Photoinduced Current in Polyvinylcarbazole

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Measurements of the electrical current associated with the return to thermal equilibrium after photoexcitation of polyvinylcarbazole (PVK), a photoconducting organic polymer, are presented and discussed. Thin sandwich layers of PVK were excited with weakly absorbed light with the electrodes shorted. After removal of the light, a voltage was applied and the current measured. The current decayed as $(time)^{-1}$ and was proportional to the electric field and dependent upon the light exposure. Discussion is presented to support the following conclusions: (a) Al and Au form blocking contacts to PVK; (b) the hole range in PVK is at least 4×10^{-6} cm^2/V; and (c) the charge carriers observed in this experiment are stored only at the surface and either recombine there or transit completely across the PVK when released. No bulk recombination or deep trapping of holes occurs. Two alternative models are proposed which produce the observed hyperbolic time dependence. One involves thermal release of charge carriers from a distribution of traps uniform in energy. A second model postulates that the current is proportional to the concentration of a bimolecularly decaying species. The existence of excitons as an intermediate state in the photoconduction process is strongly suggested.

INTRODUCTION

Since 1965 when Hoegl first reported the observation of photoconductivity in polyvinylcarbazole (PVK),[1] only modest progress has been made toward understanding the photogeneration and transport processes involved. Lardon *et al.*[2] observed a correspondence between the light absorption and photoconductivity spectra, indicating that the surface plays an important role. Regensberger[3] measured the drift mobility by xerographic techniques and found field and temperature-dependent mobilities which suggested field-assisted hopping.

The work reported here was initiated to probe the defect structure and charge transport in undoped unsensitized PVK by observing the current associated with the return to a thermal equilibrium carrier distribution after photoexcitation. Weakly absorbed light was used to excite thin (2–27 μ) layers of PVK between two metal electrodes. A voltage was applied after the light was removed and the resulting current was investigated and experimentally characterized.

The metal electrodes (Au and Al) were found to be blocking and the electric field was found to be constant in time. The photocurrent decayed hyperbolically with time and was proportional to the electric field. These results, along with the observed excitation dependence, led to the following conclusions: (a) The photoinduced carriers are holes with a range of at least 4×10^{-6} cm^2/V; (b) they are generated at the surface and travel completely through the PVK without recombining or being deep trapped

in the bulk; and (c) the electric field controls the number of released holes which actually transit the PVK. We feel that excitons (uncharged excitations of the solid) must be involved as an intermediate state in the photogeneration process and account for the surface-only generation of free holes. Two possible explanations for the observed time dependence are proposed and evaluated, one involving the release of charge from a uniform distribution in energy of traps, the other involving a current which is proportional to the concentration of a bimolecularly decaying species—not, however, to the bimolecular decay rate itself.

EXPERIMENTAL

The samples were prepared at the Xerox Research Laboratories where the PVK was coated onto polished aluminum sheets from a solution of toulene and cyclohexanone. Transparent gold electrodes (area = 0.3 cm^2) were vacuum deposited to form the top electrode. The sample was mounted on a copper block with electrical connections made as shown in Fig. 1, and maintained in a vacuum cryostat (10^{-5} Torr) at any constant temperature between -200 and $+100$ °C. The current through the sample was measured with a Cary Model 31 Vibrating Reed Electrometer. While shorted, the PVK was illuminated with light from a mercury arc lamp filtered so that only the weakly absorbed wavelengths were present. It was determined that the light was weakly absorbed because (i) the insertion of an 18-μ PVK filter in the path of the exciting radiation had no effect upon the observed current aside from that accounted for
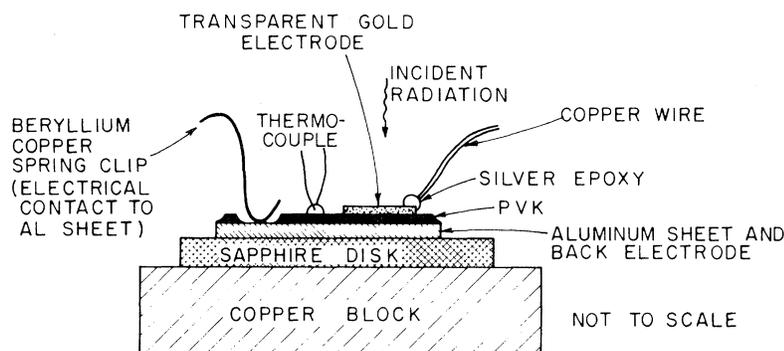
FIG. 1. Cross-sectional view of sample.

