

# Ultrafast carrier dynamics in undoped microcrystalline silicon

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## Abstract

We have studied ultrafast dynamics of photoexcited carriers in  $\mu\text{-Si:H}$  by pump and probe laser spectroscopy. We have found that the dynamics of photoexcited carriers in  $\mu\text{-Si:H}$  depend on the crystallinity of the material: in the samples with low crystalline fraction, the dynamics have a fast decay and resemble those in  $\text{a-Si:H}$ , while in the samples with high crystallinity the dynamics are slower and similar to those in  $\text{c-Si}$ . We have identified an intensity dependent bimolecular recombination in the samples with lower crystalline fraction (coefficient  $B = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for deposition with silane dilution ratio  $\approx 5\%$  at a fixed power of 6 W), and no bimolecular recombination in the samples with high crystallinity.

*Keywords:* Hydrogenated microcrystalline silicon; Ultrafast laser spectroscopy; Bimolecular recombination

## 1. Introduction

Hydrogenated microcrystalline silicon ( $\mu\text{-Si:H}$ ) [1] has attracted attention as very promising material for solar cells, thin film transistors, sensors and light emitting diodes [2]. Two properties make it superior to hydrogenated amorphous silicon ( $\text{a-Si:H}$ ), namely the enhanced light absorption in the infrared spectral region and the absence of light-induced degradation. For  $\mu\text{-Si:H}$  p-i-n solar cells stable efficiencies greater than 8.5% and in multijunction cells greater than 11% have been reported recently [2,3]. The investigation of basic physical processes in this material is still in progress. In particular, the correlation between the structure and the optical and electrical properties of the material is studied by variety of experimental techniques [2–8]. Most often the correlation between the crystalline volume fraction and the material properties is investigated. Ultrafast laser spectroscopy is a well-established tool that provides direct information on ultrafast relaxation and recombination processes in both crystalline and amorphous semiconductors. However, to our knowledge, the time-resolved optical measurements in  $\mu\text{-Si:H}$

have not yet been published.

The recombination dynamics of photoexcited carriers in  $\text{a-Si:H}$  have been extensively investigated [9–12] by a variety of techniques of time-resolved laser spectroscopy. From a number of results of pump and probe measurements, a general picture emerged [10–12]: The carrier recombination dynamics are insensitive to the pump intensities (monomolecular recombination) for injected carrier densities  $\leq 10^{17} \text{ cm}^{-3}$  per pump pulse, and they can be described well in terms of a multiple trapping model. At very high-injected carrier densities ( $\geq 10^{20} \text{ cm}^{-3}$ ) the decay rate is intensity dependent in a rather complicated way which can be understood in the framework of a plasma model. At intermediate pump intensities the recombination dynamics follow the bimolecular law, i.e. the effective decay time is inversely proportional to the injected carrier concentration. Unlike direct-gap semiconductors, the bimolecular recombination in  $\text{a-Si:H}$  is likely to be a nonradiative process [10–12], its microscopic origin being still uncertain. The bimolecular recombination has been argued to be a cause of the Staebler–Wronsky effect in  $\text{a-Si:H}$  [7,11]. Ultrafast carrier recombination in  $\text{c-Si}$  has been studied in detail [13]. Silicon, being an indirect semiconductor, has a very low value of the bimolecular coefficient and the lifetime is shortened by the nonradiative Auger process at high excitation levels.

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In this paper, we demonstrate that the dynamics of photoexcited carriers in  $\mu\text{-Si:H}$  reflect, in accordance with intuitive expectation, the degree of crystallinity of the material.

## 2. Experimental

The samples were deposited by the very high frequency glow discharge (VHF-GD) deposition technique at a plasma excitation frequency of 110 MHz using a gas purifier. The ratio of silane in total gas flow  $[\text{SiH}_4]/[\text{SiH}_4 + \text{H}_2]$  was varied between 1.25 and 7.5% keeping a fixed power of 6 W. The layer thicknesses are 1.6–2.3  $\mu\text{m}$ . We label the samples by dilution ratio 1.25, 2.5, 5, 4.5, 7.5%. The absorption spectra of the samples were studied previously [6]. We have characterized also the samples by Raman spectroscopy as shown below.

