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Reversible vs irreversible photodarkening in a-Se: the kinetics study

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Abstract The kinetics of photodarkening (PD) in amorphous selenium has been studied experimentally at different intensities of optical excitation. Comparison between the experimental results and a proposed phenomenological model reveals the characteristic rates for conversion of structural units into reversible and irreversible states. Our results show that the relaxation of the irreversible PD states occurs over a barrier of about 0.9 eV and is described by much longer characteristic times (more that one order of magnitude) than that for the reversible states.

1 Introduction

It is well known that many chalcogenide glasses may undergo photostructural transformations as a result of exposure to light. One manifestation of such transformations is the photodarkening (PD) effect [1–5]. PD is traced to the increase in the level of disorder as a result of the photostructural transformations which lead to the broadening of the band tails and hence, to the red shift in the absorption. Phenomenologically the PD effect is described as the photoinduced conversion of some structural units from the ground state configuration X (which is optically transparent) into some upper metastable state Y (which causes photodarkening) (Fig. 1a) [1, 6, 7]. Previously the PD effect in a-Se films has been observed under cooling only and was not found at room temperature (RT). [8–10] For high-quality a-Se films the PD effect is usually reversible: the original transmission of the a-Se layer is restored after the relaxation or annealing at glass transition temperature T_g [11]. This reversibility is assigned to the metastable nature of the state Y which can be easily annealed out restoring the original structural configuration and thus eliminating PD. However, it was recently shown, that prolonged exposure to light may cause stable structural transformations in high-quality a-Se layers even at RT [12, 13]. Once appear this structural modification cannot be annealed out. To get better insight into the physics of the photo-induced defects formation and into the effect of temperature on it, we performed recently a comparative study of PD effects at RT and at 35 °C (i.e. slightly below T_g) [7]. The results suggest that the relaxation of PD behaves differently at these temperatures: while at 35 °C PD exhibits reversible recovery, at RT the relaxation has both, reversible and irreversible components. This indicates that at RT there is at least one further structural unit (let us call it Z state) responsible for the irreversible component of the PD (Fig. 1b). In contrast, at 35 °C the creation of Z states is suppressed resulting in complete recovery of the transmission. In our previous work [7] we have demonstrated that the reversible component of the PD effect could be explained by the existence of the photo-induced defect with the relaxation time of ~ 8 s. The experimental results at that time however, allowed us just to speculate about the nature of the irreversible component

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of PD. The subject of this paper is to extend our knowledge on the mechanism of the irreversible PD effect in a-Se. To do this we investigate PD effect at different light intensities and compare experimental results obtained at RT (21 °C) and at 35 °C. We show that the magnitude of the reversible PD component depends linearly on light intensity proving the validity of the model of the reversible photo-induced transformation used in [7]. In contrast, the irreversible PD effect appears to be strongly non-linear although measured exactly at the same range of light intensities as a reversible one. The quantitative analysis of the observed effects provides estimates for the generation rates of Y and Z states responsible for the reversible and irreversible components of the PD effect as well as for the energy barrier E_B' which separates the metastable Z state of structural units responsible for the irreversible component of the PD effect from their ground state X.

2 Results and discussion

High quality 5–10 μm thick a-Se layers were used in this study. The kinetics of the irreversible PD effect was investigated with two laser beams, where the *pump beam* was causing PD while the *probe beam* was monitoring the simultaneous changes in transmission of light T caused by the pump beam. The details of the experimental apparatus can be found in [7]. Different intensities of the pump beam in the range from 0.36 to 2.75 W/cm^2 were used. The intensity of the probe beam was kept at low value of 0.4 mW/cm^2. The kinetics of the PD was studied by alternating exposing the a-Se to the pumping beam for cycles of 100 s separated by 100-s periods of rest. The intensity of the transmitted probe beam was measured continuously and relative changes T/T_0 were calculated, where T_0 is the initial transmission. The results of the PD measurements at RT for 10 pumping/rest cycles and for different intensities of optical excitation I are shown in Fig. 2. Both, reversible and irreversible PD components are present at this temperature (Fig. 2). The irreversible component in the PD effect is evidenced by the gradual reduction in the magnitude of T/T_0 at the end of each subsequent pumping/rest cycle (i.e. in the gradual deepening of the level $\Delta_{ir}(T/T_0)$, to which the sample transparency can be restored).

