Picosecond Photoinduced Absorption as a Probe of Metastable Light-Induced Defects in Intrinsic Hydrogenated Amorphous Silicon

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We demonstrate that picosecond photoinduced absorption probes the diffusion-limited transport of electrons in the conduction-band tail for intrinsic hydrogenated amorphous silicon. We find that the median trapping time on this scale is controlled by the number of temperature- and intensity-dependent, metastable light-induced defects. We attribute the intensity dependence of the decay to quasimonomolecular recombination and/or the generation of transient, fast-annealing light-induced defects.

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The optical and electronic properties of hydrogenated amorphous silicon (*a*-Si:H) are of considerable interest because of the application of this material to photovoltaic and thin-film electronic devices. A key issue, related to both the defect structure of *a*-Si:H and device performance, is the nature of metastable light-induced electronic defects (LID's).[1-4] We have developed a versatile, high-signal-to-noise, picosecond, photoinduced absorption (PA) technique that enables us to probe quantitatively the electronic structure and charge-carrier relaxation in intrinsic *a*-Si:H.[5] We report that the generation and rapid saturation of LID's is intrinsic to the use of this technique and we observe the systematic effect of these LID's on the short-time relaxation and recombination of photoexcited carriers in intrinsic *a*-Si:H. We demonstrate that picosecond PA monitors dispersive diffusion-limited transport of *electrons,* in the conduction-band-tail (CBT) states, to neutral traps dominated by LID's. The median trapping time for $t < 4$ ns is controlled by the number of these metastable defects which is determined by temperature. We present evidence for additional, reversible effects on the PA decay, which we ascribe to quasimonomolecular recombination and/or the generation of transient, fast-annealing LID's.

The samples used in this work were deposited in a capacitively coupled rf glow-discharge system. The steady-state optical-absorption spectra of the samples were measured by photothermal deflection spectroscopy (PDS) and transmittance and reflectance spectroscopy.[6] We have presented the details of the picosecond apparatus elsewhere.[5] Briefly, a mode-locked argon-ion laser pumped two synchronously pumped cavity-dumped dye lasers to produce independently tunable pump and probe pulses; the time resolution of the system is $\simeq 10$ ps. Typical carrier densities in the photoexcited volume were $(1-5)\times 10^{17}$ cm^{-3}. We detected the increase in absorption by a time-modulation technique to eliminate the thermal background that is present with mechanical chopping.[5] We positioned the sample so that we eliminated any interference effect, ensuring that the observed decay represented the induced absorption, $\Delta\alpha$.[5] *This step was critical in order to compare quantitatively results obtained at different temperatures.* We could reproduce the PA decays at any temperature and intensity regardless of the sample history.

In Fig. 1 we present the normalized PA decays for a low-defect-density *a*-Si:H sample obtained at a fixed pump intensity I at repetition rates of 250, 500, and 667 kHz. The PA decay over 4 ns is independent of repetition rate, R, from 150 kHz to 1.0 MHz. This feature of our observations puts a limitation on any "carrier accumulation" for $t > 1/R$. The high quality of the data permits reliable discrimination between various functional forms used to fit the decay curves. In general, the explanation for the short-time decays is either recombination or carrier population redistribution (the simplest example of which is transitions between two types of states against the background absorption[7]). The distinction between the decay mechanisms is mainly made on the details of I and t dependence.

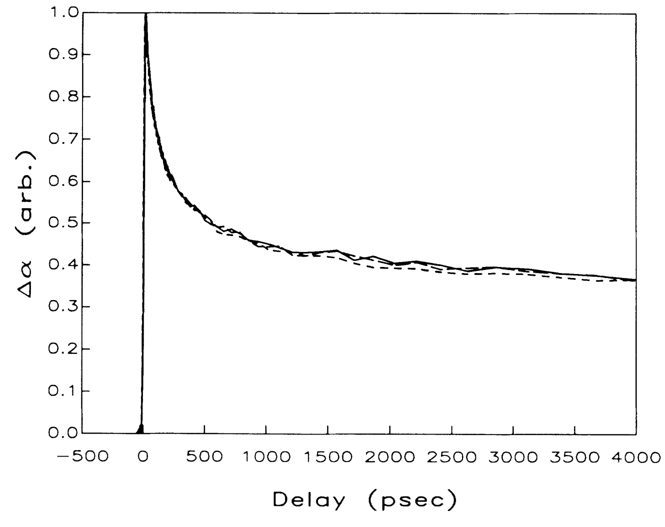

FIG. 1. The picosecond decay of photoinduced absorption for a low-defect-density sample of intrinsic *a*-Si:H at different repetition rates: 250 kHz (short-dashed line), 500 kHz (solid line), 667 kHz (long-dashed line); 295 K; pump 2.11 eV; probe, 2.01 eV.

