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# Reversible photoinduced change of photoconductivity in amorphous chalcogenide films

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Prolonged exposure to strongly absorbed light decreases the photoconductivity of well-annealed amorphous chalcogenide (Se, $As_2Se_3$, and $As_2S_3$) films, similar to the behavior observed in hydrogenated amorphous silicon and organic amorphous polysilanes. This change is removed by annealing near the glass transition temperature. The reversible change in photoconductivity appears to be an intrinsic effect in amorphous semiconductors. The optically induced defect-creation reactions responsible for this, and for light-induced changes in ac conductivity, are discussed in detail.

## I. INTRODUCTION

The reversible photostructural change, a decrease of the optical gap $E_0$ (photodarkening) after illumination and removal of the change by annealing to the glass transition temperature $T_g$, is well known in amorphous chalcogenides.[1] Several mechanisms have been proposed to account for such a reversible change.[2-4] It is evident that photoinduced reversible changes can accompany defect creation by illumination and annihilation by annealing.[2] Recent reports on electronic transport (ac conductivity, $\sigma_{ac}$) (Refs. 5 and 6) suggest also that new localized states in the band gap are induced by illumination. Such a conclusion was also reached earlier by Abkowitz and co-workers,[7,8] where a (thermally erasable) photoinduced enhancement of deep trapping of electrons and holes in *a*-Se and Se-rich alloys was observed and investigated by xerographic techniques. Consequently a decrease in photoconductivity is predicted.

In this paper we report a (reversible) photoinduced decrease in photocurrent $I_p$ in amorphous Se, $As_2Se_3$, and $As_2S_3$ films. The temporal change in $I_p$ during illumination obeys the stretched exponential form $[\exp(-Ct^{\alpha})]$, where $0<\alpha<1$, which is similar to that observed for organic amorphous polysilanes[9] and for excess band-tail carriers in hydrogenated amorphous silicon (*a*-Si:H).[10,11] We emphasize here that the reversible photoinduced change of the photocurrent appears to be an intrinsic effect for amorphous semiconductors (i.e., it is not limited to *a*-Si:H—the Staebler-Wronski effect[11]).

## II. PHOTOCONDUCTIVITY STUDIES

Thin films of amorphous Se, $As_2Se_3$, and $As_2S_3$ were evaporated onto Corning 7059 substrates. After evaporation, samples were annealed at appropriate temperatures near $T_g$. The thicknesses of the films and the annealing temperatures $T_a$ are given in Table I. Planar gap-cell electrodes using Al contacts were fabricated (gap spacing 40 μm, gap width 5 mm). A halogen lamp (480 mW/cm$^2$) for Se and $As_2Se_3$ and a high-pressure mercury lamp (54 mW/cm$^2$) for $As_2S_3$ were used with an ir-cut water filter to excite the photocurrents; the light intensities were measured at the surface of the samples using a thermopile. However, reciprocity behavior (exposure time multiplied by flux) was not examined. The applied voltages $V$ are also tabulated in Table I. The photocurrent is proportional to $V$ at these voltages.

Figure 1 shows a schematic illustration of the photocurrent $I_p$ at any measured temperature $T_m$ (90, 200, and 300 K). During illumination, $I_p$ for a well-annealed film decreases with time (*a*-*b*) and approaches a constant value $I_\infty$. After stopping the illumination, the dark state (*b*-*c*) is kept for several hours at 300 K and then the illumination is restarted at 90 or 200 K (*c*-*d*). The photocurrent returns to almost the same constant value $I_p=I_\infty$

TABLE I. Thickness, annealing temperature after evaporation and after long-time illumination, measured-applied voltage, and fitting dispersion parameter ($\alpha$).

| Chalcogenide | Thickness (μm) | Annealing temperature $T_a$ (°C) | Applied voltage $V$ (V) | Dispersion parameter ($\alpha$) |
|---|---|---|---|---|
| $As_2S_3$ | 1.0 | 170 (5 h) | 300 | 0.48 (300 K)<br>0.51 (200 K) |
| $As_2Se_3$ | 1.4 | 200 (2 h) | 5 | 0.57 (300 K)<br>0.64 (90 K) |
| Se | 1.1 | 25 (5 h) | 4 | 0.84 (90 K) |