To investigate the effect of light intensity on the magnitude of the reversible PD the a-Se sample was kept at 35 °C and the changes in T over the longer pump periods of 500 s were monitored for $I = 0.17 - 2.75$ W/cm^2 (Fig. 3). As expected, at 35 °C only the reversible component of the PD is observed that is reflected in complete restoration in T during rest periods. As it is seen from Fig. 3 the magnitude of the photodarkening measured as the drop in T/T_0 during the pump periods of each cycle depends significantly on I.

2.1 Reversible PD effect (35 °C)

In order to interpret the experimental data, we use a model of photodarkening suggested in [1, 2, 6] and developed further in [7]. According to this model the appearance of structural units in Y configuration causes the reversible PD effect (Fig. 1a) and the changes in T/T_0 are assumed to be proportional to the density of Y units. As it is proposed in [7] the relaxation occurs by thermal activation over the

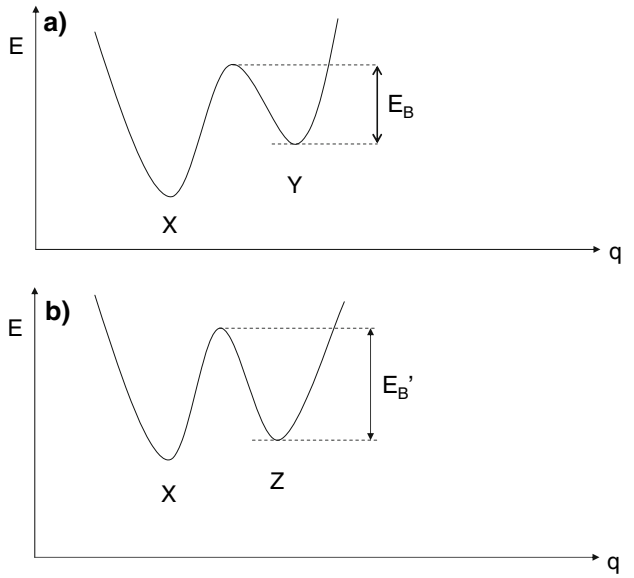

Fig. 1 Energy-configuration diagram for the proposed photoinduced "reversible" (**a**) and "irreversible (**b**) structural changes

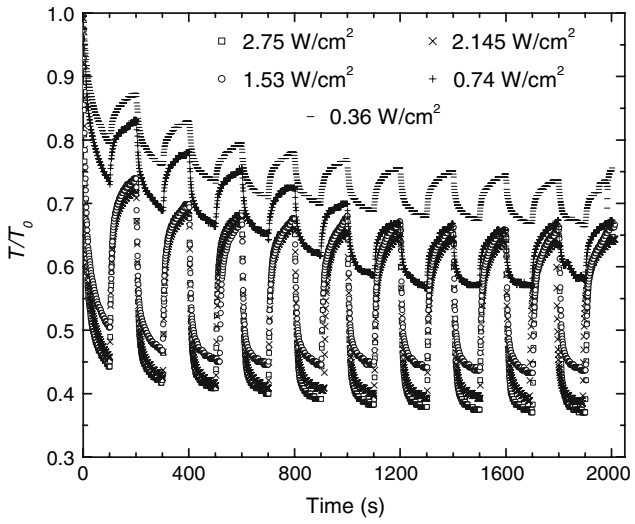

Fig. 2 Photodarkening measurements at RT for five different light intensities. Changes in T/T_0 are seen during alternating 100 s periods of pump and rest

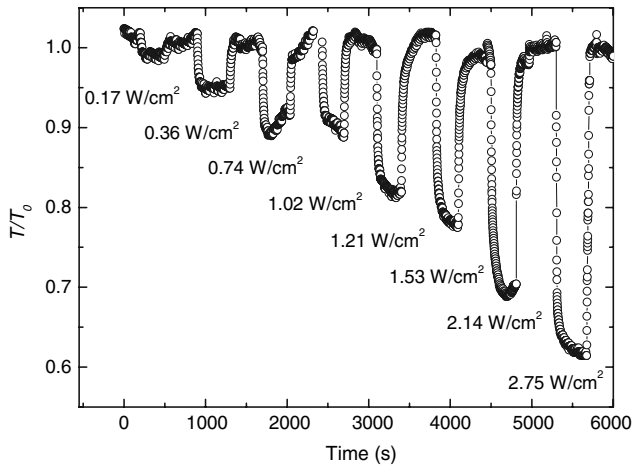

Fig. 3 Photodarkening measurements at 35 °C for eight different light intensities. The light intensity was kept constant at the level indicated for each cycle consisted of 500 s of pumping followed by 500 s of rest

energy barrier $E_B = 0.8$ eV shown in the configuration diagram in Fig. 1a.

