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Partial recovery of the fatigued photoluminescence in germanium sulfide glass

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Abstract

We report photo-induced time-dependent photoluminescence (PL) from Ge–S glass that shows not only known PL fatigue but also a PL recovery phenomenon—observed under prolonged irradiation by the excitation light, even after PL fatigue—in $\text{Ge}_{1-x}\text{S}_x$ glasses ($0.67 \leq x \leq 0.90$). The two phenomena have different time constants. Also, the fatigue process depends strongly on glass composition, excitation energy and excitation intensity, while the recovery process depends clearly only on excitation intensity. We propose a simplified functional form to describe the time dependence that is based on a model in which non-radiative recombination centres—created by the photo-excitation of the PL centres—revert to radiative centres through thermal reaction. The proposed function reproduces the experimental data for all irradiation time domains.

1. Introduction

Chalcogenide glasses are known to exhibit a wide variety of photo-induced changes in their optical properties through irradiation of bandgap or sub-bandgap light. These phenomena, which are characteristic of the chalcogenide glasses, have been the subject of intensive study in recent decades from both fundamental and practical viewpoints [1–4]. In particular, it is well known that the intensity of the photoluminescence (PL) decreases under prolonged irradiation by the excitation light. This phenomenon is called PL fatigue and has been studied extensively in relation to the photo-induced change of the electronic structure in the chalcogenide glasses.

The PL fatigue process is observed for both As-chalcogenide and Ge-chalcogenide glasses, e.g. in As–S and As–Se systems [5–8] and in Ge–Se systems [9, 10]. It has been discussed whether the origin of the process is best described by the Street–Mott model [11] or by other models [6], but this is still in dispute.

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As for the Ge-chalcogenide glasses, Mollot *et al* [9] proposed a model for the PL fatigue process and calculated the fatigue rate. However, the fatigue curves obtained by their calculations do not fit the experimental results for long time-scales. Thus, it remains for the PL fatigue in the chalcogenide glasses to be investigated.

In the present study, we choose Ge–S glasses for which PL fatigue has been studied by Tikhomirov *et al* [12]—though limited in the number of studies—and report a time-dependent PL from Ge–S glass that shows not only the PL fatigue but also PL recovery after the fatigue process, under prolonged irradiation by bandgap light. This is observed in the PL at 2.15 eV from a wide range of compositions, $0.67 \leq x \leq 0.90$, of $\text{Ge}_{1-x}\text{S}_x$ glasses, which we have reported previously [13]. We are now going to describe the time dependence using a functional form that has two time constants then present a possible simple interpretation of it. This model is derived as an extension of the fatigue-only model of Mollot *et al* [9] by adding an extra term, and can be fitted successfully to the experimental data.

2. Experimental details

Bulk glass samples were prepared by using the melt quenching technique (details are described in our previous study [13]). The samples were polished and their thickness was ~ 1 mm. They were then mounted on a specimen holder that was cooled to 77 K in a cryostat and the sample chamber was evacuated ($\sim 1.3 \times 10^{-1}$ Pa). An argon ion laser with wavelengths 457.9 nm (2.71 eV), 476.5 nm (2.60 eV), 488.0 nm (2.54 eV) and 514.5 nm (2.41 eV) was used for excitation. The intensity of the excitation light, I , was set from 5 mW (0.1 W cm^{-2}) to 50 mW (1.0 W cm^{-2}). The incident beam was chopped at 0.3 kHz for lock-in amplification. The emitted light was dispersed by a monochromator and detected by a photomultiplier.

3. Results

The time-dependent intensities for the PL, observed at 2.15 eV, are plotted in figure 1. The shape of the spectra—given in our previous publication [13]—is Gaussian-like. At first it is observed that the PL intensities decrease but, after 1000–2000 s, it is clear that they start to increase for irradiation greater than 0.4 W cm^{-2} . The decrease is faster and greater for larger irradiation intensity. It is suggested that two kinds of processes with different time constants—fatigue and recovery—exist in the mechanism of the time-dependent change in PL intensity for the Ge–S glasses and, as a result of the competition between these processes, the PL intensity finally saturates at a certain value. The fatigue and recovery time constants are evaluated and plotted in the inset of figure 1 and will be explained later.

The dependence of PL fatigue on composition is shown in figure 2. The fatigue rate increases as the S content increases, while the recovery process is independent of the glass composition.