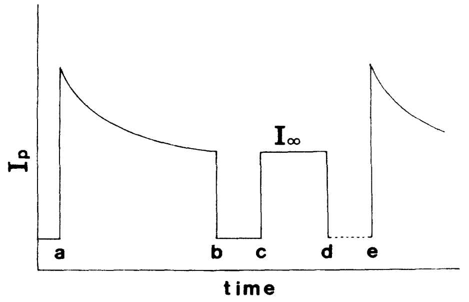

FIG. 1 Schematic illustration of the behavior of the photocurrent $I_p$ with illumination and annealing for amorphous chalcogenide materials. Illumination at the measurement temperature ($T_m < T_g$) (*a-b*, *c-d*); annealing at room temperature (*b-c*) and at $T_a \sim T_g$ (*d-e*). After annealing at $T_a$ (for values, see Table I), $I_p$ returns to the original state.

(*c-d*), suggesting that metastable localized states (stable at 300 K) are induced upon band-gap illumination for any temperature less than $T_g$. After annealing at $T_a$ (*d-e*), $I_p$ returns to the original well-annealed state. It should be noted that the photoinduced ac conductivity $\sigma_{ac}$ in *a*-$As_2S_3$ for low-temperature (90 K) illumination is destroyed by annealing at 200 K,[6] although $I_p$ here does not return to the original state after annealing at 300 K. This suggests that the induced centers controlling $I_p$ are different from those contributing to $\sigma_{ac}$. In a previous paper,[6] we have suggested that the center contributing to $\sigma_{ac}$ is the self-trapped exciton (STE), i.e., $P_4{}^+$-$C_1{}^-$, where $P$ and $C$ refer to pnictogen and chalcogen centers, respectively, and the superscript and subscript refer to the charge state and coordination number, respectively. Such STE's seem not to be stable above room temperature.

The solid circles in Figs. 2(a) and 2(b) show the time-dependent change in photocurrent $I_p$ (state *a-b*) for $As_2S_3$ measured at 300 and 200 K, respectively, where $\Delta I_p$ is defined as $I_p - I_\infty$. Here we use "current" (not conductivity), since uniform optical excitation through the films cannot always be ensured. The solid lines represent fits to the stretched exponential function given by $\exp(-Ct^\alpha)$. The values of the exponent $\alpha$ for *a*-$As_2S_3$ are 0.48 for 300 K and 0.51 for 200 K. Similar behavior is found in *a*-$As_2Se_3$ and *a*-Se. The values of $\alpha$ are tabulated in Table I. The value of $\alpha$ increases with decreasing temperature, which is contrary to that observed in organic polysilanes[9] and *a*-Si:H,[10-12] and the reason for this is not clear. A decrease in $I_p$ at 300 K is not observed in *a*-Se, and the reason for this will be discussed later. Note that the stretched-exponential functional form also appears in the photocurrent decay (after cessation of illumination) in amorphous chalcogenides.[13] It should be noted also that the stretched-exponential function has recently received renewed attention in connection with various dynamics of disordered condensed matter.[14,15]

