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PHOTO-INDUCED SHIFTS IN THE OPTICAL GAP OF a-Se THIN FILMS

L. Tichý, H. Tichá[a], P. Nagels[b], R. Mertens[b]

Joint Laboratory of Solid State Chemistry of the Academy of Sciences of the Czech Republic and the University of Pardubice, 532 10 Pardubice, Czech Republic
[a]University of Pardubice, Faculty of Chemical Technology, 532 10 Pardubice, Czech Republic
[b]RUCA, University of Antwerp, B-2020 Antwerpen, Belgium

Amorphous Se films were prepared by thermal evaporation. The photo-darkening induced by illumination with white light at various temperatures (80 K, 111 K, 146 K and 188 K, resp.) and with monochromatic light with wavelength λ = 550 nm (80 K) was studied. Photo-induced bleaching of previously-darkened samples (λ = 550 nm, 80 K) was observed at 80 K induced by illumination using light with λ = 488 nm, 671 nm, 707 nm and 768 nm, resp. It is suggested that the overall photo-darkening process is most probably a kind of self-limiting process.

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1. Introduction

Photo-induced (or photo-structural) phenomena of amorphous (a) chalcogenides are studied for more than thirty years. Various explanations and models related to the studied phenomena are summarized and discussed in a series of review articles, see e.g. Refs. [1-11]. Recently a novel explanation of photo-structural phenomena has been suggested [12,13] based on the key role of photo-induced (athermal) melting observed in amorphous selenium (a-Se) [14]. While the exact nature and mechanism of photo-structural phenomena still remain a matter of discussion, a general consensus exists that photo-structural changes, often manifested as a red shift (dE_g) of the optical gap (E_g), require p-lone-pair electron excitation over the gap and, displacement of the particular atom and its neighbours from their original position. Consequently, the magnitude of dE_g is related to the efficiency of p-lone-pair electron excitation and to the density of subsequent structural changes. Hence, the way of sample illumination should influence the measured shift of the gap.

In this communication we examine and illustrate the considerable role of the illumination conditions on the photo-induced shifts in the optical gap in a-Se thin films.

2. Experimental

Amorphous Se thin films (thickness d ≅ 1000 nm) were prepared from 5N purity Se by thermal evaporation (Balzers-BAE 250 T system, p ~ 10^{-4} Pa, rate of evaporation ~ 10 Å/s) onto glassy substrate at normal incidence. The films were stored for two months in the dark in a dessicator filled with argon gas to relax the material.

The optical properties were measured using a Beckman DU-640 UV-VIS spectrophotometer. All measurements were made in an optical cryostat Cryoson XL 500 precisely fixed in the sample compartment of the spectrophotometer. The optical transmittivity of relaxed (virgin) and illuminated samples was measured at the temperatures 80 K, 111 K, 146 K and 188 K, respectively. The

measurements were made with helium gas in the inner part of the cryostat in order to minimize any temperature fluctuation.

For illumination a halogen lamp (equipped with an infrared filter) having a maximum energy output around 550 nm was used. The overall incident power density was around 50 mW/cm^2. For illumination by monochromatic light, a Xe lamp equipped with an optical fibre and interference filters was used. In this case the incident power density was very low, around 1-2 mW/cm^2, depending on the filter used. The halogen lamp or optical fiber + interference filter were placed in the sample compartment in front of the input window of the optical cryostat. In this set-up the position of the sample in the beam was always the same. During illumination and measurements the temperature was kept nearly constant with a precision of ± 5 K.

As a measure of photo-darkening we used the shift of the optical gap induced by illumination. The values of the optical gap (E_g) were taken as the intercept of plots $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ (Tauc´s formula [15]), for $\alpha = 0$, where α is the absorption coefficient calculated from Eq.(4-32) [16]. The transmittivity below 20 % was used to determine α values. In this region the condition $\alpha d > 1$ was fulfilled. The measured room value of the reflectivity R = 23 % (a-Se) was used for calculation of α.

3. Results

3.1. Photo-darkening

In Fig.1 are summarized the dependencies of dE_g (= E_g(virgin) – E_g(illuminated)) versus illumination time. The thin curves represent a fit (see Tab.1 for the fitting parameters used) of our experimental data by a stretched exponential function (Eq.1) using standard estimation of the β and k values from a lnln ( ) function, see e.g. [17]

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

here $E_g(v)$ is the optical gap of the *virgin*–relaxed sample, $E_g(t)$ is the optical gap after illumination at time t (min), $E_g(\infty)$ is the saturated optical gap, k is the rate constant and β is the stretching parameter.

