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Persistent photocurrent in amorphous chalcogenides

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The long-term photocurrent decays following the steady-state photoexcitation have been reported in amorphous As_2Se_3, As_2S_3, GeSe, $GeSe_2$, and GeS_2 films. The photocurrent decays empirically as $\exp(-Ct^{\alpha})$ which is called the extended exponential. This behavior can be well interpreted in terms of the dispersive diffusion-controlled recombination of localized electrons and holes. The photocurrent reduces after prolonged strong photoillumination, suggesting that new localized states are induced in the band gap.

I. INTRODUCTION

Nonexponential long-term photocurrent decays ($t > 1$ s) after ceasing the steady illumination have been commonly observed in amorphous chalcogenides.[1-6] It has been found by the present author[6] that the photocurrent for amorphous As_2Se_3 decays as $\exp(-Ct^{\alpha})$, where $0 < \alpha < 1$. This functional form has recently received renewed attention, in the study of the dielectric response,[7] photoluminescence,[8,9] magnetization of spin glasses,[10-12] and the dynamics of glassy relaxation.[13]

It is not clear whether this extended exponential form can be applied to photocurrent decays for a wide variety of amorphous chalcogenides. In the present study, photocurrent decay, $I_p(t)$, for amorphous As_2S_3, GeSe, $GeSe_2$, and GeS_2 films is measured as a function of temperature. It is demonstrated that an expression for photocurrent decay $I_p(t)$ based on the dispersive diffusion-controlled recombination is able to account for all the features observed in the present amorphous chalcogenide films. By strong and long-time photoillumination which causes "photodarkening," the magnitude of $I_p(t)$ decreases; the decrease is of recombination lifetime. This suggests that new defects can be created by strong and long-time photoillumination.[14]

II. EXPERIMENTAL

Thin films were evaporated onto Corning 7059. After evaporation, samples were annealed at appropriate temperatures below the glass temperature T_g. The thickness of films and the annealing temperature T_a are given in Table I. Planar gap cell electrodes using Au contacts were fabricated (gap spacing 40 μm, gap width 11 mm). The halogen lamp (56 mW/cm^2) or the mercury lamp (39 mW/cm^2) for wide band-gap GeS_2 was used to excite photocurrent with an ir-cut filter. As the optical-absorption coefficient is around 1×10^3 cm^{-1} for the present materials, almost uniform optical excitation through the films can be ensured. The measured optical gap is also given in Table I. The applied voltage V were 3—300 V as tabulated in Table I. Note that around these voltages, the photocurrent is proportional to V.

III. MODEL FOR PERSISTENT PHOTOCURRENT DECAY

Before presenting experimental data, we summarize the dispersive diffusion-controlled recombination of localized electrons and holes in amorphous chalcogenides.[6] The assumptions adopted here are as follows: (i) The charged defects D^+ and D^- are principal centers and the other states in the gap are effectively ignored. (ii) The majority of excess electrons and holes are trapped into D^+ and D^- according to the reactions $D^+ + e \rightarrow D^0$ and $D^- + h \rightarrow D^0$, respectively.

As shown in Fig. 1(a), the quasi-Fermi levels E_{fn} for electrons and E_{fp} for holes are defined, where W_1 is the energy needed to take an electron from the valence band (VB) to turn D^0 into D^-, W_2 is the energy needed to take

TABLE I. Thickness, annealing temperature after evaporation and after long-time illumination, optical gap after annealing and measure-applied voltage.