by the small attenuation of incident intensity expected; (ii) an 18-μ layer of PVK transmitted more than 50% of the exciting radiation used; and (iii) all effects observed were polarity independent unless strongly absorbed light was intentionally used. The incident photon flux at maximum intensity was approximately 1.5×10^{17} photons/(sec cm^2). Since 50% was absorbed in 18 μ of PVK, this corresponds to 4×10^{15} photons absorbed /(μ sec). The maximum total number of electrons observed to transit the sample was approximately 6×10^{10}, so that the overall quantum efficiency was never more than 10^{-7}.

After the illumination was removed, a voltage was applied and the resulting current in excess of the capacitive charging current was measured as a function of time. In most cases, the voltage was applied within 1 sec after the removal of light excitation; in some cases the voltage was intentionally delayed, as discussed later. The dependence of the decaying photocurrent upon applied voltage, temperature, PVK thickness, light intensity, excitation time, and exposure (the product of excitation time and light intensity) was measured.

The current was *always* observed to decay with

time in a hyperbolic manner according to

$$j = A/(t + t_0) .$$ (1)

The amplitude parameter A and the time-offset parameter t_0 were determined by measuring the least-squares slope and intercept of the plot of $1/j$ vs t, since

$$1/j = (1/A) \, t + t_0/A .$$ (2)

Figure 2 shows a typical $1/j$ vs t plot for several different values of applied voltage.

The amplitude parameter A was found to be proportional to the applied electric field independent of sample thickness, as seen in Fig. 3. The amplitude parameter A also depended upon the incident light exposure independent of sample thickness, according to Fig. 4, and was thermally activated with activation energy of 0.14 eV (see Fig. 5). This activation energy is very low, only 3–5 kT over the temperature range measured. The temperature dependence could also be a $T^{4.5}$ power law, but we favor a thermally activated process.

The time-offset parameter t_0 was inherently more difficult to measure accurately than A. t_0 appeared to increase with increasing excitation time and temperature but was independent of other parameters.

All effects were polarity independent with weakly absorbed light. When strongly absorbed light was intentionally used, the currents were larger when the illuminated surface was positive, indicating that the majority of the current was due to hole flow.

Two experiments closely related to the basic experiment were performed which provided information concerning the nature of the electrical contacts and the time dependence of the electric field. The first consisted of placing a 6-μ sheet of Mylar between the top gold electrode and the top surface of the PVK to form a blocking layer. When allowance was made for the polarization of the Mylar and the associated decrease of the field in the PVK, *the photocurrent decayed with the same hyperbolic time dependence as observed without the Mylar.* It is therefore concluded that the gold and aluminum con-
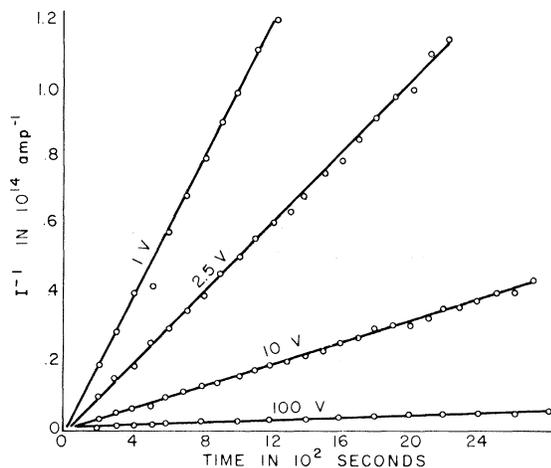
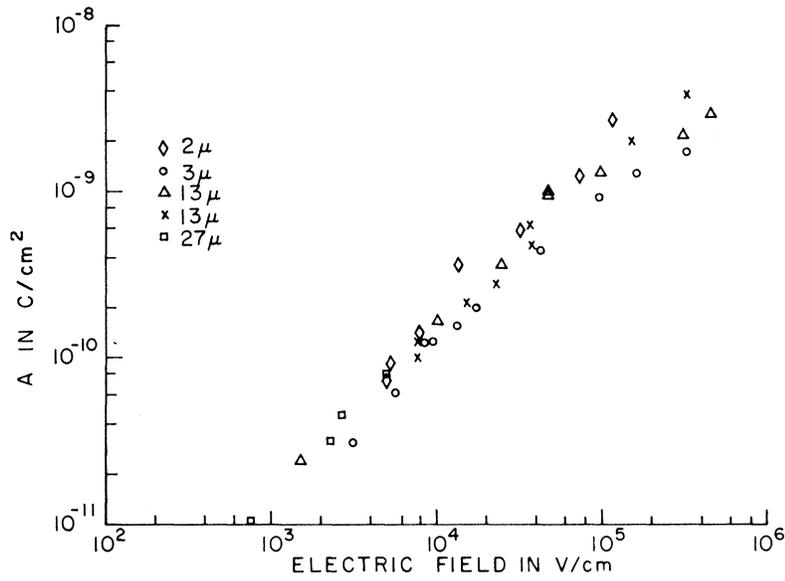FIG. 2 Current^{-1} vs time for various values of applied voltage.