The ultrafast dynamics of differential absorption were measured by a standard pump and probe technique where the transmission of the probe pulse is measured at particular delay after the pump pulse. The time delay between the pump and probe pulses was varied using an optical delay line. In the picosecond measurements, the pump pulses with the wavelength of 532 nm were used (33 ps, pulse energy  $\approx 10 \text{ mJ cm}^{-2}$ ). The absorption changes were probed at 1064 nm and 1280 nm (probe-pulse energy  $< 0.1 \text{ mJ cm}^{-2}$ ). The latter wavelength was obtained by parametric generation in KDP crystal pumped by 532 nm picosecond pulses. The diameters of the pump and the probe beams

in the sample were 0.5 mm and 0.05 mm, respectively. Their mutual angle was  $\approx 8^\circ$ . The repetition rate of pulses was 1 Hz. In the femtosecond measurements the pump pulses at 430 nm and the probe pulses at 860 nm with the time widths of  $\approx 100 \text{ fs}$  were used. The source of femtosecond pulses (repetition rate 82 MHz) was the femtosecond titanium sapphire laser (Spectra-Physics Tsunami) and BBO frequency doubler. Pump and probe beams with the average power of 40 and 10 mW, respectively, were focused by a single lens on the surface of the sample under an angle of  $\approx 5^\circ$ . The pump beam was chopped at 1 kHz, a lock-in detection was used to measure the modulated part of the probe beam. The maximum estimated photocarrier density was  $10^{18}$  and  $10^{20} \text{ cm}^{-3}$  in femtosecond and picosecond measurements, respectively. All measurements were done at room temperature.

## 3. Results and discussion

We show the results obtained on five samples of  $\mu\text{-Si:H}$  which differ in their crystallinity. In order to demonstrate clearly the differences in crystallinity between the samples we show Raman spectra of the samples studied in Fig. 1. We apply a frequently used procedure [4] to measure the crystallinity by the ratio of the Raman scattering intensity at  $\approx 520 \text{ cm}^{-1}$  to that at  $\approx 480 \text{ cm}^{-1}$ . Omitting the more elaborate way of obtaining the intensities — as the areas of several fitted Gaussian bands [4] — we have taken simply the ratio of the peak values at both wavelengths to demonstrate increasing crystalline fraction with decreasing dilution (see caption of Fig. 1). We will show in the following that different crystallinity of the samples is reflected in different dynamics of photoexcited carriers.

We report on results of measurements of transient absorption with picosecond and femtosecond time resolution. In the measurements the change in transmission of the sample is monitored by the probe pulses. In general, the change in the probe intensity is connected with a change of the complex index of refraction, i.e. both with the real index of refraction which produces a change in reflectivity and with the absorption inside sample. In analogy with measurements of silicon samples of other morphology (e.g. a-Si:H, porous silicon), we associate the measured changes of the probe pulse energy with absorption, the changes due to the reflection being at least one order of magnitude smaller [10,14]. The transmission  $T_E$  ( $T_0$ ) of the sample after (without) the pump illumination monitored by the probe pulse, are connected with the relevant absorbancies  $A_E$  or  $A_0$  as  $T_{E,0} = \exp(-A_{E,0})$ . The differential absorbance  $A_D$  is given as  $A_D = A_E - A_0$ .

The absorption connected with the excited carriers, i.e. excited state absorption, leads to the positive differ-

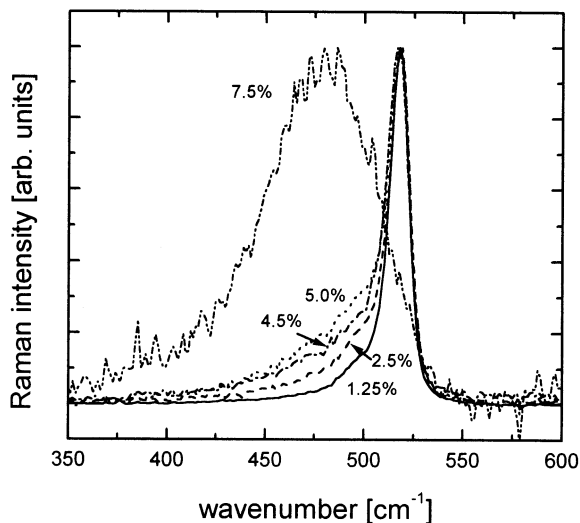


Fig. 1. Normalized Raman spectra of the studied samples grown at various silane dilution ratio at fixed power of 6 W. The crystallinity of the samples can be characterized by the ratio  $I_c/I_a$  of the Raman intensity at  $\approx 520 \text{ cm}^{-1}$  to that at  $\approx 480 \text{ cm}^{-1}$ . The values obtained from the figure are:  $I_c/I_a = 0.36$  (dilution ratio 7.5%), 5.3 (5%), 6.6 (4.5%), 9.5 (2.5%), and 21.3 (1.25%).

