

## Initial Stages of Trapping in *a*-Si:H Observed by Femtosecond Spectroscopy

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We report the first femtosecond spectroscopic investigation of ultrafast electronic processes in *a*-Si:H. By tuning the probe wavelength in a wide range around the optical gap, we are able to follow the time evolution of carrier trapping in band-tail states. At moderate injected carrier density, the band-tail states are populated by multiple trapping. As more carriers are injected, the shallow band-tail states saturate and deeper band-tail states capture carriers by direct trapping, which is a faster process (1–2 ps) than multiple trapping (10 ps).

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The electronic states of disordered solids can be divided into extended, band-tail, and deep-trap states.<sup>1</sup> An example of technological importance is *a*-Si:H. This material is now being grown very pure in a controlled manner and is of increasing use in devices.<sup>2</sup> Transport<sup>3</sup> and optical<sup>4,5</sup> measurements have revealed that thermalization within the band-tail states and trapping in the deep states occur on a time scale of 100 ps or more. So far, no experiment has had the time resolution and state specificity to observe the initial stage of thermalization and especially the transition from extended to band-tail states. The characterization and understanding of this transition are of fundamental interest because it represents the onset of localization. Furthermore, this characterization could test critically various theories (e.g., multiple trapping) and hypotheses (e.g., the possible high mobility in extended states).

In this Letter, we report the first spectroscopic measurement of the transition from extended states to band-tail states, hereafter called trapping. Our time resolution is 100 fs and our wavelength tunability from the infrared to the ultraviolet is such that we have access to extended states or localized states. Both features will prove critical for a clear determination of the trapping time and its dependence on carrier density. Additionally, we measure the cross section for intraband optical absorption as a function of wavelength and of the energy of the initial state. We then relate our measurements to previous studies and discuss our results in terms of a simple model which we compare to others.

The sample is a film of *a*-Si:H,F prepared from SiF<sub>4</sub> and H<sub>2</sub> by rf glow discharge.<sup>6</sup> The thickness of the film is 450 nm and its optical properties are shown in Fig. 1. The optical gap  $E_g$  determined from a Tauc plot is 1.82

eV, below which clear Fabry-Perot fringes are observed. The conduction band and tail parameters of the sample are identical to those of good quality *a*-Si:H.<sup>7</sup>

Time-resolved reflectivity and transmission measurements are performed simultaneously in the pump-and-probe configuration near normal incidence. The output of a colliding-pulse mode-locked dye laser is amplified in four stages by a frequency-doubled neodymium-doped yttrium aluminum garnet laser.<sup>8,9</sup> Each pulse is 100 fs long and carries 1 mJ of energy. The pulse repetition rate is 10 Hz. A fraction of the pulse at 620 nm ( $h\nu=2$  eV) is used to inject carriers above the mobility edge. The rest of the pulse is focused into a cell containing water to form a white-light continuum,<sup>8</sup> which is then spectrally filtered with interference filters to produce one of the five probe wavelengths indicated in Fig. 1. The reflectivity and transmission of the probe are monitored as a function of time delay between pump and probe pulses, up to 80 ps after excitation. The sample is held at room

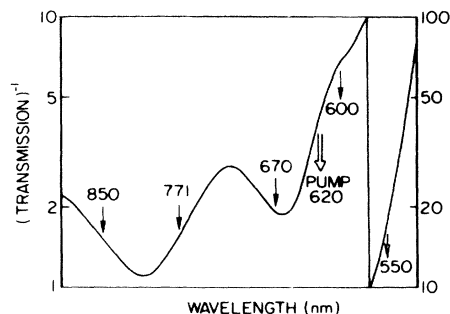


FIG. 1. Transmission spectrum of the *a*-Si:H,F film. The pump and five probe wavelengths are indicated.

