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Studies of picosecond carrier dynamics in polysilane alloys: Evidence for geminate recombination in small hydrogenated amorphous silicon clusters

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The ultrafast photocarrier dynamics in polysilane alloys, amorphous $(\text{SiH}_2)_n$, has been studied using the picosecond photoinduced absorption (PA) technique. For excitation below the optical gap, the PA response decays exponentially and is faster at low temperatures. This is interpreted in terms of e - h geminate recombination in the small clusters ($\sim 10 \text{ \AA}$) of a -Si:H embedded in the polysilane matrix. The PA response with above-gap excitation is similar to that of conventional a -Si:H; it decays much slower in the form of a power law $t^{-\beta}$ ($\beta < 1$), independent of spectral range between 1.4 and 2.2 eV. This shows that the e - h distance after above-gap photogeneration is larger than the size of the a -Si:H clusters.

The study of ultrafast relaxation processes of photoexcited carriers is of fundamental interest in amorphous materials such as hydrogenated amorphous silicon (a -Si:H) due to the presence of disorder and gap states which act as shallow traps. The short time relaxation dynamics is important for the understanding of ultrafast processes such as radiative and nonradiative recombinations, carrier localization, and transport. Photocarrier relaxation processes have been studied using transient photoconductivity (PC), photoluminescence (PL), and photomodulation (PM) techniques; the latter method is particularly useful due to its unsurpassed time resolution and its sensitivity to all excited carriers, as opposed to PL, where only radiative recombination is measured and PC, where only carriers with moderately high mobility are measured.

Previous picosecond transient PM studies of a -Si:H can be divided into two groups according to the excitation (pump) intensity used.¹⁻⁸ At all pump intensities the PM signal in a -Si:H is photoinduced absorption (PA) in which $\Delta\alpha > 0$, as opposed to crystalline materials where the signal for above-gap excitation is usually $\Delta\alpha < 0$ at short times. The PA in amorphous semiconductors has been interpreted as due to fast photocarrier localization and consequently relaxation of the \mathbf{K} conservation rule, thus enhancing reabsorption, or optical transitions to higher energy states.¹ The PA decay, however, is very different for the two pump intensity regimes: at low pump intensities,¹⁻⁵ when the photoexcited carrier density $N \leq 10^{18} \text{ cm}^{-3}$, the decay is slow and usually in the form of a power law $\sim t^{-\beta}$, where $\beta < 1$, attributed to carrier thermalization and recombination. Whereas at high pump intensities,^{6,8} when $N > 10^{20} \text{ cm}^{-3}$, an ultrafast PA decay has been observed for probe photon energies $\hbar\omega_p < E_g$, whereas for $\hbar\omega_p > E_g$ a slow decay still exists. This has been interpreted^{6,7} as due to a heating effect which dominates the spectral range $\hbar\omega_p > E_g$ and an ultrafast trapping process which is revealed in the spectral range $\hbar\omega_p < E_g$. We note, however, two distinctive advantages when working at low pump intensities:

(i) the photogenerated carrier density ($\lesssim 10^{18} \text{ cm}^{-3}$) is smaller than the density of shallow traps ($\approx 10^{20} \text{ cm}^{-3}$) and therefore no saturation of shallow traps occurs. As a result one is probing the true carrier response which figures, for example, in solar cells and other optoelectronic devices. (ii) The heat generated in the ultrafast trapping (or recombination) process at high pump intensity⁷ is not dominant at low pump intensity.

In this letter we have used the transient PM technique at low pump intensity to study carrier dynamics in thin films of polysilane alloys (PSAs). These materials have several attractive properties because they bridge between the conventional three-dimensional (3D) a -Si:H and the one-dimensional (1D) polysilane $(\text{SiH}_2)_n$ polymers.⁹ These novel films have larger band-gap E_g than a -Si:H; 1.9 eV $< E_g < 2.4$ eV, depending on preparation conditions,¹⁰ and it is quite convenient, therefore, to photoexcite carriers with photon energy $\hbar\omega_p$ above or below E_g using available picosecond excitation in the visible spectral range. For $\hbar\omega_p < E_g$ we found in PSA an exponential PA decay which is faster at low temperatures. We attribute it to carrier geminate recombination induced by carrier confinement within small a -Si:H clusters in these materials.¹⁰ For $\hbar\omega_p > E_g$ the decay is in the form of a slow power law, similar to that of conventional a -Si:H, but independent of probe wavelength. The wavelength independence proves that heating is not dominant for low pump intensities, whereas the power law decay shows that the e - h distance following photogeneration at $\hbar\omega_p > E_g$ is larger than the a -Si:H clusters size ($\approx 10 \text{ \AA}$)¹⁰ in the PSA films.