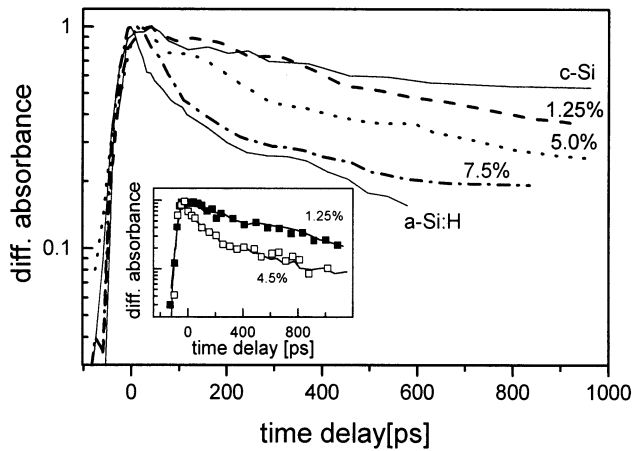


Fig. 2. Dynamics of the differential absorbance at 1064 nm of samples excited by a 532-nm picosecond pulses. The normalized curves correspond (from the top) to c-Si, to samples with dilution ratio 1.25, 5, 7.5%, and to a-Si:H. *Inset*: Comparison of normalized dynamics of differential absorbance at 1064 nm (solid curves) and 1280 nm (squares) for samples with dilution ratio 1.25 and 4.5%.

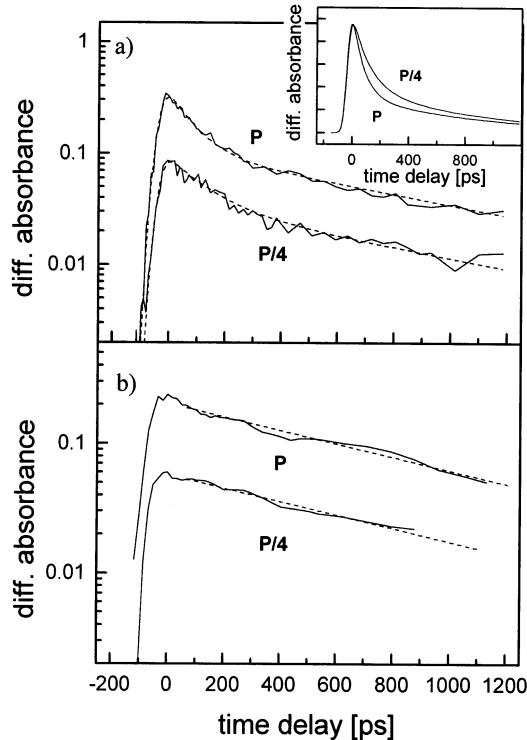


Fig. 3. Dynamics of the differential absorbance at 1064 nm excited by a 532-nm picosecond pulse. (a) Sample with 4.5% silane dilution. The dashed curve for a pump rate  $P$  is the best fit according to the model proposed, the dashed curve for  $P/4$  is computed without any adjustable parameter. *Inset*: The dashed curves from (a), displayed normalized in a linear scale. (b) Sample with 1.25% silane dilution. The dashed curves are monoexponential decay functions with time constant of 850 ps.

ential absorbance, on the contrary, the change of the occupancy of the upper and lower states due to the

excitation of carriers across the gap results in the negative differential absorbance (absorption bleaching). Our results indicate a positive differential absorbance. This can be understood recalling the fact that  $\mu\text{-Si:H}$  is basically composed of a-Si:H and c-Si. In both materials an induced absorption is observed at given wavelengths: the probe photon energy is below absorption edge in case of a-Si:H (in fact this is a standard wavelength configuration for ultrafast investigations of a-Si:H [9]), and negligible effect of bleaching can be observed in c-Si due to the fact that it is an indirect semiconductor [13]. Observing the excited state absorption we can neglect the thermal effects on measured dependencies [14].