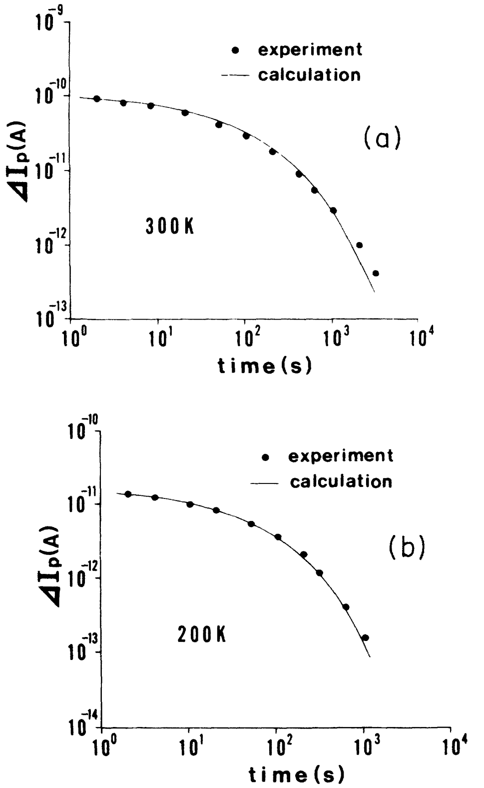

FIG. 2. Time-dependent change in $I_p$ for $As_2S_3$, where $\Delta I_p$ is defined as $I_p - I_\infty$ (see Fig. 1). The solid line is the fit to the stretched-exponential $[\exp(-Ct^\alpha)]$. (a) Measured at 300 K; (b) measured at 200 K.

## III. A MODEL FOR THE TIME-DEPENDENT LIGHT-INDUCED CHANGES IN PHOTOCONDUCTIVITY

The creation of (coordination) defects in chalcogenide glasses by optical irradiation, as opposed to excitation of preexisting defects, is well documented.[2,16] Biegelsen and Street[2] have suggested, on the basis of light-induced electron-spin-resonance (LESR) experiments that self-trapped excitons (i.e., conjugate pairs of charged defects, e.g., $P_2{}^+, C_1{}^-$ or $P_4{}^+, C_1{}^-$) are induced by illumination. Our recent work on reversible photoinduced changes in $\sigma_{ac}$ for *a*-$As_2S_3$ lends support to this picture.[5,6] The photoinduced increase in deep trapping of electrons and holes in *a*-Se observed by xerographic techniques was also explained in this manner.[7,8] The formation of a STE state is illustrated schematically in Fig. 3 for the case of *a*-$As_2S_3$ ($Y_1$ and $Y_2$). However, such STE states would not act as trapping centers for electrons or holes since they are effectively neutral (i.e., with a small capture cross section), and consequently as such would not be expected to affect the photoconductivity. On the other hand, random pairs (RP) of $D^+, D^-$ defects (e.g., $P_4{}^+, C_1^-$ or $C_3{}^+, C_1{}^-$) may result from bond-switching reactions at STE centers ($Z_1, Z_2$ in Fig. 3), and these could act as electron or hole trapping centers and hence would act to decrease the photoconductivity.

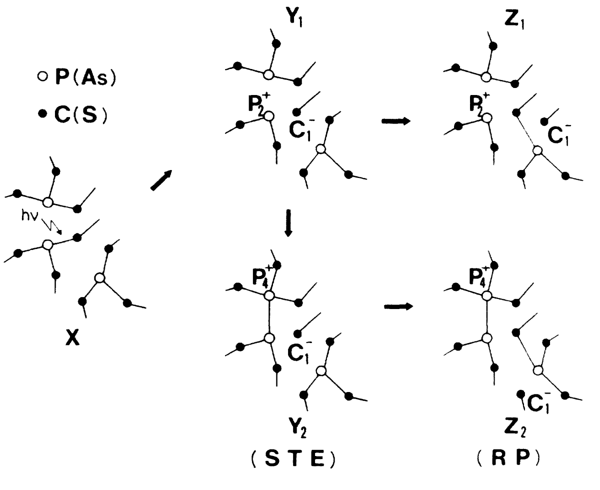

FIG. 3. Schematic illustration of the optical generation of self-trapped exciton (STE) states $(Y_1, Y_2)$ from the chemically ordered ground-state structure of $a$-$As_2S_3$ ($P \equiv As$, $C \equiv S$). Subsequent bond-switching reactions can lead to a greater separation between the charged defects, i.e., random pairs $(RP, Z_1, Z_2)$.

The potential energies relating to the ground-state $(X)$, STE $(Y)$, and RP $(Z)$ configurations are shown schematically in the configuration-coordinate diagram in Fig. 4. Note that the STE state is produced from an excited, free-exciton state by illumination,[2,4,17] *not* by the thermal energy $U_x$ shown in Fig. 4. STE states, which are formed predominantly by illumination at low temperatures, annihilate at around 200 K,[2,6] implying a small value for $V_Y$ ($\simeq kT_g$). On the other hand, if $V_z \gg kT_g$, the RP state might be quite stable at around room temperature.