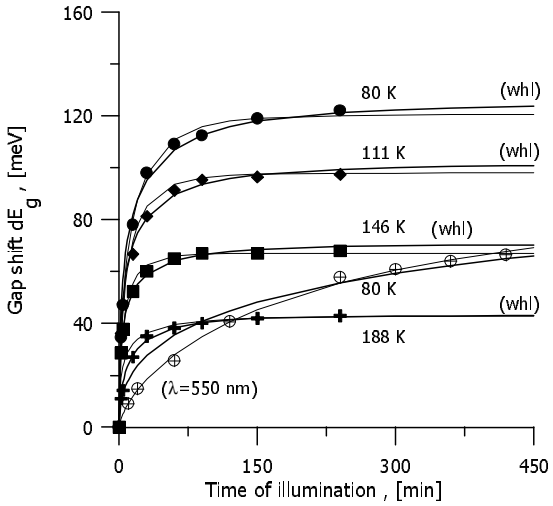

Fig. 1. The dependence of the red shift of the gap ($dE_g(t)$) induced by illumination at various temperatures. Meaning of corresponding symbols: full symbols - excitation by white light (whl), crossed circles - excitation by monochromatic over-gap light (λ = 550 nm). Thin curves – fit using standard lnln function („lnln" fit), heavy curves – fit using β = 0.43, see Eq.(1), and [19-21]. The fitting parameters, see Tab.1.

We did not obtain a good fit using a simple exponential ($\beta = 1$ in Eq. (1)) and, hence, we have to correct our recent results [18] stating that the measured photo-darkening kinetics follows a stretched exponential function and not the first-order process. Unfortunately, the stretched exponential function is a rather *flexible* one which can give comparable results for different β and k values. This fact is illustrated (see Fig. 1) in the correspondence between experimental data, heavy curves calculated using $\beta = 0.43$ [19-21], and thin curves, calculated using β values obtained from the lnln [ ] fit, see Table 1. With exception of the $dE_g(t)$ dependence induced by monochromatic light ($\lambda = 550$ nm, see Fig. 1) the agreement between the experimental values and calculated heavy curves ($\beta = 0.43$) is reasonable.

Table 1. The fitting parameters used for the calculation of the stretched exponentials (see Fig.1) the temperature (T, in (K)), the value of the saturated optical gap ($E_g(\infty)$, in (eV)), the rate constant (k, in (min^{-1})) and the values of the stretching parameter (β, see Eq.(1)).

		„lnln“ fit			$\beta = 0.43$ fit	
Excitation	T	$E_g(\infty)$	β	k	$E_g(\infty)$	k
white light	80	1.99_4	0.61	0.077	1.99_3	0.078
	111	1.99_6	0.61	0.105	1.99_3	0.098
	146	1.99_5	0.61	0.167	1.99_0	0.132
	188	1.99_5	0.5	0.125	1.99_5	0.14
$\lambda = 550$ nm	80	2.0	0.69	0.004	1.98	0.002

At the present time the understanding of the origin of photo-darkening kinetics still remains an open problem. It is out of the scope of this communication and we only use estimated $dE_g(\infty)$, see Eq. (1), for further discussion.

Two facts are evident from Fig. 1. (i) The well-known role of the temperature on the magnitude of photo-darkening, see e.g. [22,23], and (ii) a significant role of the excitation light on the magnitude of the photo-darkening at $T \cong 80$K.

The role of the wavelength (λ) of the excitation light on the dE_g shift is illustrated in Fig. 2.

