Picosecond Photomodulation Spectroscopy in Amorphous Semiconductors

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Abstract

Picosecond trapping of photogenerated carriers in gap states of doped, compensated and undoped amorphous hydrogenated silicon (a-Si:H) and of a-Si:H based superlattices was studied by the pump and probe photomodulation technique. In undoped a-Si:H the photogenerated carriers are trapped in band-tail states and in compensated a-Si:H in impurity states introduced by doping. In singly doped a-Si:H the photoexcited majority carriers are trapped in impurity states whereas the photoexcited minority carriers are trapped in charged dangling bond defects. In a–Si:H/a–SiN_x:H superlattices photocarriers are trapped in interface related defects. In all cases we found that electron trapping is about 50 times faster than hole trapping. This intrinsic property of a-Si:H originates from a larger electron hopping rate among localized states in the conduction band-tail.

Introduction

Photogenerated carriers in amorphous semiconductors dissipate their excess energy mainly by interaction with phonons. These processes can be divided into three classes: hot carrier thermalization to the band edges, trapping in gap states and non radiative recombination. Hot carrier thermalization occurs in subpicosecond range and was investigated[1,2] using subpicosecond pulses. Carrier recombination occurs at times longer than 0.1μsec and has been the subject of continuing studies in both chalcogenide glasses[3] and tetrahedrally bonded amorphous semiconductors.[4] Trapping of the photoexcited carriers occurs particularly fast in amorphous semiconductors since the density of gap states is large compared to crystalline materials. A suitable technique to study photocarriers dynamics in amorphous semiconductors is transient photomodulation (PM) because of its unparalleled time resolution.[1] A number of transient PM experiments in the picosecond time range[1,2,5-11] have indeed made significant contributions to the understanding of ultrafast carrier relaxation in amorphous semiconductors. In this paper we will focus on picosecond carrier trapping in doped and undoped hydrogenated amorphous silicon (a-Si:H) which is an important material for the optoelectronic technology.

Intrinsic traps in a-Si:H are usually separated into two kinds (Fig. 1(b)). Close to the band (mobility) edges there are shallow band-tail (BT) traps, and deeper into the gap there are deep traps. BT states have been associated with fluctuations of bond angles and interatomic distances and often have exponential energy distribution ($\sim \exp(-E/kT_0)$, where kT_0 is the distribution width). Because they are close to the bands, they strongly influence the motion of carriers close to the mobility edge making the transport dispersive.[12,13] Deep traps are due to defects in the network, such as dangling bonds (DB) which are unsatisfied chemical bonds on internal surfaces. Neutral DB defects (D^0) have spin 1/2 and therefore are ESR active. Hydrogenation reduces their density from about $10^{20}cm^{-3}$ in unhydrogenated films to less than $10^{16}cm^{-3}$ in films deposited by the glow discharge (GD) method.

Doping with donors (P,As) or acceptors (B) introduces two kinds of gap states[14]: impurity (IP) states in the BT and charged DB ($D^{\pm}$) which are much deeper; the Fermi-energy E_F is located between the IP states and the $D^{\pm}$ states. Doping in GD films is achieved by adding to SiH_4 gas a dopant gas such as PH_3 or B_2H_6, for n-type and for p-type doping respectively. The doping efficiency is small: a concentration of 10^{-3} of PH_3 gas in SiH_4 gas results in about $10^{20}cm^{-3}$ P atoms in the material, mostly P_3^0. Only $10^{18}cm^{-3}$ P atoms are in the four fold coordination.[14] Because of the simultaneous generation of DB which bind most of the elecctrons from $P_4(P_4^0 + D^0 \rightarrow P_4^+ + D^-)$ only $10^{17}cm^{-3}$ electrons are produced in the conduction band at room temperature.[15] Compensation is achieved by mixing two gases (PH_3 and B_2H_6). The films in this case contain large densities of IP states (P_4^+ and B_4^-) but the DB density is low, comparable to the DB density of undoped a-Si:H films.[14]

Experimental

For studying picosecond trapping processes we have measured photoinduced changes in transmission (ΔT) of thin a-Si:H films in the time range from 10^{-13} to 2×10^{-9}sec using the pump and probe correlation technique.[2] In our studies we have used a colliding pulse modelocked ring dye laser[16] which operates at photon-energy $\hbar\omega_P$ of 2 eV with 0.2 psec pulse duration, energy per pulse of 0.2 nJ and repetition rate of 108 MHz. For measuring ΔT we have used a fast acousto-optic modulator at 4 MHz and a fast lock-in. This technique strongly supresses the thermal background and increases the S/N ratio so that the system can resolve $\Delta T/T$ of the order of 10^{-6}. The pump and the probe beams were focused noncollinearly onto the same spot (diameter ~ 10μm) of the sample whose temperature could be changed between 10 and 300K. The two beams were carefully adjusted to maintain complete spatial overlap on the sample up to the longest delay time of 2 nsec.

