

# **Phase-Dependent Carrier Processes in Silicon-Based Photovoltaic Materials**

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# Phase-Dependent Carrier Processes in Silicon-Based Photovoltaic Materials

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## ABSTRACT

We present comparative studies of the dynamics of photoexcited carriers in a range of silicon-based materials of interest for photovoltaic applications, including crystalline silicon (c-Si), nanocrystalline silicon (nc-Si:H), amorphous silicon (a-Si:H), and “edge” materials grown at the boundary between the nanocrystalline and amorphous phases. Our femtosecond time-scale measurements show dramatic differences across this range of materials in the carrier dynamics immediately following photoexcitation. In c-Si, we detect a 240-fs exponential process corresponding to intraband carrier energy loss due to phonon emission. In contrast, a-Si:H exhibits fast thermalization processes on a distribution of time scales, together with a response consistent with bimolecular recombination. These results provide a basis for understanding the carrier processes in the more complex nanocrystalline and edge materials: we find that the carrier dynamics in nc-Si:H can be understood in terms of the component phases of this heterogeneous material, and we find that the dominant carrier processes in the edge material are likely those associated with the amorphous phase of the material.

## 1. Introduction

Time-resolved optical measurements can provide unique insight into important carrier processes in photovoltaic materials. In this work, we have studied photoexcited carrier dynamics in crystalline, amorphous, and heterogeneous silicon materials. Recently, thin-film nc-Si:H (also sometimes referred to as microcrystalline silicon,  $\mu$ c-Si) has attracted a great deal of interest as a promising material for low-cost, highly efficient, and reliable solar cells, as well as for other optoelectronic applications. The structure of nc-Si:H can be described qualitatively as a collection of nanometer- to micron-scale silicon crystallites embedded in an amorphous matrix. The composition of the films can be controlled by varying the hydrogen dilution ratio during deposition, yielding materials that span the transition from the amorphous to the nanocrystalline state, with increasingly larger grain size and crystalline fraction at higher dilution values. Of particular interest for photovoltaic applications is the “edge” material at the amorphous to nanocrystalline phase boundary. Edge materials give favorable electrical properties and show resistance to the photoinduced degradation processes characteristic of thin-film amorphous silicon, though the physical basis for these effects is still not fully understood. We have studied a series of materials in which the composition is systematically varied through the amorphous to nanocrystalline transition to better understand the nature of photocarrier processes in the edge material. Studies of c-Si and a-Si:H have allowed

us to understand the carrier processes in the heterogeneous nc-Si:H materials in terms of contributions from the component phases.

## 2. Experimental

Time-resolved differential transmittance measurements were carried out as described previously [1]. Briefly, the optical pulses were generated using an amplified Ti:sapphire laser system operating at a repetition rate of 1 kHz. Pulses 35 fs in duration centered at 800 nm (1.55 eV) were used to excite the samples, and broadband near-infrared probe pulses were generated from a compressed femtosecond white light continuum, giving an overall time resolution of  $\sim 40$  fs. Wavelength resolution was achieved by spectrally filtering the probe beam with a  $\sim 10$ -nm bandwidth interference filter after it had been transmitted through the sample. All measurements were carried out at room temperature and with mutually perpendicular pump and probe polarizations, and the pump-probe signals were measured over a range of initial excitation densities. Care was taken in the design of the experiments to minimize distortion of the measured pump-probe response by thin-film interference effects and by spatial inhomogeneity of the excited carrier distribution.

The time-resolved optical transmission measurements for crystalline silicon [2] were made using thinned Si (100) wafers, prepared by boron implantation followed by etching to a thickness of  $\sim 350$  nm. Thin films of a-Si:H were grown on glass substrates by hot-wire chemical vapor deposition (HWCVD) at a substrate temperature of 375 °C. Thin films of HWCVD nc-Si:H were grown on glass substrates: the films were deposited at a substrate temperature of 240 °C, and the hydrogen dilution ratio  $R = \text{H}_2/\text{SiH}_4$  was varied between 1 and 20 with a constant gas pressure of 30 mTorr. The resulting films were characterized by x-ray diffraction, Raman spectroscopy, optical absorption, and photoluminescence [3]. X-ray diffraction measurements indicate that the threshold for the structural transition from amorphous to nanocrystalline growth occurs at a hydrogen dilution ratio  $R = 3$ , and give an average crystallite size of greater than approximately 10 nm. The x-ray measurements, together with Raman measurements, indicate that both the grain size and crystalline fraction increase with hydrogen dilution above the amorphous to nanocrystalline transition.