The excitation energy dependence of PL fatigue is presented in figure 3. The PL fatigue occurs more strongly at higher excitation energy, while the recovery of the PL has no clear dependence on excitation energy.

4. Discussion

The plotted time-dependent PL intensities in figures 1–3 have been fitted successfully using the following function:

$$I_{\text{PL}}(t) = A \exp\left(-\frac{t}{\tau_{\text{F}}}\right) - B \exp\left(-\frac{t}{\tau_{\text{R}}}\right) + I_{\infty}, \quad (1)$$

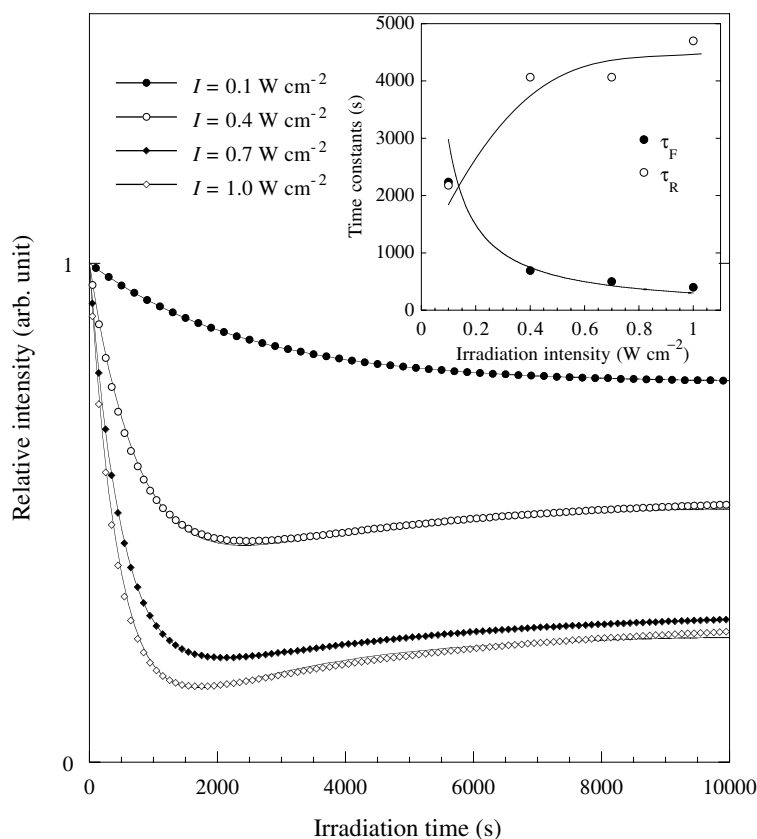


Figure 1. The time dependence of the PL at 2.15 eV from $\text{Ge}_{0.20}\text{S}_{0.80}$ at 77 K for 2.71 eV excitation and irradiation intensities of 0.1, 0.4, 0.7 and 1.0 W cm^{-2} . The full curves are the fits using equation (1). Plotted in the inset are the time constants that have been evaluated for the fatigue and recovery process. Also shown is the fit using $1/I$ for τ_F as well as a curve just to guide the eye for τ_R .

where the first term describes the fatigue process, the second term describes the recovery process, and the third term is the intensity at $t \rightarrow \infty$. These are characterized by two time constants: one for fatigue, τ_F , and one for recovery, τ_R . We can provide a possible explanation for this functional form as follows, based on the mechanism illustrated in figure 4.

It is widely known that Street and Mott [11] proposed the model of negative- U defects, which can explain many PL-related properties in chalcogenide glasses, but some exceptions exist [12]. They considered that the charged defects (D^+ and D^-) are formed in the chalcogenide glasses due to strong coupling between electrons and the lattice. These charged defects, which have energy levels in the bandgap, are responsible for the PL in chalcogenide glasses [14]. The PL fatigue is attributed to the decrease in the number of charged defects and the increase in the number of neutral defects, D^0 , which act as non-radiative recombination centres [6, 11, 14]. This is also confirmed to be applicable to the Ge–S glass in the previous study [13].

