

## Kinetics of the photostructural changes in *a*-Se films

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The kinetics of the photodarkening effect has been studied experimentally for amorphous selenium (*a*-Se) layers at room temperature and at an elevated temperature (35 °C) close to the glass transition. By switching an intense pumping light on and off with a period of 100 s, we have studied the kinetics of both the buildup of photodarkening and its relaxation (recovery). It was found that at 35 °C, only a reversible component of photodarkening has been observed. This result has been interpreted within the framework of a phenomenological model assuming that photodarkening is caused by light-induced transitions of structural units from their ground states into metastable states. Our estimate for the energy barrier  $E_B$  between these states obtained for the photodarkening process ( $E_B \sim 0.8$  eV) coincides with that obtained from the analysis of the relaxation process. At room temperature, an irreversible component of photodarkening has been observed along with the reversible one. The energy barrier responsible for the relaxation of the reversible component at room temperature appears the same as at 35 °C. This suggests that the energy barrier identified represents a fundamental feature of the photoinduced structural metastability in amorphous selenium.

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### I. INTRODUCTION

Recently there has been a growing interest in photoinduced processes in amorphous selenium (*a*-Se). This is due to an expanding field of applications in modern imaging devices that became possible as a result of the development of photoconductor quality *a*-Se (i.e., stable avalanche gain and negligible trapping). One of the most important applications of the avalanche multiplication process in *a*-Se is in high-field avalanche rushing photoconductor (HARP) video tubes for optical imaging cameras. Currently HARP cameras are produced for high-definition television broadcasting,<sup>1,2</sup> and HARP-based technologies are planned for use in medical x-ray and gamma-ray imaging applications.<sup>3,4</sup> One important requirement for HARP targets is *a*-Se stability under illumination. However, there is some evidence that prolonged usage of HARP targets, especially at ambient temperatures lower than room temperature (RT), results in the appearance of white blemishes on images.<sup>5,6</sup> Such blemishes are undesirable because they degrade image quality. It has been found

empirically that the appearance of white blemishes can be prevented by keeping *a*-Se at 35 °C during camera operation.<sup>5</sup> This shows that the stability of the *a*-Se HARP structure is significantly improved by heating to 35 °C. In order to get a better insight into the mechanisms a comparative study of the photoinduced effects in *a*-Se at RT and at 35 °C has been performed. In this work we focus on the photodarkening (PD) effect since it is known to be caused by photoinduced changes in the material structure.<sup>7-15</sup> Indeed, it is well known that *a*-Se, like many other chalcogenide glasses, may undergo photostructural transformation as a result of prolonged exposure to light. Therefore light-induced structural metastability is a candidate for the root cause of the initiation of white blemishes in the HARP camera image.

In this study we measured changes in optical transmission brought about by the photodarkening effect and compared experimental results at RT with those at 35 °C at a given light intensity. We analyzed our experimental data using a model based on photoinduced metastability in *a*-Se.<sup>11,14,15</sup> Our observations allow us to conclude that at RT there are both reversible and irreversible components of PD. Furthermore, the quantitative analysis of the observed effects

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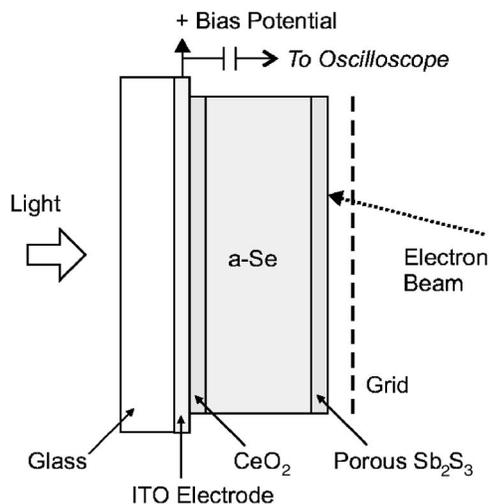


FIG. 1. The structure of a high-field avalanche rushing photoconductor (HARP) target.

provides an estimate of the energy barrier which separates the metastable state of structural units responsible for the reversible component of the PD effect from their ground state. While we were initially motivated by the practical significance of photoinduced effects in the HARP operation, there is also a scientific interest in elucidating the fundamental microscopic mechanisms of photostructural changes in *a*-Se, which have not been fully characterized to date despite extensive work over several decades.