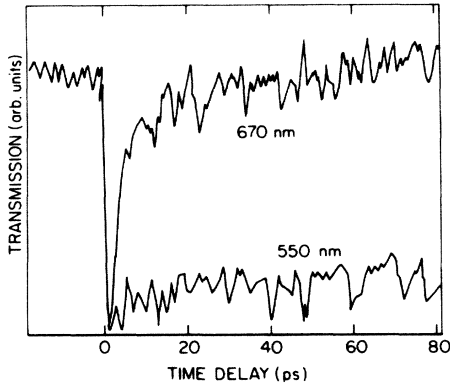


FIG. 2. Transmission of a probe beam above (550 nm) and below (670 nm) the mobility gap as a function of time following injection of  $5 \times 10^{19}$  carriers/cm<sup>3</sup>. Above the gap,  $T$  is a step function, and below the gap,  $T$  recovers in a few picoseconds.

temperature. The intensity of the pump is varied over a factor of 40. In order to minimize cumulative heating or damage, the sample is continuously translated, resulting in a decrease of the exposure rate by a factor of 10. We have observed no laser-induced Staebler-Wronski effect during the entire experiment.<sup>10</sup>

Figure 2 shows the transmission of a probe beam above  $E_g$  and below  $E_g$  after excitation with a 100-fs-long pump pulse at 620 nm. In each case, the initial transmission dip is as abrupt as the convolution of the pump and probe pulses. However, for  $h\nu < E_g$ , the transmission recovers in a few picoseconds, whereas for  $h\nu > E_g$ , there is little or no recovery even after 80 ps. The longest three probe wavelengths display a similar recovery while the shortest two probe wavelengths display a similar step function. Below  $E_g$ , strong Fabry-Perot fringes are observed (see Fig. 1). After pumping, the reflectivity actually increases at 771 nm and decreases at 670 and 850 nm: This indicates an increase in the real part of the refractive index  $n$  of the film. However, the change in reflectivity is much smaller than the change in transmission, and it is an excellent approximation to interpret the decrease in transmission as induced absorption.<sup>11</sup> If we do so, the fact that the initial transmission dip at all five wavelengths is approximately constant for a fixed pump intensity (the dip tends to be smaller for  $h\nu > E_g$ ) can be interpreted as a wavelength-independent induced absorption. We have also varied the pump intensity  $I_p$  over nearly 2 orders of magnitude. As shown in Fig. 3, the magnitude of the transmission dip is found to be proportional to  $I_p$ . At the highest  $I_p$ 's, which corresponds to injection of about  $10^{20}$  carriers/cm<sup>3</sup>, the transmission recovery is faster and a net bleaching is even observed after 10–20 ps. Figure 4 shows normalized transmission curves that clearly illustrate that observation.

In the interpretation of our data, one must remember that both electrons and holes are injected. The optical

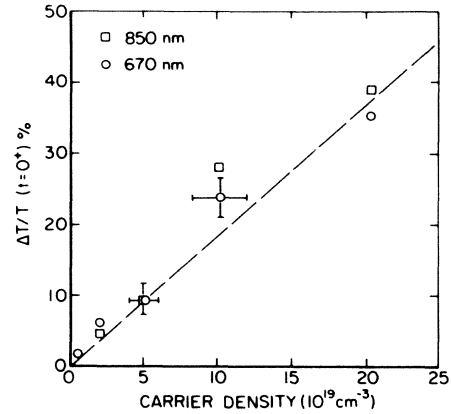


FIG. 3. The magnitude of the transmission dip at  $t=0^+$  is proportional to the pump intensity, that is, to the injected carrier density, as one would expect if it is produced by intraband absorption with a constant absorption cross section.

probe is sensitive to the joint density of states and there is no straightforward way to separate the dynamics of the electrons from that of the holes. We will then for simplicity consider only one kind of carrier throughout the analysis (namely the electrons). This assumption is justified because the trapping of holes is thought to occur instantaneously.<sup>3</sup> The total absorption is the sum of band-to-band absorption and of intraband absorption which can be written as

$$\alpha = \alpha_{vc}(f_e f_h) + \alpha_{intra}(N), \tag{1}$$

where  $f_e$  ( $f_h$ ) is the Fermi occupation probability of the final (initial) state. Just after pumping ( $t=0^+$ ), the carriers have less than 100 meV excess energy compared to the mobility edge<sup>12</sup> and for each probe wavelength, the absorption coefficient for transitions from the valence band to the conduction band  $\alpha_{vc}$  remains essentially un-