Based on this background, the configuration coordinate diagram for this process is illustrated in figure 4. The excitation process—represented by the transition from a to b in this diagram—occurs through the irradiation, then a local distortion occurs (the process b to c). The excited state of a , a^* , either undergoes a radiative recombination process from c

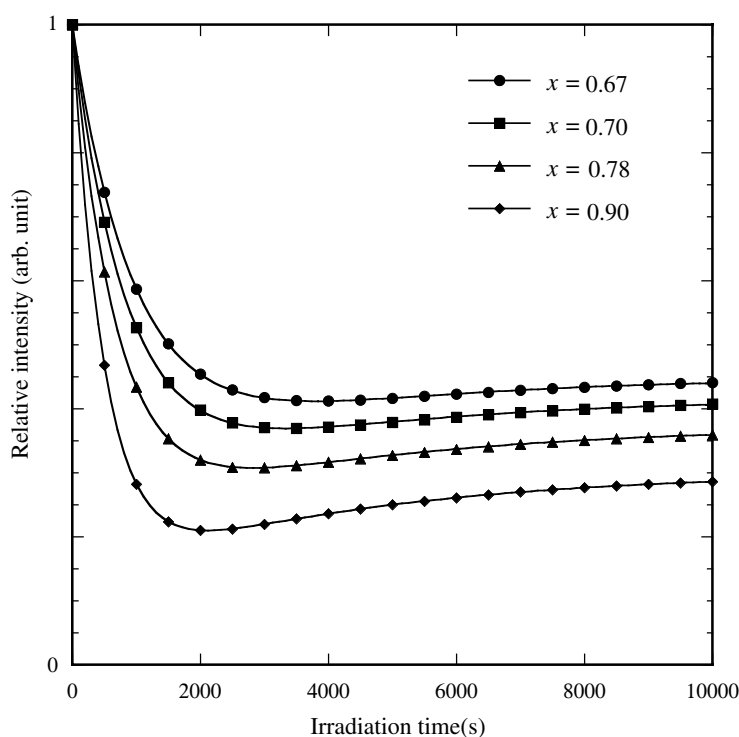


Figure 2. The time dependence of the PL, observed at 77 K for various compositions: (a) $x = 0.67$, (b) $x = 0.70$, (c) $x = 0.78$ and (d) $x = 0.90$. The excitation energy was 2.71 eV and the excitation intensity was 0.7 W cm^{-2} . The full curves are fits using equation (1).

to d or, if the photo-excited carriers are trapped by the charged defects around the excited region, a transition occurs through another distortion at e to the metastable state f , in which case radiative recombination is impossible. This state is considered to be more stable at low temperatures.

However, some of the metastable states also relax to their ground states by overcoming the activation energy E_{Δ} that corresponds to the energy difference between g and f in figure 4. When the temperature rises by through irradiation these relaxation process becomes more frequent and, therefore, recovery of the PL is expected to occur. As reported by Tanaka *et al* [15] and Messaddeq *et al* [16], the photo-bleaching (PB) effect is also observed in Ge–S and Ge–Ga–S glasses. If PB occurs in the present case during prolonged illumination, then the same excitation wavelength approaches the edge of the band. According to our previous study [13, 19], it is also expected that this results in the higher intensity of PL due to an increase in the relative efficiency. Nevertheless, the present measurement was executed at 77 K and $1.3 \times 10^{-1} \text{ Pa}$, as described in the experimental section, for which—according to the study of the Ge–S system by Tanaka *et al* [15]—it is hard to observe PB. Besides, since the time constant for the recovery process is completely independent of the excitation energy (as we will show later on), it is very hard to connect this process to any phenomena related to photoexcitation. Therefore, we proceed with the model that does not have any connection with PB.

On the basis of the present model in figure 4, we suppose that the rate of change of the radiative centre density, $dn(t)/dt$, is expressed by the following equation:

$$\frac{dn}{dt} = -FIn + R \exp(-E_{\Delta}/k_{\text{B}}(T_0 + \Delta T)), \quad (2)$$

