RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 34, NUMBER 4 15 AUGUST 1986

Systematic investigation of picosecond photoinduced absorption in hydrogenated amorphous silicon

W. B. Jackson, C. Doland, and C. C. Tsai
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 20 May 1986)

A systematic study of the dependence of picosecond photoinduced absorption (PA) and transmission in hydrogenated amorphous silicon on sample thickness, doping concentration, and excitation intensity has been undertaken. Investigations demonstrated that the picosecond PA decays are not caused by recombination at the sample surface nor by deep trapping. The decays are consistent with thermalization within the band tails and doping-induced band-tail states.

The study of ultrafast relaxation of excited carriers is of fundamental interest in semiconductors, particularly in amorphous materials such as hydrogenated amorphous silicon (*a*-Si:H), due to the presence of disorder and distributions of traps. This short-time relaxation dynamics is important for the understanding of luminescence, recombination, and transport. The carrier relaxation process has been studied using time-resolved luminescence, transient photoconductivity, and photoinduced absorption (PA). Of the three techniques, PA is particularly useful due to its subpicosecond time resolution and sensitivity to all the excited carriers.

Previous PA studies, covering the time range from picoseconds to seconds, have been performed on a variety of undoped and doped samples.[1-9] Early work interpreted the decays in terms of holes thermalizing within the band tails.[1] Subsequently, the photoinduced absorption was interpreted in terms of bimolecular recombination with multiple trapping; the intensity and time decays were consistent with this interpretation.[2] More recently, a fairly extensive model has been developed which attributes decays of photoinduced absorption to deep trapping.[5,6] In the case of undoped material, the trapping states are neutral dangling bonds, while in the case of doped material, the trapping centers for minority carriers become charged dangling bonds. The most recent interpretation for the PA decays involves thermalization in the band tails and donor states for compensated material.[8] In this intrepretation, the donor states in singly doped material, despite being similar to those found in compensated, are presumed to be unimportant. In addition to these interpretations, recent transient grating experiments[9] have been interpreted in terms of carrier diffusion to the sample boundary. For large grating spacings, the grating decay should be similar to the decay of transient reflectivity and/or photoinduced absorption.

The goal of this paper is to eliminate some of these models and help understand underlying mechanisms for PA in the picosecond and nanosecond time regime. In light of the previous work which demonstrated that mutually exclusive models can yield equally good fits, the present study uses samples prepared under a wide variety of deposition and doping conditions to check consistency of the experimental trends with those predicted by the various models. We find evidence that all PA decays in the picosecond time range can be interpreted in terms of thermalization within the band tails and, in the case of doped material, into donor and acceptor levels located in the band tails. The results do not seem to be consistent with deep trapping or recombination at the sample boundaries.

The characteristics of the PA experimental setup consisted of the following. The 614-nm laser pulses were produced by a synchronously pumped cavity dumped dye laser system with an energy up to 8 nJ, a 12-psec pulse width, and a 800-kHz repetition rate. The beam was focused to a 30-μm-diam spot giving rise to carrier densities in the range of $10^{18}-10^{19}$ carriers per cm^3. The pump beam was modulated at 10 kHz, and PA absorption was determined from the synchronous modulation of a weak probe beam (5% of the pump intensity) passing through the sample. Delays up to 8 nsec could be obtained using a feedback stabilized delay line which ensured overlap of the pump and probe spots over the entire delay.[10] The series of samples used in this study will be described later. For most studies, thick samples were used to minimize the distortion in the decays due to etalon effects.[11]

We first tested the model of carrier diffusion for explaining the PA decays. If the PA decays are caused by carrier diffusion to the sample boundaries, one would expect slow decays for thicker samples, or if the carriers were generated deeper within the sample. This prediction was tested by measuring PA decays on a series of undoped low defect samples of thicknesses ranging from 200 nm to 2.5 μm. Furthermore, the generation depth of the carriers was changed by a factor of 3 by altering the laser wavelength. In both cases, no change in the observed decays was observed within experimental uncertainty. This indicates that unlike the case for thin films in Ref. 9, the decays are not due to carrier diffusion to, and recombination at, the sample boundaries. This result also eliminates the possibility of thermal diffusion and/or pressure effects observed in other materials[12] giving rise to the decay, since such mechanisms would also predict a slower decay for thicker samples. Hence, we can conclude the decays are due to some bulk electronic relaxation process.