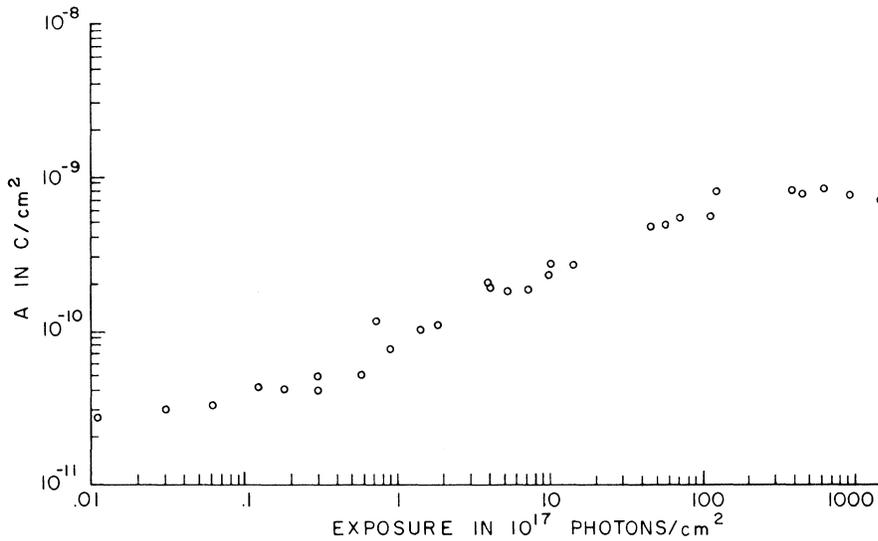FIG. 3. Log A vs log electric field (V/L) for various thickness samples.