For the picosecond PM experiments we have used the polarized pump and probe technique¹ with two laser systems. One system is based on a mode-locked CPM dye laser with pulse duration of about 70 fs, 0.1 nJ energy per pulse, photon energy of 1.98 eV, at a repetition rate of 85 MHz. The second laser system consists of two synchronously pumped dye lasers, each pumped by the second harmonic of a mode-locked Nd-YAG laser. The two lasers

are tunable from 0.57 to 0.9 μm , operate at 76 MHz with up to 0.5 nJ energy per pulse and pulse autocorrelation of about 2 ps; the cross correlation of the two dye lasers, however, is somewhat larger, 5 ps, due to the time jitter between the lasers. To improve the signal to noise we have used a fast modulation scheme for the pump beam⁴ (4 MHz) combined with a fast photodiode and lock-in amplifier to measure the photoinduced changes ΔT in the probe transmission T ; our signal limit was $\Delta T/T \approx 10^{-6}$. Two translation stages with short and long delays were used to introduce variable optical delays between the pump and probe pulses, with maximum time resolution over the full 3 ns optical delay. The samples were positioned in a helium exchange gas cryostat where the temperature could be controlled between 2 and 300 K.

The PSA films were deposited at low substrate temperatures T_s on sapphire substrates by the glow discharge of disilane gas in a 13.6 MHz inductively coupled system. The films thickness was about 3 μm and T_s was between 30 and 80 $^\circ\text{C}$. Typical absorption curves,¹¹ obtained using optical reflectance and PDS techniques, yield a Tauc-gap E_0 of 2.05 eV and an Urbach edge which extends from 1.4 to 2.0 eV. In our experiments we have used pump excitation at $\hbar\omega_p = 1.98$ eV which is inside the Urbach edge, and at $\hbar\omega_p = 2.14$ eV which is above E_0 . The amount of $(\text{SiH}_2)_n$ in the films was obtained by measuring the ratio r of the IR absorption strengths of the two lines at 850 and 890 cm^{-1} ; these are the wagging mode of Si-H₂ and the bending mode of Si-H [and $(\text{SiH}_2)_n$], respectively.^{10,11} For the PSA films used in our studies, $r \approx 0.8$ which corresponds to about 40 at. % hydrogen in the films and formation of polysilane $(\text{SiH}_2)_n$ ($n > 2$).

It is theoretically and experimentally known¹⁰ that E_g of polysilane chains is in the UV spectral range (3.4–6 eV). However E_g of the PSA films is much lower ($E_g = 1.9$ –2.4 eV). In order to explain this difference in E_g , Matsumoto *et al.*¹⁰ have introduced a 3D quantum well model for PSA. They assumed that the films are macroscopically heterogeneous consisting of 3D a -Si:H clusters embedded in a matrix of polysilane chains. The higher E_g values for the a -Si:H clusters in PSA ($E_g > 1.9$ eV) compared with conventional a -Si:H ($E_g \approx 1.7$ eV), have been explained by a quantum size effect of the Si:H clusters which have to be of order 10 \AA ; similar quantum size effects have been known to occur in a -Si:H/ a -Si_{*n*}:H multilayers.¹² The proposed model also explains other distinctive properties of PSA films, such as high efficiency PL which remains high even at RT,¹⁰ softness of the backbone structure which is manifested in moderately large pressure dependence for the electronic states,⁹ and a high PL fatigue which may be associated with large hydrogen content in PSA.¹³

Typical picosecond transient responses at 20 and 300 K in a PSA film excited and probed at $\hbar\omega = 1.98$ eV are plotted in Fig. 1. $\Delta T/T \approx 2 \times 10^{-5}$ which is about 100 times smaller than in a typical a -Si:H using the same laser system. This leads to an estimate $\approx 10^{16}$ cm^{-3} for the initial photocarriers density. The PA response ($\Delta\alpha > 0$) is generated instantaneously within our time resolution of 50 fs. The PA decay is exponential. The exponential time con-

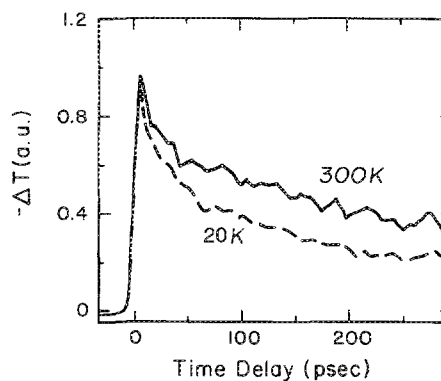


FIG. 1. Transient photoinduced absorption (PA) at $\hbar\omega_p = 1.98$ eV in a PSA film ($E_g = 2.05$ eV) at 20 and 300 K, up to 280 ps.

stant τ is 220 ps at 300 K and is smaller at 20 K; $\tau(20 \text{ K}) = 60$ ps. This was concluded by carefully measuring more than four decades in time (0.1 ps to 3 ns) and plotting the response on logarithmic scales as in Fig. 2. In contrast to the exponential decay in PSA, the PA in a -Si:H (Fig. 2) exhibits a power law decay $t^{-\beta}$ ($\beta \approx 0.6$) reflecting different carrier dynamics for these two materials.