Sample	Thickness (μm)	Annealing temperature T_a (°C)	Optical gap (eV)	Voltage (V)
As_2Se_3	2.0	200	1.72	3
As_2S_3	0.90	170	2.42	300
GeSe	0.76	150	1.25	5
$GeSe_2$	0.37	150	2.10	30
GeS_2	0.64	350	3.09	300

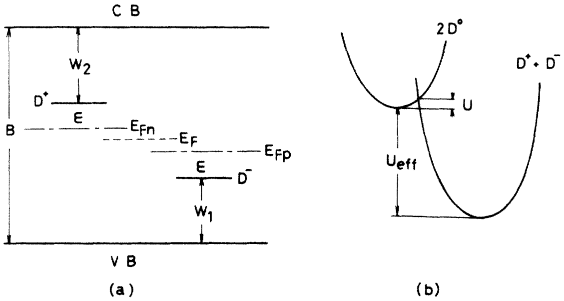

FIG. 1. (a) Thermal energy levels and (b) configurational-coordinate diagram for tunneling associated with D^+, D^0, and D^-. E_{fn} and E_{fp} are the quasi-Fermi levels for electrons and holes, respectively. U_{eff} is the effective negative correlation energy $(B-W_1-W_2)$.

an electron from D^0 to the conduction band (CB).[15]

The density of D^0, n_t', is given by

$$n_t' = \Delta n_t + n_t = N_t \exp(-\varepsilon/kT) , \qquad (1)$$

where Δn_t is the excess density of D^0, n_t the equilibrium density of D^0, and $\varepsilon = E_{fp} - W_1$, and N_t the total density of charged defects $(=[D^+]+[D^-])$. Holes could dominate photocurrents since E_{fp} for holes is closer to VB than E_{fn} for electrons to CB ($W_2 > W_1$ was implicitly assumed).[15]

The density of free holes p' is given by

$$p' = \Delta p + p_0 = N_v \exp(-E_{fp}/kT) , \qquad (2)$$

where Δp is the excess density of free holes, p_0 the equilibrium density of free holes, and N_v the effective density of states of VB. Δp is then obtained from Eqs. (1) and (2),

$$\Delta p = \Delta n_t N_v \exp(-W_1/kT)/N_t . \qquad (3)$$

Equation (3) predicts that the photocurrent ($\propto \Delta p$) is proportional to the excess density of D^0 (Δn_t).

After cessation of illumination , Δn_t decrease by the recombination process, $2D^0 \rightarrow D^+ + D^-$. Before recombination, D^0 (a trapped hole and/or an electron) could hop (tunneling of a hole from D^0 to D^- and tunneling of an electron from D^0 to D^+). These processes are just the reactions of $D^0 - h \rightleftarrows D^-$ and $D^0 - e \rightleftarrows D^+$: The location of D^0 is converted to those of D^- and D^+. This type of recombination should be represented by the bimolecular reaction. However, if the interpair separation of trapped electron-hole pairs is larger than the intrapair separation, a geminatelike monomolecular recombination would predominate.[16] It is hence assumed that both the bimolecular and monomolecular reactions dominate recombination of excess D^0 (Δn_t). If the diffusion of the trapped carrier is dispersive, the recombination rate can be given as[17]

$$b = 1/\tau_r = A(T) t^{-(1-\alpha)} , \qquad (4)$$

where $A(T)$ is the temperature-dependent parameter and α the dispersion parameter.

The rate equation for recombination of excess Δn_t (excess density of D^0) is hence given by

$$\frac{d\Delta n_t}{dt} = -A(T) t^{-(1-\alpha)} (\Delta n_t)^2 - B(T) t^{-(1-\alpha)} \Delta n_t , \qquad (5)$$

where $B(T)$ is also the temperature-dependent parameter. Note that the first and second terms are the bimolecular and monomolecular processes, respectively. The solution of Eq. (5), Δn_t, is written as

$$\Delta n_t = \frac{C \dfrac{B(T)}{A(T)} \exp\left[-\dfrac{B(T)}{\alpha} t^{\alpha} \right]}{1 - C \exp\left[-\dfrac{B(T)}{\alpha} t^{\alpha} \right]} , \qquad (6)$$