FIG. 4. Log A vs log exposure. Several points near center of curve vary by three orders of magnitude in light intensity.
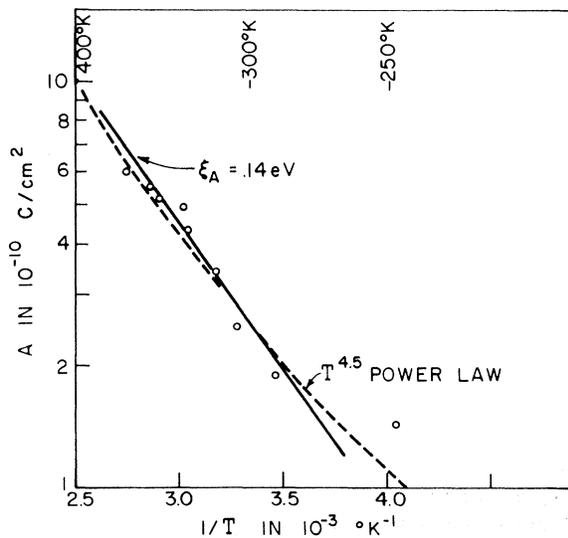
FIG. 5. $\mathrm{Log_{10}}\,A$ vs $1/T$. Solid line is predicted by thermally activated process with activation energy equal to 0.14 eV. Dotted line is predicted by $T^{4.5}$ power law.
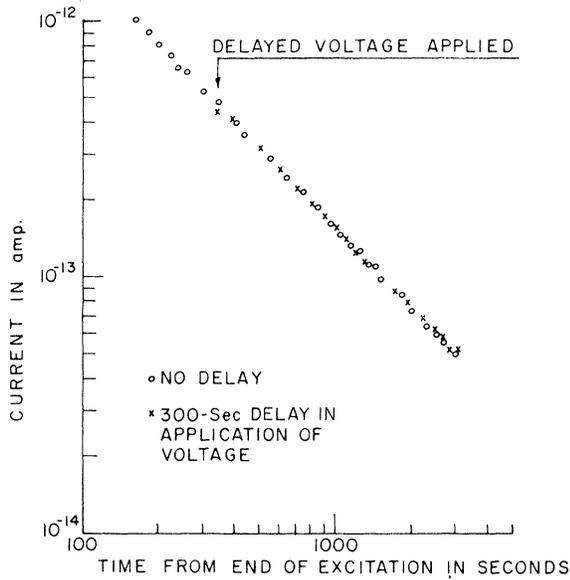
FIG. 6. Log current vs log time since excitation removed for no delay (O) and for 5-min delay (×) before applying voltage.

tacts were also blocking.

The second experimental variation consisted of allowing a time interval between the removal of the light and the application of the voltage. As seen in Fig. 6, the current depends only upon the time elapsed since the light was removed and is insensitive to the time of voltage application. *Only an electric field constant in time is consistent with these results.*

DISCUSSION

The manner in which the observed currents scale with sample thickness can provide information about the spatial properties of the postexcitation charge carrier generation and carrier transport mechanisms. The explicit thickness dependence can be easily determined when current is expressed as the product of the free-charge volume-generation rate R and the average distance the charge moves, w, integrated over the sample thickness:

$$j(t) = \frac{1}{L} \int_0^L R(x, t) \, w(x, t) . \tag{3}$$

This analysis assumes that R and w change negligibly in the time required for an excited carrier to move a distance w.

Two simple limiting models for R and w will be assumed and the explicit thickness dependence scaling laws determined. The postexcitation carrier generation can be either (a) uniform throughout the bulk, in which case the total generation rate will be proportional to sample thickness, or (b) limited to the surface region with the total generation independent of sample thickness. The two limiting cases for w are (i) short range where w is much less than L and field dependent $[w = L(1 - e^{-rE/L}) = Lf(E/L)$ and r is the range or the average distance traveled per unit field]; or (ii) long range where the charge travels from its point of generation to the electrode without being deep trapped or recombining. The four different combinations and the appropriate thickness scaling laws are shown in Table I.

As shown in Fig. 3, the experimentally observed scaling law is $j \propto E$ independent of L. Therefore either the bulk-generation short-range model or the surface-generation long-range model could be appropriate. However, the former would result in the generation of space charge in the PVK bulk which for the current observed would very substantially alter the electric field in the course of the experiment. This contradicts the experimental observation that the electric field does not change with time. The observed current, therefore, is likely due to surface generation of free charge which subsequently travels completely across the sample without deep trapping or recombination. Since no departure from the $j \propto E$ scaling law was observed for the lowest fields providing reliable measurements (7×10^2 V/cm) in the thickest sample (27 μ), the hole range in PVK must be at least 4×10^{-6} cm^2/V. In principle, the hole range could be determined by studying progressively thicker samples or lower voltages until a departure from $j \propto E$ and/ or evidence of time-varying fields were observed. The lower limit for the range quoted above was determined using the thickest sample available to us and the lowest voltage permitted by the sensitivity of the charge measuring apparatus used.

Since the carriers go all the way across the sample, then according to (3) the current density is just the surface-generation rate for free carriers. This generation rate must account for the time, excita-

TABLE I. Summary of explicit thickness dependences predicted by simple limiting models for generation and transport. R_0 is the uniform bulk-generation rate; $\mathcal{R}_0$ is the surface-generation rate.