## II. EXPERIMENT

### A. The *a*-Se avalanche phototarget

The structure of the HARP camera target is shown schematically in Fig. 1. The photoconductive layer is deposited using vacuum evaporation technique on a glass plate with an indium tin oxide (ITO) layer that serves as the transparent front positive electrode.<sup>16</sup> Normally the *a*-Se layer is confined between the CeO<sub>2</sub> and porous Sb<sub>2</sub>S<sub>3</sub> layers that act as blocking contacts to permit high electric fields to be applied across the HARP target. The CeO<sub>2</sub> layer prevents hole injection from the ITO, and Sb<sub>2</sub>S<sub>3</sub> prevents electron injection from the electron beam that is used in HARP tubes for the latent charge readout and to stabilize the potential of the free surface to ground potential.

HARP targets with 15 μm thick *a*-Se were used in our study. Targets with and without CeO<sub>2</sub> and Sb<sub>2</sub>S<sub>3</sub> layers were both used so that the observed effects could be differentiated from those due to bulk *a*-Se properties and those from the specific (multilayer) HARP target structure.

### B. Photodarkening

The standard method for investigation of PD effects is to monitor changes in transmission as a function of exposure to light. Our study was carried out using the apparatus shown in Fig. 2. Two He-Ne laser beams (633 nm) were used to illuminate the same area of the sample. The less powerful (0.4 mW/cm<sup>2</sup>) *probe beam* was used to monitor changes in transmission of light *T*. Before being incident on the *a*-Se

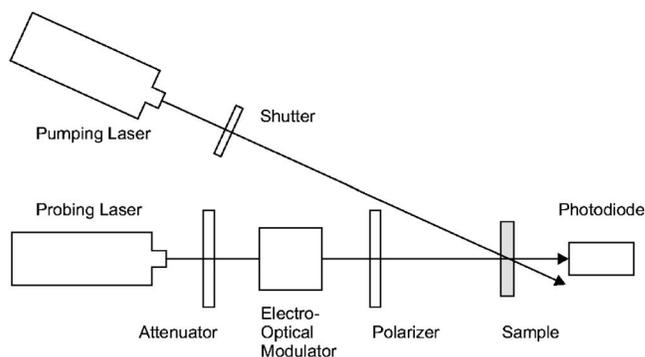


FIG. 2. Experimental apparatus for photodarkening measurements.

sample, light first passed through an electro-optical modulator and polarizer, which together permitted the modulation of light intensity between zero and the maximum value at a frequency of 1 kHz. After emerging from the sample the probe beam was incident on a Si photodiode that was used to measure the photoinduced transmission. 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 more powerful (2.75 W/cm<sup>2</sup>) *pump beam* was used to produce PD. The kinetics of the PD was studied by alternately exposing the *a*-Se to the pumping beam for cycles of 100 s separated by 100 s periods of rest. These alternating periods were produced using a shutter. Throughout the experiment  $T/T_0$  was measured synchronously with the modulation of the pumping beam.

## III. RESULTS AND DISCUSSION

The results of the PD  $T/T_0$  measurements are shown in Fig. 3 as a function of time for several pumping/rest cycles. At RT, the ratio  $T/T_0$  is reduced by 30% during the first 100 s of pumping. During the following 100 s rest period,  $T$  is partially recovered, but remains <80% of  $T_0$ . In subsequent cycles, this decrease followed by partial recovery is repeated although with reduced magnitude of recovered  $T$ , producing a gradual overall decrease in transmission. At 35 °C the PD effect is distinctly different. The initial de-

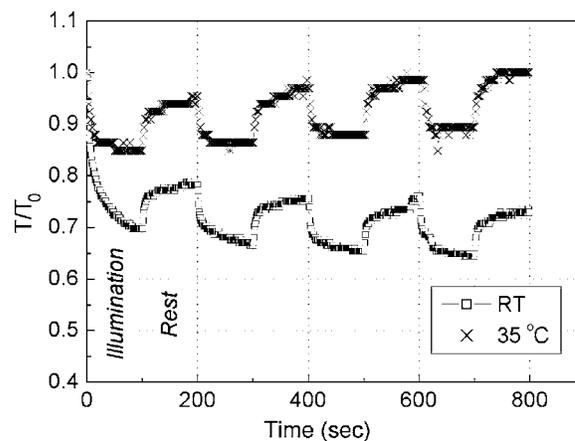


FIG. 3. The changes in transmission of a HARP target during alternating periods of illumination and rest.

