerable fraction of bonds (76.1%(1), 64.6%(2)) forming the sample network (([As-Se]+[As-As])/ 125.5 = 0.761(1), 0.646(2)) has the bond enthalpy less than the photon energy of the monochromatic light (λ = 523 nm, $\hbar\omega_{Ph}$ = 2.371eV) we used for illumination. Also in whl used for illumination the energy of a part of photons, see dashed area in Fig. 1, exceeds the bond enthalpy of As-Se and As-As bonds. Hence, we assume that such photons can more significantly influence the sample network namely they can induce some bond reconstruction and/or creation of some defects originating from broken As-Se and As-As bonds. In Fig. 3 infrared transmission spectra and differential infrared (dir) spectra are shown: for virgin (v) and annealed (a1) film, (Fig. 3a), for annealed film illuminated by whl up to the saturated state, (Fig. 3b), for this film subsequently annealed, (a2), (Fig. 3c) and finally for the annealed film illuminated up to the saturated state by "near gap" sub-gap light (λ = 660 nm, $\hbar\omega_{Ph}$ = 1.878eV), (Fig. 3d), respectively.



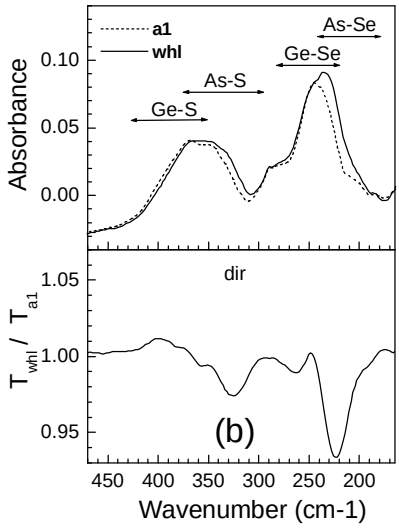


Fig. 3a,b. Upper part - far infrared transmission spectra in absorbance versus wavelength co-ordinates for virgin (v) and annealed (a1) film (Fig. 3a), for annealed (a1) and subsequently illuminated by whl (whl) film, (Fig. 3b). The horizontal arrows indicate the region of main infrared features corresponding to stretching motion in Ge-S, As-S, Ge-Se and As-Se based networks. Lower part – corresponding differential infrared spectra (dir = T(after treatment)/T(before treatment)).

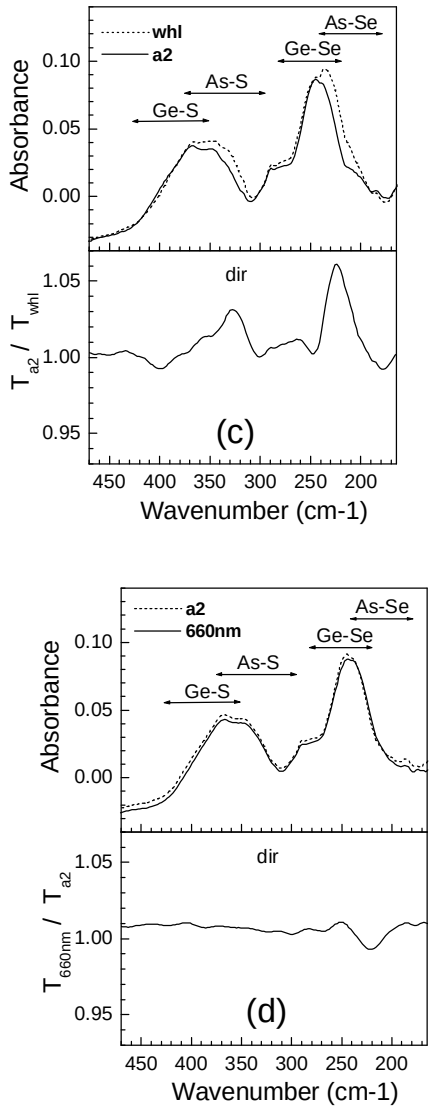


Fig. 3c,d. Upper part - far infrared transmission spectra in absorbance versus wavelength co-ordinates for the film illuminated by whl (whl) and subsequently bleached by annealing (a2), (Fig. 3c), for annealed (a) film subsequently darkened by "near gap" sub-gap photons (λ=660 nm) (660 nm), (Fig. 3d.). The horizontal arrows indicate the region of main infrared features corresponding to stretching motion in Ge-S, As-S, Ge-Se and As-Se based networks. Lower part – corresponding differential infrared spectra (dir = T (after treatment) /T(before treatment)).