Subsequently, the deep-trapping model was considered. In this model, the PA decay occurs when the carriers thermalize out of the band-tail states into dangling bond deep traps. The deep traps are assumed to have smaller optical cross sections than the band-tail states. The observed decay is due to thermalization of carriers from the band tails into these deep traps. In this model, the number of band-tail carriers, dominated by multiple trapping, is described by the relation[5,6]

$$\Delta\alpha(t)=A\{R/[1+(t/\tau)^{\alpha}]+1\}\ , \qquad (1)$$

where R is a ratio of cross sections and is negative for doped films and positive for undoped films, α is the dispersion parameter, and τ is the deep-trapping lifetime and has the dependence given by $\tau\sim(N_s)^{-\alpha}$, where N_s is the density of dangling bonds. Since $0.3<\alpha<1$, the decay rate should increase rapidly as N_s increases.

This dependence of the decay time on deep-trap density was tested in a number of ways. First, the defect density was altered by changing the substrate temperature during deposition. The defect density changed from 3×10^{15} to 3×10^{17} dangling bonds per cm^3.[13] The decays were longer for the higher defect films—the opposite of the results expected from deep trapping. The defect density was also altered by doping. When the phosphorus gas phase doping density is increased from 0 to 1×10^{-5}, the defect density increases two orders of magnitude to $\sim5\times10^{17}$ defects per cm.$^{-3}$ The corrresponding decays, however, did not change [Fig. 1(a)]. Upon increasing the doping density further, the photoinduced absorption made an abrupt transition to photoinduced transparency (PT) for 10^{-3} P-doped films. The defect density, however, changed only by a factor of 10. The expected dependence of the decay on doping, including the dependence of the defect density on doping, is indicated in Fig. 1(b). It is evident that the deep-trapping model predicts that the largest changes occur for the lower doping range, while the experiment indicates that the changes are largest for the higher doping levels. The independence of the decays with power discussed below demonstrates that trap saturation cannot explain these results.

Even more striking are the decays observed in Fig. 1(c) for films with various levels of compensated doping (equal concentrations of B and P doping). The curves are nearly identical to comparable concentrations of P doping except that the transition to PT occurs more rapidly in the 10^{-3} compensated sample than in the 10^{-3} P-doped sample. The compensated samples, however, have up to three orders of magnitude fewer defects than the corresponding P-doped films, indicating, again, that the density of traps does not influence the observed decays as predicted by the deep-trapping model. These results also indicate that the position of the Fermi level is not important. Finally, it should be pointed out that for low defect and compensated films, the number of carriers excited by the laser is several orders of magnitude larger than the density of deep traps. Consequently, the decays cannot be due to thermalization of band-tail carriers into deep traps with smaller cross sections.

The above results leave three possibilities remaining to explain the decay: bimolecular band-to-band recombination, cross-section changes due to carrier thermalization within the band tails, or monomolecular luminescence. Evidence against the first possibility is shown in Fig. 2, where the carrier density has been changed by a factor of 4 with no discernible changes in the decay rate. Furthermore, the ratio of the PA signal to the long-time thermal signal, caused by band-gap changes, is independent of power (Fig. 2). If significant bimolecular recombination occurred on a time scale faster than the experiments, the PA signal amplitude would decrease relative to the