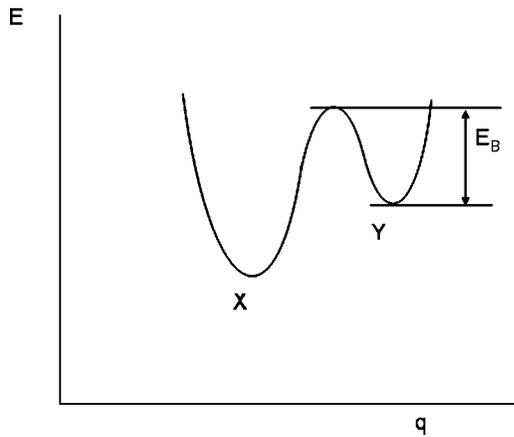


FIG. 4. Energy-configuration diagram for the proposed photoinduced structural changes.

crease in  $T$  during pumping is smaller ( $\sim 15\%$ ), and the subsequent recovery of transmission is almost complete after several rest periods. Thus only a reversible PD component is present at  $35^\circ\text{C}$ , while at RT there are both reversible and irreversible components.

We start the theoretical interpretation of the data by discussing the results at  $35^\circ\text{C}$ , when only the reversible PD component is present. In order to interpret the experimental data, we use a model of photodarkening, suggesting that there is some given concentration  $N_0$  of structural units which are photoinduced to transform from their ground state configuration  $X$  into a state  $Y$  that corresponds to the upper or the metastable state. The corresponding energy-configuration diagram is shown in Fig. 4. This causes the PD effect, and the changes in  $T/T_0$  are assumed proportional to the density of units in the  $Y$  configuration.<sup>12-14,17,18</sup> Let the rate of the transitions from  $X$  into  $Y$  under continuous pumping be  $G$  and the relaxation time for a transition back into  $X$  be  $\tau_0$ . This relaxation occurs by thermal activation over the energy barrier  $E_B$  in the configuration diagram shown in Fig. 4. Hence it is reasonable to assume that the time for relaxation  $\tau_0$  depends on the temperature  $T$  in an Arrhenius fashion which can be expressed as

$$\tau_0(T) = \nu_0^{-1} \exp(-E_B/k_B T), \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $\nu_0$  is the attempt-to-escape frequency usually assumed to be of the order of phonon frequency  $\sim 10^{12} \text{ s}^{-1}$ .

The time dependence of the concentration  $n(t)$  of units in the  $Y$  state under continuous pumping can be described by the following differential equation:

$$\frac{dn(t)}{dt} = G[N_0 - n(t)] - \frac{n(t)}{\tau_0}, \quad (2)$$

with the solution

$$n(t) = G\tau N_0[1 - \exp(-t/\tau)], \quad (3)$$

where the characteristic excitation (darkening) time constant  $\tau$  is

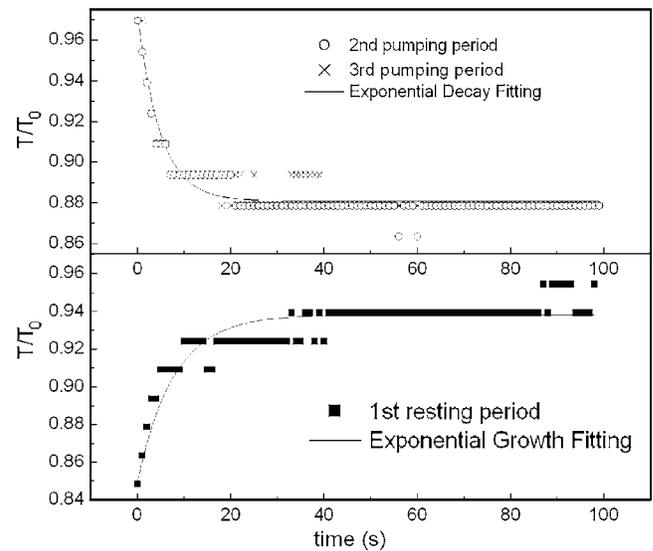


FIG. 5. The decay (upper part) and the restoration (lower part) of the optical transparency for different pumping/resting periods at  $35^\circ\text{C}$ .

