Picosecond trapping of photocarriers in amorphous silicon

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Trapping of photoexcited carriers in the picosecond and subnanosecond time domains was studied by measuring the decay of photoinduced absorption (PA) in *a*-Si, *a*-Si:F, *a*-Si:H, and *a*-Si:H:F. We found that when the midgap density of states decreases, both the trapping time and its temperature dependence increase. The observed PA decays are compared to the picosecond photoconductivity decays, and the differences in the response curves are explained. The possibility that geminate recombination might explain our results is ruled out.

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Photogenerated carriers in semiconductors dissipate their excess energy usually by interaction with phonons. These processes can be divided into three classes: hot carrier themalization to the band edges, trapping in states inside the band gap, and nonradiative recombination. Their time evolution can be studied by optical methods since the optical absorption coefficient depends on the occupation of states ("band filling") and on the absorption cross section of the excited carriers, which is usually a function of their energy. In crystalline semiconductors the band filling effects often prevail leading to photoinduced bleaching. In amorphous semiconductors the relaxation of *k*-vector conservation enhances the absorption cross section of the excited carriers, leading to photoinduced absorption.[1,2] In addition the presence of states in the gap causes trapping that often does not have a counterpart in crystalline semiconductors. We studied carrier themalization processes in *a*-Si (Ref. 2) and trapping processes in doped *a*-Si:H.[3] In this letter we report our results on carrier trapping that occurs after hot carrier thermalization in the time range from 1 ps to 1.4 ns in undoped *a*-Si, *a*-Si:H, *a*-Si:F, and *a*-Si:H:F prepared by different methods. The data show that the time response and its temperature dependence are related to the total density of states in the gap.

We measured the decay of the photoinduced absorption (PA) with the pump and probe technique, using a cavity dumped passively mode-locked dye laser.[1,4] The photon energy was 2 eV for both the pump and probe beams, the pulse duration was 0.8 ps, the energy per pulse was 2 nJ, and the repetition rate was 5×10^{5} s^{-1}. The pump beam was chopped at 2 kHz and the probe beam was mechanically delayed with respect to the pump beam. The two beams were focused noncollinearly onto the same spot (diameter $\simeq$40 μm) of the sample whose temperature could be changed between 80 and 300 K. The pump and probe beams were carefully adjusted to maintain complete spatial overlap on the sample up to the longest delay time of 1.4 ns. The average intensity was 25 W/cm^{-2}, the peak intensity was 0.3 GW cm^{-2}, and the carrier density per pulse was on the order of 5×10^{17} cm^{-3}. The samples were nonhydrogenated, hydrogenated, fluorinated, and hydrogenated fluorinated *a*-Si thin films (thickness about 1 μm) deposited on transparent substrates by different techniques as summarized in Table I where the different samples used are arranged in decreasing level of density states in the gap.

The PA decay rates up to 100 ps for two *a*-Si samples and an *a*-Si:F sample (samples Nos. 1–3 in Table I) at room temperature are shown in Fig. 1. $\Delta\alpha$ is induced instantaneously. The finite pulse duration of about 1 ps broadens the response near $t = 0$. After $t = 0$, the *a*-Si (SP) and the *a*-Si:F samples have a decay of $\Delta\alpha$ in a characteristic time t_p to a saturated level $\Delta\alpha_s$. For *a*-Si (SP) t_p is about 14 ps and for *a*-Si:F it is about 30 ps. Note that when t_p is larger, $\Delta\alpha_s$ is smaller. The measurements shown in Fig. 1 have a resolution of about 1 ps and they do not show any decay for *a*-Si (EV). Nevertheless, higher resolution measurements taken near $t = 0$ indicate that *a*-Si (EV) has a fast decay lasting less than 1 ps. After 1 ps $\Delta\alpha$ is saturated for at least several hundred picoseconds. For all three samples, the decays did not depend on the pump beam intensity when it was changed by an order of magnitude. The decays measured at 80 K were found to be the same as at 300 K for the two *a*-Si samples and only slightly longer for the *a*-Si:F sample.

The decays are slower for the two *a*-Si:H samples as shown in Fig. 2. We deduced $t_p \simeq 300$ ps for the *a*-Si:H (SP) sample and $t_p > 1.4$ ns for the *a*-Si:H (GD) sample.

The temperature dependence of the decay is shown in Fig. 3 for an *a*-Si:H (SP) sample. Around $t = 0$, the responses at 300 and 80 K are equal showing densities of photoexcited carriers at both temperatures but the decay is much slower at the lower temperature.