Let the concentration of structural units which are photo-induced to transform from their ground state configuration X into a state Y be N_0, the rate of the conversion from X into Y under continuous pumping be G_{XY} and the relaxation time for a transition from Y back into X be τ_{0r}. Then, the time dependence of the concentration of units in the metastable Y state under continuous pumping $n_Y(t)$ can be described as:

$$\frac{dn_Y(t)}{dt} = G_{XY}[N_0 - n_Y(t)] - \frac{n_Y(t)}{\tau_{0r}} \tag{1}$$

with the solution:

$$n_y(t) = G_{XY} \cdot \tau_r \cdot N_0[1 - \exp(-t/\tau_r)] \tag{2}$$

where the characteristic darkening time constant τ_r for the reversible PD process is:

$$\tau_r = \frac{\tau_{0r}}{G_{XY} \cdot \tau_{0r} + 1}. \tag{3}$$

At 35 °C $\tau_{0r} \cong 8$ s [7]. This allows us to estimate quantitatively the generation rate G_{XY} for different pumping light intensities I. Consider, for instance, the data at $I = 0.74$ W/cm^2 (Fig. 3). During the pumping periods the average changes in the transmission $\Delta_r(T/T_0) \cong 0.1$. According to our model, the change in $\Delta_r(T/T_0)$ is equal to n_Y/N_0, i.e. to the fraction of the structural units in the state Y of the total amount N_0. On the other hand, according to Eqs. 2 and 3 under stationary pumping

$$\frac{n_Y}{N_0} = G_{XY} \cdot \tau_r = G_{XY} \frac{\tau_{0r}}{G_{XY} \cdot \tau_{0r} + 1} \cong 0.1 \tag{4}$$

giving $G_{XY} \cdot \tau_{0r} \cong 0.111$. Since $\tau_{0r} \cong 8$ s [7], $G_{XY} \cong 0.014$ s^{-1} at $I = 0.74$ W/cm^2. G_{XY} for different pump beam intensities I were derived in a similar manner and are plotted in Fig. 4 together with the corresponding values for $\Delta_r(T/T_0)$ in the steady-state conditions. As it is seen from the Fig. 4, both $\Delta_r(T/T_0)$ and G_{XY} are linearly proportional to I. This is consistent with the previously observed similarity in τ_{0r} and τ_r [7]. Indeed, according to the Eq. 3 $\tau_{0r} \approx \tau_r$ imposes the condition of $G_{XY} \cdot \tau_{0r} \ll 1$ which in its turn requires $\Delta_r(T/T_0)$ to depend linearly on the conversion rate G_{XY}. As it is seen from the Fig. 4 this condition is met proving the validity of the proposed model for the reversible PD effect observed at 35 °C.

2.2 Irreversible PR effect (RT)

Let us now turn to the analysis of the irreversible PD. Assuming that a certain metastable state Z of the structural units responsible for the PD causes the irreversible component of the PD effect as shown in Fig. 1b, we can suppose that the magnitude of the irreversible PD effect is proportional to the number $n_Z(t)$ of structural units in Z states. By analogy with Eq. 1–3 we can write:

$$\frac{dn_Z(t)}{dt} = G_{XZ}[N_{0Z} - n_Z(t)] - \frac{n_Z(t)}{\tau_{0ir}} \tag{5}$$

$$n_Z(t) = G_{XZ} \cdot \tau_{ir} \cdot N_{0Z}[1 - \exp(-t/\tau_{ir})] \tag{6}$$

$$\tau_{ir} = \frac{\tau_{0ir}}{G_{xz} \cdot \tau_{0ir} + 1}, \tag{7}$$

where N_{0Z} is the concentration of structural units, which can be converted into states Z and provide the irreversible PD effect; G_{XZ} is the conversion rate from state X into state Z, τ_{0ir} is the relaxation time for transitions from Z state back into the ground X states, τ_{ir} is the characteristic