where C is given by

$$C = \frac{\Delta n_t(0)}{\dfrac{B(T)}{A(T)} + \Delta n_t(0)} , \qquad (7)$$

where $\Delta n_t(0)$ is a constant which depends on illumination intensity. Combining Eqs. (3) and (6), the photocurrent $I_p(t)$ is given as

$$I_p(t) \propto \Delta n_t N_v \exp(-W_1/kT)/N_t . \qquad (8)$$

Equations (6) or (8) predict that the extended exponential decay of photocurrent is observed in longer time delay,

$$I_p(t) \propto \Delta p = C' \exp(-W_1/kT) \exp[-B(T) t^{\alpha}/\alpha] , \qquad (9)$$

where C' is a constant which depends on illumination intensity.

IV. RESULTS AND DISCUSSION

A. Photocurrent decay $I_p(t)$

Solid circles in Fig. 2 shows the photocurrent $I_p(t)$ for As_2Se_3 after stopping steady illumination.[6] Note that $I_p(t)$ is the net photocurrent, $I_p(t) = I(t) - I_d$, where $I(t)$

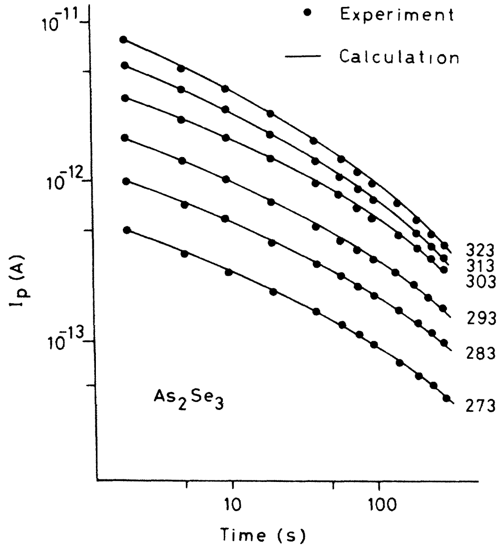

FIG. 2. Decays of photocurrent $I_p(t)$ after stopping the steady illumination in As_2Se_3. Data are from Ref. 6.

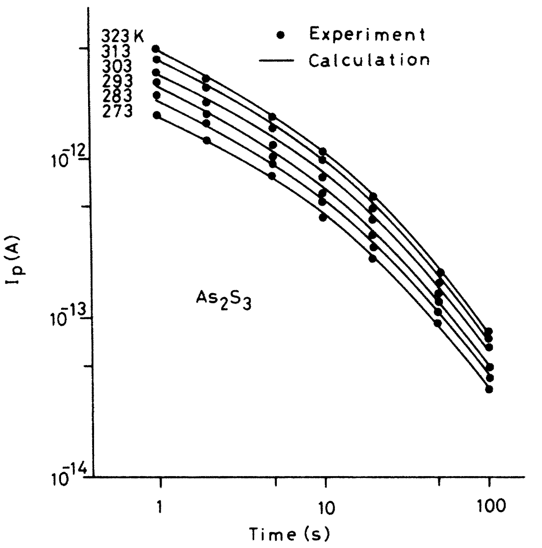

FIG. 3. Photocurrent $I_p(t)$ as a function of temperature in As_2S_3.

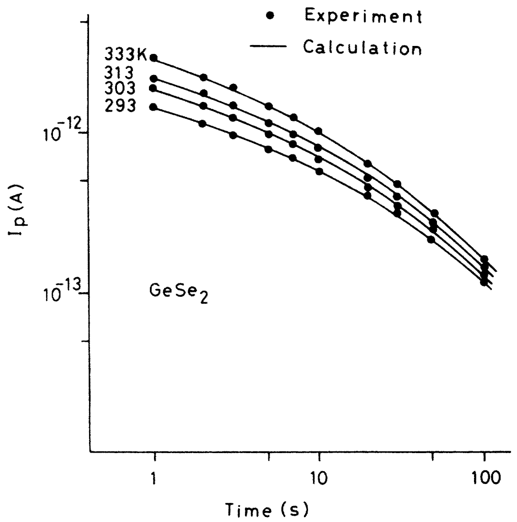

FIG. 5. Photocurrent $I_p(t)$ as a function of temperature in $GeSe_2$.

