Ultrafast carrier trapping in microcrystalline silicon observed in optical pump–terahertz probe measurements

P. Uhd Jepsen[a)]
Department of Molecular and Optical Physics, Universität Freiburg, Hermann-Herder-Strasse 3, D-79104 Freiburg, Germany

W. Schairer, I. H. Libon, U. Lemmer, and N. E. Hecker
Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universität München, D-80799 Munich, Germany

M. Birkholz and K. Lips
Silizium-Photovoltaik, Kekuléstrasse 5, Hahn-Meitner-Institut Berlin, D-12489 Berlin, Germany

M. Schall
Freiburg Materials Research Center (FMF), Universität Freiburg, Stefan-Meier-Strasse 19, D-79104 Freiburg, Germany

(Received 1 March 2001; accepted for publication 25 June 2001)

We report on direct evidence of ultrafast carrier dynamics displaying features on the picosecond time scale in microcrystalline silicon (μc-Si:H). The dynamics of photogenerated carriers is studied by using above-band-gap optical excitation and probing the instantaneous carrier mobility and density with a THz pulse. Within the first picoseconds after excitation, the THz transmission transients show a fast initial decay of the photoinduced absorption followed by a slower decrease due to carrier recombination. We propose that the initial fast decay in the THz transients is due to carrier capture in the trapping states. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1394953]

Microcrystalline (μc-Si:H) silicon has attracted a great deal of attention for use in photovoltaic applications,[1,2] as well as light-emitting diodes,[3] sensors,[4] and thin-film transistors.[5] It combines the properties of crystalline silicon (c-Si), currently the most important material for electronic applications, with those of low-cost thin-film technology, which makes it attractive for large-area applications. For each of the applications mentioned, knowledge of charge carrier dynamics is of vital interest for improving the efficiency of the devices. It can be expected that carrier dynamics depends strongly on the material properties, which are influenced by the deposition technique, deposition temperature, grain size, crystallinity, and other aspects of sample preparation. Very few results are found in the literature that treat the dynamics of carriers in μc-Si:H on a subpicosecond time scale.[6]

μc-Si:H is a heterogeneous material consisting of small crystallites with sizes in the range of 10–15 nm. These nanocrystals form columns which have a diameter of, typically, 100–200 nm, and tend to grow perpendicularly to the surface.[7,8] At the surface of the columns and at the boundaries between crystallites trapping centers such as dangling bonds or tail states can exist that strongly influence the carrier dynamics of the material.[9–11]

In this letter, we report on optical pump/THz probe experiments that allow us to monitor the temporal evolution of the charge carrier density on a time scale down to 300 fs. The experiments are carried out in a nominally undoped μc-Si:H sample. Because the THz photon energy is so low (1 THz=4.1 meV), resonant processes such as interband absorption do not play a role, and absorption is, in this case, mainly due to mobile electrons.

The measurements presented in this letter were performed with a transient terahertz time-domain spectrometer (THz TDS), which is described in Ref. 12. The spot size of the THz beam on the sample is approximately 2 mm. The sample is mounted in an 8-mm-diam aperture placed at a 45° angle with respect to the THz beam axis, and is optically excited with a 100 fs laser pulse at the back surface with respect to the THz beam propagation direction. The μc-Si:H layer faces the optical excitation beam.

In the present work, we are interested in the temporal development of the frequency-integrated THz transmission through the sample subsequent to optical excitation of charge carriers. The experimental data reported here were obtained by monitoring changes of the peak field strength of the transmitted THz pulse at different excitation powers. At the peak of the THz pulse, all frequencies within the bandwidth of the pulse are approximately in phase. Therefore, the transmission of the peak represents a measure of the average transmission through the sample within the bandwidth of the detected THz pulse.

Thin-film μc-Si:H samples were prepared on quartz glass by electron-cyclotron resonance (ECR) plasma-enhanced chemical-vapor deposition (PECVD) from silane–hydrogen mixtures. The sample investigated in this work was deposited at a rate of 17.5 nm/min at a temperature of 475 °C for a total thickness of 2.1 μm. The sample consists of an initial 20–50-nm-thick amorphous-silicon (α-Si) layer,[13] followed by the dominating μc-Si:H portion, and finally, a