Following facts are evident: (i) Fig. 3a. In the region of most intensive infrared (IR) response for Ge-S and As-S based network the annealing leads to a narrowing of a broad IR feature composed by an overlap of Ge-S and As-S main stretching motion. This observation we attribute to an increase in structural arrangement of the film network namely to a decrease in dispersion in both the bond distances and valence angles in GeS_4 tetrahedra and AsS_3 pyramids. Simultaneously in the region of the most intensive infrared response for Ge-Se and As-Se based network annealing leads to a considerable broadening of the IR feature composed by an overlap of Ge-Se and As-Se stretching motion. This observation we attribute to an increase in disorder due to a decrease in the structural arrangement in the Ge-Se and As-Se part of the network. (ii) Fig. 3b. Illumination of annealed film by whl leads to an apparent increase in absorption namely in the region 300 cm^{-1} to 380 cm^{-1} and in the region 180 cm^{-1} to 280 cm^{-1} which we, however, suppose is mainly due to a broadening of both overall IR features due to light induced increase in the film network disorder. (iii) Fig. 3c. Annealing of the film darkened by whl leads to the film bleaching accompanied by a decrease in overall absorption (in both 300 cm^{-1} to 380 cm^{-1} and 180 cm^{-1} to 280 cm^{-1} regions) which one is mainly due to a narrowing of both IR features. It means that light induced disorder of the film network decreases by annealing. (iv) Fig. 3d. Contrary to structural changes induced by whl light in annealed film (Fig. 3b) the structural changes induced by illumination of annealed film by "near gap" sub-gap light (λ = 660 nm, $\hbar\omega_{Ph}$ = 1.878 eV) are very weak. Only very small change in absorption, a weak increase in absorption centred around 220 cm^{-1} is seen in dir spectra despite the fact that darkening in this case reaches in the saturated state the value dE_g= 116 meV, see Table 1. We suppose that differences observed in the film response to the illumination by whl and by "near gap" sub-gap light are associated with following processes: (a) Contrary to "near gap" sub-gap light the over-gap photons of whl can excite also the deeper states in the valence band, namely some weak bonds like As-Se and As-As bonds can be broken which may assist to a light induced bond reconstruction and disorder increase in the film network. (b) Over-gap photons of whl are absorbed, depending on the actual penetration depth, in a narrow region which can enhance a probability of structural changes due to a co-operative two-photon process, see e.g. [13]. (c) The "near gap" sub-gap light (λ = 660 nm, $\hbar\omega_{Ph}$ = 1.878 eV) can excite only the states from an upper part of valence band or, more probably, from the tail states of the valence band, while the bonding states are nearly intact by the excitation light. Consequently in this case the light induced structural changes reflect only those changes associated with nonbonding lone pairs excitation and/or defect states in the gap. Because the density of these states is lower than the overall density of states which can be excited by the gap and over-gap photons of the whl, the darkening for the "near gap" sub-gap light is lower than the overall darkening induced by whl.

4. Conclusions

In amorphous $Ge_5As_{41}S_{15}Se_{39}$ film we observed reversible photo-darkening induced by illumination by white light and by "near gap" sub-gap photons. The magnitude of photo-darkening (dE_g) induced by white light illumination exceeds those induced by "near gap" sub-gap photons (dE_g= 116 meV) by about 54 meV.

Infrared transmission spectra indicate structural changes induced by white light illumination, while very weak structural changes are seen induced by "near gap" sub-gap light. The differences observed in magnitude of photo-darkening, in the structural changes seen in infrared transmission spectra and in kinetics of photo-darkening are tentatively attributed to different states excited by gap and over-gap photons of white light and by "near gap" sub-gap photons.

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