Carrier thermalization is improbable in PSA because the a -Si clusters are isolated¹⁰ within the polysilane matrix and lower electronic states are not easily accessible, especially when excited in the Urbach edge with no excess energy over E_g . Therefore we tentatively attribute the picosecond decays in PSA for $\hbar\omega_p < E_g$ to e - h geminate recombination induced by carrier confinement in the small a -Si clusters of order 10 \AA . The microscopic confinement leads to fast geminate recombination in the clusters, similar to the case of a -Si:H based multilayers.¹² This can also explain the high PL efficiency in PSA.¹⁰ That the PA decay in a -Si:H is not exponential may indicate therefore that carrier recombination in this material is not geminate.¹

At low temperatures the electronic levels increase in energy and because the excess energy is lower, tighter

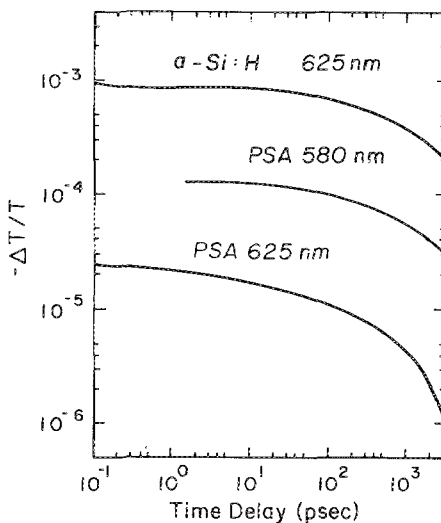


FIG. 2. Room-temperature PA responses in PSA (excited at 580 and 625 nm) compared with that of conventional a -Si:H, plotted on logarithmic scales.

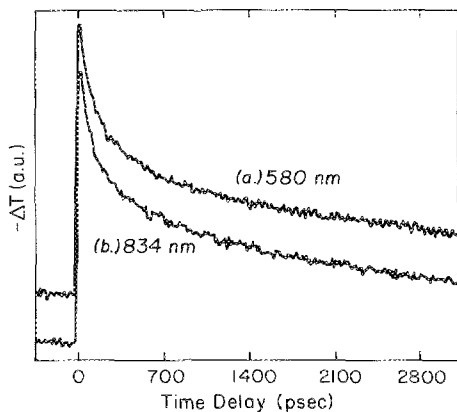


FIG. 3. Transient PA in PSA at 300 K, excited with pump $\hbar\omega_p = 2.14$ eV ($> E_g$). (a) probe $\hbar\omega_r = 2.14$ eV, carrier density $N = 2 \times 10^{17}$ cm^{-3} , (b) $\hbar\omega_r = 1.49$ eV, $N = 2 \times 10^{16}$ cm^{-3} .

$e-h$ pairs might be generated at $\hbar\omega_p = 1.98$ eV; this would explain the faster decay at 20 K (Fig. 1). We have checked this assumption by measuring the PA decays at 300 K excited at lower $\hbar\omega_p$ (tighter $e-h$ pairs are formed), using the sync. pump laser system. The decay kinetics down to $\hbar\omega_p = 1.8$ eV were the same as at 1.98 eV (Fig. 1), thus disproving the above assumption. We tentatively attribute the faster decay at low temperatures to larger capture cross section of charged carriers.¹⁴ For example, the capture cross section for positive dangling bonds in $a\text{-Si:H}$ was measured to vary as T^{-3} .

In Fig. 3 we show two ΔT responses of PSA excited with $\hbar\omega_p = 2.14$ eV, which is larger than E_g . The two responses differ in the probe photon energies $\hbar\omega_r$, and the photoexcited carrier densities N . In one case, $N \approx 2 \times 10^{17}$ cm^{-3} and $\hbar\omega_r = 2.14$ eV; in the second case, $N \approx 2 \times 10^{16}$ cm^{-3} and $\hbar\omega_r = 1.49$ eV. These responses have been chosen to illustrate that in PSA the decay rate is independent on N and $\hbar\omega_r$. This is in contrast to conventional $a\text{-Si:H}$, where the decay rate has been shown to increase with N .⁵ Since this includes the PSA film's transparent region, the $\hbar\omega_r$ independence proves that a thermal effect affecting the

decays is improbable, due to the weak interband transitions for $\hbar\omega_r < E_g$. In the case $\hbar\omega_p > E_g$ photocarriers are probably not confined within the $a\text{-Si}$ clusters and this means that the $e-h$ distance following photogeneration is larger than the clusters size of about 10 Å.¹⁰

In summary, we have studied the ultrafast photocarrier dynamics in PSA films with excitation over and below the energy gap. We showed that the response kinetics for both cases reflects carrier recombination in the $a\text{-Si:H}$ portions rather than a thermal effect. For $\hbar\omega_p < E_g$ we observed geminate recombination induced by carrier confinement in the $a\text{-Si:H}$ clusters (< 10 Å). For $\hbar\omega_p > E_g$ the response in PSA is similar to that in $a\text{-Si:H}$ showing that the $e-h$ distance following photogeneration is larger than the clusters size.

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