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.[1] 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.[2] Transport[3] and optical[4,5] 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_4 and H_2 by rf glow discharge.[6] 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.[7]

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.[8,9] 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,[8] 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

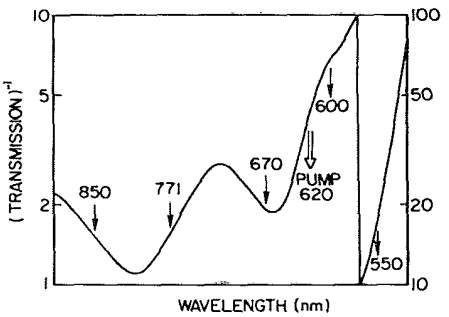

FIG. 1. Transmission spectrum of the *a*-Si:H,F film. The pump and five probe wavelengths are indicated.

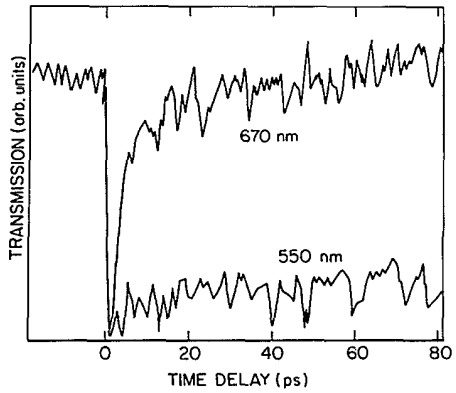

FIG. 2. Transmission of a probe beam above (550 nm) and below (670 nm) the mobility gap as a function of time following injection of 5×10^{19} carriers/cm^3. Above the gap, T is a step function, and below the gap, T recovers in a few picoseconds.

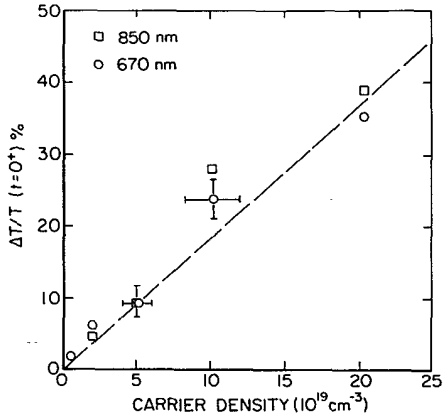

FIG. 3. The magnitude of the transmission dip at $t=0^+$ is proportional to the pump intensity, that is, to the injected carrier density, as one would expect if it is produced by intraband

changed because the occupation of the initial and final states of the transition is unchanged. However, intraband absorption α_{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 $h\nu > E_g$, α_{vc} remains unchanged and intraband absorption is still possible. For a probe such that $h\nu < E_g$, α_{vc} is bleached because the final (initial) state is occupied, while intraband absorption is still possible. If α_{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 σ is a constant.

At this point, it is necessary to compare our results to those obtained by Vardeny, Strait, and Tauc[13] 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} cm^{-3}. Their time resolution of 1 ps was nearly 2 orders of magnitude better than in time-resolved photoluminescence experiments[4,5] but nearly 1 order of magnitude worse than in our case. They found a photoinduced absorption starting at 10 cm^{-1} for 5×10^{17} carriers/cm^3, which decays on a 1-ns time scale. Their results indicate that σ is equal to 2×10^{-17} cm^2 and decreases slowly as the carriers are trapped in deeper and deeper states. At the five probe wavelengths, we find σ to be in the range of $(4\text{–}6)\times10^{-17}$ cm^2 for a carrier concentration ranging from 5×10^{18} to 2×10^{20} 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.*[14]

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, $N_c = 4\times10^{21}$ cm^{-3} eV,[15] and $E_0 = 30$ meV,[3] the total density of states in the band tail is 1.2×10^{20} 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.[3,16] With the assumption of a constant capture cross section σ_{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 $kT \ln \nu_0 t$, where the escape frequency $\nu_0 = 10^{13}$ s^{-1}.[16] States 100 meV below the mobility 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 σ_{capt} decreases with increasing localization, a physically sound assumption[17] that is usually not made in a multiple trapping model for computational simplicity and for a lack of knowledge of the functional dependence of σ_{capt}.

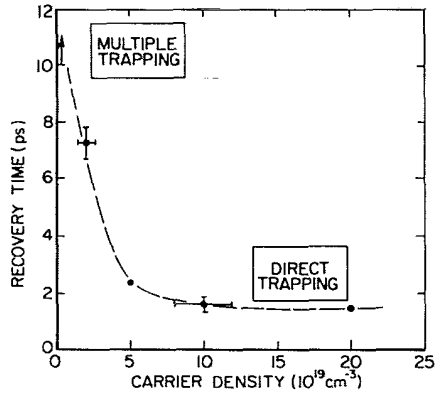

FIG. 5. Recovery time of the transmission curves vs injected carrier density at 670 nm. The recovery time is the time it takes T to recover to within $1/e$ of its initial value. At high density, direct trapping dominates and at moderate density, multiple trapping becomes predominant. At the lowest density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

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 σ_{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 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$,[3] the electron will travel 60 Å in 1 ps. Since the average distance between states 100 meV or deeper in the band tail is ~60 Å, it is reasonable that the electron be captured in 1 ps by DT, much faster than by MT. Assuming a constant σ_{capt}, we had computed it takes 5 ps to populate those states by MT. Since σ_{capt} decreases with increasing localization, and since the assumed ν_0 of 10^{13} 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 α_{vc} larger than α_{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 $(4-6)\times10^{-17}$ cm^2, nearly independent of wavelength and state energy.

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[12]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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