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Role of dangling-bond defects in early recombination in hydrogenated amorphous silicon

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Relaxation of photoexcited carriers is studied in a-Si:H with the use of photoinduced ir absorption. The role of the dangling-bond defect in recombination is investigated with samples of defect density from 10^{15} to $>10^{18}$ cm^{-3}. We find that during the first microsecond the dangling bond does not cause rapid recombination, but rather actually slows recombination by acting *indirectly* through its influence on the density and shape of the exponential distribution of states near the band edge.

Dangling-bond (DB) defects are the focus of many investigations dealing with tetrahedrally bonded amorphous semiconductors.[1] Such defects, whose density can be measured by electron-spin resonance (ESR), correlate strongly with luminescence quenching,[2] short free carrier lifetime,[3] increased subgap absorption,[4] and the shape of the absorption edge.[5,6] DB defects can be passivated in amorphous silicon (a-Si) by alloying with hydrogen (a-Si:H). The defect density is controlled by material deposition conditions; it is increased with hydrogen evolution and is partially diminished by rehydrogenation.

There is strong circumstantial evidence from several experiments that DB defects play an active role in electron-hole recombination in amorphous silicon[1] analogous to the role of defects in crystalline materials. In particular, at low temperatures fast recombination by direct tunneling of carriers to DB defects is assumed to be the main mechanism which limits carrier lifetime and quenches luminescence.[2] In this Communication we present evidence that DB defects are not fast recombination centers. We emphasize that the dispersive influence of the exponential distribution of localized states extending into the gap (the band tail) dominates the recombination process in the multiple trapping model (MTM).[7]

Photoexciting carriers across the gap in a-Si:H allows infrared (ir) absorption by the nonequilibrium population of electrons and holes, as these carriers make transitions to the extended states deeper in the bands. Photoinduced absorption (PA) data have been reported previously for a-Si:H for times from 0.5 μsec and have been interpreted in terms of multiple trapping.[8,9] Our data span the time regime from 4 to 500 nsec. This time regime is important for a number of reasons: Very few carriers have actually recombined, although trapping processes and luminescence quenching have begun, and carrier thermalization is important.

We used a 10-Hz Nd:YAG pumped dye laser with 4-nsec full width at half maximum (FWHM) pulses of 2.2-eV photons to photoexcite a carrier density of $\sim 10^{18}$ cm^{-3} in a-Si:H. A cw ir beam (0.9 to 1.45 eV) from a filtered tungsten lamp was passed through this carrier population, and changes in the ir transparency were detected by a fast Ge photodiode with a risetime of 1.5 nsec. Changing the spectral width of the incident ir with a crystalline Si filter had no effect on the PA response. The change in detector photocurrent was digitized by a Tektronix 7912AD. At low temperatures, luminescence is unavoidably emitted into the photodiode optics, but it was separately recorded and subtracted. Data were taken for undoped samples of various defect densities over a temperature range of 10 to 300 K.

Figure 1 shows the PA data for representative a-Si:H samples. The defect density N_S is measured by ESR at $g=2.0055$. A power law describes the PA decay of these samples over this time period very well with an exponent of "α." The rate of decay

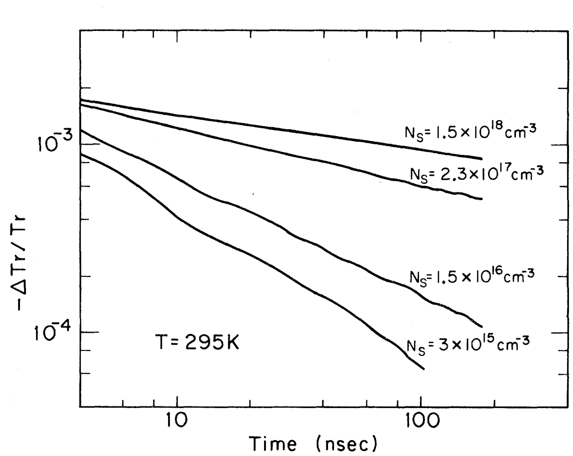

FIG. 1. Relative change in transmission (photoinduced absorption) vs time delay for samples of various defect densities showing a power-law decay $t^{-\alpha}$.

systematically decreases with increasing defect density. This trend is *opposite* to that expected if DB defects were controlling recombination.