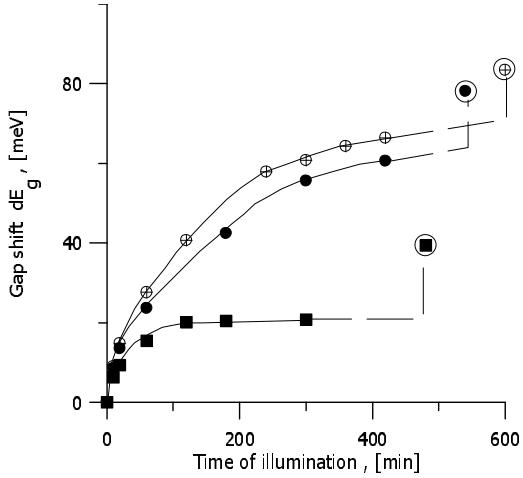

Fig. 2. The $dE_g(t)$ dependence at T = 80 K for excitation by light with $\lambda = 550$ nm, crossed circles ⊕ – illumination from the film side, full circles • – illumination from the substrate side and full squares ■ - excitation by light with $\lambda = 488$ nm. By encircled symbols the dE_g shift induced by illumination from the reverse side is shown, see text. Dashed lines only indicate a jump-like change in dE_g induced by illumination from the reverse side. The curves are only guide for the eye.

The crossed circles correspond to $dE_g(t)$ values for illumination by the light with λ = 550 nm from the film side. The full circles correspond to $dE_g(t)$ values for illumination by light with λ = 550 nm from the substrate side and full squares correspond to $dE_g(t)$ values for illumination by light λ = 488 nm from the film side. The last encircled points indicate the $dE_g(t)$ values for illumination of the relevant sample from the reverse side. The sample was turned around over 180 ° in the cryostat and the response was measured after illumination from the reverse side. Two features are evident. Firstly, no significant role of the substrate is observed on the dE_g values since the $dE_g(t)$ values for illumination from the film side (⊕) and from the substrate side (•) are very close. Secondly, the magnitude of photo-darkening depends on the penetration depth of the light. For the excitation light with λ = 488 nm, the penetration depth is estimated to be one order of magnitude lower than that one for the light with λ = 550 nm. Therefore, the darkening significantly continues if the sample is illuminated from the opposite side (see Fig. 2). For light with λ = 550 nm, the penetration depth is probably still smaller than the sample thickness (d) but it is closer to d. Consequently, dE_g induced by illumination from the reverse side of a sample is lower in comparison with the one observed by light illumination with λ = 488 nm.

In Fig. 3 are summarised the measured experimental dE_g values corresponding with the longest time of illumination together with the calculated $dE_g(\infty)$ values (fits according to Eq.(1)) for white light illumination (whl), for λ = 550 nm and λ = 488 nm excitation light plotted in co-ordinates dE_g versus T_i/T_g (see [22]), where T_i is the temperature of illumination and T_g is the glass-transition temperature of a-Se.

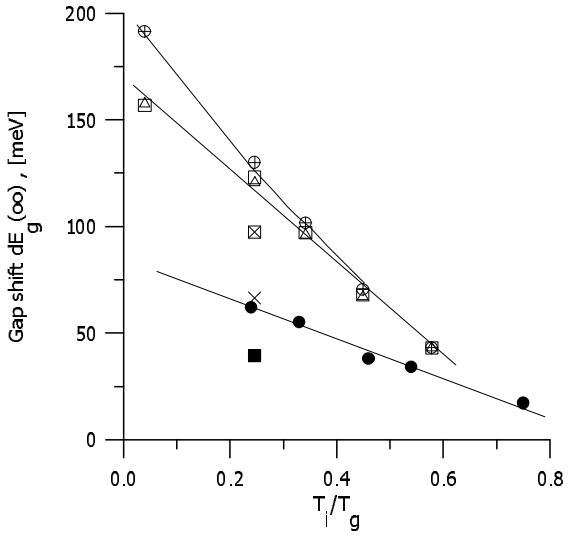

Fig. 3. The dE_g dependencies for various experimental or calculated values of the red shift of the gap as a function of the illumination temperature (T_i) normalized to the glass-transition temperature (T_g). ⊕: β = 0.43, „JCP“ fit, (whl); Δ: β = 0.5-0.61, „lnln“ fit, (whl); □: last experimental value,(whl); □: β = 0.69, „lnln“ fit, (550 nm); x: last experimental value, (550 nm); ■: last experimental value, (488 nm); •: Tanaka´s values, Ref. [22]. The lines are nly guide for the eye.