These results are summarized in Table I. The samples are characterized by the density of unpaired spins N_s which, however, we did not measure in our samples; the values in Table I are taken from the literature as typical for the method of preparation.[5] Three clear trends are seen in the data: (i) the decay time t_p is longer if N_s is smaller; (ii) $\Delta\alpha_s$ is smaller when N_s is smaller; (iii) the temperature dependence is larger if N_s is smaller.

We explain these results as the trapping of carriers in states in the gap whose absorption cross section σ_1 decreases with energy from the band gap. The decay time t_p is the time required for carriers to fall into these deep traps. For larger N_s, t_p is shorter because the trapping rate has to increase if the trap density increases. In the case of *a*-Si (EV), N_s is so large that carriers are trapped in less than a picosecond. Since it is believed that hot carriers in *a*-Si thermalize to the

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TABLE I. Electronic relaxation properties for different amorphous silicon samples ($T = 300$ K).

Sample No.	Sample	N_s(cm^{-3})	t_p	T dependence	t_{pc}
1	a-Si (EV)	10^{19}–10^{20}	< 1 ps		< 4 ps
2	a-Si (SP)	10^{18}–10^{19}	14		16
3	a-Si:F (SP)		30	some	
4	a-Si:H:F (SP)		80	large	
5	a-Si:H (SP)	10^{17}	300	large	
6	a-Si:H (GD)	$< 10^{16}$	> 1400	large	> 200

EV, SP, and GD mean preparation by evaporation in ultrahigh vacuum, by sputtering in Ar gas and by glow discharge. N_s is the estimated spin density. t_p is the trapping time measured by PA. T dependence is the temperature dependence of t_p. t_{pc} is the relaxation time deduced from picosecond photoconductivity (Ref. 8).

band edge in less than 1 ps,[2] this means that the carriers in the evaporated sample are trapped almost immediately after they arrive at the band edge. In the other samples with smaller N_s, the trapping is delayed after hot carrier thermalization.

We note in Fig. 1 that the saturation values $\Delta\alpha_s$ to which the signals decrease are smaller if N_s is smaller. This means in samples with higher N_s the carriers are trapped in higher energy states where their cross section σ_1 is larger. Thus the high density of states in these samples extends over the whole gap.

The PA decay rate depends on the speed of carriers motion towards the deep traps. This motion is determined by carriers trapping in shallow states close to the mobility edge,[3] since the initial trapping populates them first.[6,7] If the shallow trap distribution is sharp (e.g., exponential as in the multiple trapping model[6,7]), only carriers that are released from the shallow traps into the band can diffuse and are captured by the deep traps. In this case the trapping and thermal reexcitation produce a temperature-dependent mobility.[3,6] This is apparently the case of a-Si:H and a-Si:H:F samples. Moreover, in a-Si the density of shallow states does not decrease sharply enough and the temperature dependence of t_p is not observed (because of the high density of shallow traps, the motion probably occurs by tunneling between the traps). The a-Si:F sample exhibits some temperature dependence, showing that the density of states is somewhat reduced by fluorination but not as much as by hydrogenation.

In Table I the PA data on a-Si are compared with the picosecond photoconductivity (PC) decay data of Johnson *et al.*[8] The PA and PC data on the EV material were taken on samples prepared under the same conditions; the SP and a-Si:H (GD) samples were prepared in different laboratories and are expected to be only roughly similar. The comparison shows that the general trend of the decay rate is similar for PC and PA: the smaller N_s the longer the decay. This agrees with the interpretation of the decays in both cases as due to trapping. However, there is a difference between the two effects. In PA, all carriers contribute (recombination occurs at much longer times) but the contribution of carriers in different states is weighted with the absorption cross section $\sigma_1(E)$ which decreases rather slowly when the carriers become trapped in deeper and deeper states. In most cases, $\Delta\alpha$ decreases from the maximum value of $\Delta\alpha(0)$ to $\Delta\alpha_s$, which corresponds to the carriers in some deep states in which they remain until recombination occurs. However, when the density of states close to the band edge is high the saturation corresponds to carriers in traps whose σ_1 differs little from σ_1 at the band edge ("mobility" edge) because the energy difference is small. This is apparently the case for a-Si (EV) in Fig. 1. In PC, the contribution of carriers in different states is weighted with the mobility $\mu(E)$. $\mu(E)$ is a much steeper function of energy than $\sigma_1(E)$; only carriers above the mobility edge contribute significantly to the PC response and therefore one observes the decay of their density. The difference between PC and PA is clearly seen in the difference of responses in a-Si (EV). In PC, the decay is observed because the