Consistent, good quantitative fits to all the picosecond PA transients, $\Delta\alpha(t)$, have been obtained with a simple power-law decay,

$$\Delta\alpha(t)=\frac{n_0(\Delta\sigma_1-\Delta\sigma_2)}{1+(t/\tau)^\beta}+n_0\Delta\sigma_2\ . \tag{1}$$

From the fits we propose a physical interpretation based on the two-state model from the pioneering work of Vardeny *et al.*[7] which has the novel feature that the transition between the states $(1\rightarrow 2)$ is limited by dispersive diffusion.[8] In the model, n_0 is the initial number of excited carriers; $\Delta\sigma_{1(2)}$ is the difference in the cross sections between the ground state and excited state 1 (2); τ is the median trapping time; and β is the dispersion parameter. The strength of the interpretation depends on the self-consistent dependences of all the parameters in Eq. (1) on changes in T, I, R, and defect density (i.e., different samples).

The most stringent test of the model is to establish β as an *intrinsic* dispersion parameter. At fixed T the dispersion parameter was found to be the same at each intensity within the uncertainty of the fit. In Fig. 2(a) we plot the values for β as a function of T. The relation is linear, $\beta=T/T_0$, with an offset at $T=0$ that is equivalent to zero within the uncertainty of the fit. We note that the lack of intensity dependence of β indicates that the transport process is independent of metastable defect density *(vide infra)*. The relation $\beta=T/T_0$ indicates that the dispersion is due to multiple trapping from an exponential density of states with distribution width kT_0. We plot the value of kT_0 (or kT/β) in Fig. 2(b) for a number of samples, each designated by E_0, the slope of the PDS absorption. The value of E_0 as measured in PDS is dominated by the width of the valence-band tail (VBT) since it is broader than the CBT; typical values are $\simeq$43 meV for the width of the VBT and $\simeq$30 meV for the width of the CBT.[9] In Fig. 2(b) the solid line represents the anticipated trend in the data if the picosecond PA experiment were monitoring the width of the VBT (i.e., holes). The slopes of the dashed lines correspond to the ratio of the CBT to the VBT width based on time-of-flight[9] and electron-spin-reso-

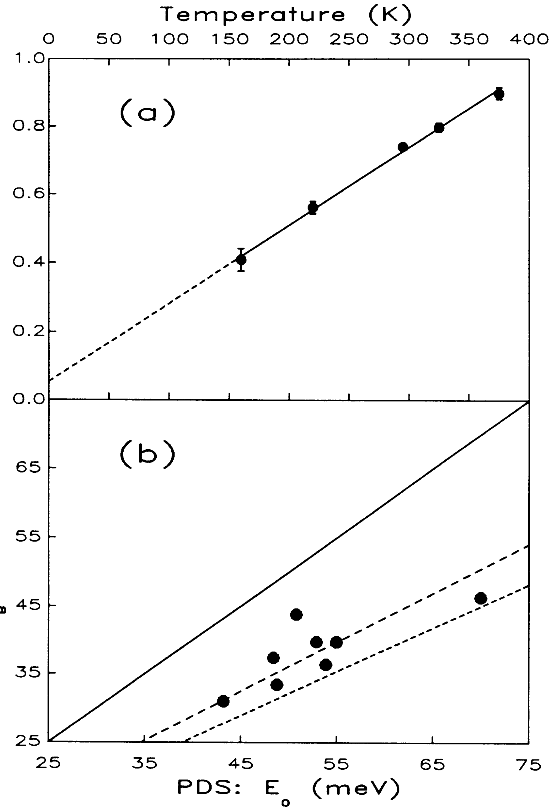

FIG. 2. (a) The temperature dependence of the dispersion parameter β for a low-defect-density sample of intrinsic *a*-Si:H. The solid line is a linear best fit to the data; the dashed line is the extrapolation to zero. (b) kT_0 $(\equiv kT/\beta)$ from picosecond PA vs the slope of the band-tail states from PDS (E_0) for intrinsic *a*-Si:H samples of varying quality.