For the readers convenience, in Fig. 3 are also shown the $dE_g(T_i/T_g)$ values (saturated states for band-gap light) for a-Se taken from Ref. [22] and the $dE_g(\infty)$ value calculated from the experimental data of photo-induced darkening of a-Se at 13 K [24]. It is evident that the photo-induced gap shift strongly depends on the details of illumination. For example, our last experimental value dE_g (T ~ 80 K, marked by x in Fig. 3) agrees well with $dE_g(\infty)$ (T ~ 80 K) reported by Tanaka [22]; however, from Fig. 1 (see dE_g values for λ = 550 nm) it is clear that even after 7 hours of illumination the sample is not in a saturated state. Note, that the calculated value of $dE_g(\infty)$(T ~ 80 K) for our gap light was found close to 95 meV (Fig. 3). We observed a nearly saturated value around 120 meV for dE_g(T ~ 80 K) induced by white light illumination, very close to calculated $dE_g(\infty)$ = 125 - 130 meV. We relate the observed differences in $dE_g(\infty)$ values to the number of

effective photons capable to excite susceptible sites of a sample. For white light with the light intensity 50 mW/cm^2 there is a broad spectrum of photons and also a sufficient number of photons to excite more susceptible states than in the case of gap light with intensity around 2 mW/cm^2. Moreover, in the case of photo-darkening induced by gap light, the light penetration depth should decrease during the darkening process (the absorption coefficient increases), while in the case of white light there are other photons with energy more relevant to affect the partly darkened state of the sample.

3.2. Photo-bleaching

In Fig. 4 the photo-induced bleaching induced by below-gap (λ = 671, 707, 768 nm, resp.) and over-gap (λ = 488 nm) photons of a previously - darkened sample by *small* over-gap photons (λ = 550 nm) is shown. The bleaching is considerable, especially for light with λ = 671 nm. The result is interesting especially since according to Averianov et al.[23] in materials with excess chalcogen the temperature dependent probabilities of optical transitions from the ground state to the metastable state (the darkened state) and vice versa change in an identical way. Therefore no optical bleaching is observed in these materials. A surprising result is the small but well resolved bleaching induced by over-gap illumination.

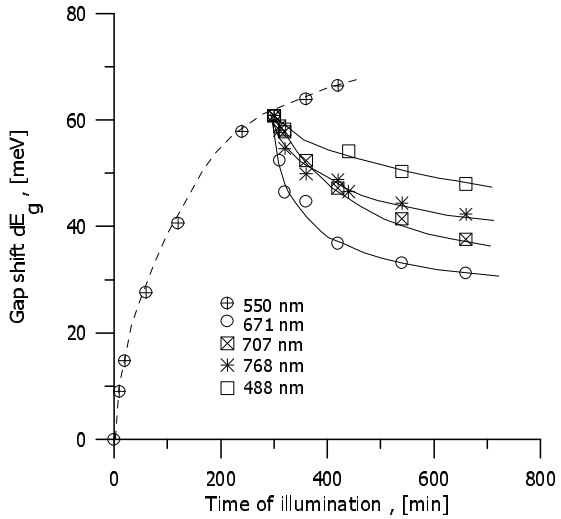

Fig. 4. The $dE_g(t)$ shift – darkening at T = 80 K induced by illumination using "small over-gap light" (λ = 550 nm) – crossed circles, and bleaching induced by illumination using „over-gap light" (λ = 488 nm) and using „below-gap light" (λ = 671, 707, 768 nm, resp.). The curves are only guide for the eye.

4. Discussion

We suppose that the observed role of the excitation light on the process of the photo-induced shift of the gap can be qualitatively explained within a slightly modified *single-double well* model of Tanaka (SDW) [5] (see Fig. 5), also taking into account the energy-co-ordinate model by Averianov et al. [23]. By suitable light energy ($\hbar\omega_1 \geq E_g$) some sample states are excited from the ground state (GS) to a transient excited state (ES). After a process of excited carrier energy dissipation, the carriers recombine non-radiatively into a new quasi-stable state (QSS) which is the darkened state. The degree of darkening (dE_g) is given by a volume fraction of ES and QSS which is manifested by the role of the penetration depth of the light used for the sample illumination. The process marked in Fig. 5 by 1 is the true darkening process.