In Fig. 2, the results of pump and probe measurements with picosecond pulses are shown. The samples were excited by single 35-ps pulses with the wavelength of 532 nm well above the absorption edge. The absorption changes were monitored by a probe pulse at 1064 nm. An increase in the absorption connected with excited state absorption is observed. In order to verify the negligible effect of possible bleaching connected with below-gap states matching 1064 nm absorption, we used also the probe pulses with the wavelength of 1280 nm. The time dependence of differential absorbance is identical for 1064 and 1280 nm probe as shown in the inset of Fig. 2 for two samples. From Fig. 2 it is clear that the overall decay rate of differential absorbance in  $\mu\text{-Si:H}$  gets faster with decreasing crystalline fraction of silicon (cf. Fig. 1). For comparison, also the results of measurements under the same experimental conditions in c-Si and a-Si:H are shown in Fig. 2, illustrating the fact, that the decay rates of differential absorbance lie between those of c-Si (slow) and a-Si:H (fast). In semilog scale used one can observe also an exponential character of the decay for samples with high crystalline fraction, and a nonexponential decay for more amorphous samples.

We have studied also the role of the pump intensity on the dynamics of differential absorbance. The dynamics of the samples with high and lower crystalline fractions for two pump intensity levels are displayed in Fig. 3. The dynamics of the sample with high crystalline fraction (Fig. 3b) have the decay rate independent of the pump intensity, which is consistent with its monoexponential character. The dashed straight lines in Fig. 3b are the monoexponential fits with the decay constant of 850 ps. On the contrary, the decay gets faster with increasing pump intensity in the sample with smaller crystalline fraction (Fig. 3a). The decay is clearly nonexponential and the effective decay time decreases with the pump intensity which can be seen in the inset of Fig. 3a where the two dashed curves from Fig. 3a are normalized and plotted in a linear scale.

Before discussing the dynamics of  $\mu\text{-Si:H}$  we would like to comment on the carrier dynamics of c-Si and

a-Si:H. In c-Si under strong picosecond pumping the recombination of carriers is dominated by the Auger recombination (the Auger constant of  $4 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$  leads to the initial decay time of 25 ns for photoexcited carrier density of  $10^{19} \text{ cm}^{-3}$ , the bimolecular recombination results in microsecond decay constants due to rather small value of the coefficient of bimolecular recombination  $B = 2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ) [13]. In a-Si:H, the recombination at photocarrier densities exceeding  $5 \times 10^{18} \text{ cm}^{-3}$  the bimolecular recombination is the major mechanism of recombination of photoexcited carriers. The values of relevant coefficient  $B$  reported range between  $7 \times 10^{-10}$  [15] and  $7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  [16]. On the basis of femtosecond measurements an even higher value of this constant was found [10].

The dynamics of differential absorbance in  $\mu\text{c-Si:H}$  with lower crystalline fraction (e.g. 7.5% sample or 4.5% sample) have some features of dynamics in a-Si:H, namely the decay rate is pump-dependent. Similarly as in a-Si:H, the dynamics can be interpreted in terms of a bimolecular recombination process. We discuss in detail the results obtained on the sample with 4.5% dilution ratio. In Fig. 3a, the dashed curve for a pump rate  $P$  is the best fit according to the rate equation model including the bimolecular recombination. The dashed curve for  $P/4$  is computed without any adjustable parameters using the best-fit values of the fit for  $P$ . Our model is described in detail in [14] where we used it for a-Si:H. The rate equation for photoexcited carrier density  $N$  includes a quadratic (bimolecular) term  $\approx -BN^2$  and a linear term  $\approx -N/\tau$ . We have obtained the value of excited state absorption cross-section  $\sigma = 8 \times 10^{-18} \text{ cm}^2$ , the decay constant of linear decay  $\tau = 900 \text{ ps}$  and the bimolecular coefficient  $B = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . The value of excited state absorption cross-section agrees well with those at 1064 nm found in c-Si ( $\sigma = 5 \times 10^{-18}$

$\text{cm}^2$  [13]) and a-Si:H ( $\sigma = 3 \times 10^{-18} \text{ cm}^2$  [9]). The value of the decay constant  $\tau$  agrees very well with that in Fig. 3b and is comparable with that found in a-Si:H [14], but its value from present measurement has a low precision due to the short interval of the measurement. The value of bimolecular recombination constant is smaller than those found in a-Si:H (see above) and agrees very well with value found on basis of transport measurements in  $\mu\text{c-Si:H}$  [7].