TRANSPORT / GENERATION	RANGE-LIMITED $w = Lf(E/L)$ $w \ll L$	ELECTRODE-LIMITED $w = L - x$ (x IS POINT OF GENERATION)
UNIFORM, BULK GENERATION (PROPORTIONAL TO L)	$j = R_0 \cdot L\, f(E/L)$ THICKNESS INDEPENDENT PLOT: j/L vs E/L	$j = (L/2)\, R_0(E)$ PLOT: j/L vs E
SURFACE GENERATION (INDEPENDENT OF L)	$j = \mathcal{R}_0 f(E/L)$ PLOT: j vs E/L	$j = \mathcal{R}_0(E)$ PLOT: j vs E

$$\left[j = (1/L) \int_0^L R(x,t) w(x,t)\, dx \right]$$

SCALING LAWS

tion, and field dependences observed. The time dependence will be considered first. Bimolecular processes are commonly called upon to explain $1/t$ decays.[4] A bimolecular process is one in which the decay of the nonequilibrium concentration of a species is proportional to the square of the concentration:

$$\frac{dn}{dt} = -an^2 . \tag{4}$$

Integration yields

$$n(t) = \frac{1}{at + 1/n_0} = \frac{1/a}{t + 1/an_0} . \tag{5}$$

This is similar to the time dependence of the observed current. However, if one postulates that the free carriers are produced by the bimolecular decay of some species, e.g., mutual annihilation of two excitons to form a hole-electron pair, then the generation rate of free carriers would go as the *decay rate* of the species which is given by

$$j \propto \frac{-dn}{dt} = \frac{1/a}{(t + 1/an_0)^2} . \tag{6}$$

Clearly this is not the time dependence observed and therefore this *direct* bimolecular model is inadequate.

However, the similarity of the time dependence of the concentration of a bimolecularly decaying species, Eq. (5), to the observed time dependence of the current decay demands more attention. One can postulate a model in which bimolecular decay
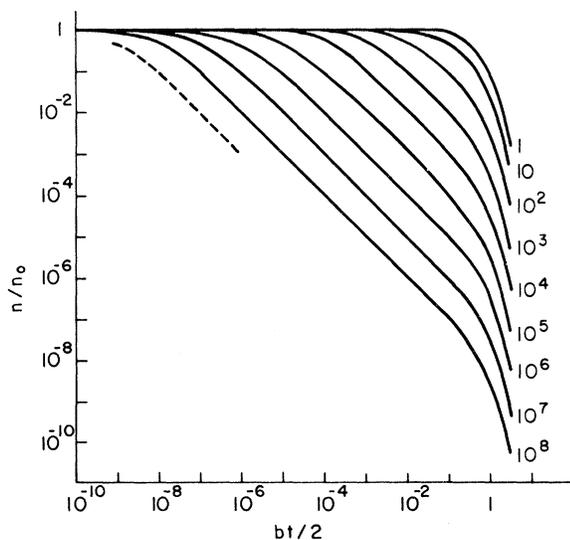

FIG. 7. $\text{Log}(n/n_0)$ vs $\log(bt/2)$ for various values of $2an_0/b$ for the case of a perturbed bimolecular process $(\dot{n} = -an^2 - bn)$. Dashed line shows form of observed current.

occurs and the current is proportional to the concentration. A "catalytic" process in which the release of carriers from a surface reservoir is proportional to the concentration of some species, say, excitons, at the surface is an example of such a process. Another closely related process is a perturbed bimolecular process in which the decay of a species is basically bimolecular but which also has a small monomolecular decay component which produces free carriers. The rate equation is then

$$\frac{dn}{dt} = -an^2 - bn , \tag{7}$$

the first term dominating at all observable values of n. Integration of (7) yields the following transcendental equation:

$$\tan[\tfrac{1}{2}\operatorname{arcsec}(2an/b + 1)]$$

$$= \exp\left(\frac{bt}{2}\right)\tan[\tfrac{1}{2}\operatorname{arcsec}(2an_0/b + 1)] . \tag{8}$$

Figure 7 is an evaluation of (8) in the form of a plot of $\log(n/n_0)$ vs $\log(bt/2)$ for various values of $2an_0/b$. Clearly there are values of an_0/b and $bt/2$ such that n decays with a form close to $1/(t + t_0)$ over a wider time range than we could make measurements. Note that provided $n/n_0 > b/2an_0$, $n \propto 1/(t + t_0)$ with $bt_0/2 = b/2an_0$. Thus, a perturbed bimolecular decay will be hyperbolic provided $an > b$. The time-offset parameter t_0 is $1/an_0$, just as we might expect from (5).