[a)]Electronic mail: jepsen@uni-freiburg.de

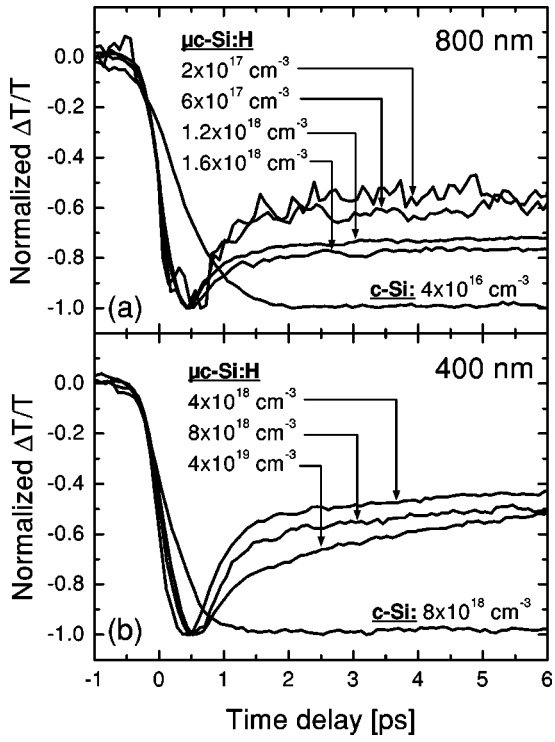

FIG. 1. Normalized THz transmission transients obtained subsequent to (a) 800 nm and (b) 400 nm excitation. Transients recorded on c-Si are shown for comparison. Excitation densities are indicated with arrows in the figure.

natural surface oxide layer of less than 5 nm thickness. The thin α-Si and oxide layers surrounding the μc-Si:H layer may play a significant role in the trapping behavior of the photoexcited carriers.

Excitation experiments were carried out at 400 and 800 nm, respectively. For comparison, transients were also taken on a high resistivity ($\rho = 10\,\mathrm{k}\Omega$ cm) 2-mm-thick silicon wafer. Both photon energies were sufficient to induce indirect optical transitions in Si (indirect band gap, 1.1 eV). THz transmission transients were taken at room temperature with different excitation fluences to investigate carrier density dependent variations in the THz transmission.

The THz transmission transients, normalized to the maximum transmission change, are shown in Figs. 1(a) and 1(b) for 800 and 400 nm excitation wavelengths, respectively. Normalized THz transmission transients recorded on c-Si are also shown. The initial carrier densities indicated in Figs. 1(a) and 1(b) are estimated from the photon fluence and optical penetration depths [$\delta \approx 10\,\mu$m at 800 nm, $\delta \approx 0.1\,\mu$m at 400 nm in crystalline Si (Ref. 14)].

After the initial decrease in transmission at $t=0$ due to photoinjection of carriers, the transients recover, representing a combination of changes in mobility and carrier concentration. We interpret the initial decrease of $\Delta T/T$ immediately following excitation as the result of thermalization of the carriers on a time scale less than the temporal resolution of the experiment. At $t > 0.5$ ps, the dynamics of the THz transients is controlled by recombination and trapping of the thermalized carriers. It is clear from Fig. 1 that the dynamics depends strongly on the initial carrier concentration.

We propose that the fast transmission recovery observed in the measured THz transients for the μc-Si:H sample is due to the trapping of the photoexcited carriers since mainly free carriers contribute to THz absorption. This interpretation is strengthened by the conclusions of the work by Prabhu *et al.*,[15] who used a similar technique to study carrier dynamics subsequent to photoexcitation in low-temperature-grown GaAs.

The following observations support our interpretation that ultrafast trapping accounts for the main characteristics of the transmission transients. Both for 800 and 400 nm excitation, we observe a reduced recovery of the transient as the excitation fluence is increased. The overall recovery behavior for both excitation wavelengths may be accounted for by an inhomogeneous distribution of trapping sites in the sample, with low trap site density in the μc-Si:H layer and a high trap density in the surface oxide layer and in the α-Si layer at the glass/Si interface. In the case of 800 nm excitation the sample is nearly homogeneously excited, and the effective trap site density is relatively low, effectively on the order of $10^{17}\,\mathrm{cm}^{-3}$, judging from the recovery saturation at lowest fluences in Fig. 1(a). A fast intrinsic trapping time (<1 ps) may account for the initial fast recovery at $t<2$ ps. As the excitation fluence is increased, the available trapping sites fill up, leaving only recombination as a drain for the charge carriers. The result is a slower recovery and a saturation at larger values of $|\Delta T/T|$. In the case of 400 nm excitation the optical penetration depth is much shorter. Because of the proximity of the surface oxide layer we, therefore, expect that the carrier dynamics is dominated by a higher local trap density. In this case, diffusion of carriers may also play a role. Typical column mobilities of electrons in μc-Si:H are of the order of $10^2 - 10^3\,\mathrm{cm}^2/\mathrm{V\,s}$,[9] which allows carriers within the 100-nm-thick excited layer either to diffuse to the surface where the trap density is high or into the μc-Si:H layer with a lower trap density on a picosecond time scale. This process may account for the recovery behavior observed at the highest carrier densities in Fig. 1(b). Here, the recovery does not saturate at a constant level as is seen in Fig. 1(a), instead we observe a gradual decrease in $|\Delta T/T|$ which is still much faster than the recombination time.