The rate equation for inducing randomly paired states (via STE) can be written as

$$\frac{dN_{RP}}{dt} = k_p(N_T - N_{RP}) - k_r N_{RP} , \tag{1}$$

where $N_{RP}$ is the number of pairs of induced RP centers, $N_{RP} = [D^+] = [D^-]$, $N_T$ the total participating site density, $k_p$ the promotion rate, and $k_r$ the recovery rate toward the ground state. If the reaction is dispersive in nature, which may result from cooperative processes or from fluctuations of the potential barriers for forward and reverse processes $(U_y, V_z)$, the rate constant can be time dependent and can be written as $k_P = At^{\alpha-1}$ and $k_r = Bt^{\alpha-1}$, where $A$ and $B$ are constants including thermal population factors $\exp(-U_Y/kT)$ and $\exp(-V_Z/kT)$, respectively, and the dispersion parameter[9,10,13] $\alpha$ is assumed to be the same for both creation and annihilation reactions. The solution of Eq. (1) under such dispersive conditions is given by[7]

$$N_{RP} = \frac{A}{A+B} N_T[1 - \exp(-Ct^{\alpha})] , \tag{2}$$

where $C = (A+B)/\alpha$.

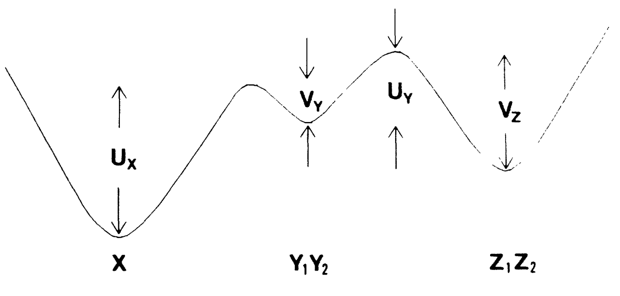

FIG. 4. Configurational-coordinate potential-energy diagram illustrating schematically the relative energies of the ground-state $(X)$, and STE $(Y)$ and RP $(Z)$ configurations.

Free holes, which are the dominant carriers in thermal equilibrium in amorphous chalcogenides, will be trapped by the induced RP centers and hence the concentration of free holes at time $t$ is given by

$$n_p(t) = n_p(0) - N_{RP} , \tag{3}$$

where $n_p(0)$ is the initial hole density in the band states. Substitution of Eq. (2) into Eq. (3) yields

$$\begin{aligned} \Delta n_p(t) &= n_p(t) - n_p(\infty) \\ &= \frac{A}{A+B} N_T \exp(-Ct^{\alpha}) . \end{aligned} \tag{4}$$

Hence the origin of the experimentally observed empirical form for $\Delta I_p(t)$ appearing in Figs. 2(a) and 2(b) is explained by Eq. (4) since $I_p$ is proportional to $n_p$.

Alternatively, a stretched-exponential time dependence of the density of free holes, and hence of the photoconductivity, can also be obtained from a consideration of the behavior of the quasi-Fermi level under photoexcitation. In the case of holes being the majority carriers, let $E_v$ be the energy corresponding to the valence-band (mobility) edge (set to zero for convenience), $E_t$ that of a trapping level in the gap near the valence band, and $E_{FP}$ the position of the hole quasi-Fermi level, with $N_v$ and $N_t$ being the effective densities of states for the valence-band states and trapping states, respectively, and with corresponding values for electron-related quantities pertaining to the conduction band. The quantities $E_{FP}$ and $N_t$ are time dependent. Then, charge neutrality dictates that

$$N_v \exp(-E_{FP}/kT) + N_t(t) \exp[-(E_{FP} - E_t)/kT] = C , \tag{5}$$

where $C$ is a constant, equal to the equivalent of Eq. (5) in terms of electron quantities. The concentration of photogenerated free holes at time $t$, $n_p(t)$, is given by

$$n_p(t) = N_v \exp(-E_{FP}/kT) \tag{6}$$

or, substituting from Eq. (5), by

$$n_p(t) = \frac{C}{\left[1 + \frac{N_t(t)}{N_v} \exp(E_t/kT)\right]} . \tag{7}$$