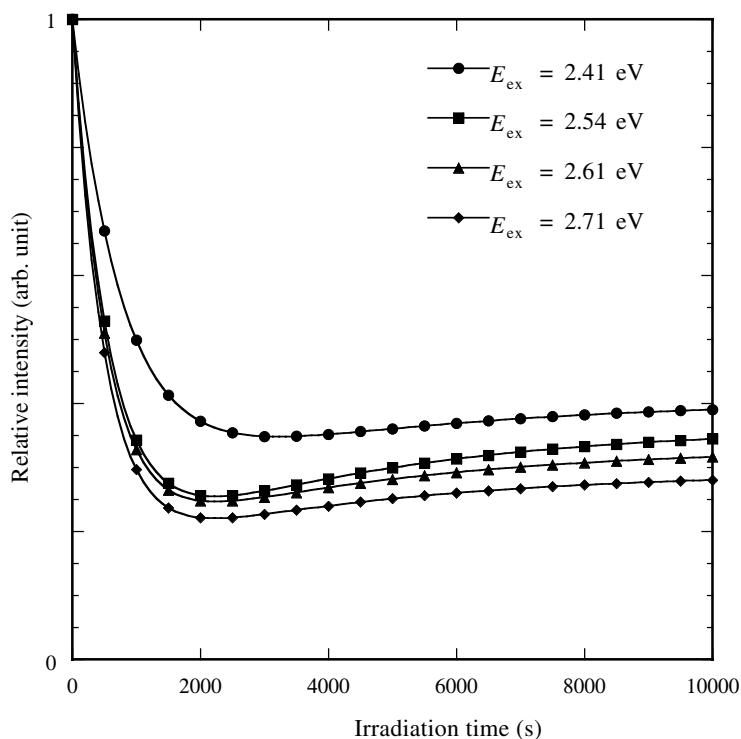


Figure 3. The time dependence of the PL from $\text{Ge}_{0.22}\text{S}_{0.78}$, observed at 77 K for various excitation energies: (a) 2.41 eV, (b) 2.54 eV, (c) 2.60 eV and (d) 2.71 eV. The excitation intensity was 0.7 W cm^{-2} .

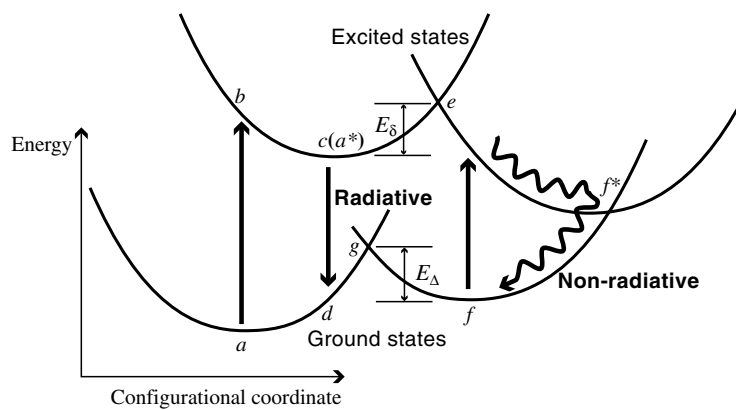


Figure 4. The configuration coordinate diagram for the PL processes.

where F and R are coefficients for the fatigue and recovery intensities, respectively, T_0 is the ambient temperature (which is equal to 77 K), and ΔT is the temperature increase induced by the irradiation. A possible justification for this equation is given in appendix A.

We assume that the spatial distribution of all the parameters can be neglected. Furthermore, the effect of self-absorption [10] is also assumed to be negligible. For the present case these

assumptions do not affect the final functional form, as shown in appendix B where the same equation is derived in a more general form. The cross section of the PL fatigue, F , which was originally introduced by Mollot *et al* [9], has the dimension of area. The second term in the right-hand side of equation (2) represents the annealing effect of the irradiation, which corresponds to the relaxation process at g in figure 4. The coefficient R depends on the total density of non-radiative centres, $N(t)$. This is expressed as $N(t) = N_0 + n_0 - n(t)$, where N_0 is the density of the intrinsic neutral defects and n_0 is the density of the PL centres that existed before the excitation, i.e. $n(0)$. We assume here that the density of intrinsic neutral defects is much larger than the density of photo-created neutral defects, i.e. $N_0 \gg n_0 - n(t)$, and therefore R is considered to be independent of n_0 and $n(t)$. Exceptionally, unlike other chalcogenides, Ge-S glasses are known to yield an electron-spin resonance (ESR) signal and the intrinsic neutral defects exist stably [17].

From the heat capacity for Ge-S glasses reported [18], the temperature increase in our present experiment is estimated to be less than 3 K at most. Therefore it is acceptable to expand the second term in equation (2) for the temperature increase ΔT based on the assumption that $\Delta T/T_0$ is small.