The samples used in our studies were thin films (thickness of ~ 1μm) of n-type, p-type, compensated and undoped a-Si:H and also films of a–Si:H/a–SiN_x:H multilayers with various silicon sublayer thicknesses on transparent substrates. The films were prepared by B. Abeles from Exxon Research using the GD technique. The transmission T at 2 eV for most of the samples was between 1 and 5%; ΔT was proportional to the change $\Delta\alpha$ in the absorption coefficient α and was little effected by the changes in the surface

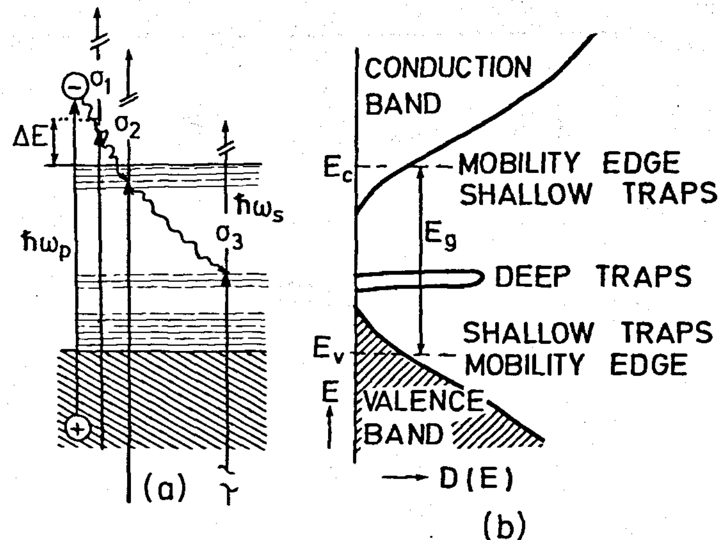

Fig. 1: Electronic relaxation processes in amorphous semiconductors. (a) Generation of a hot electron-hole pair followed by their thermalization into shallow traps and then into deep traps with different absorption cross-section. (b) Density of states D(E) in an amorphous semiconductor.

reflectivity.[17] The initial photoexcited carrier density per pulse was estimated to be about $10^{18}cm^{-3}$.

The model used to analyze the ultrafast PM responses[2] is summarized in Fig. 1(a). The pump photon produces an electron-hole pair and the probe measures the changes of optical transmission as the carriers thermalize (only electrons are shown in the figure). The photogenerated carrier in a certain state blocks the transitions which can exist in the dark. This effect increases the transmission and is referred to as "bleaching"; it may be characterized[18] by a photoinduced bleaching (PB) cross-section σ_{PB}. Another process is photoinduced absorption (PA) characterized by a cross-section σ_{PA}; this corresponds to a process in which the probe produces a transition into a higher energy state. If the density of carriers is n,

$$\Delta\alpha = (\sigma_{PA} - \sigma_{PB})n = \sigma n \qquad (1)$$

where σ is the effective cross-section which can have both signs depending on which process (PA or PB) prevails. In Fig. 1(a) we show various effective σ: for hot carriers (σ_1), for carriers in BT(σ_2) and for carriers in deeper traps (σ_3).

The processes described in Fig. 1(a) occur in a-Si:H at short times (< 10 nsec) before recombination becomes important.[2,4] Therefore the total carrier concentration is constant (Eq. (1)) and hence the PA response corresponds to the time evolution of the distribution of carriers over states with different σ.