From arguments similar to those leading to Eq. (2), the carrier concentration in the traps, $N_t(t)$, is given by

$$N_t(t)=a[1-\exp(-bt^{\alpha})] , \tag{8}$$

where $a$ and $b$ are constants. Thus, if $N_t(t)\exp(E_t/kT)/N_v \gg 1$, from Eq. (8),

$$n_p(t) \simeq \frac{CN_v \exp(-E_t/kT)}{a[1-\exp(-bt^{\alpha})]} \tag{9}$$

and

$$n_p(\infty)=\frac{CN_v}{a}\exp(-E_t/kT) . \tag{10}$$

Thus

$$\Delta n_p(t)=n_p(t)-n_p(\infty)=\frac{CN_v \exp(-E_t/kT)\exp(-bt^{\alpha})}{a} \tag{11}$$

when $\exp(-bt^{\alpha}) \ll 1$.

## IV. DISCUSSION

It is proposed that the reversible time-dependent changes in the photoconductivity of chalcogenide glasses caused by optical illumination result from the initial creation of self-trapped exciton pairs of charged defects, followed by bond-switching reactions leading to widely separated, metastable "random pairs" of defects (Fig. 3). These defects are presumed to be the origin of the trapping levels controlling the photocurrent. In general, it is expected that such RP states would be metastable, and would only anneal out if the temperature of the samples is raised to near $T_g$, as found experimentally (see Table I). The fact that a light-induced decrease in photoconductivity is *not* observed in the case of *a*-Se illuminated at 300 K is understandable in this context since the glass transition temperature for this material is comparable to room temperature; thus the rates of inducing and annealing of the change in photoconductivity would be comparable at 300 K and no net effect is therefore expected. Relaxation times should increase rather rapidly, however, as the temperature is lowered below $T_g$, and so a light-induced decrease in the photoconductivity in *a*-Se should begin to be observed at temperatures a few tens of degrees below $T_g$, although this has not yet been investigated. (A pronounced effect is observed at a measurement temperature of 90 K—see Table I.)

At this point, we should also discuss the possible (microscopic) reasons for the observation of a stretched-exponential decay law for the time evolution of the photocurrent under conditions of constant illumination (Fig. 2). As shown in Sec. II, this behavior can be understood in terms of time-dependent rate constants governing the kinetics of creation $[k_p(t)]$ and annihilation $[k_r(t)]$ of the optically induced RP centers believed to be responsible for controlling the photoconductivity [Eq. (1)]. We believe that these time-dependent (power-law) rate constants could arise from the defect diffusion processes illustrated in Fig. 3 which are necessary to stabilize photocreated charged defects against mutual annihilation by causing them to become spatially separated or, conversely, which are involved in the diffusive motion towards each other leading eventually to annihilation. This process of diffusive transport is analogous to the hopping motion of electrons in disordered media which can be treated in terms of the continuous-time random-walk model of Scher and Montroll.[18] In this, a waiting-time distribution function $\psi(t)$ characterizes the motion and, under the conditions where stretched-exponential relaxation behavior arises (i.e., for "fractal" times[19]), $\psi(t)$ has a power-law time dependence.[18,19] We would expect, therefore, $k_p(t)$ and $k_r(t)$ to have a similar time dependence to that of $\psi(t)$ and, moreover, to have the same functional form as each other since the diffusive motions involved in creation and annihilation of RP charged defects are essentially the same (Fig. 3).