The behaviour of the temperature in the irradiated region can be expressed as follows:

$$\frac{d\Delta T}{dt} = \gamma I - \frac{\Delta T}{\tau_R}, \quad (3)$$

where the coefficient γ represents the efficiency of the absorbed photon in heating, and τ_R is the relaxation time of the temperature decrease.

The PL intensity is described as follows:

$$I_{\text{PL}}(t) = YVIn(t), \quad (4)$$

where Y is the quantum efficiency and V is the volume of the irradiated region. From equations (2) to (4) we obtain the PL intensity in the form of equation (1) as follows:

$$I_{\text{PL}}(t) = A \exp\left(-\frac{t}{\tau_F}\right) - B \exp\left(-\frac{t}{\tau_R}\right) + I_\infty, \quad (5)$$

where

$$A = I(n_0 + B - I_\infty), \quad (6)$$

$$B = \frac{R \exp(-E_\Delta/k_B T_0) E_\Delta \gamma I^2 \tau_R}{(FI - 1/\tau_R) k_B T_0^2}, \quad (7)$$

$$I_\infty = \frac{R \exp(-E_\Delta/k_B T_0)}{FI} \left(1 + \frac{E_\Delta \gamma I \tau_R}{k_B T_0^2}\right), \quad (8)$$

and

$$\tau_F = 1/FI. \quad (9)$$

From figures 1 to 3, the curve calculated using equation (1) gives a close fit even in the long time domain, in contrast to the previous study of Ge-Se glasses [9]. We consider that the disagreement between the experimental results and the calculation in the previous study can be explained by introducing the thermal effect term that we have demonstrated.

The dependences of the calculated time constant τ_F on the excitation energy and the excitation intensity for various compositions are presented in figures 5 and 6. Note that the time constant τ_R shows no clear dependence on the excitation energy and shows weak dependence on composition, as seen in figure 7. As shown in the inset of figure 1, it depends on intensity at the lower end but seems to saturate quickly. In contrast, τ_F shows a striking dependence on

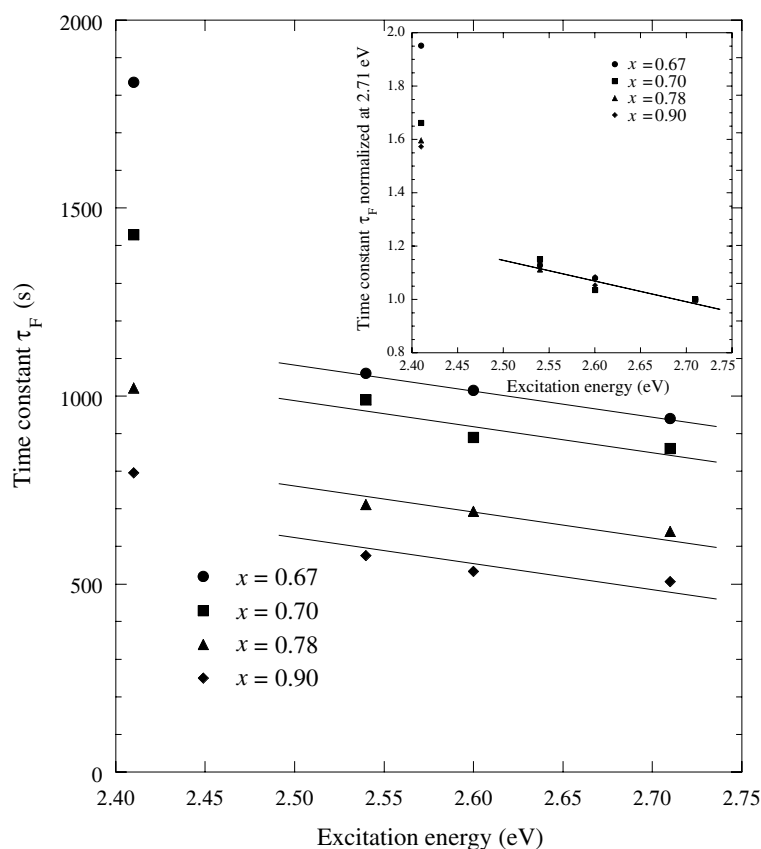


Figure 5. The time constant versus excitation energy for various glass compositions. The excitation intensity is 0.7 W cm^{-2} . Plotted in the inset is the normalized time constant of the PL fatigue versus excitation energy for various glass compositions. The lines are to guide the eye.

irradiation and composition, which is caused by the wide variation in cross section of the PL fatigue, F .