We can, however, successfully interpret these results in terms of multiple trapping[7] with a distribution of localized trapping states $N_t(E)$ whose density declines exponentially into the gap; $N_t(E) = N_0 \exp(-E/E_0)$, where E is the depth of the trap level from the band edge and E_0 is the width of this band tail. There is evidence that this is the case not only for *a*-Si:H but also for a large number of amorphous and disordered crystalline systems. Upon photoexcitation, the carriers are quickly trapped into the band tails,[3] acquiring an exponential energy distribution which parallels the density of trap states. The top of the trapped distribution thermalizes; the level at which thermalization begins, E_d, descends through the distribution as $E_d = k_B T \ln \nu t$, where ν is an attempt-to-escape frequency on the order of 10^{13} sec^{-1}. Capture by carriers of opposite charge or deeper levels which are not part of the band tail competes with retrapping; when the probability of capture there exceeds the probability of retrapment at states below E_d, the population in the band tail diminishes as $t^{-\alpha}$, where $\alpha = T/T_0$, and $T_0 = E_0/k_B$. This time dependence is observed from our earliest time of 4 nsec.

The shape of the trap distribution, then, determines the exit rate of the carriers from the band tail. Other experiments have shown that increasing the DB defect density leads to widening of the band edge, increasing E_0.[5,6] Since E_d descends through the band tail at a rate independent of trap or defect density, a larger fraction of carriers are localized below E_d in a high-defect-density material than in a low-defect-density material at comparable times. The high-defect-density material holds carriers in the band tail longer.

A test of this interpretation is to decrease the temperature. In Fig. 2 we plot "α," obtained from the power-law fit to PA at 200 nsec, as a function of temperature for one sample. As predicted by the MTM, "α" varies linearly with temperature between 50 and 250 K. A similar temperature dependence has already been observed at longer times.[8] Figure 2 shows that $E_0 = 46$ meV ($T_0 = 534$ K).

We have also measured E_0 directly from optical absorption and in Fig. 3 compared $k_B T/E_0$ with the "α" from PA. Since the optical-absorption data represent a joint density of states involving both the valence and conduction bands, the convolution of a narrow feature of one band with a broad feature of the other band will map out the broad feature in the absorption spectrum. The broader of the two band tails will dominate the optical-absorption edge; in *a*-Si:H this is the valence-band edge.[10] Thus the excellent agreement in Fig. 3 for all but the lowest-defect-density samples ($< 10^{16}$ cm^{-3}) indicates that the shape of the valence-band tail determines the rate of PA decay. O'Connor and Tauc[11] have concluded that they are not observing electrons in their PA experiments on *a*-Si:H. We interpret our results as strong and direct evidence that the PA decay is due to hole activity. In the lowest-defect-density samples, the PA decays faster than the rate predicted by optical absorption, indicating that hole movement is not the limiting rate that it is in the samples with more defects. This suggests that electron transport assists band-to-band recombination in the lowest-defect-density samples, and that the faster decay perhaps yields information on the conduction band instead of the valence band.

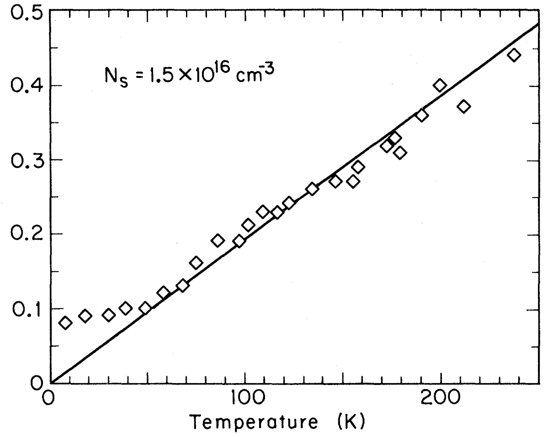

FIG. 2. Temperature dependence of α. The weakening of the temperature dependence at low temperature is most likely due to a competing local-to-local recombination process.