is the total current and I_d the dc current. Solid lines show the calculated results by taking $\alpha = 0.16$ (temperature independent), $W_1 = 0.52$ eV. The values of C' are chosen as fitting to experimental data. Good agreement between calculations and experimental data have been obtained, suggesting that the persistent photocurrent decay for amorphous As_2Se_3 is dominated by dispersive diffusion-controlled recombination. It is of interest to clear whether the proposed model [Eq. (9)] is applicable for other chalcogenide materials. Solid circles in Figs. 3—6 show experimentally obtained $I_p(t)$ at several temperatures for As_2S_3, GeSe, $GeSe_2$, and GeS_2, respectively. $I_p(t)$ decreases with decreasing temperature T. Solid lines in Figs. 3—6 show the calculated results. Fitting Eq. (9) to experimental data produces the values of W_1 and temperature-independent parameter α. Note that the dispersion parameter $(0 < \alpha < 1)$ which appeared in the drift mobility study is almost temperature independent for chalcogenides.[15] These values are tabulated in Table II. Except for GeS_2, features are very similar to that obtained for As_2Se_3. $I_p(t)$ for GeS_2 is almost temperature independent ($W_1 \simeq 0$), which will be discussed later.

In Figs. 7—9, $I_p(t)$ as a function of illumination intensity are shown for As_2S_3, GeSe, and GeS_2, respectively. Curves of the extended exponential are shown by the solid lines. $I_p(t)$ decreases with decreasing illumination intensity, while the value of α is independent of illumination intensity, suggesting also the validity of the present model

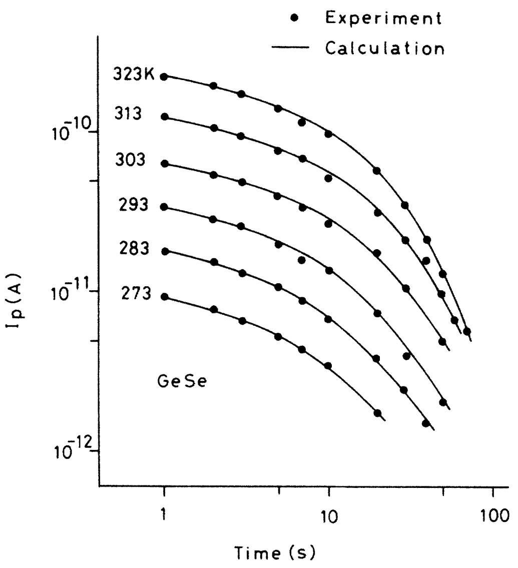

FIG. 4. Photocurrent $I_p(t)$ as a function of temperature in GeSe.

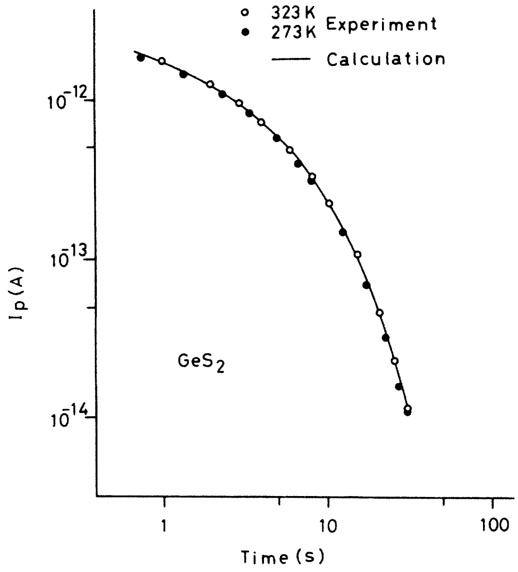

FIG. 6. Photocurrent $I_p(t)$ at temperatures of 273 and 323 K in GeS_2.