## 3. Results and Discussion

Measurements of the time-resolved differential transmittance for HWCVD a-Si:H are presented in Fig. 1. In this material, photoexcitation of carriers results in an induced absorbance signal, presented in the figures as a negative differential transmittance,  $-\Delta T/T$ , where  $\Delta T$  is the

change in transmittance due to the action of the pump pulse, and  $T$  is the transmittance of the sample in the absence of the pump pulse. The response was probed at a detection wavelength of 940 nm (1.32 eV). In the small signal limit, the differential transmittance measurements are expected to be proportional to the photoinduced carrier population, and the time course of the signal reflects the dynamics of the photoexcited carrier distribution. The sharp features near  $t = 0$  include contributions from nonlinear effects that occur during the temporal overlap of the pump and probe pulses, and are excluded from the interpretation of the population dynamics.

As discussed in our previous work on a-Si:H and related materials [4], the time-dependent optical response for pump-probe delay times greater than  $\sim 1$  ps is well characterized by bimolecular recombination. This is the dominant contribution to the response, consistent with a large body of earlier work on a-Si:H. The high time resolution of our measurements has also allowed us to detect a new process occurring on a subpicosecond time scale that is associated with fast carrier thermalization.

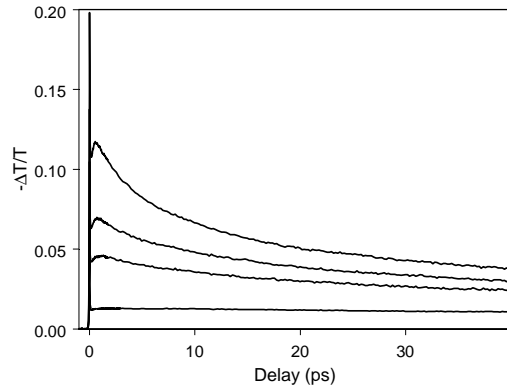


Fig. 1. Time-resolved differential transmittance response of a-Si:H, measured over a range of initial excitation densities.

In contrast to the response seen in a-Si:H, time-resolved differential transmittance measurements on c-Si made under similar conditions show an increase in transmission that forms with a simple exponential time constant of  $\sim 240$  fs, independent of excitation density [2]. This response can be identified as the characteristic time scale for intraband carrier energy loss due to phonon emission as the photoexcited carriers relax toward the band edge.

Representative data for nc-Si:H are shown in Fig. 3. The response includes a rapid, sub-picosecond component together with a more slowly varying response. We find that the dynamics in nc-Si:H are well characterized by the model

$$n(t) = ae^{-t/\tau} + n_0/(1 + n_0kt) + c$$

This model corresponds physically to three separate components: a population that undergoes a simple exponential decay with time constant  $\tau$ , a population  $n_0$  that undergoes bimolecular recombination with an associated rate constant

$k$ , and a component of amplitude  $c$  that decays slowly compared to the time scale of the measurements.

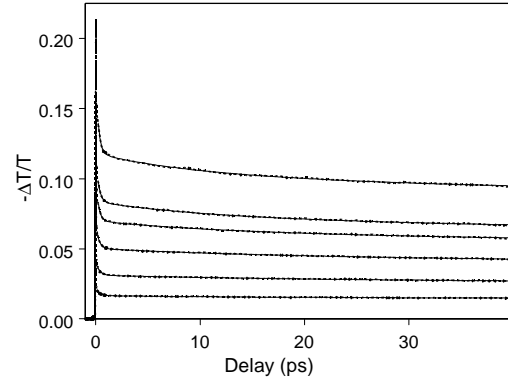


Fig. 2. Time-resolved differential transmittance response for nc-Si:H prepared at a hydrogen dilution ratio  $R = 4$ , measured at a series of initial carrier densities. The solid lines correspond to fits to a multi-component model.

In all of the nc-Si:H materials studied, the fast exponential decay component fits to a time constant of 240 fs, allowing us to identify it as originating in the crystalline phase of the material. The bimolecular recombination component yields a value for the recombination constant consistent with that found for a-Si:H, indicating that this part of the response originates from the amorphous fraction of the material. The slowly varying component  $c$  likely includes contributions from long-lived carrier states associated with the grain boundary regions. As the composition of the nc-Si:H material is varied in samples prepared at higher dilution ratios, we find that the relative amplitudes of the three components change in a manner consistent with the change in composition, allowing us to interpret the carrier dynamics in terms of contributions from the component phases. Remarkably, even though edge material shows evidence of some degree of microcrystallinity in the x-ray diffraction and Raman measurements, the optical response of the photoexcited carriers is largely characteristic of a-Si:H, suggesting that, on a microscopic level, the relevant carrier processes for the photoexcitations are those associated with the amorphous phase of the material.

#### Acknowledgments

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