Mat. Res. Soc. Symp. Proc. Vol. 664 © 2001 Materials Research Society

Femtosecond Carrier Dynamics in Nanocrystalline Silicon Films: The Effect of the Degree of Crystallinity

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ABSTRACT

We present studies of the ultrafast dynamics of photoexcited carriers in HWCVD nanocrystalline silicon thin films to address the underlying physics of carrier relaxation and recombination processes in this heterogeneous material. The degree of crystallinity is controlled by varying the H-dilution during deposition, yielding materials with increasingly larger grain size and crystalline fraction at higher dilution values. Time-resolved measurements of the carrier dynamics were made using a femtosecond pump-probe method, in which a short pump pulse excites carriers in the sample and a time-delayed probe pulse measures the resulting change in the optical properties as a function of the pump-probe delay time. Photoexcitation of carriers with pulses 35 fs in duration centered at 1.55 eV results in a net induced absorbance signal in the near-infrared that is analyzed in terms of a multi-component response that includes contributions from the silicon crystallites and the amorphous matrix.

INTRODUCTION

Thin film hydrogenated nanocrystalline silicon (nc-Si:H), comprised of nanoscale crystallites of silicon embedded in a hydrogenated amorphous silicon (a-Si:H) matrix, has attracted interest due to its potential optoelectronic applications as well as the physical properties that result from its heterogeneous nature. This material is promising for photovoltaic applications, especially given its high efficiency and resistance to the photoinduced degradation characteristic of thin-film amorphous silicon. An important issue in the physics of this heterogeneous material is the extent to which its optical and electronic properties can be understood simply as a combination of the properties of the separate phases, and in particular, the role of the grain boundary regions.

The characteristics of nc-Si:H, including the size of the crystallites and the crystalline fraction, or ratio of the volumes of the crystalline and amorphous components, can be directly controlled via the film deposition conditions. We have carried out systematic studies of photoexcited carrier dynamics in nc-Si:H as a function of its composition, and we find that the fast optical response can be understood in terms of contributions from each of the separate phases in the material.

MATERIALS

Thin film nc-Si:H samples were grown by the hot-wire assisted chemical vapor deposition (HWCVD) technique, and the composition of the films was controlled by variation of the hydrogen dilution ratio $R = H_2 / SiH_4$ during deposition. The films were deposited at a substrate temperature of 240 °C on Corning 7059 glass, and the hydrogen dilution ratio was varied at a gas pressure of 30 mTorr. X-ray diffraction measurements indicate that the threshold for the transition from amorphous to nanocrystalline growth occurs at a dilution ratio R = 3. For R > 3, the average crystallite size is greater than 10 nm, and the x-ray measurements, together with Raman measurements, show that both the grain size and the crystalline fraction increase with R. Since the average grain size in all samples is larger than the threshold of ~ 5 nm for quantum confinement effects in silicon, bulk-like properties may be expected in the crystalline grain regions. All of the nc-Si:H samples show nearly identical optical absorption spectra, with a monotonic increase over the measured range of 0.8 to 2.0 eV [1]. We note that similar materials have sometimes been referred to in the literature as microcrystalline silicon (μc-Si); here we use the designation nc-Si, since this more accurately reflects the size scale of the crystalline inclusions.

EXPERIMENT

Time-resolved measurements of the carrier dynamics were carried out using a femtosecond pump-probe technique, in which a short pump pulse excites carriers in the sample and a time-delayed probe pulse measures the resulting change in transmission as a function of the pump-probe delay time. 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. Variable-wavelength probe pulses were produced by using a portion of the amplified 800-nm beam to generate a femtosecond white light continuum, and the near-infrared components of the continuum were compressed using a fused-silica prism delay line to give an overall time resolution of ~ 40 fs in the pump-probe measurements. Wavelength resolution was achieved by spectrally filtering the probe beam with a 10-nm bandwidth interference filter after it had been transmitted through the sample.

For this study, all measurements were carried out at room temperature and with mutually perpendicular pump and probe polarizations. Since the dynamics of the photoexcited carriers depend on excitation density, the relative pump and probe spot sizes were chosen to minimize distortion of the measured pump-probe response by spatial inhomogeneity of the excited carrier distribution. Care was also taken to minimize distortion of the measured pump-probe response by thin-film interference effects [2].

RESULTS

Measurements of the time-resolved change in transmission following excitation at 1.55 eV for a series of nc-Si:H films are displayed in Figures 1-3. The data are presented as the negative of the differential transmittance, corresponding to a net induced absorbance signal that results from the photoexcited carrier population. In all cases, the carrier response was probed at a detection wavelength of 940 nm (1.32 eV). 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 analysis of the population dynamics.

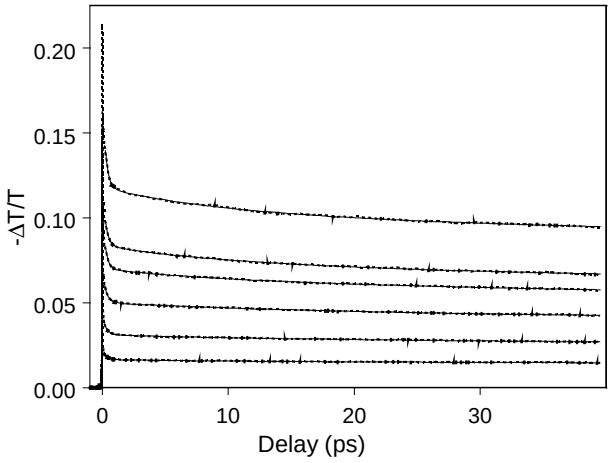

Figure 1. Time-resolved negative differential transmittance of a nc-Si:H thin film with dilution ratio R = 4. The data traces correspond to initial carrier densities of approximately 2.4 x 10^{19} cm^{-3}, 1.8 x 10^{19} cm^{-3}, 1.5 x 10^{19} cm^{-3}, 1.2 x 10^{19} cm^{-3}, 9.0 x 10^{18} cm^{-3}, and 6.0 x 10^{18} cm^{-3}. The solid lines correspond to fits to the multi-component model described in the text.