Figure 1 shows that at 295 K, the low-defect-

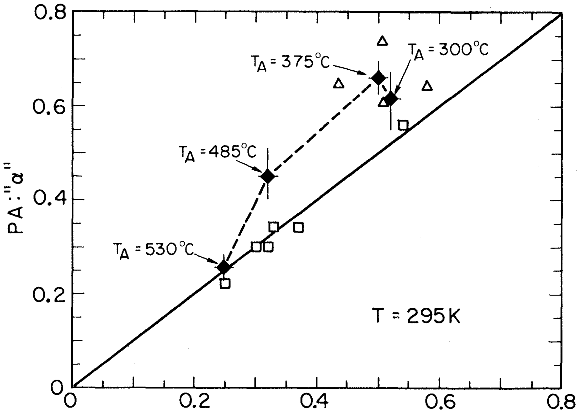

FIG. 3. α from transient photoinduced absorption compared with $k_B T/E_0$ from optical absorption at 295 K. Open symbols represent samples deposited under a range of conditions which vary N_s (ESR), triangles are "optimal," low-defect-density samples. Solid symbols show the effect of evolving H from a single sample.

density sample relaxes much more quickly than the high-defect-density sample. Below 50 K both samples are relaxing at about the same rate, $\alpha \sim 0.07$ (very slowly), and the PA signal is approximately equal for *all* samples near 10 nsec. This is in sharp contrast to luminescence experiments which show that the low-defect-density material has a luminescence quantum efficiency near unity for the 1.4-eV emission and the high-defect-density material has a weaker band at 0.9 eV.[12] One interpretation of this has been that the carriers are rapidly tunneling to the DB defects which act as nonradiative recombination centers. The PA results indicate this is not happening. At low T, the highest-defect-density sample's ir absorption is reduced only 50% at 2 μsec; yet the luminescence is weak and decays rapidly. Correlation of band tail widths with PA decay rates is quite good. We conclude that the DB defect is not a rapid recombination center in undoped amorphous silicon, but instead influences the recombination process indirectly by its effect on the width of the band tail.

We can only suggest alternative quenching mechanisms for the luminescence such as charged defect electric field quenching,[13] DB induced strains, or tightly localized carriers in the higher-defect-density material. We do not completely rule out the possibility that the electrons are rapidly captured by DB defects followed by a slower capture of holes. Yet serious difficulties exist with all of these suggestions and will be discussed in a future paper.

In order to separate the role of defects from the effects of various deposition conditions used in the samples in Fig. 3, we created defects by stepwise evolving hydrogen from an initially low-defect-density sample by annealing it to temperatures of 300 to 530° C. This widened the optical-absorption edge (increased E_0) as the DB defect density increased.[5] The dashed line of Fig. 3 follows the comparison between the PA "α" and $k_B T/E_0$ as the sample is annealed to higher temperatures. The comparison is complicated by the faster decay noted for the lower-defect-density material, but the trend to slower PA decay with increasing E_0 is confirmed.

We find it unlikely that PA and luminescence do not arise from the same population of electrons and holes due to the following considerations. (1) Assuming oscillator strengths of unity for the ir cross sections over the bandwidth used, we find a minimum estimate for the population observed when PA is at its highest (earliest) level. We obtain a value from an integrated absorption estimate[4] that is $\sim 80\%$ of that expected from the photoexcited carrier density. Coupled with an estimated luminescence efficiency of 50–100% in low-defect-density material, this argues against separate populations. (2) PA and luminescence have very similar temperature quenching dependences. (3) Similar PA maximum amplitudes (within 20%) near 10 nsec and 10 K for all the samples support the argument that nearly all of the photoexcited population is being observed. (4) Luminescence recombination kinetics have been observed to change from monomolecular to bimolecular at a photoexcited carrier density N_P of $1-2 \times 10^{18}$ cm^{-3}.[2,14] We have discovered[15] a similar change in recombination kinetics at the same density of 1×10^{18} cm^{-3}, where the PA amplitude shifts from $N_p^{0.9}$ to $N_p^{0.5}$ with increasing excitation density.

There may be another deep gap state more important in recombination than the DB since even at $N_s > 10^{18}$ cm^{-3} the recombination is slow. Evidence for other states exists in the light-induced Staebler-Wronski states[16] and the hole trap state deduced from photoconductivity.[17] The luminescence line due to oxygen is occasionally reported but other impurities may exist at significant densities in a typical sample. Surface states may also play a role, but clearly more work is needed.

In conclusion, our PA data show that the band tail of a-Si:H plays a more important role in the early recombination process than does the DB defect density and that DB defects are not fast recombination centers. We suggest another more important recombination channel may exist, although we acknowledge the difficulty of reconciling the evidence from non-PA experiments that seem to imply otherwise. Luminescence does not detect carriers which do not radiatively recombine and photoconductivity does not detect carriers which are immobilized in deep traps; thus PA is a complementary probe for studying the time evolution of the carrier population. If the DB defects are not important nonradiative recombination centers, then other roles proposed for this state[18] must be more carefully considered.

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