The cross section F can be interpreted as the efficiency of photo-creation of the non-radiative centres, i.e. of the neutral defects from the charged defects. In S-rich samples this is large, which leads to the smaller time constant τ_F , as shown in figure 5. Therefore, in S-rich samples, where the intrinsic charged defects are relatively abundant as S increases, the photo-excitation process of these defects proves to be comparatively prevalent. On the other hand, when irradiated with excitation light of higher energy, the photo-excited electron-hole pairs are mobile and are trapped by the neutral defects, as discussed in the previous study [13]. Therefore, F increases as the excitation energy increases, as seen in figure 5. This is more clearly observed in the normalized plot in the inset of figure 5, which shows similar behaviour to the PL excitation spectra given in [13, 19], though further detailed study of this similarity may be needed. In addition, if F does not depend on the irradiation intensity I , then our model predicts that τ_F is proportional to the inverse of I , as given in equation (9). This is supported on the whole, as in the inset of figure 1 and in figure 6.

As for the recovery time constant τ_R , in the present model it stems directly from the thermal relaxation time in equation (3). Therefore, there is no demand from the model for dependence on I or E_{ex} . The observed τ_R in figure 7 clearly shows the absence of any dependence on

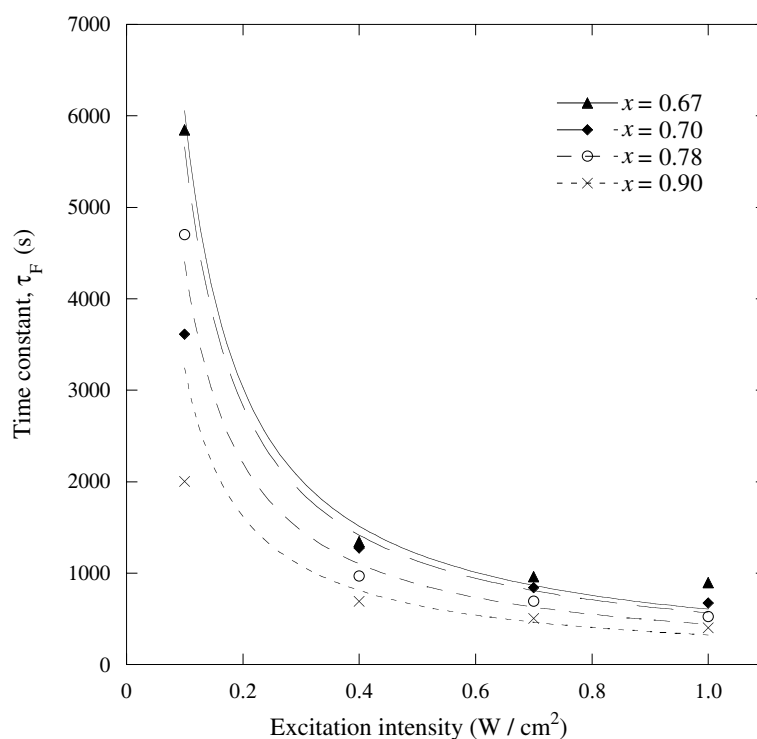


Figure 6. The time constant of the PL fatigue versus excitation intensity for various glass compositions. The excitation energy is 2.71 eV. Also shown are the fits using $1/I$.

excitation energy. This fact supports the present model for the recovery process, which occurs between ground states with no excitation process involved.

5. Conclusion

The time dependence of the PL intensity in Ge–S glasses through prolonged irradiation by the excitation light is explained by the coexistence of two processes with different time constants: the fatigue process and the recovery process. The fatigue process depends strongly on the composition, excitation intensity and excitation energy, while the recovery process depends only on the excitation intensity. We attribute the former process to the photo-induced reaction of radiative centres to non-radiative centres, and the latter process to the thermal effect of the irradiation. The fatigue–recovery curve of this model yields a close fit to the experimental results for all time domains.

