Picosecond Photoinduced Transmission Associated with Deep Traps in Phosphorus-Doped *a*-Si:H

Z. Vardeny, J. Strait, D. Pfost, and J. Tauc
Division of Engineering and Department of Physics, Brown University, Providence, Rhode Island 02912

and

B. Abeles
Exxon Research and Engineering Company, Corporate Research Laboratory, Linden, New Jersey 07036
(Received 1 February 1982)

Photoinduced transmission was observed in the picosecond time domain in phosphorus-doped *a*-Si:H and connected with deep hole traps produced by doping. The hole transport was found to be dispersive starting before 5 ps and temperature dependent. This shows that the energy distribution of shallow traps is exponential beginning below 10^{-2} eV from the valence-band top. The deep traps are negatively charged defects, the trapped holes are removed from the recombination process, and their distribution peaks at 0.45 eV above the valence-band top.

PACS numbers: 71.55.Fr, 72.20.Jv, 72.80.Ng, 78.50.Ge

We found that doping of *a*-Si:H profoundly changes its electronic relaxation response in the picosecond domain. In undoped *a*-Si:H we have always observed induced absorption ($\Delta\alpha > 0$) decaying in time.[1] The introduction of a sufficient level of phosphorus, boron, or both dopants dramatically accelerates the decay and the response eventually changes its sign becoming induced transmission ($\Delta\alpha < 0$). In this communication we report results in phosphorus-doped (P-doped) samples which are interpreted as absorption by photogenerated carriers that after thermalization are trapped in the deep states produced by doping. This effect enabled us to study the transport of carriers in a time domain much shorter than accessible by other methods [time of flight[2] (TOF), photoconductivity[3,4] (PC), photoluminescence[5] (PL), and midgap photoabsorption[6] (PA)]. For the first time we found evidence that dispersive transport[7] starts at very short times (before 5 ps). In addition, we obtained information about the deep states produced by P doping. They are hole traps, negatively charged when empty, and they remove the holes from the recombination process. By measuring steady-state PA we found that the trapped holes form a band situated about 0.45 eV above the valence-band top.

The picosecond measurements were done in the time domain of 2 to 200 ps with the pump and probe technique by using a cavity-dumped passively mode-locked dye laser.[1] The photon energy was 2 eV, the pulse duration 2 ps, the pulse energy 1 nJ, and the repetition rate 5×10^5 s^{-1}. The *a*-Si:H:P films with thicknesses $d \simeq 1$ μm were prepared by glow-discharge (GD) decomposition of SiH_4 doped with PH_3 in the concentration range of 10^{-3} to 10^{-2} in the gas, with substrate temperature kept at 250 °C. The photogenerated carrier densities per pulse $\simeq 3\times10^{17}$ cm^{-3}.

The photoinduced responses are shown in Fig. 1 ($\Delta\alpha = -\Delta T_s/T_s d$, where T_s is the optical transmission and ΔT_s the induced change). The absorption ($\Delta\alpha > 0$) is induced instantaneously (the pulse width broadens the response close to $t = 0$). For $t > 0$ $\Delta\alpha$ decays; at 300 K it decays more rapidly than at 80 K, passes through zero, and changes into induced transmission ($\Delta\alpha < 0$). The decay is faster when the doping is higher.

In the induced-absorption region the excited carriers have a higher optical absorption cross section σ_1 than the cross section σ_0 for the excitation from the ground states (band to band transition); this is the case for hot carriers thermalized at the band edges.[8] We associate the induced transmission with carriers trapped in the deep states produced by P doping[5] where their absorption cross section is $\sigma_2 < \sigma_0$. The decay corresponds to the transport of carriers from the band edge into these states. In this picture,

$$\Delta\alpha(t) = n_0(\sigma_0 - \sigma_2) \times[(\sigma_1 - \sigma_2)n(t)/(\sigma_0 - \sigma_2)n_0 - 1], \quad (1)$$

where n_0 is the total photoexcited carrier density and $n(t)$ is the density of thermalized carriers near the band edge.