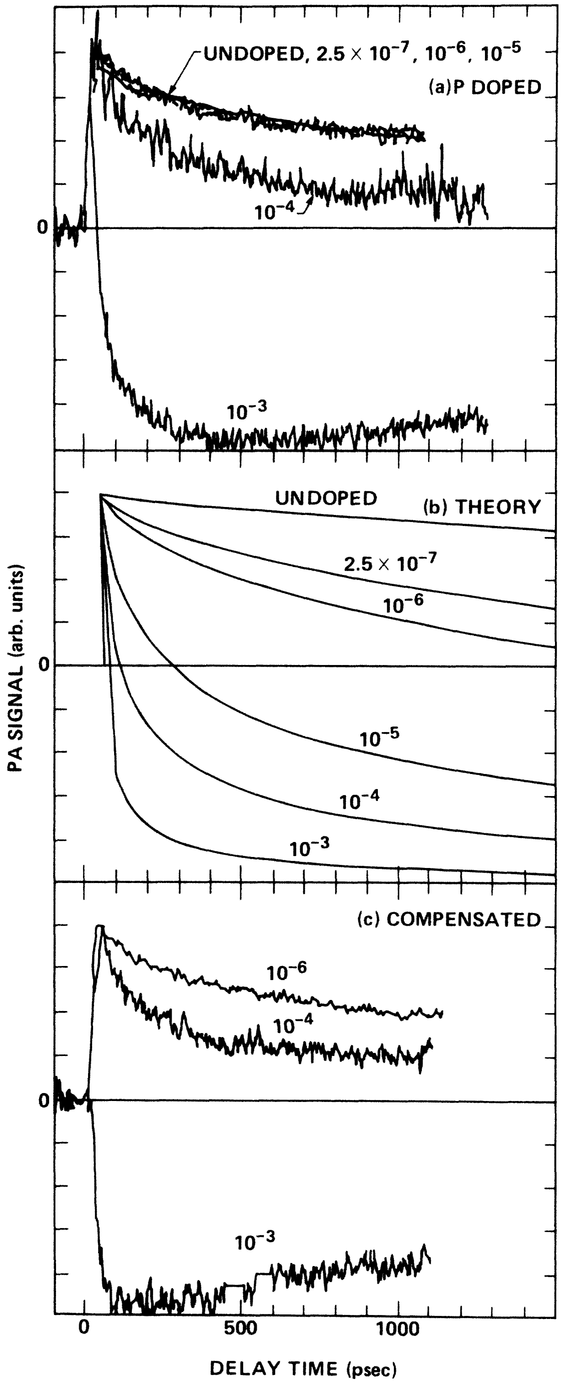

FIG. 1. (a) Photoinduced absorption vs delay for various P-doped samples. (b) Calculated decays using the parameters from Refs. 5 and 6 and the defect densities from photothermal deflection spectroscopy (Ref. 13). (c) Photoinduced absorption for various levels of compensated doping.

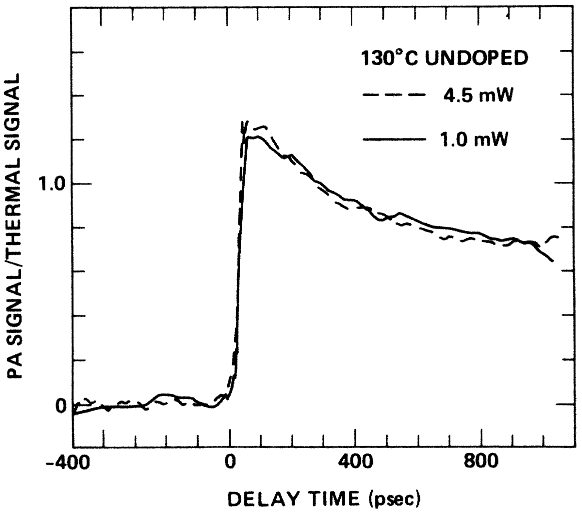

FIG. 2. The ratio of the PA signal to the thermal signal vs delay for various carrier densities.

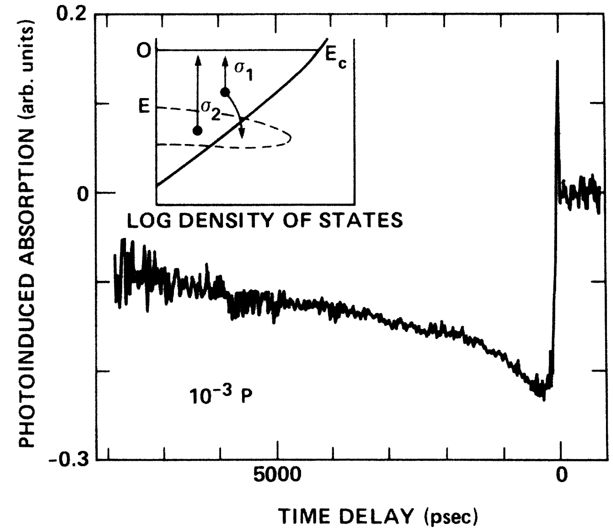

FIG. 3. Long-time PA decay vs delay for 10^{-3} P-doped sample. Inset shows the possible origin of the negative PA signal due to a donor level with a cross section which is less than the unexcited material.

thermally induced signal which depends linearly on power. Some smaller changes with intensity have been observed in Ref. 11, changes for lower carrier densities and longer times. In addition, bimolecular decays cannot explain the transition from PA to PT, although bimolecular decays probably play a role in determining the precise form of the decays. Finally, the fraction of carriers recombining by luminescence on a picosecond time scale at room temperature has previously been shown to be insignificant.[14] This leaves cross-section changes as the most likely cause of observed decays at short times.

