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# Photocarrier dynamics in compensated hydrogenated amorphous silicon

C. Thomsen, H. Stoddart, T. Zhou, and J. Tauc
*Department of Physics and Division of Engineering, Brown University, Providence, Rhode Island 02912*

Z. Vardeny
*Department of Physics and Solid State Institute, Technion, Haifa, Israel*

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The photocarrier dynamics in compensated $a$-Si:H is studied using the time-dependent photomodulation technique in the subpicosecond-to-millisecond time range. We find that photocarriers are quickly trapped in shallow impurity levels for $t < 10$ psec, similar to the behavior in singly doped materials. However, their recombination kinetics for $t > 10$ nsec and their steady-state properties are not substantially different from those in undoped materials. This behavior is explained by fast trapping in donor and acceptor states and thermalization into deeper band-tail states which are similar to those in undoped materials.

A question of much current interest in hydrogenated amorphous silicon ($a$-Si:H) is the nature of defect states introduced into the material by doping.[1] Recently, Street[2] has put forward a successful model for explaining the doping mechanism in $a$-Si:H which treats both charged and neutral impurity states by the same stability criterion, namely, the modified "8-$N$ rule." Within this model, the neutral fourfold-coordinated donors $P_4^0$ or acceptors $B_4^0$ are unstable, and pairs of $P_4^+$ or $B_4^-$ with charged dangling bonds (DB), $D^-$ or $D^+$, are formed ($P_4^+D^-$ or $B_4^-D^+$). The Fermi energy $E_F$ is pinned in between the $P_4^+$ and $D^-$ (or $B^-$ and $D^+$) energy levels.[1] This explains the increase of the DB density with doping in both $p$-type and $n$-type materials, as observed in many experiments.[3,4]

Surprisingly, it was observed[4] that compensated $a$-Si:H samples (achieved by doping with equal concentrations of phosphorus and boron) do not contain large DB densities even at high doping levels. This can be readily explained if the charged donors and acceptors are incorporated into the material by exchanging electrons so that formation of oppositely charged DB's is not needed for this system. This also explains why doping efficiency in compensated $a$-Si:H is higher than in singly doped samples, while $E_F$ remains at midgap.[1] Various observations, however, have indicated that large densities of localized states different from DB's are introduced upon compensation. For example, compared to undoped $a$-Si:H the Urbach tail in the absorption spectrum is broader,[4] the band-edge luminescence peak shifts to substantially lower energies,[3] and the mobility activation energies of holes and electrons double.[5] Street[1] considers two kinds of states in the gap of a compensated sample, both of which are relatively shallow. One is the donor or acceptor states which may form a band; we will refer to them as "impurity" states. The other is the band-tail states which are similar to those in undoped samples, although their concentration may be increased. More direct studies of these states are difficult because the steady-state properties of the compensated and undoped materials are similar. For example, the defect luminescence (at 0.8–0.9 eV) is absent,[3] the electron spin resonance signal is weak,[3] the light-induced electron spin resonance signal shows electrons and holes trapped in regular tail states[6] and the recombination kinetics as revealed by the luminescence decay,[3] and luminescence quenching at high temperatures[3] is similar to that in undoped material. The reason for the difficulty of observing the localized states with steady-state techniques is that these states are shallow and photocarriers stay in them for a short period of time. Transient experimental techniques are more suitable tools for studying the interaction of carriers with these states.

We have investigated the dynamics of photocarriers in compensated $a$-Si:H using time-dependent photomodulation techniques in the subpicosecond to tens of milliseconds time range. We found that in the subnanosecond time range the photocarrier dynamics is similar to that of singly doped materials. The carriers are quickly trapped in states introduced by doping. However, at longer times the excess-carrier recombination kinetics is similar to that of undoped materials. This puzzling result can be explained if compensated samples contain impurity states similar to those in singly doped materials, which, however, are occupied by photocarriers only for a short period of time ($< 10$ nsec).

For the photomodulation measurements in the subnanosecond range we have used the pump and probe technique[7] with a colliding pulse mode locked ring dye laser with pulses 0.2 psec long, an energy per pulse of 0.2 nJ at $\hbar\omega = 2$ eV, and a repetition rate of 110 MHz. The illuminated spot size diameter was about 10 $\mu$m. The pump beam was modulated at 4 MHz and the changes $\Delta T$ in the probe beam transmission $T$ were detected with a fast lock-in amplifier. The nominally compensated samples obtained from Xerox (Palo Alto) and Exxon (Annandale) were thin films (about 1 $\mu$m thick) deposited on quartz or on crystalline silicon by the glow-discharge technique with phosphine and diborane concentrations of $10^{-3}$.