The dynamics of the samples with higher crystalline fraction have apparently no features of bimolecular recombination. The  $\mu\text{c-Si:H}$  can be understood as composite of silicon crystallites with typical dimensions 10–100 nm in the a-Si:H host [4,8]. On this basis one could expect that the dynamics of excited carriers — to the first approximation — can be interpreted as a mixture of dynamics in c-Si and in a-Si:H with the relative weights corresponding to the ratio of relevant fractions. Our data shown above suggest that this is really the case. However, using entirely this model we should expect the bimolecular recombination to be apparent in all the samples with the same coefficient as in a-Si:H. The smaller value of bimolecular coefficient and apparent absence of bimolecular recombination in samples with higher crystallinity can be explained by capture of carriers into Si crystallites [4]. The recombination of carriers in crystallites should be similar to that in bulk c-Si, though modified by the presence of surface states. The surface recombination has monomolecular character that is consistent with data in Fig. 3b.

In Fig. 4 the results of pump and probe measurements with femtosecond time resolution are shown. The absorption changes were probed by 860 nm pulses after 430-nm excitation. The dynamics of differential absorbance do not display any subpicosecond feature, their effective decay times are 25, 50 and 150 ps for samples with the dilution ratio of 7.5, 5 and 1.25%, respectively. The same trend of decay rates with crystalline fraction as in picosecond measurements is observed, that is the higher crystalline fraction means the slower decay. The 25 ps decay in sample 7.5% is in very good agreement with that found under similar experimental conditions in a-Si:H [10,12,14] where it was interpreted in terms of bimolecular recombination with higher coefficient ( $B = 2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ) [10]. Results of our femtosecond measurements indicate again the importance of relative weights of the crystalline and the amorphous fractions. More experiments are needed to detail the process of possible carrier exchange between the crystalline and amorphous fractions in  $\mu\text{c-Si:H}$ .

We have found small (in the samples with low crystalline fraction) or negligible (in the samples with high crystalline fraction) bimolecular recombination. At the same time no creation of photoinduced effects was

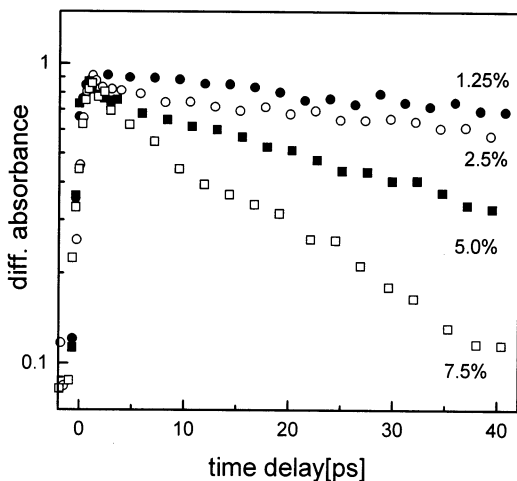


Fig. 4. Dynamics of differential absorbance measured by femtosecond pump and probe technique (probe 860 nm, pump 430 nm, pulse widths  $\approx 100 \text{ fs}$ ).

reported in  $\mu\text{-Si:H}$  [2,5]. It has been argued in literature that the bimolecular recombination of the photoexcited carriers can cause the formation of metastable light-induced defects in  $\text{a-Si:H}$  [7,11]. Our present results are consistent with this suggestion.

In conclusion, we have studied ultrafast dynamics of photoexcited carriers in  $\mu\text{-Si:H}$  by pump and probe laser spectroscopy. We have found that the dynamics of photoexcited carriers in  $\mu\text{-Si:H}$  depend on the crystallinity of the material: in the samples with low crystalline fraction, the dynamics have a fast decay and are similar to those in  $\text{a-Si:H}$ , while in the samples with high crystallinity the dynamics are slower and very much like those in  $\text{c-Si}$ . In particular, we have identified a bimolecular recombination in the samples with lower crystalline fraction (coefficient  $B = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the sample with 4.5% dilution), and no bimolecular recombination in the samples with high crystallinity.

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