The curves in Fig. 1 could not be fitted with an exponential function for $n(t)$, but their shape and dependence on temperature and doping could be fitted with expressions following from the disper-

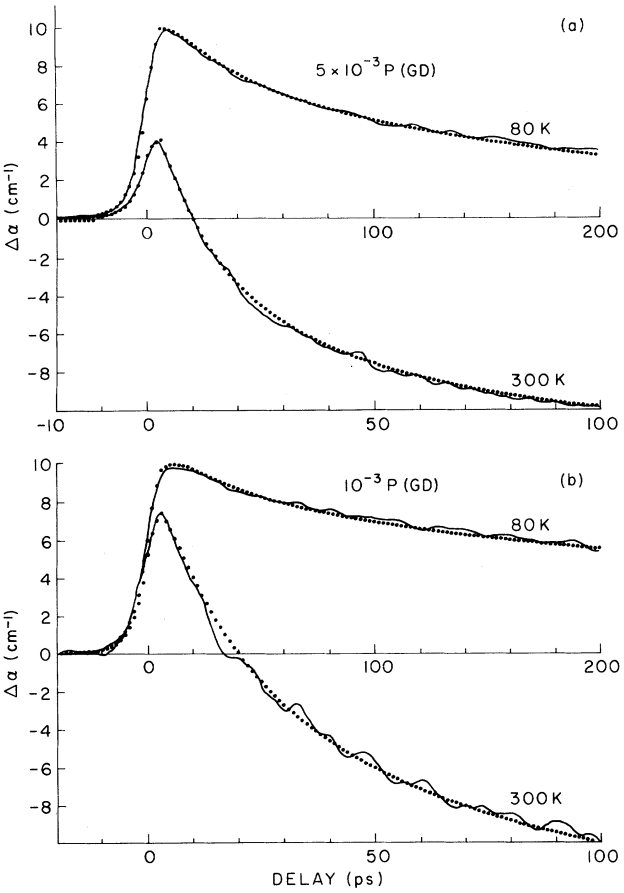

FIG. 1. Time dependence of photoinduced absorption in P-doped GD a-Si:H. Solid lines are experimental; dotted lines are calculated. Note the different time scales for different temperatures.

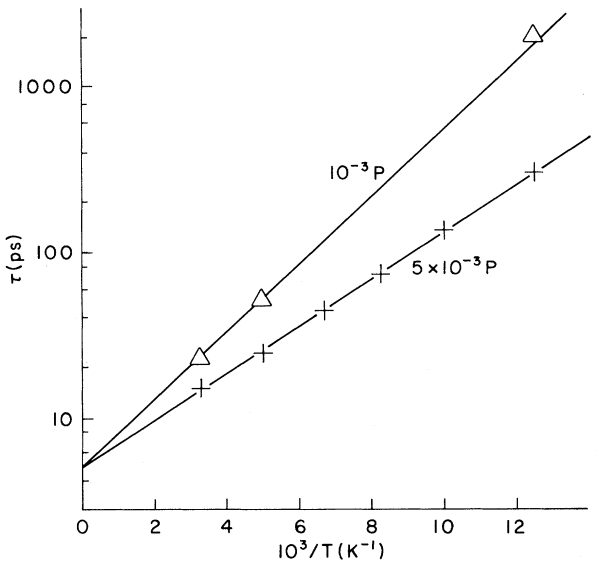

FIG. 2. Temperature dependence of the trapping time τ derived from fitting the decays.

sive transport theory.[7] A simple version of this theory, the multiple trapping (MT) model,[9] gives strikingly good agreement. This agreement means that the motion of a photogenerated carrier towards the deep trap is dominated by the trapping in the shallow traps close to the band edge. From our results it follows that this kind of transport becomes operative in the first few picoseconds after carrier thermalization. We can explain the time and temperature dependence shown in Fig. 1, by assuming that the distribution of the shallow traps is exponential $g(E)=(N_t/kT_0)\exp(-E/kT_0)$; N_t is the concentration of shallow traps, kT_0 is the width of the distribution, and E is measured from the band edge. The rate equation for the deep trapping process is identical to the equation for the monomolecular recombination. In both cases carriers are removed from the shallow traps and no longer take part in the MT process. Only carriers that are in the band ("free carriers") participate in the transport and are subject to capture by shallow traps or by deep traps with trapping coefficients b_t and b_p, respectively. We assume that neither kind of trap is saturated. The solution for the monomolecular recombination in the MT framework was found by Orenstein and Kastner[10] and we interpret it for our case:

$$n(t)=\frac{n_0}{1+(t/\tau)^{T/T_0}}, \tag{2}$$

where the trapping time constant is

$$\tau=\nu_0^{-1}\exp(E_a/kT) \tag{3}$$

with the activation energy

$$E_a=kT_0\ln(b_tN_t/b_pN_p); \tag{4}$$

N_p is the density of deep traps, and ν_0 is the attempt frequency of the carriers to be released from shallow traps.