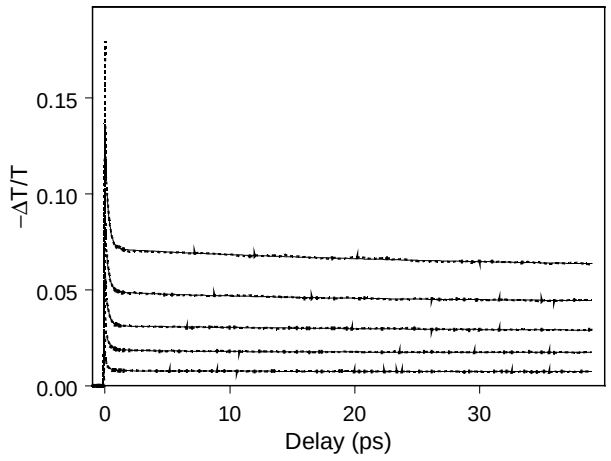

Figure 2. Time-resolved negative differential transmittance of a nc-Si:H thin film with dilution ratio R = 5. The data traces correspond to initial carrier densities of approximately 1.5 x 10^{19} cm^{-3}, 1.2 x 10^{19} cm^{-3}, 9.0 x 10^{18} cm^{-3}, 6.0 x 10^{18} cm^{-3}, and 3.0 x 10^{18} cm^{-3}. The solid lines correspond to fits to the multi-component model described in the text.

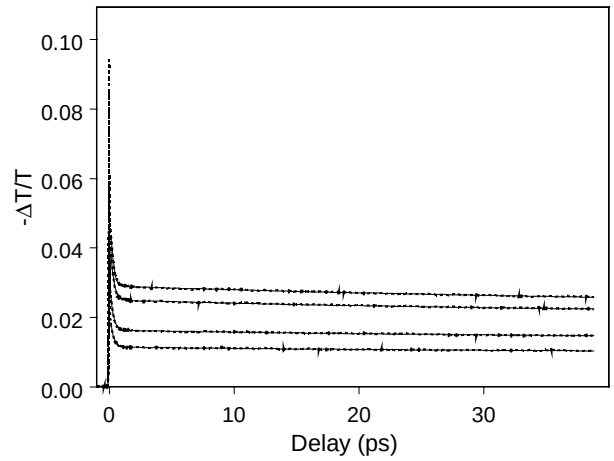

Figure 3. Time-resolved negative differential transmittance of a nc-Si:H thin film with dilution ratio R = 10. The data traces correspond to initial carrier densities of approximately 1.8 x 10^{19} cm^{-3}, 1.5 x 10^{19} cm^{-3}, 1.2 x 10^{19} cm^{-3}, and 9.0 x 10^{18} cm^{-3}. The solid lines correspond to fits to the multi-component model described in the text.

DISCUSSION

In the small signal limit, the differential transmittance measurements are expected to be proportional to the photoinduced carrier population, and the data are fit to a multi-component expression:

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

This form for the time-dependent signal corresponds physically to three separate components: a population that undergoes a simple exponential decay with time constant τ, 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. Fits to this expression are shown superposed on the data traces in Figs. 1-3, and it can be seen that this functional form provides an excellent representation of the response.

The fits to Eqn. (1) allow the ultrafast photoexcited carrier dynamics in nc-Si:H to be understood in terms of contributions from each of the component phases of this heterogeneous material. The exponential decay component fits to a time constant $\tau \sim 240$ fs in all of the materials studied here. This temporal response corresponds to the time scale for intraband carrier relaxation in crystalline silicon [3], and the relative amplitude of the component increases with dilution ratio R, indicating that this part of the observed signal originates in the crystalline phase of the material. The second term in Eqn. (1) represents the time dependence of a carrier population that undergoes bimolecular recombination, giving rise to a decay rate that depends on excitation density. The resulting value of the bimolecular recombination constant k is consistent

with that determined using a straightforward rate equation analysis in previous studies of a-Si:H and related materials [4-7]. Although the detailed nature of the relaxation processes in these materials is still under discussion [see, for example, Refs. 6-8], the correspondence with the characteristic response of a-Si:H indicates that the excitation-density-dependent portion of the nc-Si:H response originates from the amorphous fraction of the material, and the relative amplitude of this response varies appropriately with dilution ratio R. The constant *c* in Eqn. (1) corresponds to a component that decays slowly on the measured time scale, effectively giving rise to a constant offset on a picosecond time scale. This component may include a contribution from lattice heating due to energy relaxation of the photoexcited carriers, but given its amplitude, it likely also includes contributions from long-lived carrier states associated with the grain boundary regions.

CONCLUSIONS

We have studied the dynamics of photoexcited carriers in HWCVD nc-Si:H films of varying composition, and find that the carrier processes can be understood in terms of contributions from each of the separate phases in the material. In particular, nc-Si:H exhibits a fast optical response distinct from that observed in a-Si:H as a result of the fast carrier relaxation response associated with the silicon crystallites.

ACKNOWLEDGMENTS

This work was supported by a subcontract from the US Department of Energy National Renewable Energy Laboratory and by the National Science Foundation Division of Materials Research.

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