We turn now to a brief discussion of the photoinduced changes in ac conductivity observed experimentally.[5,6] Previously,[5,6] we have ascribed the photoinduced changes in $\sigma(\omega)$ to the photocreation of STE defects, such as $P_4{}^+, C_1{}^-$ ($Y_2$ in Fig. 3). The identity of such a defect pair is preserved upon exchange of two electrons, as required in the correlated-barrier-hopping (CBH) model of ac conductivity[20] in amorphous chalcogenides, although the relative positions of the $P_4{}^+$ and $C_1{}^-$ centers are reversed, leading to a change in dipole moment (Fig. 5). (N.B. This preservation of symmetry does not occur for other types of defect pairs in compound chalcogenides.) The varying separations between $P_4{}^+$ and $C_1{}^-$ centers necessary[20] to give rise to the nearly linear frequency dependence of $\sigma(\omega)$ could arise from the defect-preserving, bond-switching reaction shown in Fig. 3 ($Y_2 \rightarrow Z_2$), although the pairs of centers which contribute to the ac loss response are in fact rather close, with a separation of 5–10 Å.[20,21]

It was found that the photoinduced increase in $\sigma(\omega)$ for *a*-$As_2S_3$ was greater when illumination was carried out at 90 K rather than at 300 K, yet the change induced at 90 K annealed out at ~200 K, whereas that induced at 300 K was stable to an annealing temperature corresponding to $T_g$ (~440 K).[6] We ascribe this difference in behavior to the fact that, under low-temperature conditions of illumination, there is insufficient thermal energy available for the bond-switching reactions shown in Fig. 3 ($Y_2 \rightarrow Z_2$) to take place to any significant extent; as a result, the high densities of relatively close pairs of charged centers (STE) induced at low temperatures will be very susceptible to mutual annihilation via the reverse reaction of that shown in Fig. 3 ($Y_2 \rightarrow X$) at relatively low

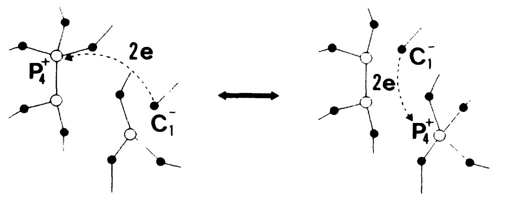

FIG. 5. Schematic illustration showing the two-electron exchange between $P_4{}^+$ and $C_1{}^-$ centers giving rise to ac conductivity in the CBH model (Ref. 18). Note that the identity of this pair of defects is preserved under two-electron interchange.

temperatures, i.e., $\simeq 200$ K. However, illumination at more elevated temperatures would tend to produce fewer but more stable defects since the bond-switching reactions leading to the more separated RP centers would be promoted. In such a case, it would only be at annealing temperatures near $T_g$ that sufficient atomic mobility could be introduced to facilitate mutual annihilation of the charged defects.

## V. CONCLUSIONS

We have observed reversible changes in the photoconductivity of amorphous chalcogenides after optical illumination and subsequent thermal annealing. These changes are ascribed to the creation and annihilation of widely separated random pairs of positively and negatively charged defect centers (most likely $P_4^+$ and $C_1^-$ or $C_3^+$ and $C_1^-$ defects), which act as recombination (trapping) centers. The time dependence of the decrease in photoconductivity under constant illumination follows a stretched-exponential law. This behavior has been explained in terms of time-dependent creation and annihilation rate constants (having a power-law time dependence) arising from defect-diffusion (bond-switching) reactions after the optical creation of self-trapped exciton states. Such STE states arise from bond-breaking and consist of neighboring positively and negatively charged dangling-bond defects (e.g., $P_2^+, C_1^-$). Thus a photoinduced decrease in the photoconductivity is not a feature unique to *a*-Si:H,[12] but appears to be a common behavior for most disordered semiconductors.

We also discuss the reversible photoinduced changes in ac conductivity observed in amorphous chalcogenide materials.[5,6] We ascribe this behavior also to the photogeneration of diamagnetic, i.e., charged, coordination defects, as for photoconductivity. However, it should be stressed that these bond-breaking mechanisms, and others giving rise to light-induced ESR,[22] do not account for all photoinduced phenomena in amorphous chalcogenides. In particular, photodarkening most likely results from changes in interchain interactions not involving covalent bond breaking.[4,23]

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