TABLE II. Energies W_1 and δ ($=U$) related to the charged defects D^+ and D^-. α is the dispersion parameter. γ is the parameter appearing in relation to $I_p(0) \propto L^\gamma$ (measured at 303 K).

Sample	W_1 (eV)	δ (meV)	α	γ
As_2Se_3	0.52	40	0.16	0.48
As_2S_3	0.17	22	0.30	0.53
GeSe	0.48	43	0.63	0.68
$GeSe_2$	0.20	30	0.28	0.69
GeS_2	~ 0		0.58	0.57

[see Eq. (9)]. The steady photocurrent $I_p(0)$ was proportional to L^γ, where L is the illumination intensity and γ the parameter. The values of γ measured at 303 K are also given in Table II.

Equation (9) predicts that $I_p(t)\exp(Bt^\alpha/\alpha)$ is thermally activated and falls to the same curve. To clearly see this, the temperature dependence of $I_p(t)\exp(Bt^\alpha/\alpha)$ as a function of time t for As_2S_3 and for GeSe are shown in Figs. 10 and 11, respectively, indicating the validity of Eq. (9). From these figures the values of W_1 are estimated and are given in Table II.

The temperature dependences of the rate, $b = B(T)t^{-(1-\alpha)}$, for As_2S_3 and GeSe, as examples, are plotted in Fig. 12. As shown in the figure, the rate b is proportional to $\exp(-\delta/kT)$ with $\delta = 22$ meV for As_2S_3 and 43 meV for GeSe. The same temperature dependence of b is also obtained for the other examined materials. The values of δ are given in Table II. δ may be the potential barrier height for localized-localized tunneling recombination ($2D^0 \rightarrow D^+ + D^-$), U in Fig. 1(b).

Next, we should consider the cause of $W_1 \simeq 0$ for GeS_2. $W_1 = 0$ may be out of the problem in the charged defect model. The decay kinetic of photocurrent for GeS_2 is suggested to be different from that for the other materials. The temperature dependence of steady photocurrent $I_p(0)$ is very weak for GeS_2; the activation energy of $I_p(0)$ is 0.08 eV. $I_p(0)$ may be dominated by a hopping transport in localized tail states.[18] The kinetic of $2D^0 \rightarrow D^+ + D^-$ cannot be the principal recombination path in GeS_2.

$I_p(t)$, due to a hopping transport, can be expressed as

$$I_p(t) \propto \Delta p_t(t) \mu_0 \exp(-\Delta/kT) , \qquad (10)$$

where $\mu_0 \exp(-\Delta/kT)$ is the mobility of holes in tail states and $\Delta p_t(t)$ is its concentration which is given as $\Delta p_t(0)\exp(-Bt^\alpha/\alpha)$ if the dispersive diffusion-controlled monomolecular recombination is dominant for electrons and holes in localized tail states. Almost temperature independent $I_p(t)$ is thus expected. It is not clear, however, why only $I_p(t)$ for GeS_2 is dominated by a hopping transport.

B. Effect of strong and long-time photoillumination on $I_p(t)$

Prolonged exposure to strongly absorbed light induces reversible photostructural change (photodarkening) in chalcogenide glasses.[19] The photodarkening may accompany with creating new localized states.[14] In fact, a new