Picosecond PM in doped a-Si:H

Typical PM decays in an undoped a-Si:H film at 80 and 300K are shown in Fig. 2 up to 1.8 nsec after photoexcitation. The onset of $\Delta\alpha$ is instantaneous (on our time scale) and $\Delta\alpha(t=0)$ is positive ($\sigma_1 > 0$); this is in contrast to many crystalline materials[2] where $\sigma_1 < 0$. The decay of $\Delta\alpha$ is non-exponential with characteristic times of ~ 2 nsec at 300K and ~ 6 nsec at 80K. Since the photoexcited carrier density ($10^{18}cm^{-3}$) is much larger than the DB density in this film ($\approx 10^{16}cm^{-3}$), the observed PA decay cannot be due to deep trapping. We believe that the PA decays shown in Fig. 2 are due to photocarrier themalization within the BT states[6] where σ is smaller for deeper BT states. Photocarrier thermalization is slower at lower temperature and this explains the slower PA decay at 80K (Fig. 2). We note that the picosecond photoconductivity response as a function of temperature has also been analyzed[19] in terms of carrier thermalization within BT states.

In contrast to undoped a-Si:H we have observed in doped[5] and compensated[11] a-Si:H a much faster decay of $\Delta\alpha$ which at higher temperatures becomes negative (PB prevails) as seen in Fig. 3. The film is a-Si:H doped with 2×10^{-2} phosphine in the gas mixture. Picosecond decays in singly doped films depend strongly on previous light exposure as has been shown by Strait and Tauc.[20] The measurements reported in this paper were done on spots exposed to prolonged illumination which stabilizes the responses. The decays are non-exponential and are faster at higher temperatures and higher doping level.[6] In the first study[6] of a-Si:P:H it was assumed that the photoexcited carriers decay into deep states in the gap (charged dangling bond) which had very small σ_{PA}. However, later work[9,11] gives convincing arguments that PB is associated with the impurity states. The fast decays turning into PB have been observed also in compensated a–Si:H[11] in which the DB concentration is very low (Fig. 4). On the other hand, bleaching was not observed in a-Si:H heavily damaged by electron bombardment[21] which contains a large concentration of DB. We conclude that the bleaching process is associated with a process in which a photogenerated electron is trapped on P_4^+ and removes the transition of an electron from the valence band into this center.[4]

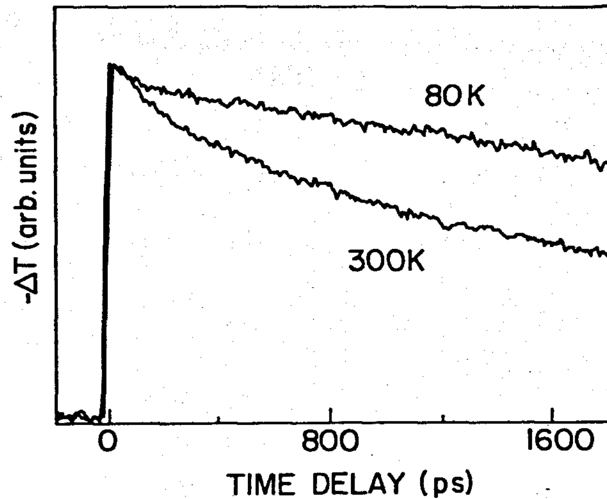

Fig. 2: PM decays in a-Si:H at 80 and 300K.

The photomodulation spectrum of doped a-Si:H at longer time[5] ($t > 10^{-8}$sec) indicates that photoexcited holes are trapped in charged DB centers. This trapping process has been recently observed[22] in our laboratory when we extended the measurements to longer times. In Fig. 5 we show the PB decay at 300K for 10^{-3}P and 2×10^{-2}P up to 1.8 nsec. The PA signal close to t=0 is hardly resolved. The important point to note is that the PB signal does not remain constant but relaxes back towards zero level; the relaxation is faster for higher doping levels (Fig. 5) and at higher temperatures (Fig. 3). In the samples with 2×10^{-2}P, the PB signal at 300K crosses the zero baseline (Figs. 3 and 5); this rules out that the observed response is due to fast recombination. We interpret the PB relaxation as hole trapping into D^- states where they have a larger cross-section than in BT states. This explains the dependence on doping level seen in Fig. 5; the holes are trapped faster when the DB density is larger. Also the similar temperature dependence for the two decays shown in Fig. 3 indicates that the hole and electron trapping processes are dominated by the same carrier kinetics.

We have also studied the dependence of the fast PM decay and the slow PM decay on light exposure. It has been observed[20] that the picosecond PM responses in doped a-Si:H became faster when the exposure time to the laser beam is longer. The changes have been attributed[21] to laser induced break-up of donor-silicon pair into charged IP and DB thus making equally many additional trapping centers available for electrons (IP) and holes (DB). We have indeed observed[22] that both the fast and the slow decays became faster with light exposure. These results show that the two decays are strongly correlated and that the fast PA decay is due to electron trapping into P_4^+ and the slow PB decay is due to hole trapping with D^-.