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Appendix A. Model for the rate of change of PL radiative centre density

Here, we label the radiative and the non-radiative recombination centres P and NR, respectively. Those labelled P^* and NR^* are their excited states. The state a in figure 4 is such that a centre

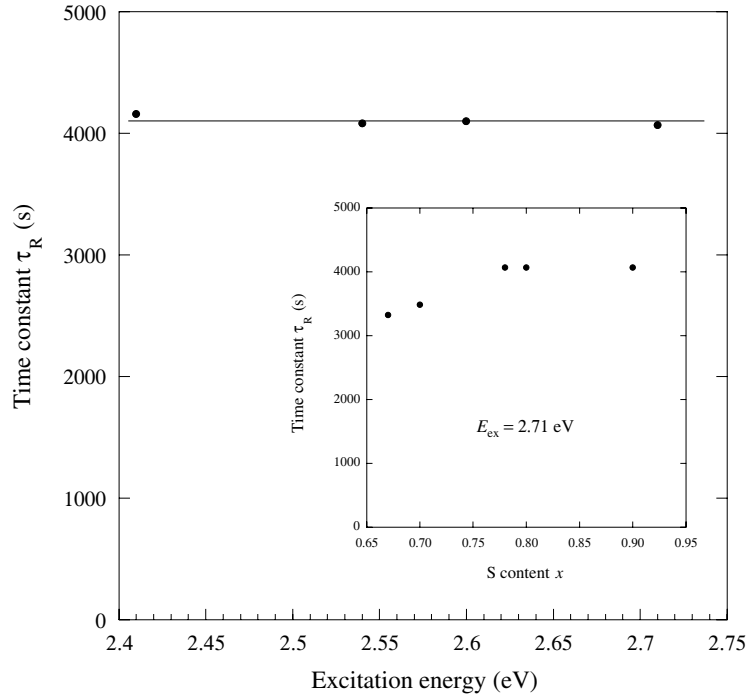


Figure 7. The time constant of PL recovery versus excitation energy. The excitation intensity is 0.7 W cm^{-2} . The plot in the inset is for various glass compositions and an excitation energy of 2.71 eV .

is P; when the centre becomes NR, it is then converted to a state f . We assume that P becomes NR through the reaction with Q and that its reverse also occurs:



Our previous results [13] suggest that P and NR correspond to D^- and D^0 , respectively, in the Street–Mott model [11]. In such a case, Q corresponds to D^+ .

The contribution of the fatigue process to the rate of change of radiative centres is given by

$$k_{\rightarrow}[P^*][Q] = c_Q \times k_{\rightarrow} \times c_e I[P] \equiv -FI[P], \tag{A.2}$$

where $[P^*]$ and $[Q](\equiv c_Q)$ are the local density of P^* and Q, k_{\rightarrow} is the velocity constant of the $P \rightarrow \text{NR}$ reaction (forward reaction) in equation (10), and c_e is a constant when we suppose that the photoexcitation from P to P^* occurs as

$$[P^*] = c_e I[P]. \tag{A.3}$$

Here, we consider that the forward reaction only occurs at the photoexcited P, i.e. P^* , and depends only on $[P^*]$. As has been shown by Mollot *et al* [9], the fatigue process can be described successfully by supposing that the rate of change of the local radiative centre density decreases linearly with the local density itself and the local illumination.

The recovery process is described by the $\text{NR} \rightarrow P$ reaction in equation (10) (backward reaction), which is the f -to- a transition between the ground states in figure 4. If the activation energy for the forward reaction is E_{δ} and that for the backward reaction is E_{Δ} , then the

temperature dependence of the velocity constants for the forward reaction, k_{\rightarrow} , and the backward reaction, k_{\leftarrow} , can be described by the following Arrhenius-type formula:

$$k_{\rightarrow} \propto \exp\left[-\frac{E_{\delta}}{k_{\text{B}}(T_0 + \Delta T)}\right], \quad k_{\leftarrow} \propto \exp\left[-\frac{E_{\Delta}}{k_{\text{B}}(T_0 + \Delta T)}\right]. \quad (\text{A.4})$$

Nevertheless, when E_{δ} is smaller than E_{Δ} , the temperature dependence of k_{\rightarrow} becomes much weaker than k_{\leftarrow} . In this case, within the estimated range of temperature increase through laser-light irradiation (less than 3 K, estimated from the heat capacity of Ge-S glasses [18]) it can be neglected and supposed to be a constant. In this case, F is also a constant versus ΔT and the rate of change for the radiative centre, P, is

$$\frac{d}{dt}[\text{P}] = -FI[\text{P}] + k_{\leftarrow}[\text{NR}]^2. \quad (\text{A.5})$$

The density of NR, $[\text{NR}]$, can be divided into ΔN and $[\text{NR}] - \Delta N \equiv N_0$, where ΔN is the density increase through the forward reaction and N_0 is the density that is originally present. If we make a further supposition that ΔN is much smaller than N_0 , then $[\text{NR}]$ can be regarded as a constant and equation (14) becomes equation (2) when $n(t)$ is $[\text{P}]$.