We fitted the experimental data by Eqs. (1) and (2). Since the laser pulses had finite width, we first deconvoluted the intensity autocorrelation function[1] (measured by second-harmonic generation in potassium dihydrogen phosphate) from our data to obtain the true impulse response function.[8] From our fit we obtained the same values for the following three parameters for all temperatures and doping levels: $\sigma_1-\sigma_0=4\times10^{-17}$ cm^2, $(\sigma_1-\sigma_2)/(\sigma_0-\sigma_2)=1.8$, and $T_0=350$ K. The value of τ varied with temperature and doping as shown in Fig. 2. The activation energies are 28 meV for P doping of 5×10^{-3} and 40 meV for 1×10^{-3}. In Fig. 2,

both lines intercept at one point for $1/T = 0$ giving $\nu_0 = 2\times10^{11}$ s^{-1} which is in reasonable agreement with the values obtained from TOF[2] and picosecond PC[4] measurements. Street, Biegelsen, and Knights[5] have shown that N_p increases 1.5 times when the nominal P concentration in the gas is increased from 1×10^{-3} to 5×10^{-3}. According to Eq. (4) the corresponding decrease in the activation energy E_a should be $kT_0 \ln 1.5 = 12$ meV as observed.

From our data we can obtain information about the deep traps. Since the measured E_a is close to kT_0, it follows from Eq. (4) that the ratio $b_t N_t / b_p N_p \simeq 3$. If we use the estimated values of $N_t \simeq 10^{20}$ cm^{-3} (Ref. 2) and $N_p \simeq 10^{18}$ cm^{-3} (Ref. 5) we find that the ratio b_p/b_t has to be large ($\simeq 10^2$). This means that the capture cross section of deep traps is substantially larger than that of shallow traps. An estimate of the latter[2] is 10^{-15} cm^2 so that the capture cross section of deep traps should be of order 10^{-13} cm^2. Such large capture cross sections are expected for charged traps.[11] During the time range of our experiment (200 ps) the induced transmission measured at 300 K did not start to return to $\Delta\alpha = 0$. Therefore, the energy E_p of deep traps (measured from the band edge) has to be sufficiently large to explain the lack of carrier release. If the release time $t_r = \nu_p^{-1} \times \exp(E_p/kT)$ is larger than 200 ps at 300 K then E_p has to be larger than 0.25 eV. In this calculation, we took $\nu_p \simeq 100\nu_0$, since, as detailed balance shows,[10,11] the attempt frequency is proportional to the trapping coefficient b. Actually, as we show below, $E_p \simeq 0.45$ eV which corresponds to a release time $t_r \simeq 3$ μs.

We can estimate the upper limit of the drift mobility of carriers in thermal equilibrium with deep traps by using $\mu = \mu_0 (N_0/N_p) \exp(-E_p/kT)$, where μ_0 is the band mobility and N_0 is the effective density of states at the band edge. Taking the maximum reported[2] $\mu_0 \simeq 13$ cm^2/V s, $N_0 \simeq 10^{20}$ cm^{-3}, and $N_p \simeq 10^{18}$ cm^{-3}, we obtain $\mu \simeq 2 \times 10^{-5}$ cm^2/V s. This value is several orders lower than the drift mobility of about 4×10^{-2} cm^2/V s obtained by PC measurements[3] in a-SI:H:P at $t = t_r = 3$ μs. We conclude that the carriers trapped in deep traps cannot be the carriers responsible for the PC response. Since PC in P-doped a-Si:H is due to electrons the induce transmission is due to trapped holes. Therefore the deep traps are negatively charged when empty.

For finding the energy of the deep traps E_p we measured the steady-state midgap PA.[12] The sample was excited with a cw Ar$^+$ laser ($\hbar\omega_l = 2.4$ eV, intensity 200 mW/cm^2, chopping frequency 150 s^{-1}). The PA spectrum was measured with a monochromator using an incandescent light source in the spectral range 0.3 to 1.2 eV. In this experiment, $\Delta\alpha$ is always positive because σ_0 at these subgap energies is very small. In undoped a-Si:H $\Delta\alpha_{PA} \sim (\hbar\omega - E_t)^{1/2}/\hbar\omega$ and was ascribed to transitions of holes from the shallow traps into the valence band.[12] The hole concentration is peaked at the quasi Fermi level E_t which is strongly temperature dependent. This is seen in Fig. 3 where $(\hbar\omega\Delta\alpha_{PA})^2$ is plotted versus $\hbar\omega$. In the undoped sample E_t changes from 0.2 to 0.7 eV when T increases from 80 to 300 K. However, in the P-doped sample $E_t \simeq 0.45$ eV and within the accuracy of the measurement is temperature independent. These data indicate that E_t is pinned by the high concentration of states introduced by P doping and that the hole density peaks at about 0.45 eV above the valence band, in agreement with the recent measurements of the density of states in the gap by the deep-level transient spectroscopy technique.[13]