$$\tau = \frac{\tau_0}{G\tau_0 + 1}. \quad (4)$$

In Eqs. (2) and (3) the origin of the time scale is set to the start of the pumping process. When the pumping light is switched off, the system relaxes forward to the ground state  $X$  and the concentration of  $Y$  states depends on  $t$  as

$$n(t) = n(0)\exp(-t/\tau_0), \quad (5)$$

with a characteristic time  $\tau_0$  given by Eq. (1). In Eq. (5) the origin of the time scale is set to the end of the pumping. Under the assumption that  $T \propto N_0 - n(t)$  (the concentration of  $X$  states), we can fit the experimental results with Eqs. (1)–(5).

Figure 5 shows the decay of  $T/T_0$  with time during the pumping phase at  $35^\circ\text{C}$  and its recovery during the relaxation phase (rest period when pumping is switched off). The saturation in the changes in  $T/T_0$  with a plateau at the second half of each period is present. Solid curves in this figure are theoretical fits in accordance with Eq. (3) for the photodarkening process and Eq. (5) for the relaxation phase. The kinetics in both phases can be described as single exponentials. Furthermore, the magnitude of the characteristic time  $\tau \approx 7.6 \pm 0.6 \text{ s}$  obtained in the darkening phase is identical within experimental error to  $\tau_0 \approx 7.8 \pm 0.6 \text{ s}$  obtained in the relaxation phase. According to Eq. (4),  $\tau_0 \approx \tau$  requires  $G\tau_0 \ll 1$ . Then, the theory predicts that the height of the plateau in the time dependence of  $T/T_0$  in the pumping phase that corresponds to the solution of Eq. (3) at  $t \gg \tau$  is proportional to the conversion rate  $G$  of  $X$  to  $Y$  (see Fig. 5, upper part). It would be useful, in a future study, to check how the magnitude of  $T/T_0$  at the plateau region depends on the pumping intensity  $I$ . A linear dependence would mean a linear relation between  $G$  and  $I$ . If, however, it deviates from a linear dependence, nonlinear effects for the conversion rate  $G$  come into play.<sup>19</sup>

Using the relaxation time  $\tau_0 \approx 7.8 \text{ s}$ , experimentally obtained at  $T = 35^\circ\text{C}$ , the height of the energy barrier  $E_B$  that

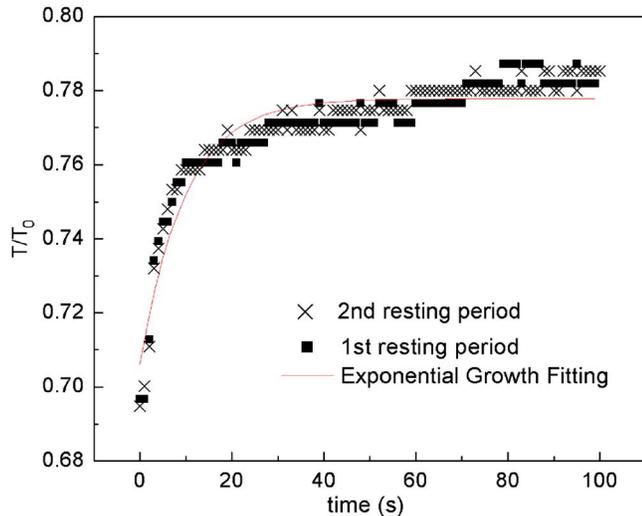


FIG. 6. The relaxation of the reversible component of the photodarkening effect at room temperature.

separates metastable states from the ground states can be estimated using Eq. (1). Assuming  $\nu_0 = (1-5) \times 10^{12} \text{ s}^{-1}$  we obtain  $E_B \approx (0.81 \pm 0.02) \text{ eV}$ . Variation in a choice of  $\nu_0$  (from  $10^{12}$  to  $5 \times 10^{12} \text{ s}^{-1}$ ) does not affect this estimate significantly since the dependence of  $E_B$  on  $\nu_0$  is logarithmic.