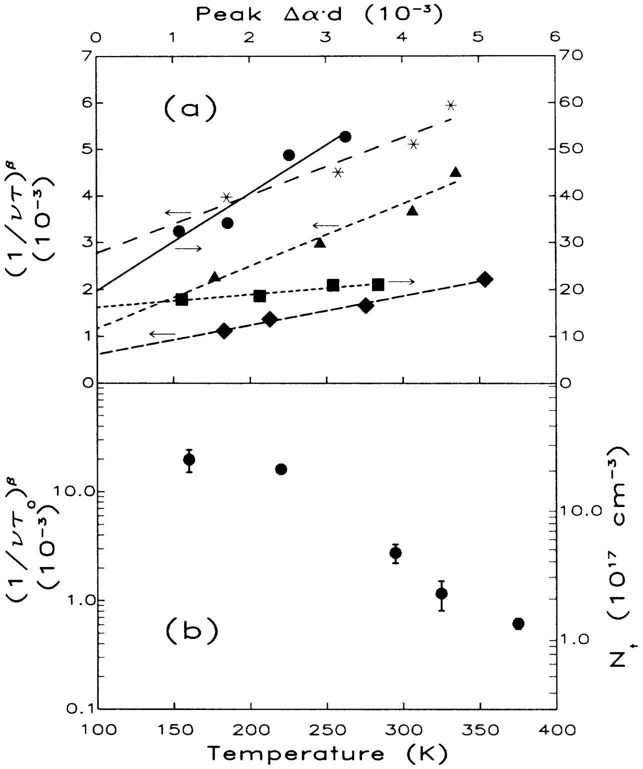

FIG. 3. (a) The intensity dependence of $(1/\nu\tau)^\beta$ at various temperatures for a low-defect-density sample of intrinsic *a*-Si:H. On right ordinate, 160 K (circles), 220 K (squares); on left ordinate, 295 K (asterisks), 325 K (triangles), 375 K (lozenges); $\nu=10^{13}$ s^{-1}; d is the sample thickness. (b) The values of $(1/\nu\tau_0)^\beta$ obtained by a linear extrapolation to zero from the intensity dependence of $(1/\nu\tau)^\beta$ at various temperatures. The trap density (right ordinate) is calculated with use of $N_c=1.2\times10^{19}$ cm^{-3} and $b_t/b_c=0.3$.

nance[10] experiments. The correlation between the data and the dashed lines indicates that the carriers dominating the PA in intrinsic a-Si:H, over the 4-ns range, are electrons.

While the shape of each normalized PA transient versus t/τ is independent of I, the time scale of the decay, τ, is not. Consistent with the model of diffusion-limited trapping, $\ln(\nu\tau)$ should be proportional to $\beta^{-1}\ln[(b_tN_t)^{-1}]$, implying an Arrhenius T dependence for τ for $\beta = T/T_0$. (ν is the escape frequency, N_t is the density of trap states, and b_t is the capture coefficient.) The variation of τ with I presents a difficulty in our establishing the functional form of $\tau(T)$. We adopt the following approach: The relation between τ and b_tN_t holds and we use this relation to establish important aspects of the dependence of N_t on T and I, i.e.,

$$(\nu\tau)^{-\beta} = b_tN_t(T,I)/b_cN_c, \tag{2}$$

where N_c is the density of states and b_c the capture coefficient in the CBT. In Fig. 3(a) we plot $(\nu\tau)^{-\beta}$ vs I and demonstrate a linear variation at each T, i.e.,

$$b_tN_t(T,I) = [b_tN_t]_0 + \delta(b_tN_t), \tag{3}$$

where $\delta(b_tN_t) = a(T)I$. The value $\nu = 10^{13}$ s^{-1} is used in Fig. 3(a) and is consistent with other results.[11] To first establish $\tau(T)$, we eliminate the complication caused by $\delta(b_tN_t)$ by linear extrapolation to $I=0$ to determine $[b_tN_t]_0/b_cN_c$ $[\equiv(\nu\tau_0)^{-\beta}]$. In Fig. 3(b) we plot $(\nu\tau_0)^{-\beta}$ as function of T. We see that there is an appreciable T dependence, with a transition at $T \simeq 250$ K from an essentially constant value to an order of magnitude lower one for $T \gtrsim 325$ K. We interpret this behavior in terms of a trap density with an intrinsic temperature dependence $N_t(T)$. There are two candidates for this behavior: thermal-equilibrium defects[12] and LID's.[13,14] We will show that the data in Fig. 3(b) are in remarkable agreement with the annealing kinetics established for LID's.[14] The numerical values for N_t depend upon the choices for N_c and b_t/b_c. Using the accepted band-edge value of the density of states[15] of $g_0 = 2\times10^{21}$ eV^{-1}cm^{-3} we determine $N_c = 5\times10^{19}$ cm^{-3} (at 295 K). We limit the factor b_t/b_c with the assumptions that the trap levels correspond to states in the upper half of the gap, near the CBT states, and are neutral when empty. Hence, $b_t/b_c \lesssim 1$. The scale for N_t on the right of Fig. 3(b) is fixed with $b_t/b_c = 0.3$. This reasonable choice for the capture rate ratio yields a value for the low-temperature saturation of N_t of 2×10^{18} cm^{-3} which is the same as that determined in a systematic study of LID's under conditions of cw low-intensity illumination with very long exposure times.[16] The comparison of $N_t(T)$ in Fig. 3(b) with studies of the kinetics of LID annealing[14] independently verifies our association of N_t with LID's. The close agreement at $T = 295$ K with $N_t = 5\times10^{17}$ cm^{-3} and $T = 375$ K with $N_t = 1.5\times10^{17}$ cm^{-3} is somewhat surprising considering the very different conditions of light exposure in our experiment. Further evidence that the N_t can be associated with LID's was obtained by low-temperature photoluminescence measurements with the pump pulsed laser as the excitation source. The results are consistent with previous measurements using photoluminescence to study LID's.[2] At room temperature and higher, the saturation of the LID's occurs rapidly, with an exposure time of < 100 s, as can be monitored directly by the amplitude of the PA at various fixed delay times.[11]