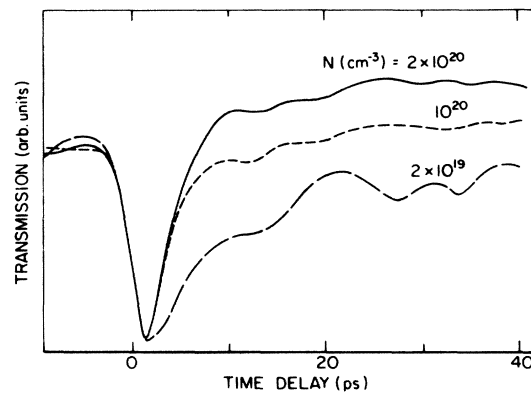


FIG. 4. Transmission at 850 nm following various carrier injections. Net bleaching and faster recovery are observed at high intensities. The curves have been normalized to give the same transmission dip at  $t=0^+$ .

changed because the occupation of the initial and final states of the transition is unchanged. However, intraband absorption  $\alpha_{\text{intra}}$  becomes possible because "free" carriers have been produced. The opacity of the sample increases and the transmission decreases. After a few picoseconds, the carriers have lost energy, as discussed below, and they populate states relatively deep in the band tail. For a probe such that  $h\nu > E_g$ ,  $\alpha_{vc}$  remains unchanged and intraband absorption is still possible. For a probe such that  $h\nu < E_g$ ,  $\alpha_{vc}$  is bleached because the final (initial) state is occupied, while intraband absorption is still possible. If  $\alpha_{\text{intra}}$  does not change much as carriers get trapped deeper in the band tail, we predict a step function of time for transmission above  $E_g$  and at least a partial recovery below  $E_g$ , in agreement with Fig. 2. We thus deduce that the intraband absorption cross section  $\sigma$  is a constant.

At this point, it is necessary to compare our results to those obtained by Vardeny, Strait, and Tauc<sup>13</sup> in undoped *a*-Si:H. Their experiments were also performed in the pump-and-probe configuration, but with both pulses at 620 nm. Their injected carrier density was below  $10^{18}$   $\text{cm}^{-3}$ . Their time resolution of 1 ps was nearly 2 orders of magnitude better than in time-resolved photoluminescence experiments<sup>4,5</sup> but nearly 1 order of magnitude worse than in our case. They found a photoinduced absorption starting at  $10 \text{ cm}^{-1}$  for  $5 \times 10^{17}$  carriers/ $\text{cm}^3$ , which decays on a 1-ns time scale. Their results indicate that  $\sigma$  is equal to  $2 \times 10^{-17} \text{ cm}^2$  and decreases slowly as the carriers are trapped in deeper and deeper states. At the five probe wavelengths, we find  $\sigma$  to be in the range of  $(4-6) \times 10^{-17} \text{ cm}^2$  for a carrier concentration ranging from  $5 \times 10^{18}$  to  $2 \times 10^{20} \text{ cm}^{-3}$ . For  $h\nu > E_g$ , little or no recovery is observed up to 80 ps after excitation, also in agreement with Vardeny, Strait, and Tauc's results. Despite our better time resolution, we do not observe any short-lived transient that can be identified with hot-carrier thermalization above the mobility edge. This negative result agrees with the reflectivity and transmission of *a*-Si:H measured with 100-fs pulses at 620 nm by Kuhl *et al.*<sup>14</sup>

A better understanding of the trapping mechanisms may be gained from our data. If the band-tail density of states has the usual exponential form  $g_{\text{BT}} = N_c \exp(-E/E_0)$ , where we have defined the zero of energy at the mobility edge,  $N_c = 4 \times 10^{21} \text{ cm}^{-3} \text{ eV}$ ,<sup>15</sup> and  $E_0 = 30 \text{ meV}$ ,<sup>3</sup> the total density of states in the band tail is  $1.2 \times 10^{20} \text{ cm}^{-3}$ , which is comparable to the maximum injected carrier density. A multiple trapping model has been proposed to explain thermalization within the band tail.<sup>3,16</sup> With the assumption of a constant capture cross section  $\sigma_{\text{capt}}$ , the states below the mobility edge become uniformly populated by the trapped carriers. As the carriers are preferentially released from the shallow states by the thermal activation, the average carrier energy  $\langle E \rangle$  changes with time as  $kT \ln v_0 t$ , where the escape frequency  $v_0 = 10^{13} \text{ s}^{-1}$ .<sup>16</sup> States 100 meV below the mobility