Typical photomodulation decays for the compensated $a$-Si:H samples at 300 K are shown in Figs. 1(a) and 1(b) in the picosecond and nanosecond time ranges. Figure 1(a) shows an initial increase in absorption $\Delta\alpha > 0$ [photoinduced absorption (PA)] followed by a nonexponential decay to states where $\Delta\alpha < 0$ [photoinduced bleaching (PB)]. The decay to PB can be fitted by a power law in time $t^{-\beta}$, where $\beta = 0.9 \pm 0.2$. This fast decay is similar to the decays observed in heavily doped materials[7] with two important distinctions: The decays in compensated materials are temperature independent and also insensitive to the total illumination time.[8] In both singly doped[7] and compensated materials we associate the $\Delta\alpha > 0$ close to $t = 0$ with carriers

 

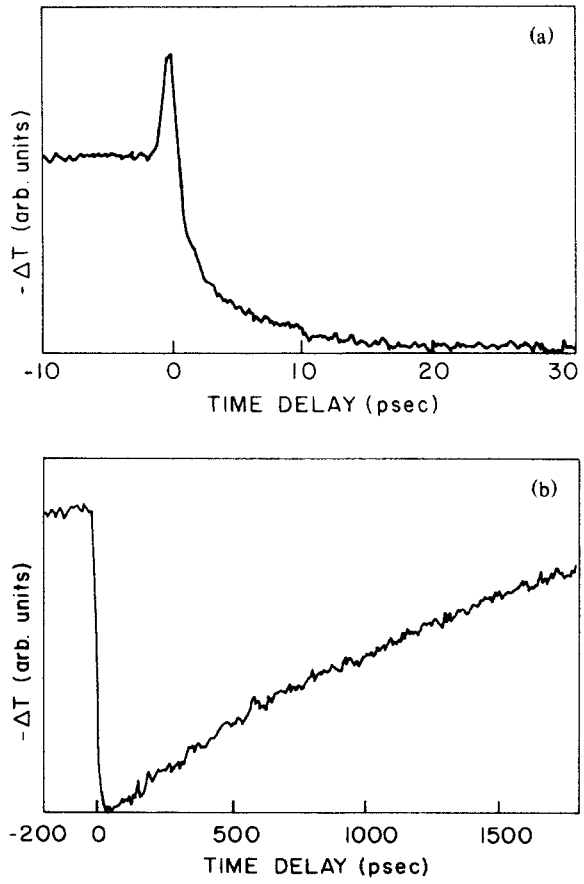


FIG. 1. Decay of the photoinduced change in transmission for the compensated $a$-Si:H at 300 K (a) in the picosecond time range, (b) in the nanosecond time range. $\Delta T < 0$ corresponds to induced absorption ($\Delta\alpha > 0$).

close to the bottom of the band (the mobility edge). These carriers then relax into the impurity states. Filling these states ($P_4^+ + e \rightarrow P_4^0$, $B_4^- + h \rightarrow B_4^0$) reduces optical transitions from the opposite band, and a strong bleaching effect is produced. An origin of the power law may be tunneling of carriers into impurity states which involves a broad distribution of relaxation times. The temperature-independent decay indicates that trapping in compensated materials is not governed by thermally activated transport as it is in singly doped material.[7,8] The reason might be the much higher impurity densities obtained by compensation. This also explains the insensitivity to exposure time, in contrast to the behavior of singly doped materials.[8]

Figure 1(b) shows the relaxation of the PB signal; we note that the fast $\Delta\alpha > 0$ part observed in Fig. 1(a) is not resolved in Fig. 1(b). The relaxation time (a few nanoseconds) appears to be insensitive to the doping level in the range of $10^{-4}$–$10^{-2}$ and to the Fermi-level position. This was verified by checking several $n$-type, $p$-type, or compensated $a$-Si:H samples. We interpret this relaxation as due to trapping of the carriers released from the impurity states in deeper-lying band-tail states for which the bleaching effect is weaker. The carriers stay in these states until recombination occurs at much longer times.

The recombination process was studied in the micro-

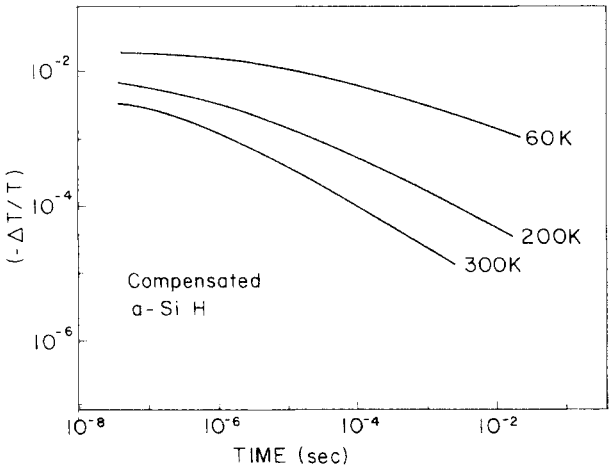


FIG. 2. Decay of photoinduced absorption in compensated $a$-Si:H measured using a probe with a broad spectrum (0.8–1.1 eV), at three different temperatures.