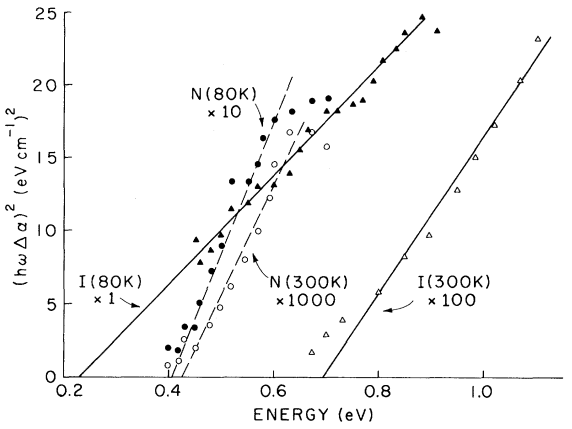

FIG. 3. Photoinduced absorption excited by a cw Ar$^+$ laser plotted as $(\hbar\omega\Delta\alpha)^2$ vs $\hbar\omega$ in undoped (I) and 5 $\times10^{-3}$ P-doped (N) GD a-Si:H at 80 and 300 K. Experimental data have been multiplied by factors shown in the figure.

The properties of the deep traps explain the increase of the recombination time of electrons by P doping as seen in PC measurements.[3] Holes are quickly trapped in these negatively charged deep traps and are practically removed from the recombination process. Recombination is more probable for holes which are thermally released into the valence band. For times longer than t_r and $n_0 < N_p$, their density is $p = n_0 (N_0/N_p) \exp(-E_p/kT) \simeq 10^{12} n_0/N_p$ (at 300 K). Therefore the recom-

bination time increases with increasing N_p.

In conclusion, we found that P doping of a-Si:H leads to induced transmission that is associated with deep traps which have a low optical absorption cross section for photon energy of 2 eV. We presented arguments for ascribing the observed effects to hole trapping. In this picture, the trapped-hole distribution peaks at 0.45 eV above the valence band, the empty traps are negatively charged defects, and the trapped holes are removed from the recombination process. We found that dispersive transport begins before 5 ps and is temperature dependent. This means that the distribution of shallow traps near the valence band is exponential starting with energies smaller than 10^{-2} eV from the band edge.

We thank T. R. Kirst for technical assistance. This work was supported in part by the National Science Foundation under Grant No. DMR 79-09819 and the Materials Research Laboratory.

[1]D. E. Ackley, J. Tauc, and W. Paul, Phys. Rev. Lett. 43, 715 (1979).

[2]T. Tiedje, T. M. Cebulka, D. L. Morel, and B. Abeles, Phys. Rev. Lett. 46, 1425 (1981).

[3]T. M. Hvam and M. H. Brodsky, Phys. Rev. Lett. 46, 371 (1981).

[4]A. M. Johnson, D. H. Auston, P. R. Smith, T. C. Bean, J. P. Harbison, and A. C. Adams, Phys. Rev. B 23, 6816 (1981).

[5]R. A. Street, D. K. Biegelsen, and T. C. Knights, Phys. Rev. B 24, 969 (1981).

[6]Z. Vardeny, P. O'Connor, S. Ray, and J. Tauc, Phys. Rev. Lett. 44, 1267 (1980).

[7]H. Scher and E. W. Montroll, Phys. Rev. B 12, 2445 (1975).

[8]Z. Vardeny and J. Tauc, Phys. Rev. Lett. 46, 1223 (1981).

[9]T. Tiedje and A. Rose, Solid State Commun. 37, 49 (1981); J. Orenstein and M. Kastner, Phys. Rev. Lett. 46, 1421 (1981).

[10]J. Orenstein and M. Kastner, Solid State Commun. 40, 85 (1981).

[11]A. Rose, *Concepts in Photoconductivity and Allied Problems* (Krieger, Huntington, N.Y., 1978).

[12]P. O'Connor and J. Tauc, Solid State Commun. 36, 947 (1980).

[13]D. V. Lang, J. D. Cohen, J. P. Harbison, and A. M. Sergent, Appl. Phys. Lett. 40, 474 (1982).