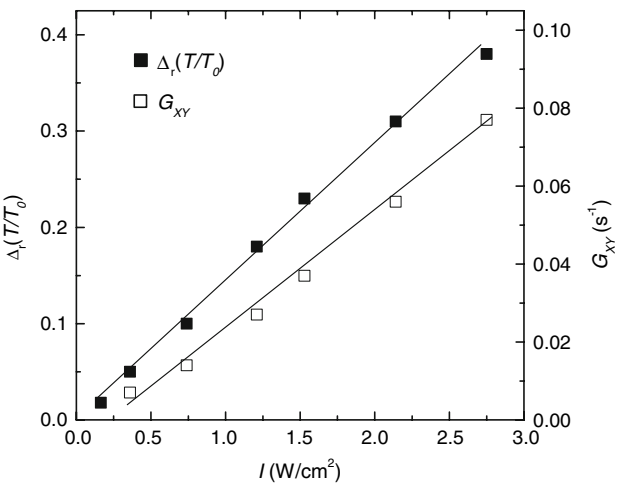

Fig. 4 The magnitude of the reversible PD effect (filled squares) and the conversion rate from the ground state configuration X into the configuration Y responsible for reversible PD component (open squares) as function of the light intensity

darkening time constant for the irreversible PD effect. In contrast to the reversible PD component whose magnitude gradually increases with increase in I, the behaviour of the irreversible PD is strongly non-linear. As it is seen from Fig. 2, the change in intensity by two (from $I = 0.36$ to 0.74 W/cm^2) results just in slight changes in the overall decrease in T/T_0. With further increase in I irreversible PD saturates rapidly, as is reflected in the same level to which T can be restored after six pump/rest cycles: $\Delta_{ir}(T/T_0) = \frac{n_Z}{N_{oZ}} \cong 0.35$ for all $I \geq 0.74$ W/cm^2 (see Fig. 5). The saturation in the magnitude of the irreversible PD component suggests that the number of units in Z state does not change anymore after six successive cycles meaning that for this range of exposure X-to-Z conversion process is limited by the total number of units N_{0Z} which can be potentially converted. Thus, in the last four cycles the drop in T during the pump period is accounted for by the reversible PD component only.

The saturation in $\Delta_{ir}(T/T_0)$ allows us to quantify the irreversible PD process. Fitting of the experimental $\Delta_{ir}(T/T_0)$ to the Eq. 6 gives $\tau_{ir} \cong 400$ s at $I = 0.74$ W/cm^2 and $\tau_{ir} \cong 200$ s for $I \geq 1.53$ W/cm^2 (Fig. 5). Using these values for τ_{ir} we can estimate the conversion rate G_{XZ}. Indeed, saturation in the changes of the magnitude of the PD with time corresponds to the steady-state condition:

$$\frac{n_Z}{N_{0Z}} = G_{XZ} \cdot \tau_{ir}(G_{XZ}) \tag{8}$$

Equating (8) to the final $\Delta_{ir}(T/T_0)$ of 0.35 gives $G_{XZ} \cong 9 \times 10^{-4}$ s^{-1} for $I = 0.74$ W/cm^2 and $G_{XZ} \cong 2 \times 10^{-3}$ s^{-1} for $I \geq 1.53$ W/cm^2. This in turn permits for the estimation of the relaxation time τ_{0ir} (Eq. 7) which appears to be $\sim$600 and $\sim$300 s, respectively. A decrease in τ_{0ir} with increase in the rate of X-to-Z conversion is attributable to the fact that the height E_B' of the potential barrier which separates X ground state and Z metastable state (Fig. 1b) slightly decreases with the gradual accumulation of structural units in Z configuration. Using the final value of the relaxation time $\tau_{0ir} \approx 300$ s, E_B' can be estimated:

$$\tau_{0ir} = \nu_0^{-1} \exp(E_B'/k_B\Theta), \tag{9}$$

where k_B is Boltzmann constant, Θ is the temperature and ν_0 is the attempt-to-escape frequency of the order of phonon frequency $\sim 5 \times 10^{12}$ s^{-1}. This estimation suggests that the relaxation from Z state responsible for the irreversible PD effect back to initial X state occurs by thermal activation over the energy barrier $E_B' \approx 0.9$ eV.