second range. The pump beam used for studying the decays in this range was a dye laser which produced pulses of 10 nsec duration, with 400 $\mu$J of energy per pulse at $\hbar\omega = 2.1$ eV with a repetition rate of 20 Hz; the diameter of the pump beam was about 2 cm. The probe beam was an incandescent light source. The changes in transmission $\Delta T(t)$ were measured in the energy range of 0.8–1.1 eV, using a Ge detector, a silicon filter, and fast electronics. The decays of $\Delta T$ are shown in Fig. 2 for three different temperatures. The decays depend on temperature, being faster at higher temperature. At long times, the decay curves can be described by a power law $t^{-\beta}$, where $\beta < 1$; $\beta$ increases from 0.3 at 60 K to 0.5 at 300 K. The power-law decays, the strong temperature dependence, and the values of $\beta$ are similar to $\Delta T$ decays in undoped $a$-Si:H,[9] but different from the decays in singly doped materials.[9] Since the decays in this time range are associated with recombination,[9] the similarity to the undoped material indicates that carrier recombination kinetics is the same for both undoped and compensated materials. The same conclusion was reached by comparing the band-edge PL decay in both materials.[3]

Figure 3 shows the steady-state photomodulation spectrum of compensated $a$-Si:H at 12 K deposited on crystalline silicon; the doping level in the gas was $10^{-3}$. The interference fringes[10] were small in this case and the spectrum could be easily averaged. The spectrum was obtained using a chopped (75-Hz) $Ar^+$ laser with an intensity of 100 mW cm$^{-2}$ as a pump beam, while the probe beam was an incandescent light source dispersed by a monochromator. $\Delta T$ was measured using Ge and cooled InSb detectors and a lock-in amplifier. The spectral response was normalized by dividing by $T$ ($-\Delta T/T$ is proportional to $\Delta\alpha$). The spectrum in Fig. 3 contains a single PA band with a relatively gradual onset at 0.2 eV. The PA signal, measured at 0.9 eV, decreases by about two orders of magnitude when the temperature increases from 12 to 250 K. The PA band and its temperature dependence are similar to those in undoped materials,[10] but differ substantially from those in singly doped material where the PA band occurs at smaller $\hbar\omega$, and its temperature dependence is much weaker.[11,12] This shows again that the electron states occupied by the photo-

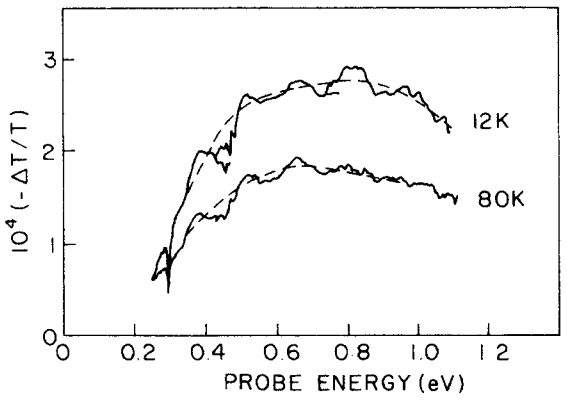


FIG. 3. cw photomodulation spectrum of compensated $a$-Si:H at 12 K. The periodic structure is due to interference.

carriers at longer times in compensated and in undoped $a$-Si:H are similar.

In conclusion, our time-resolved and cw photoinduced spectra in compensated $a$-Si:H can be explained by a model in which the compensation introduces donor and acceptor states superimposed on band tails.[1] Picosecond data show a fast decay of photoinduced absorption into bleaching which is similar to that in singly doped $a$-Si:H. It is therefore ascribed to trapping in impurity states. At longer times, the decays in compensated samples are similar to those observed in undoped $a$-Si:H. This is interpreted as evidence that the recombination processes are similar in both materials because they involve carriers in the band tails which are similar. In singly doped $a$-Si:H the recombination process is different because the minority carriers are quickly trapped on oppositely charged DB's (producing $D^0$), while the majority carriers are trapped in impurity states (producing $P_4^0$ or $B_4^0$). The slow recombination observed in photomodulation,[9] photoconductivity,[13] and photoluminescence[3] experiments in singly doped samples may be due to the slow charge transfer between $D^0$ and $P_4^0$ (or $B_4^0$). The observed cw spectra and temperature dependences of the decays and of the spectra are in agreement with this picture.

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