From the dynamics of the trapping processes we can obtain information about subnanosecond carrier transport in doped a-Si:H. The photogenerated carriers are first trapped in BT states with effective optical cross-section σ' and then decay into doping related defects having a cross-section σ^*. In this case[5]

$$\Delta\alpha(t) = \sigma' N(t) + \sigma^* \left[N(0) - N(t)\right] \tag{2}$$

where N(t) is the transient carrier density in BT states. Eq. (2) can be used separately for electrons and holes since the two decays occur on two different time scales (Figs. 3 and 5). N(t) decays with time as[5]

$$N(t) = N(0) / \left[1 + (t/\tau)^{\alpha}\right] \tag{3}$$

where τ is the deep trapping time constant and $\alpha (< 1)$ is the dispersion parameter. Eq. (3) fits the decays[2] for carriers which thermalize in BT states either by direct hopping to deeper states[23] (α is temperature independent) or by multiple trapping[12,13] ($\alpha = T/T_0$).

We used[22] Eqs. (2) and (3) to fit our data. We found for the PM decays in P-doped a-Si:H that α depends linearly on temperature $\alpha(T) = \alpha(0) + T/T_1$ for both electrons and holes; for electrons $\alpha = 0.18 + T/280$ whereas for holes $\alpha = 0.15 + T/635$. This form of $\alpha(T)$ is justified when during the trapping process carrier thermalize within BT states both by direct hopping to deeper states[23] (which gives the temperature independent part α_1) and by a multiple trapping process[12,13] (which gives the temperature dependent part T/T_1). We note that T_1 is twice as large for holes than for electrons and this is in agreement with other measurements[24] in a-Si:H showing larger width for the valence BT.

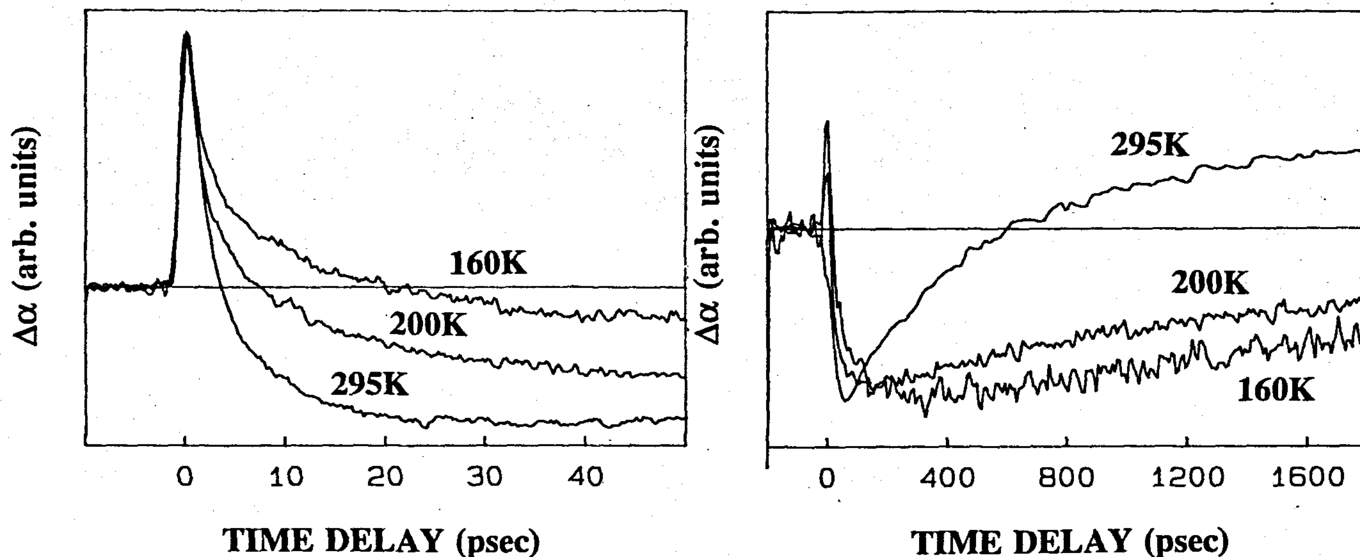

Fig. 3: Fast and slow PM decays in 2×10^{-2} phosphorus doped a-Si:H at various temperatures.