The results presented here alone will not allow us to determine the nature and spatial distribution of traps in the μc-Si:H film. However, pulsed electron spin resonance experiments on similar μc-Si:H samples[16] has distinguished several defect states which may be responsible for the fast THz transmission recovery. Among them are dangling bonds that provide states in the center of the band gap as well as valence- and conduction-band tail states.[9–11]

A simple model which includes saturable traps located near the conduction band in the band gap can reproduce the general tendencies which we observed for the temporal evolution of the THz transmission of the μc-Si:H sample. Assuming that the THz absorption is proportional to the number of free carriers times their mobility, and that the trapping time τ_{trap} is dependent on the number of available identical traps N_{trap} such that

$$\tau_{\mathrm{trap}} = \frac{\tau_{\mathrm{trap,max}}}{1 - N_{\mathrm{trap}}/N_{\mathrm{trap,max}}}, \tag{1}$$

the carrier dynamics can be modeled by the following set of rate equations:

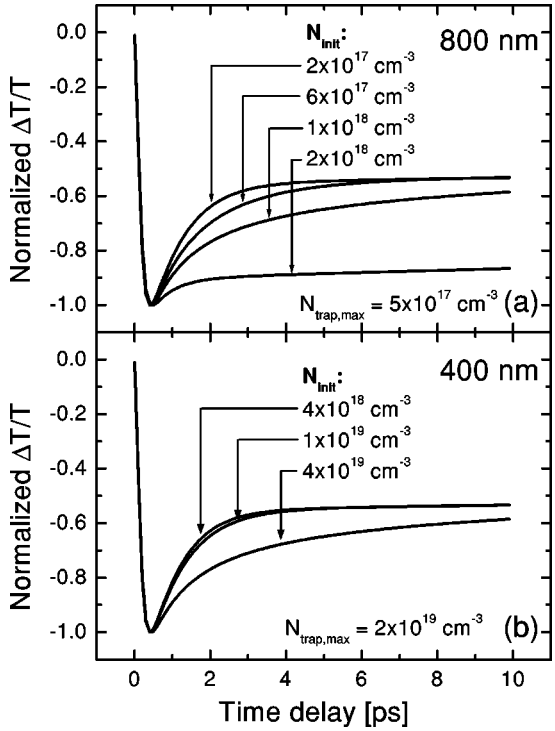

FIG. 2. (a) Numerically calculated transients using parameters as in Fig. 1(a) for 800 nm excitation, and (b) parameters as in Fig. 1(b) for 400 nm excitation.

$$\dot{N}_1 = G(t) - N_1/\tau_{\mathrm{cool}}, \tag{2}$$

$$\dot{N}_0 = N_1/\tau_{\mathrm{cool}} - N_0/\tau_{\mathrm{trap}} - N_0/\tau_{\mathrm{rec}}, \tag{3}$$

$$\dot{N}_{\mathrm{trap}} = N_0/\tau_{\mathrm{trap}} - N_{\mathrm{trap}}/\tau_{\mathrm{rec}}, \tag{4}$$

where N_1 is the density of hot carriers, N_0 is the density of carriers in the conduction-band minimum, N_{trap} is the density of carriers in trap states, $G(t)$ is the generation rate given by the excitation pulse, τ_{cool} is the carrier relaxation time, τ_{trap} is the carrier trapping time, and τ_{rec} is the band-to-band carrier recombination time.