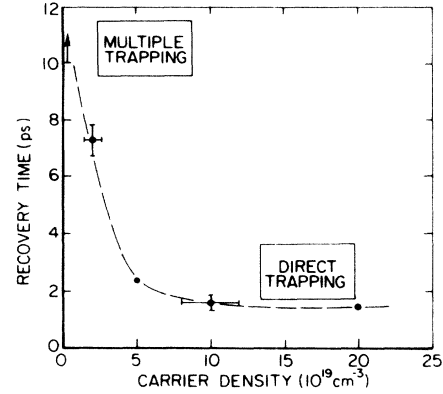


FIG. 5. Recovery time of the transmission curves vs injected carrier density at 670 nm. The recovery time is the time it takes  $T$  to recover to within  $1/e$  of its initial value. At high density, direct trapping dominates and at moderate density, multiple trapping becomes predominant. At the lowest density ( $5 \times 10^{18} \text{ cm}^{-3}$ ), the recovery exceeds 10 ps. The dashed line is a guide to the eye.

edge would be populated after 5 ps. Experimentally, we observe that these relatively deep states are occupied in 5–10 ps under moderate injection and in 1–2 ps under high injection. We propose that this is evidence for *direct* trapping (DT) under high injection, not *multiple* trapping (MT) (or hopping, which is even slower at room temperature). Our model requires that  $\sigma_{\text{capt}}$  decreases with increasing localization, a physically sound assumption<sup>17</sup> that is usually not made in a multiple trapping model for computational simplicity and for a lack of knowledge of the functional dependence of  $\sigma_{\text{capt}}$ .

Consider an electron at or just above the mobility edge. If most localized states are empty, the electron will most likely be captured by a shallow state. If, however, all shallow states are occupied by already captured electrons, but most deep states remain empty because their  $\sigma_{\text{capt}}$  is smaller, then the electron will stay in the extended states until it is captured by a deep state. With the assumption of a mobility of  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>3</sup> the electron will travel  $60 \text{ \AA}$  in 1 ps. Since the average distance between states 100 meV or deeper in the band tail is  $\sim 60 \text{ \AA}$ , it is reasonable that the electron be captured in 1 ps by DT, much faster than by MT. Assuming a constant  $\sigma_{\text{capt}}$ , we had computed it takes 5 ps to populate those states by MT. Since  $\sigma_{\text{capt}}$  decreases with increasing localization, and since the assumed  $v_0$  of  $10^{13} \text{ s}^{-1}$  is quite high, that time may be much longer. In Fig. 5, we plot the recovery time of the transmission as a function of injected carrier density. This plot clearly supports the transition between DT and MT.

We also wish to mention that the net bleaching observed at high carrier density is explained by the combined effect of DT and MT which makes the decrease in  $\alpha_{vc}$  larger than  $\alpha_{\text{intra}}$ . Our results are also inconsistent with recombination on a picosecond time scale.

In conclusion, we have performed the first femtosecond spectroscopic measurement of the optical properties of  $a$ -Si:H,F after carrier injection above  $E_g$ . The time evolution of the photoinduced absorption depends dramatically on whether extended or localized states are probed. States 100 meV or more below the mobility edge are populated in 10 ps by multiple trapping but in only 1–2 ps by direct trapping. This implies a capture time from extended states to shallow band-tail states much shorter than 1 ps, in agreement with our failure to observe thermalization within the extended states. The optical intraband absorption cross section is also found to be  $(4-6) \times 10^{-17} \text{ cm}^2$ , nearly independent of wavelength and state energy.

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<sup>7</sup>Dark conductivity  $= 1 \times 10^{-10} \text{ S cm}^{-1}$ , its activation energy  $= 0.85 \text{ eV}$ ; electron drift mobility  $= 1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , its activation energy  $= 0.13 \text{ eV}$ .

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<sup>12</sup>In amorphous semiconductors, where there is no conservation of  $k$  vector, the injected carriers will be distributed in energy but on average, the excess energy  $h\nu - E_g$  is equally shared by electrons and holes above the mobility edge. In addition, the mobility gap, which defines the mobility edge, is usually somewhat larger than  $E_g$ .

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