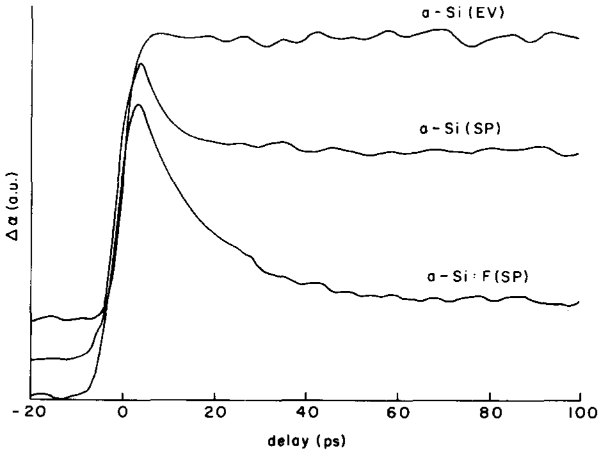

FIG. 1. Photoinduced absorption $\Delta\alpha(t)$ in a-Si (EV), a-Si (SP), and a-Si:F (SP) (Samples Nos. 1–3 in Table I) at 300 K up to 100 ps.

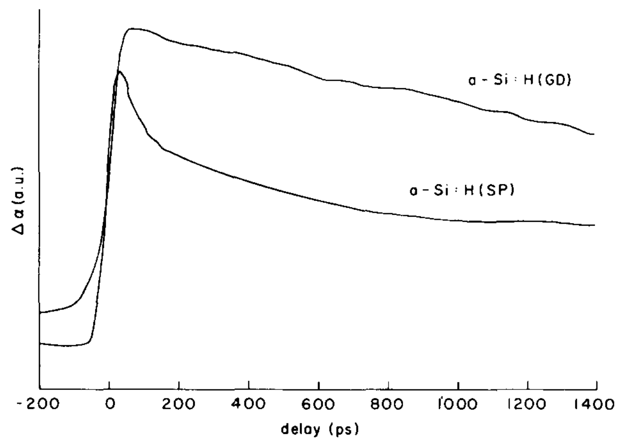

FIG. 2. $\Delta\alpha(t)$ in a-Si:H (SP) and a-Si:H (GD) (Samples Nos. 5 and 6 in Table I) at 300 K up to 1.4 ns.

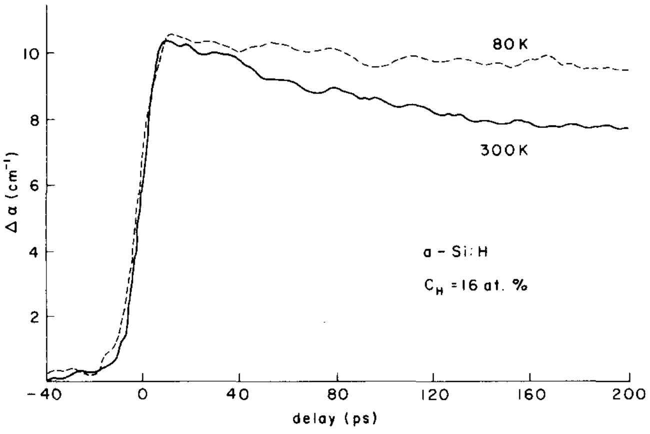

FIG. 3. $\Delta\alpha(t)$ in *a*-Si:H (SP) (No. 5 in Table I) at 80 K and 300 K up to 200 ps.

mobility of trapped carriers is very small, even if the traps are close to the edge.

Finally, we comment on geminate recombination which might be a conceivable alternative interpretation of our data. Mort *et al.*[9] interpret their Xerographic measurements and delayed-collection field technique in *a*-Si:H as evidence that at 300 K about 50% of the carriers recombine geminately[10] even when they are excited by photons with energies larger than the gap. Our results do not fit a geminate recombination process. In that process higher N_s would result in a lower drift mobility and a slower recombination rate, which is just the opposite of what we found. In addition the geminate recombination model[9] predicts higher recombination rate for lower temperature which cannot explain the observed temperature independent decay for samples with high N_s. One might argue that the high photoexcited carrier density ($> 3\times 10^{17}$ cm^{-3}) screens the Coulomb attraction between geminate pairs but this cannot explain the intensity independent decays we observed. We conclude that our data show that geminate recombination, if it occurs at all, would occur at times longer than 1.4 ns (but shorter than 50 ns according to the data of Mort *et al.*[9]).

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