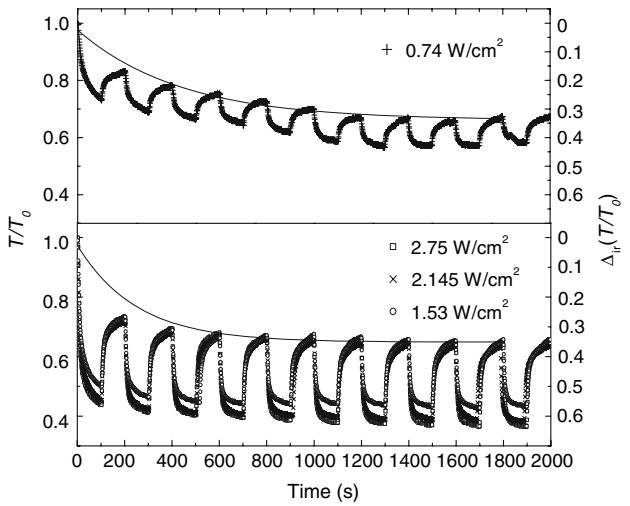

Fig. 5 Fitting of the photodarkening measurements at room temperature to the Eq. 6 (solid lines). Upper part ($I = 0.74$ W/cm^2): $\tau_{ir} \cong 400$ s. Lower part ($I \geq 1.53$ W/cm^2): $\tau_{ir} \cong 200$ s

3 Conclusions

We have studied the PD phenomena in a-Se films at room temperature (RT = 21 °C) and at temperature close to the glass transition temperature $T_g = 35$ °C under different light intensities between $I = 0.17$ W/cm^2 and $I = 2.75$ W/cm^2. The PD effect is described as the photoinduced conversion of some structural units from the initial states X (which are optically transparent) into the metastable states Y and Z (which cause reversible and irreversible PD components, respectively). Our quantitative analysis shows that the generation rate of the reversible PD effect, i.e. the rate of transitions from X into Y states, increases linearly with the intensity of light. In contrast, the generation rate for the irreversible component (from X to Z) is almost independent of light intensity for the same exposure range and is more than an order of magnitude smaller. Furthermore, the relaxation of the irreversible PD component is characterized by a much longer time constant and appears to occur over the barrier of about 0.9 eV which separates X and Z states.

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References

1. K. Tanaka in *Photo-Induced Metastability in Amorphous Semiconductors*, ed. by A.V. Kolobov (Wiley, Weinheim, 2003), p. 69
2. K. Tanaka, A. Odajima, J. Non-Cryst. Solids **46**, 259 (1981)
3. S.G. Bishop, U. Strom, P.C. Taylor, Phys. Rev. Lett. **34**, 1346 (1975)
4. S.G. Bishop, U. Strom, P.C. Taylor, Phys. Rev. B **15**, 2278 (1977)
5. V.M. Lybin, M. Klebanov, I. Bar, S. Rosenwaks, V. Volterra, L. Boehm, Z. Vagish, Appl. Surf. Sci. **106**, 502 (1996)
6. K. Shimakawa, S. Inami, S.R. Elliott, Phys. Rev. B **42**, 11857 (1990)

7. A. Reznik, S.D. Baranovskii, V. Lyubin, M. Klebanov, B.J.M. Lui, S.O. Kasap, O. Rubel, Y. Ohkawa, T. Matsubara, K. Miyakawa, M. Kubota, K. Tanioka, T. Kawai, J.A. Rowlands, J. Appl. Phys. **100**, 113506 (2006)
8. V.L. Averianov, A.V. Kolobov, B.T. Kolomiets, V.M. Lyubin, Phys. Stat. Sol., **a 57**, 81 (1980)
9. K. Tanaka, A. Odajima, Solid State Commun. **43**, 962 (1982)
10. R.T. Phillips, J. Non-Cryst. Solids **70**, 359 (1985)
11. M. Frumar, B. Frumarova, T. Wagner, P. Nemec, in *Photo-Induced Metastability in Amorphous Semiconductors*, ed. by A.V. Kolobov (Wiley, Weinheim, 2003), p. 23
12. A. Ganjoo, K. Shimakawa, K. Kitano, E.A. Davis, J. Non-Cryst. Solids **299–302**, 917 (2002)
13. A. Reznik, B.J.M. Lui, V. Lyubin, M. Klebanov, Y. Ohkawa, T. Matsubara, K. Miyakawa, M. Kubota, K. Tanioka, T. Kawai, J.A. Rowlands, J Non-Cryst. Solids **352**, 1595 (2006)