The change in b_tN_t with I can be attributed to either (or both) of two likely mechanisms: One applies to any trap distribution, the other is specific to the annealing kinetics of LID's. First, as N_t is considered neutral before electron trapping, the capture of a hole in the N_t states can change b_t by as much as 2 orders of magnitude. Therefore, an initial capture of the photogenerated holes into as little as 1% of the N_t trap density could account for the maximal change in $\delta(b_tN_t)$ in Fig. 3(a). This density of captured holes, at most temperatures, corresponds to a very small percentage, less than 1%, of n_0 [in Eq. (1)]. The linear dependence on I of $\delta(b_tN_t)$ follows from the linear dependence of $n_0(I)$, i.e., quasimonomolecular recombination.[17]

The other possible source of change for b_tN_t involves an increase in N_t due to the generation of LID's with fast annealing rates. As shown in Fig. 2 in Ref. 14 the LID's have a broad distribution of annealing barriers. The saturation value of $N_t(T)$ is determined by that part of the distribution corresponding to annealing times much larger than the nominal time of observation. The spectral distribution of $N_t(T)$ narrows with increasing T. At any temperature, one can generate LID's over the entire spectral range (of annealing barriers heights) but outside the distribution that determines the steady-state saturation $N_t(T)$; these are transient species. In the transient PA method the electron trapping can interrogate these transient species. Thus the pulse sequence can generate and even saturate a part of the distribution of LID's which subsequently decays between nominal measurement periods of $\Delta\alpha(t)$ at a given T. It is not obvious that this increment to N_t during these periods should follow a linear I dependence. A full kinetic modeling, under the conditions of the transient PA measurement, will be included in a future report.

In summary, the early-time relaxation of photoexcited carriers in intrinsic a-Si:H has been observed in the range from $\simeq 10$ ps to 4 ns. The high quality of the two-wavelength pump-probe data acquisition[5] (Fig. 1) permits a reliable and reproducible quantitative fit of $\Delta\alpha(t)$. We determined that the induced-absorption decay is dominated by electrons and the exponent in the power law decay, β, is strictly proportional to T [Fig. 2(a)]. The I independence of β insures that it is an intrinsic property. The $T_0 (= T/\beta)$ is in excellent agreement [Fig. 2(b)] with other transport measurements (at much longer times) of the width of the CBT. Hence, the exponential density of states can be extrapolated to at least within 0.15 eV of the mobility edge. We have used a self-consistent means of unraveling the I and T dependence of τ [Fig. 3(a)]. The *a posteriori* justification that the extrapolated values of $N_t(T,I\rightarrow 0)$ $[\equiv N_t(T)]$ can be interpreted as a neutral trap density is the close agreement of $N_t(T)$ [Fig. 3(b)] with the saturated value of LID's reported in Ref. 14. Independent evidence for this association has been obtained in low-T luminescence quenching and PA amplitude relaxation (at fixed delay) measurements.[11] Thus, starting with a very low-defect-density film of a-Si:H one can induce defects, generic to the material, in a reproducible and controlled way (i.e., by I and T). Since the electronic relaxation (i.e., τ^{-1}) scales with these defects one can now use the transient PA as a sensitive and quantitative probe of further dynamic processes: early recombination and/or a fuller spectral range of (transient) LID's. In future experiments, by studying $\Delta\alpha(t)$ as a function of probe and pump wavelength, we hope to locate the position of these defects in the gap. It is assumed that a large fraction of N_t is located near or in the CBT. If the traps are deep it is difficult to understand the recombination of a density n_0 of electrons and holes within each repetition period.[18]

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