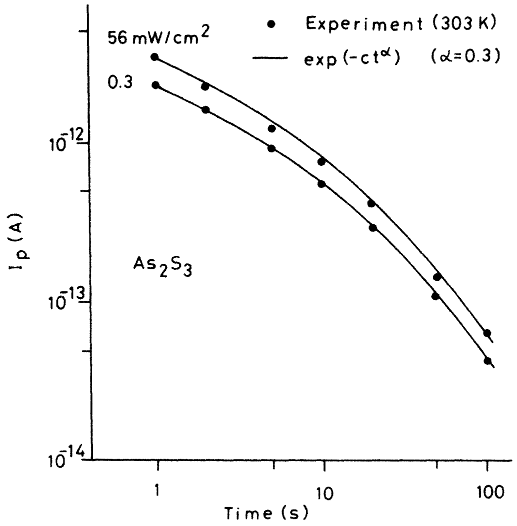

FIG. 7. Dependence of illumination intensity on $I_p(t)$ at 303 K in As_2S_3 (solid circles). The extended exponentials $\exp(-Ct^\alpha)$, with $\alpha = 0.3$ are shown by the solid lines.

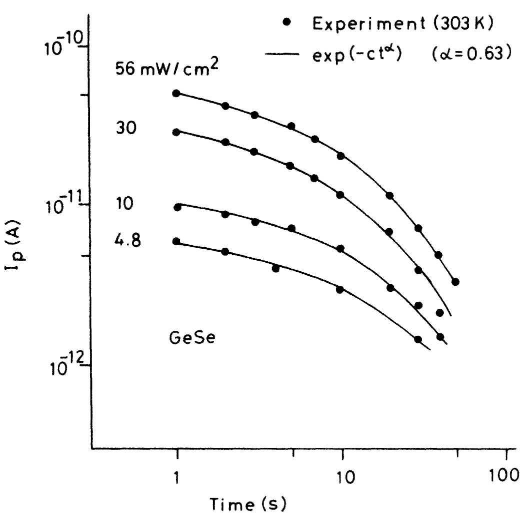

FIG. 8. Dependence of illumination intensity on $I_p(t)$ at 303 K in GeSe (solid circles). The functions $\exp(-Ct^\alpha)$, with $\alpha = 0.63$ are shown by the solid lines.

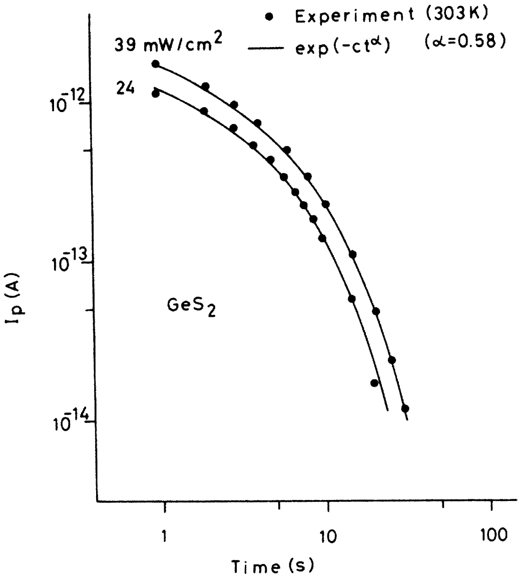

FIG. 9. Dependence of illumination intensity on $I_p(t)$ at 303 K in GeS$_2$ (solid circles). The functions $\exp(-Ct^{\alpha})$, with $\alpha=0.58$ are shown by the solid lines.

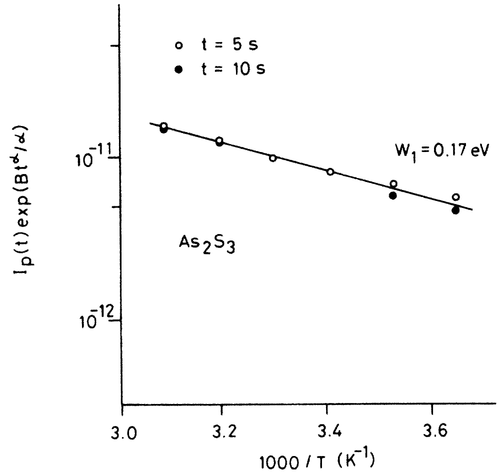

FIG. 10. Temperature dependence of $I_p(t)\exp(Bt^{\alpha}/\alpha)$ for $t=5$ and $t=10$ s in As$_2$S$_3$.