Another model which can produce the observed time and space dependence postulates surface traps distributed uniformly in energy with energy-independent capture cross section. If the surface density of occupied uniform traps is $n_0(\text{cm}^2\ \text{eV})^{-1}$, then the release rate R is given by[5]

$$R = n_0 kT/t . \tag{9}$$

This relation arises from the wide range of trap release times which exist for traps widely distributed in energy. The release rate from any given level is the number of traps releasing divided by the release time, and the total release rate is the sum over all the traps. But only those traps whose release time is of the order of the time since the emptying process started (since the light was removed) will contribute significantly to this sum since all traps with shorter release times are already empty, and all those with longer release times have a negligible contribution. Since we have assumed the same capture cross section for all traps, the release time defines the depth of the traps which dominate the release at any time. The number of traps contributing to release at any time will be those whose energies lie in the band of width kT at this depth. In addition, for $t < \tau_{\text{top}}$, the release time of the shallowest filled traps at the end of excitation, the

release rate is constant:

$$R_{t < \tau_{top}} = n_0 kT / \tau_{top} . \qquad (10)$$

Combining (9) and (10), the over-all release rate is

$$R(t) = n_0 kT / (t + \tau_{top}) . \qquad (11)$$

Eq. (11) is identical to (1) where $A = n_0 kT$ and $t_0 = \tau_{top}$.

Let us now consider the excitation dependence. The amplitude factor A depends upon incident light exposure. A model for the exposure dependence which can be incorporated into either the bimolecular decay or uniform trap view point involves the filling of deep normally empty states during the photoexcitation. If the states are deep enough so that thermal emptying during the exposure time is negligible, the rate equation is

$$\frac{dn}{dt} = \gamma I [N - n(t)] , \qquad (12)$$

where N is the total number of the states, I is the light intensity, and γ is a constant. Integration yields

$$n(t) = N(1 - e^{-\gamma I t_{exc}}) , \qquad (13)$$

where t_{exc} is the excitation time. Since It_{exc} is the exposure, the filling of deep states will depend upon exposure in much the same manner as the observed photocurrent depends upon exposure.

We have already ruled out a bimolecular process in which the decaying species results directly in the generation of free charge. Therefore, a perturbed bimolecular model in which the current is proportional to the concentration must necessarily have a charge reservoir which is filled by the light and from which the release of free charge is controlled by the concentration of the bimolecularly decaying

species. The concentration of filled states is this reservoir can be exposure dependent.

The uniform trap distribution model can also exhibit this exposure dependence since the traps with release times greater than τ_{top} meet the deep-trap requirement.

Another aspect of the excitation dependence is the observed increase of the time-offset parameter t_0 with excitation time. The bimolecular model predicts a time offset of $1/an_0$. If anything, this would predict a decrease in time offset with increasing excitation time—the opposite of that observed. For the uniform trap model, the time-offset parameter t_0 is associated with the release time of the shallowest filled traps, τ_{top}, which can depend upon excitation time and intensity in a rather complicated manner. Simulation of the trap-filling process by computer yielded the results shown in Fig. 8, which shows a tendency for τ_{top} to increase as excitation time increases.

A consideration which detracts from the uniform trap model is that, to be consistent with the observed hyperbolic time decays, the density in energy of these states must be uniform to within 5% over at least 0.26 eV. It seems unlikely to us that this stringent requirement would be met—especially for all ten of the samples studied in detail.