The cross section, in turn, depends on the matrix element and the density of final states. Since the carriers are thermalizing within the band tails as $k_B T \ln \nu t$ over an energy range of only ~0.2–0.4 eV, and the density of final states is roughly linear in energy,[15] the changes due to the final-state density would have the form $A - B \ln \nu t$. The observed form is somewhat different, suggesting the possibility that the observed decay is due to changes in the optical matrix element as carriers thermalize within the band tails. The less localized states near the mobility edges have a somewhat larger cross section than deep states.

The model which best explains the observed dependence of the PA decays on material properties is the following. The decays at short times are caused by changes in the optical cross section as the carriers thermalize within the band tails (inset, Fig. 3) and explain why the decays become slower at lower temperatures and in high defect samples with more disorder. The transition to transparency for singly doped and compensated samples occurs when the phosphorus donor band occupation becomes comparable or exceeds the band-tail states. Hyperfine measurements are consistent in indicating that the donor level exceeds the band-tail densities for doping levels near the 10^{-4} range.[16] The induced transparency is due to the smaller optical cross section for the donor level compared to band-to-band transitions. Because the compensated and P-doped films both contain donor levels, the observed decays are similar. At sufficiently long times, which depend on the distribution of donor level and band-tail states, the carriers thermalize out of the donor level into deep traps and/or deeper band tails, and the PA magnitude decreases as shown in Fig. 3 for a 10^{-3} P-doped sample. The donor level is deeper and distributed wider in energy for the compensated samples explaining the slow return to equilibrium and the lack of temperature dependence of the decay. The observation of metastable changes in 10^{-3} P-doped material indicates an increase in the P donor level upon light illumination, rather than metastable changes in deep-trap densities. This metastable increase of donor levels is observed in hyperfine measurements of P-doped samples as well.[17]

The explanation proposed above that the short PA measures the thermalization of the carriers within the band tails is similar to the model proposed in Ref. 8 for compensated material, except that rather than having a different decay mechanism for undoped, singly doped, and compensated, the present model attributes all short-time decays to thermalization within the band tails, with perhaps some modification due to bimolecular recombination depending on the excitation intensity—the effects of deep traps must appear at longer times.

We would like to thank R. Street, M. Stutzmann, J. Tauc, and T. Gustafson for helpful discussions. This work was supported in part by Solar Energy Research Institute Contract No. XB-3-03112-1.

[1] D. E. Ackley, J. Tauc, and W. Paul, Phys. Rev. Lett. **43**, 715 (1979).

[2] Z. Vardeny, P. O'Connor, S. Ray, and J. Tauc. Phys. Rev. Lett. **44**, 1267 (1980).

[3] Z. Vardeny, J. Strait, D. Pfost, J. Tauc, and B. Abeles, Phys. Rev. Lett. **48**, 1132 (1982).

[4] D. Pfost, Z. Vardeny, and J. Tauc, Phys. Rev. Lett. **57**, 376 (1984).

[5] J. Strait, Ph.D. thesis, Brown University, 1985 (unpublished).

[6] J. Strait and J. Tauc, Appl. Phys. Lett. **47**, 589 (1985).

[7] D. R. Wake and N. M. Amer, Phys. Rev. B **27**, 2598 (1983).

[8] C. Thomsen, H. Stoddart, T. Zhou, J. Tauc, and Z. Vardeny, Phys. Rev. B **33**, 4396 (1986).

[9] V. J. Newell, T. S. Rose, and M. D. Fayer, Phys. Rev. B **32**, 8035 (1985).

[10] C. Doland, W. B. Jackson, and A. Anderson (unpublished).

[11] D. M. Roberts and T. L. Gustafson, J. Non-Cryst. Solids **77 & 78**, 551 (1985); D. M. Roberts, J. F. Palmer, and T. L. Gustafson (unpublished).

[12] C. Thomsen, J. Strait, Z. Vardeny, H. Maris, and J. Tauc, Phys. Rev. Lett. **53**, 989 (1984).

[13] W. B. Jackson and N. M. Amer, Phys. Rev. B **25**, 5559 (1982).

[14] B. A. Wilson, P. Hu, J. P. Harbison, and T. M. Jedju, Phys. Rev. Lett. **50**, 1490 (1983).

[15] W. Jackson, S. M. Kelso, C. C. Tsai, J. W. Allen, and S.-J. Oh, Phys. Rev. B **31**, 5187 (1985).

[16] M. Stutzmann and R. Street, Phys. Rev. Lett. **54**, 1836 (1985).

[17] W. B. Jackson, M. Stutzmann, and C. C. Tsai, in *Proceedings of Seventh Photovoltaic Advanced Research and Development Project, Denver, 1986* [J. Sol. Cells (to be published)].