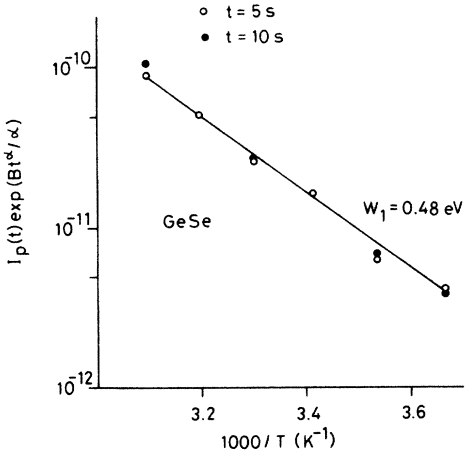

FIG. 11. Temperature dependence of $I_p(t)\exp(Bt^{\alpha}/\alpha)$ for $t=5$ and $t=10$ s in GeSe.

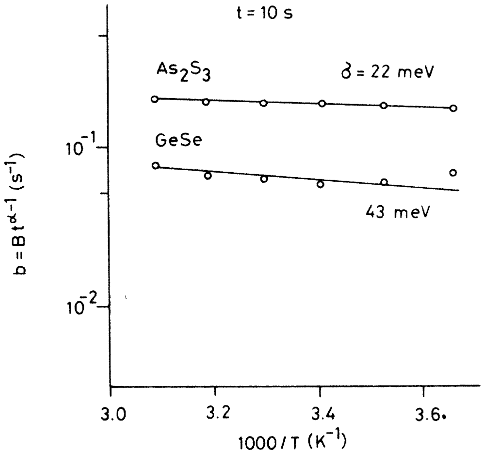

FIG. 12. Temperature dependences of the decay rate $Bt^{\alpha-1}$ at $t=10$ s in As$_2$S$_3$ and GeSe.

ESR signal has been observed after strong and long-time photoillumination.[14] Biegelsen and Street[14] have suggested that these new localized states are close pairs of the charged D^+ and D^- centers. If new localized states are created, the photocurrent would decrease after strong illumination. To our knowledge, photoinduced change of the photocurrent has not yet been reported in amorphous chalcogenides. We examined the photoinduced effect of $I_p(t)$ for As$_2$S$_3$ and GeSe$_2$. The steady photocurrent $I_p(0)$ decreases with increasing exposure time. $I_p(t)$, of course, decreases after long-time illumination.

Solid circles in Fig. 13 show $I_p(t)$ before and after long-time illumination (56 mW/cm^2 by mercury lamp, 90 min at 303 K) in As$_2$S$_3$. Note that the specimen used here is different from those used in Sec. IV A (Figs. 3 and 7). The optical gap decreases by an amount of 0.07 eV.

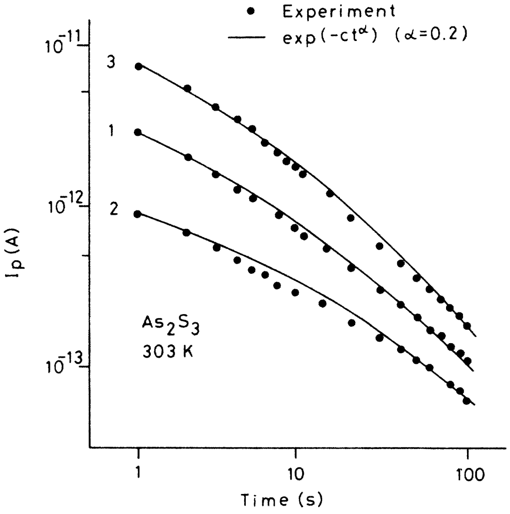

FIG. 13. Effects of prolonged illumination and annealing on $I_p(t)$ measured at 303 K in As$_2$S$_3$. Solid circles denoted by 1, 2, and 3 are $I_p(t)$ for the original, the prolonged illumination, and the annealed states, respectively. The functions $\exp(-Ct^{\alpha})$, with $\alpha=0.2$ are shown by the solid lines.