The experiments show that the time and field dependence of the carrier release are separable, that is, $R(t, E) = f(t) \cdot g(E)$. Thus, although the field controls the *observed* carrier generation, *the kinetics of the underlying return to a thermal equilibrium distribution are not field dependent.* A model for the observed field dependence which can also be incorporated into both models for the time dependence involves a surface recombination process which competes with the conduction process for the re-
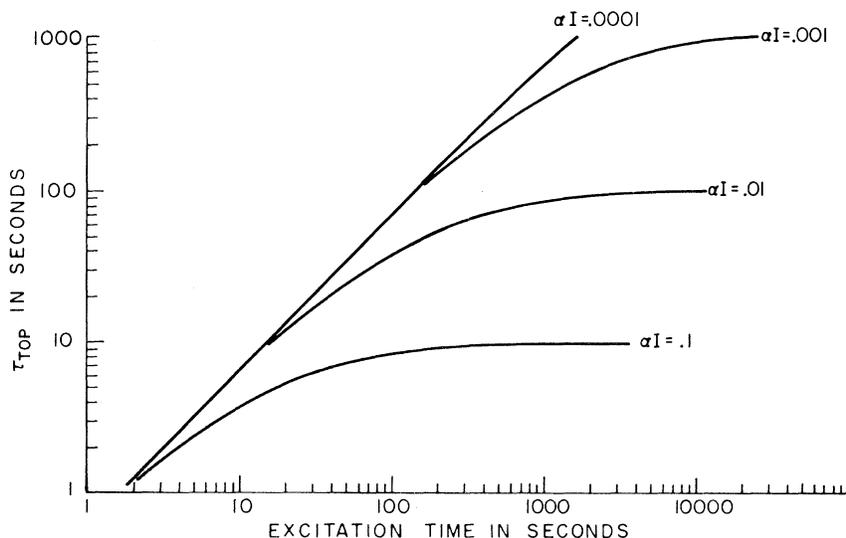

FIG. 8. Log release time of the shallowest occupied traps vs log excitation time for various light intensities as calculated for a uniform distribution in energy of traps.

leased holes. In this model most of the released carriers recombine and the electric field diverts a small number which transit the sample and contribute to the current. With no applied field, all released carriers recombine. Assuming that a quasi-steady-state condition applies at the surface, the surface density of free carriers is given by

$$n_s(t) = \frac{R_0(t)}{q(s + \mu E)} \quad , \qquad (14)$$

where $R_0(t)$ is the release rate from the charge reservoir, s is the surface recombination velocity, and μ the hole drift mobility. If $s/\mu E \gg 1$, then the current density is given by

$$j(t) = \frac{\mu E}{s} R_0(t) . \qquad (15)$$

Even though the light is weakly absorbed, all free carriers are observed to come from the surface. The models for the excitation dependence which we have been able to develop require a trapped carrier reservoir which, therefore, must be at the surface. The reservoir might be filled in one of three ways: (a) direct optical absorption in the surface states—possible considering the very large light fluxes used in sample excitation; (b) redistribution of carriers in surface states by excitons diffusing to the surface; or (c) by the ambipolar diffusion of electrons and holes to fill the surface states. The last alternative seems especially unlikely in the light of what is known about electron nontransport in PVK.

SUMMARY

Decaying photocurrents have been observed which decay as $1/t$, are proportional to the electric field, and depend upon light exposure. The electric field is found to be constant in time. This fact, along with the observed thickness scaling laws, leads to the conclusion that the free holes are generated at the surface and travel completely across the PVK without being deep trapped or recombining. A hole range of at least 4×10^{-6} cm^2/V is required. The time, field, and excitation dependences must all be explained by the model for free-charge generation. The field dependence is likely due to a surface recombination process which competes for the released holes. The exposure dependence is likely due to the filling process of a surface charge reservoir.

Two models, either of which can explain the observed hyperbolic time dependence and both of which have drawbacks, have been presented and discussed. One involves bimolecular decay of a species such as excitons, with the release rate from the surface charge storage reservoir being proportional to the concentration of the bimolecularly decaying species. This model predicts a dependence of the time-offset parameter upon excitation time opposite to that observed.

An alternate explanation of the hyperbolic time dependence is a uniform distribution in energy of trap states which make up the charge reservoir.

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