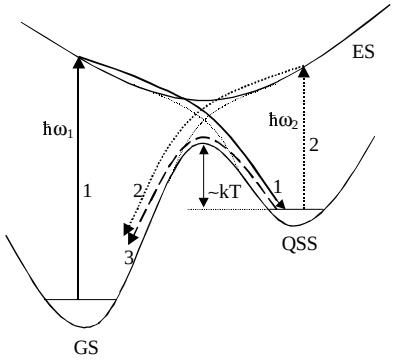

Fig. 5. Tanaka´s SDW energy – co-ordinate diagram with suggested non-radiative transitions responsible for photo-darkening (process 1), for photo-bleaching (process 2), and for pure thermal bleaching (process 3). GS – a ground state, QSS – a quasi-stable state, ES – an excited transient-like state. Possible radiative (direct-vertical) transitions ES → GS and ES → QSS are not shown here. We note that the direct-vertical transition ES → QSS, not shown there, is in fact relevant to Tanaka´s $n_0 \rightarrow i_3 \rightarrow l_0 \rightarrow n_0$ transition [25].

The GS and QSS are separated by a barrier 3 with a barrier energy proportional to kT. As the GS is much deeper than the QSS, effective thermal transition is only possible from QSS to GS, that is the true thermal bleaching. If the darkened sample is illuminated by photons with energy $\hbar\omega_2$, and $\hbar\omega_2 < \hbar\omega_1$, the QSS can be excited back to ES and analogously to the process 1, after some energy dissipation, the carrier can recombine non-radiatively back to GS. Hence, some part of QSS is transferred back to GS and photo-induced bleaching is observed, see Fig. 4. A direct vertical recombination from ES to QSS, like the $n_0 \rightarrow i_3 \rightarrow l_0 \rightarrow n_0$ transition mentioned by Tanaka [25], is also possible. This transition is, however, ineffective for the bleaching process. We observed also bleaching induced by over-gap light illumination ($\hbar\omega_2 > \hbar\omega_1$). We suppose that a possible reason for such behaviour is associated with the higher stability of GS in relation to QSS and also with the number of states susceptible of excitation in both the GS and QSS. If for given light wavelength, in our case the light with λ = 480 nm, the overall number of the states susceptible for excitation from GS to QSS is less (available states were excited by the light with λ = 550 nm, see Fig. 2, for the difference in dEg induced by the illumination using light with λ = 480 nm and λ = 550 nm) than the number of states susceptible of excitation back from QSS to GS, the sample is bleached even by over-gap light. The bleaching will proceed until a new dynamical equilibrium state relevant to the last light used for illumination is reached.

According to Averianov et al. [23] the photo-induced bleaching, that is the process 2, requires some kT energy because with increase of the temperature the photo-bleaching becomes enhanced. From our experiments it is evident that even in this case the temperature of 80 K is sufficient for photo-induced bleaching in a-Se. If both processes 1 and 2 are operative and Tanaka's SDW model can be applied to the process of photo-induced phenomena in amorphous chalcogenides, then for any photon with energy susceptible to excite GS into ES with subsequent transition into QSS will proceed simultaneously both the darkening, process 1 and the bleaching, process 2. It means that the overall process of photo-darkening is a *self-limiting* process. This *self-limiting* process is not only due to a reduction of GS states in the course of the over-gap illumination but, it is also due to a dynamical equilibrium between process 1 and 2.

5. Conclusions

(i) The kinetics of photo-darkening of an a-Se film follows a stretched exponential form for white light and gap light illumination.

(ii) The magnitude of photo-darkening depends on the light intensity and penetration depth of effective photons that is the photons susceptible to create photo-darkening. For excitation by white

light we observed a considerable shift of the gap by about 120 meV at the temperature 80 K in a saturated state. This value exceeds the saturated state reported by Tanaka [22] (band gap light excitation, T ~ 80 K) by about 60 meV. We attribute the difference in the saturated states to the higher light intensity of our white light (50 mW/cm^2), (Tanaka used a light intensity around 10 mW/cm^2), and also to the broad spectrum of effective photons in the white light.

(iii) We observed that the photo-darkened state can be bleached by below-gap and over-gap photons. This finding leads us to the conclusion that photo-darkening is in fact a self-limiting process where simultaneously proceed the optical excitations from a ground state to a quasi-stable darkened state and vice versa.

(iv) We speculate that the sensitivity of photo-structural changes to the light penetration depth could be of interest for some technical applications. For example, by changing the light wavelength a different depth of the sample is affected, and by etching profiles of different depth can be prepared. In principle also *writing* and *reading* (in reflection mode) could probably be realized simultaneously from both sides of a film for convenient excitation light with penetration depth less than e.g. 1/3 of the film thickness.

Acknowledgements

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