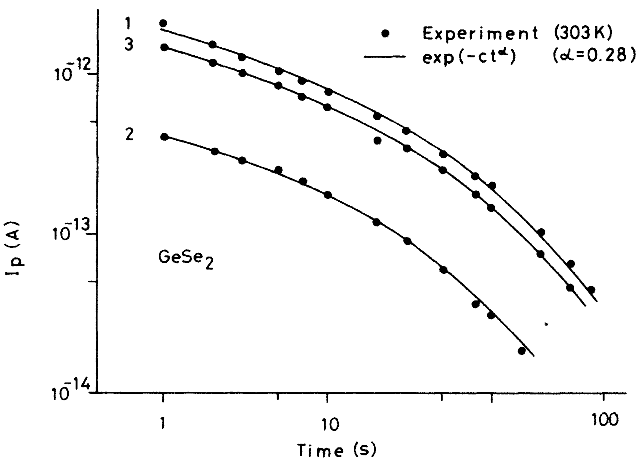

FIG. 14. Effects of prolonged illumination and annealing on $I_p(t)$ measured at 303 K in $GeSe_2$. Solid circles denoted by 1, 2, and 3 are $I_p(t)$ for the original, the prolonged illumination, and the annealed states, respectively. The functions $\exp(-Ct^{\alpha})$, with $\alpha = 0.28$ are shown by the solid lines.

The magnitude of $I_p(t)$ reduces after long-time illumination, suggesting that new localized states in the gap are induced. Solid lines are the extended exponentials for the same α ($=0.2$), showing the shape of $I_p(t)$ does not change after long-time illumination. The similar behaviors are also obtained for $GeSe_2$ after illumination (56 mW/cm^2, 90 min at 303 K) as shown in Fig. 14. The optical gap decreases by an amount of 0.03 eV. Solid lines are the extended exponentials for the same α ($=0.28$). The same shape of $I_p(t)$ before and after long-time illumination suggests that both the recombination mechanisms (before and after long-time illumination) are essentially the same. This suggests that new created localized states are the same centers which dominate recombination process for the original states.

Solid circles denoted by 3 in Figs. 13 and 14 show $I_p(t)$ after isothermal annealing (170 °C, 60 min for As_2S_3, and 150 °C, 60 min for $GeSe_2$). $I_p(t)$ for $GeSe_2$ almost returns to the original state (before illumination), suggesting the reversible change of $I_p(t)$. $I_p(t)$ for As_2S_3 after annealing, however, becomes large as compared with that of the original state. Probably, the original state for As_2S_3 could be ill annealed. It should be stressed that the reversible nature is similar to the photodarkening effect. It is shown that the photodarkening accompanies the decrease of the photocurrent $I_p(t)$. This suggests also that prolonged and strong exposure of light induces new localized states in the gap.

It is not clear from the present study whether created new states are the close pairs of D^+ and D^- as suggested by Biegelsen and Street.[14]

V. CONCLUSIONS

It has been demonstrated that the persistent photocurrent $I_p(t)$ for amorphous chalcogenides is described empirically by the extended exponential $\exp(-Ct^{\alpha})$. This behavior was explained by the dispersive diffusion-controlled tunneling reaction of excess D^0s ($2D^0 \rightarrow D^+ + D^-$) for the most of amorphous chalcogenides. The magnitude of $I_p(t)$ decreases after prolonged exposure to strongly absorbed light, while the shape of $I_p(t)$ does not change. These predict that charged defect states D^+ and D^- are induced by strong and long-time photoillumination.

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