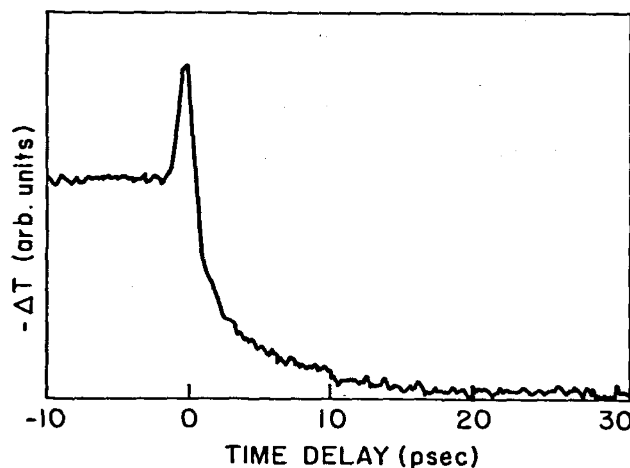

Fig. 4: PM decay in compensated (10^{-3} phosphorus and boron doping) a-Si:H at room temperature. [From Ref. 11]

From the transient PM responses at room temperature (Fig. 3) we measure for 2×10^{-2}P $\tau = 2.5$ psec for electron trapping whereas $\tau = 125$ psec for holes. Electron trapping remains[22] ≈50 times faster than hole trapping regardless of the sample temperature, exposure to the laser light, doping level, doping type (P-doped, B-doped or compensated) or the nature of the trap centers (IP states, charged or neutral DB). This indicates that the fast decays for electrons and the slow decays for holes is an *intrinsic* property of a-Si:H. In most of the trapping processes mentioned above carriers thermalize within BT states by direct hopping to deeper states.[22] The trapping rate into doping related defects in this case is proportional to the defect density and the hopping rate ν among BT states. Doping in a-Si:H is known to introduce as many electron traps as hole traps[14] and therefore only different ν for electrons and holes can explain the asymmetry in electron and hole trapping rates. ν depends exponentially on the extent of the wave function r_0 and on the distance between adjacent hopping sites R_t :[23]

$$\nu \sim \exp(-2R_t/r_0) \ . \qquad (4)$$

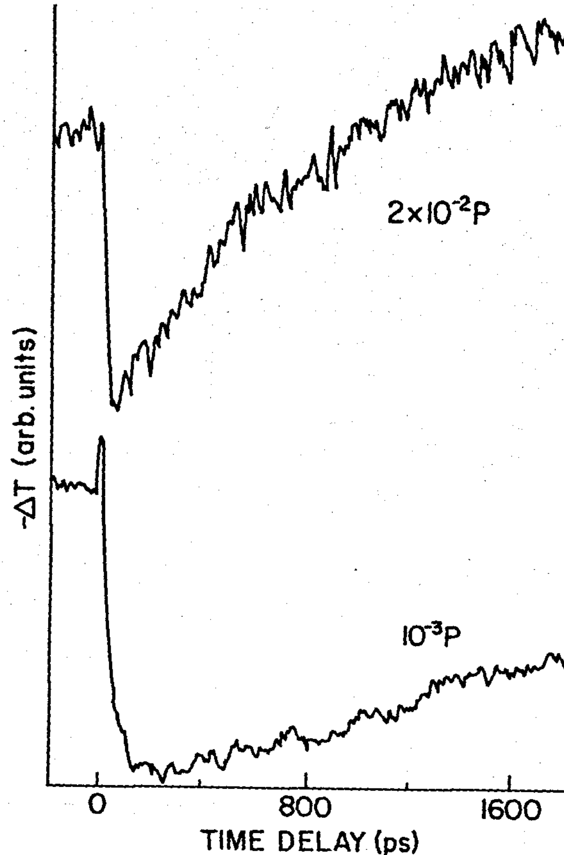

Fig. 5: Room temperature PB relaxations in phosphorus doped a-Si:H with (a) 10^{-3}P and (b) 2×10^{-2}P.