We may treat the temperature dependence of the velocity constants in a more sophisticated way than in equation (13). In this case, the resulting rate of increase in equation (2)—and then the recovery term in equation (1)—becomes more complicated. The fits in figure 1 show that the present form is sufficient for the actual data analysis in this case.

The above assumption that E_{δ} is smaller than E_{Δ} for k_{\rightarrow} to be constant is also supported by the fact that the fatigue process is faster than the recovery process (i.e. $\tau_{\text{F}} < \tau_{\text{R}}$), as can be seen in figure 1.

Appendix B. PL intensity obtained by taking the intensity variation into account

The PL intensity, I_{PL} , is obtained when the dependence of the light intensity, I , on the depth in the sample is taken into account, as follows:

$$I(x) = I_0 \exp(-\alpha x), \quad (\text{B.1})$$

where I_0 is the irradiated intensity at the surface, x is the depth from the surface of the samples and α is the absorption coefficient.

The density of the PL centres $n(x, t)$ is obtained from equation (2) as

$$n(x, t) = C_1 \exp(-Fit) - C_2 \exp(-t/\tau_{\text{R}}) + C_3 \quad (\text{B.2})$$

where

$$C_2 = \frac{\gamma \tau_{\text{R}} I R E_{\Delta} \exp(-E_{\Delta}/k_{\text{B}}T_0)}{(FI - 1/\tau_{\text{R}})k_{\text{B}}T_0^2},$$

$$C_3 = \frac{R \exp(-E_{\Delta}/k_{\text{B}}T_0)}{FI} \left(1 + \frac{\gamma \tau_{\text{R}} I E_{\Delta}}{k_{\text{B}}T_0^2}\right),$$

and

$$C_1 = n_0 + C_2 - C_3.$$

The PL intensity is given by

$$I_{\text{PL}} = \int_0^d Y S n(x, t) I(x) dx, \quad (\text{B.3})$$

where d is the thickness of the samples, Y is the quantum efficiency and S is the area of the irradiated region.

Then I_{PL} is obtained as

$$I_{\text{PL}} = A' \frac{\exp\{-F I_0 t \exp(-\alpha d)\} - \exp(-F I_0 t)}{F I_0 t} - B' \exp(-t/\tau_R) + I'_{\infty}, \quad (\text{B.4})$$

where

$$A' = \frac{C_1 Y S I_0}{\alpha},$$

$$B' = \frac{\gamma \tau_R Y S R E_{\Delta} \exp(-E_{\Delta}/k_B T_0)}{k_B T_0} \left[\frac{I_0}{F \alpha} [1 - \exp(-\alpha d)] + \frac{1}{F^2 \alpha \tau_R} \ln \left| \frac{1 - F I_0 t}{\exp(-\alpha d) - F I_0 t} \right| \right],$$

and

$$I'_{\infty} = \frac{Y S R \exp(-E_{\Delta}/k_B T_0)}{F} \left[d + \frac{\gamma \tau_R I_0 E_{\Delta}}{k_B T_0^2 \alpha} [1 - \exp(-\alpha d)] \right].$$

Here we neglect the dependence on x of the coefficient C_1 in equation (16).

When we assume that αd is small, i.e. the excitation absorption is assumed to occur at the edge of the bands and α is small enough, then the calculated right-hand side of equation (17) can be expanded by αd and I_{PL} becomes the Morse-like function as

$$I_{\text{PL}} = A' \alpha d \exp\left(-\frac{t}{\tau_F}\right) - B' \exp\left(-\frac{t}{\tau_R}\right) + I'_{\infty}, \quad (\text{B.5})$$

which is equation (1) when $A = A' \alpha d$, $B = B'$ and $I_{\infty} = I'_{\infty}$.

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