In contrast to the  $T=35^\circ\text{C}$  case above, the photodarkening phenomenon at RT has both reversible and irreversible components. It is interesting to check whether the same two states,  $X$  and  $Y$ , can be responsible for the reversible component of the PD effect at RT as well as at  $T=35^\circ\text{C}$ . Figure 6 shows the recovery phase of the reversible part of PD plotted and then fitted with a single-exponential dependence. The exponential fit required a characteristic time  $\tau_0 \approx 13 \text{ s}$ . Given this value of  $\tau_0$  at  $T=25^\circ\text{C}$  (RT) and the attempt-to-escape frequency  $\nu_0 = (1-5) \times 10^{12} \text{ s}^{-1}$ , we again use Eq. (1) to estimate the height of the energy barrier, which turns out to be  $0.80 \pm 0.02 \text{ eV}$  that is identical to the  $E_B$  value found at  $T=35^\circ\text{C}$ . This allows us to conclude that the relaxation process of the reversible component of the photodarkening effect at RT is identical to the relaxation process at  $35^\circ\text{C}$  and occurs over the energy barrier  $E_B \approx 0.8 \text{ eV}$  between the metastable state and the ground state of structural units responsible for the PD effect.

The irreversible component of the PD effect appears only in the RT data. We can only speculate on the cause of irreversible effect. Data in Fig. 3 show that at RT, some fraction of the structural units is converted by pumping into structural configurations that are different from the  $Y$  state shown in Fig. 4. These structural configurations are responsible for the irreversible component at RT since they cannot relax back into ground states  $X$  over the time scale of 100 s used in our experiments. In contrast, at  $T=35^\circ\text{C}$  such states cannot be created. The peculiarity of  $T=35^\circ\text{C}$  lies in the fact that it is very close to the glass transition temperature  $T_g$  of  $a\text{-Se}$ , which is estimated to be  $36^\circ\text{C}$  for the HARP structure<sup>20</sup> ( $T_g$  of  $a\text{-Se}$  depends on the heating rate, but its range is typically from  $35$  to  $40^\circ\text{C}$ ). Thus, at  $35^\circ\text{C}$ , the  $Y$  states are the only defects that can be created since they are introduced by illumination due to the double-well nature of

the structural units considered here.<sup>14,19</sup> The double-well structure gives the highly probable pathway for this photoinduced changes to occur, while other types of defects might be instantaneously annealed. In contrast, RT does not restrict the creation of a variety of defect types.<sup>21</sup> Furthermore, due to slower relaxation rates into the ground states at RT than at  $T=35^\circ\text{C}$ , the structural units associated with the metastable states, denoted as  $Y$  in Fig. 4, can agglomerate and produce clusters with high activation energy.<sup>22</sup> Relaxation of these states therefore cannot occur over the time scale of our experiments ( $\sim 100 \text{ s}$ ).

It is important to emphasize that we assume that the characteristic time  $\tau_0$  does not depend on the structure itself, i.e.,  $\tau_0$  is independent of  $n(t)$ . In support of this assumption we note that if  $\tau_0$  depends on the structure, then we would lose the simple exponential kinetics that appeared in the model and is confirmed experimentally. In the case of  $\tau_0$  independent of  $n(t)$ , the kinetics of the PD effect would be described by a stretched exponential function.

#### IV. CONCLUSIONS

We have studied the PD phenomena in  $a\text{-Se}$  films at RT and at temperature close to the glass transition temperature  $T_g \approx 35^\circ\text{C}$ . We found that PD at  $35^\circ\text{C}$  exhibits reversible recovery, whereas at RT, the relaxation has reversible and irreversible components. We used a model based on the photoinduced transformation of structural units from the ground state (which is optically transparent) into the metastable states (which cause photodarkening) with a thermally activated relaxation back to the ground state. Relaxation occurs over the barrier of height  $E_B$  which separates the metastable state from the ground state. The model has a single relaxation time  $\tau_0$  that is thermally activated (with an activation energy  $E_B$ ) but is independent of the concentration of photoactivated units. Our experimental results strongly support the validity of the presented model. Indeed, the relaxation time  $\tau_0$  is about  $7.7 \text{ s}$  at  $35^\circ\text{C}$  and about  $13 \text{ s}$  at RT—both values give the identical value for the height of the barrier  $E_B$  of about  $0.8 \text{ eV}$ . Thus, the energy barrier between metastable and ground states with an activation energy of about  $0.8 \text{ eV}$  represents a fundamental feature of the photoinduced structural metastability in amorphous selenium. At RT there is a slow or an irreversible component in the relaxation process due to photocreation of certain high-activation-energy structural units; that is, they have longer relaxation times than the time scale of the present experiments (100 s).

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