R_t is the same for electrons and holes (the total density of localized BT states N_t for the valence band and the conduction band is the same) and therefore only different r_0 can explain the difference in ν. As shown above, electron trapping is faster than hole trapping by a factor of ≈50. Assuming N_t≈5×10^{19}cm^{-3} (R_t≈22Å) and r_0 twice larger for conduction BT states than for the valence BT states[25] we calculate from Eq. (4) r_0≈12Å and r_0≈6Å for shallow (BT) electron and hole traps respectively, in good agreement with the values of r_0 deduced from photoluminescence studies in a–Si:H.[26]

Picosecond PM in amorphous multilayer structures

We have recently studied[27] the subnanosecond photocarrier dynamics in a–Si:H/a–SiN_x:H multilayer structures as a function of the Si sublayer thickness (d_S). The superlattice (SL) films were deposited[28] by plasma assisted chemical vapor deposition technique where pure SiH_4 was used for the Si sublayers and a 5:1 mixture of NH_3 to SiH_4 for the a–SiN_x:H sublayers. The superlattice repeat distance was varied while keeping the ratio d_S/d_N constant (= 0.85). The number of layers was adjusted so as to keep the film thickness ~1μm; interface effects are clearly brought out in this series because the average composition of the films is kept constant.

Typical subnanosecond PA decays at 300K for SL with d_S = 204Å, 78Å and 25Å are shown in Fig. 6. Similarly as in doped a-Si:H (Fig. 3) Δα(> 0) increases instantaneously at t=0 followed by a non exponential decay which is slower at lower temperatures. However, in contrast to doped a-Si:H we never observed that the PA signal crosses the zero baseline changing into PB. Fig. 6 also shows that the decay for d_S = 78Å is much faster than for d_S = 204Å, but the decay slows down considerably for d_S = 25Å. It is instructive to define a decay time constant $\tau_{1/2}$, where $\Delta T(\tau_{1/2}) = 1/2\Delta T(0)$, for comparison of the different SL. $\tau_{1/2}$ at 300K is plotted in Fig. 7 vs. d_S. A striking feature of this plot is that $\tau_{1/2}$ has a minimum for d_S around 60Å; $\tau_{1/2}$ decreases from a value of 160 psec for d_S = 204Å to 10 psec for d_S = 78Å and then increases again to 160 psec for d_S = 25Å. Although $\tau_{1/2}$ is the same for d_S = 204A and d_S = 25Å, Fig. 6 shows that the decays in these two samples are very different. The PA decay in the SL with d_S = 25Å is much faster for short times than the one for d_S = 204Å, but at longer times (t > 400 psec) the decay for d_S = 25Å becomes much slower. The same behavior is observed when one compares the decays in the SL with d_S = 39Å and 78Å. This indicates that the PM decay kinetics for SL with d_s < 50Å is different from that of SL with d_S > 50Å.

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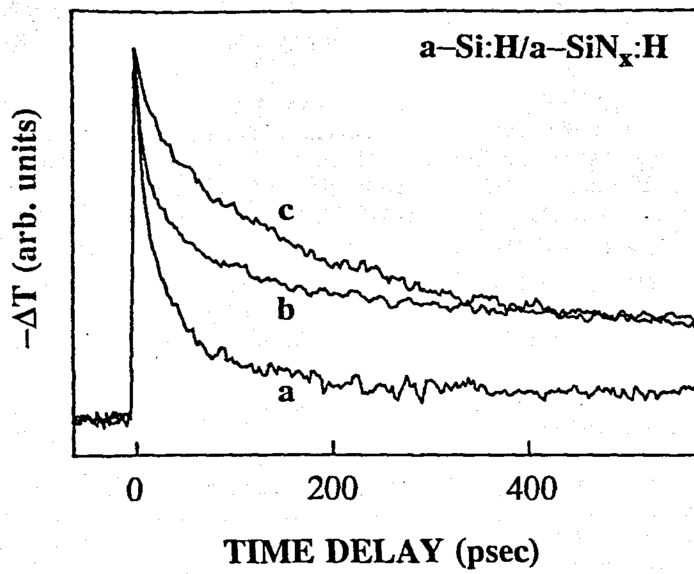

Fig. 6: Room temperature PM decays in superlattices of a–Si:H/a–SiN$_x$:H with various silicon sublayer thickness d_S. (a) d_S = 78Å (b) d_S = 25Å (c) d_S = 204Å