The results of the numerical calculations are shown in Fig. 2. While this simple model reproduces the very fast decay of the THz absorption and saturation of the recovery, it does not quantitatively reproduce the data. This is most likely due to our oversimplification of identical values of τ_{trap} for all traps, a constant trap density throughout the sample, and the exclusion of diffusion processes. Nevertheless, with realistic values $\tau_{\mathrm{trap}} = 0.7\,\mathrm{ps}$ and $N_{\mathrm{trap,max}} = 5\times10^{17}$ and $2\times10^{18}\,\mathrm{cm}^{-3}$ for 800 and 400 nm data, respectively, the shape of the THz transients can be qualitatively reproduced. The level at which the transients saturate at late times is determined by the degree of trap filling and, hence, the amount of remaining mobile carriers.

Based on our experimental and numerical results, we attribute the fast initial THz transmission recovery to ultrafast trapping of carriers. Variation of the wavelength, i.e., absorption length within the sample, indicates that the μc-Si:H film exhibits depth dependent electronic properties which are manifest in the measured THz transmission transients. Interestingly, the dynamics that we observe within the first picoseconds after excitation was not observed in earlier pump–probe measurements utilizing visible and near-IR pulses on μc-Si:H.[6] While differences in the measured samples cannot be excluded as a reason for the differences, pump–probe measurements with visible/near-IR pulses rely on electronic excitation of carriers from any given state in order to induce an absorption change. Hence, it is not expected *a priori* that it is possible to distinguish between carriers at the conduction-band minimum from carriers in trap states in the band gap. A THz probe, in contrast, is sensitive to the carrier density and mobility. It should not be surprising that these two types of experiments do not show the same results. Therefore, optical pump–THz probe studies may be a useful alternative approach for elucidating the trapping process in μc-Si:H and other materials where trapping plays a role.

The authors thank E. Conrad for technical assistance with the deposition of the μc-Si:H samples, and J. Feldmann for stimulating the work on this project. Two of the authors (P.U.J. and M.S.) acknowledge support from the Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 276, TP C14.

[1] O. Vetterl, P. Hapke, O. Kluth, A. Lambertz, S. Wieder, B. Rech, F. Finger, and H. Wagner, Solid State Phenom. **67-68**, 101 (1999).
[2] H. Keppner, J. Meier, P. Torres, D. Fischer, and A. Shah, Appl. Phys. A: Mater. Sci. Process. **69**, 169 (1999).
[3] T. Fugati, T. Matsumoto, M. Katsuno, Y. Otha, H. Mimura, and K. Kitamura, Appl. Phys. Lett. **63**, 1209 (1993).
[4] M. Vieira, E. Morgado, A. Macarico, S. Koynov, and R. Schwarz, Vacuum **52**, 67 (1999).
[5] P. Roca i Cabarrocas, R. Bernot, P. Bulkin, R. Vanderhagen, B. Drévillon, and I. French, J. Appl. Phys. **86**, 7079 (1999).
[6] J. Kudrna, P. Malý, F. Trojánek, J. Štěpánek, T. Lechner, I. Pelant, J. Meier, and U. Kroll, Mater. Sci. Eng., B **69-70**, 238 (2000).
[7] G. Willeke, in *Amorphous and Microcrystalline Semiconductor Devices*, edited by J. Kanicki (Artech House, London, 1991), p. 55.
[8] M. Luysberg, P. Hapke, R. Carius, and F. Finger, Philos. Mag. A **75**, 31 (1997).
[9] S. Brehme, P. Kanschat, K. Lips, I. Sieber, and W. Fuhs, Mater. Sci. Eng., B **69-70**, 232 (2000).
[10] S. Brehme, P. Kanschat, T. Weis, K. Lips, and W. Fuhs, in *Polycrystalline Semiconductors VI—Bulk Materials, Thin Films, and Devices*, Solid State Phenomena Series, edited by O. Bonnaud, T. Mohammed-Brahim, H. P. Strunk, and J. H. Werner (Scitech, Uettikon am See, in press).
[11] W. Fuhs, P. Kanschat, and K. Lips, J. Vac. Sci. Technol. B **18**, 1792 (2000).
[12] M. Schall and P. Uhd Jepsen, Opt. Lett. **25**, 13 (2000).
[13] M. Birkholz, B. Selle, E. Conrad, K. Lips, and W. Fuhs, J. Appl. Phys. **88**, 4376 (2000).
[14] S. M. Sze, *Semiconductor Devices: Physics and Technology* (Wiley, New York, 1985), p. 257.
[15] S. S. Prabhu, S. E. Ralph, M. R. Melloch, and E. S. Harmon, Appl. Phys. Lett. **70**, 2419 (1997).
[16] P. Kanschat, H. Mell, K. Lips, and W. Fuhs, Mater. Res. Soc. Symp. Proc. **609**, A27.3 (2000).