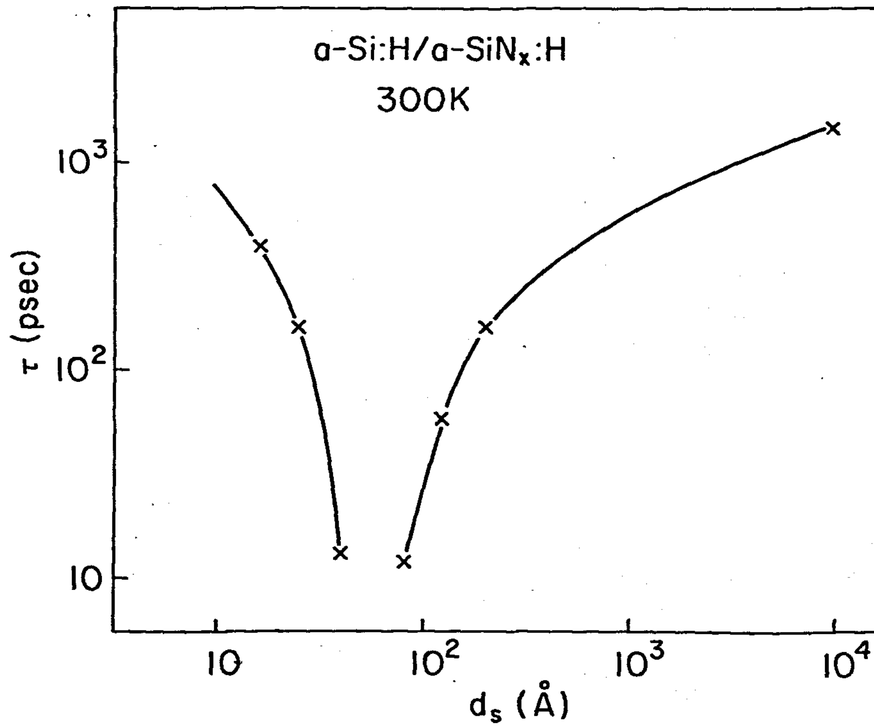

Fig. 7: The decay time constant $\tau_{1/2}$ at 300K as a function of silicon sublayer thickness d_S. [From Ref. 27]

We have found[27] that the PA signal at longer times ($t > 10^{-7}$sec) is unusually large and it is therefore unlikely that the subnanosecond PA decay is due to carrier recombination. We interpret it as due to carrier trapping in deep states with lower σ (Fig. 1(a)). Since PB is never observed, these states are different from the impurity states in doped a-Si:H.

We will discuss separately the right hand and left hand branches in Fig. 7. The right hand branch can be interpreted as carrier trapping at the defect states associated with the interfaces. The carriers are homogeneously generated in the a-Si:H sublayers and then move towards the interfaces. The transport process may be diffusion but perhaps a contribution of drift is important because of the presence of internal electric fields.[29] The relaxation time $\tau_{1/2}$ is determined by the duration of this transport process and therefore $\tau_{1/2}$ decreases with decreasing d_S. The diffusion process is dispersive. It is hoped that its detailed understanding will lead to a method for studying transport processes over very short distances.

One may speculate what the trapping states are. There are strong indications that the interfacial defects are negatively charged dangling bonds D^-. The spin density does not increase for films with increasing interface density[30] while E_F in the a-Si:H sublayers can increase as much as 0.4 eV relative to the a-Si:H film.[31] The defects are therefore spinless when charged which is a property of DB.[18]

The left hand branch in Fig. 7 is more difficult to understand. It is necessary to assume that such very thin a-Si:H layers are structurally different from regular a-Si:H and are becoming more and more disordered as their thickness decreases; the disorder slows down the trapping process. This disorder has been observed in Raman scattering[32] and also in the broadening of the Urbach tail and photoluminescence bandwidths.[28] There are various possibilities for interpreting the PA decays. The simplest one is that in such highly disordered layers the trapping occurs through the whole film and it does not make sense to speak about more disordered interfaces. Then the simple multiple trapping may apply; in fact, in a preliminary way we could fit the data with Eq. (3). It is hoped that this analysis will contribute to an understanding of the very intriguing question about the nature of the disorder in very thin films of a-Si:H.

Acknowledgements

We thank B. Abeles for providing us most of the samples used in our studies. The work was supported in part by the National Science Foundation grant DMR 82-09148; we have also benefited from the use of the Optical Facility of the NSF Materials Research Laboratory at Brown University.

* On sabbatical leave from the Technion, Haifa, Israel.

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