

Picosecond dynamics of photoexcited carriers in free-standing porous silicon

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Abstract

We study the ultrafast dynamics of photoexcited carriers in luminescent free-standing porous silicon at room temperature using the experimental techniques of picosecond absorption and luminescence spectroscopy. Both the luminescence intensity and transient absorption signals show a fast decay on the scale of hundreds of picoseconds, followed by a slower nanosecond decay. We identify the faster signals as being due to a bimolecular recombination process in the core of Si nanocrystallites with a quasi-direct gap energy structure (bimolecular recombination coefficient of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$), while the slower component is likely to be due to recombination via surface states.

Keywords: Optical spectroscopy; Silicon

1. Introduction

Porous silicon (PS), emitting strong visible light at room temperature, is being intensively studied with the prospect of achieving all-silicon-based optoelectronics. Although successful preparations of PS-based light-emitting elements [1] and photodetectors [2] have already been reported, the very microscopic nature of radiative recombination in PS is still a matter of controversy. Further investigations of recombination processes in PS are therefore needed. Recently we reported a transmission study of the picosecond photocarrier dynamics in free-standing PS [3]. In the present paper we extend the spectral range of our investigations and include fast photoluminescence (PL) decay measurements.

2. Experimental details

The samples of free-standing PS were prepared from B-doped 1–2 $\Omega \text{ cm}$ (100) wafers. We shall concentrate on two representative samples (#2 and #36) in this paper. The wafers were electrochemically anodized in HF acid solution ($\text{HF}:\text{H}_2\text{O} = 3:1$) with current densities

of 30 mA cm^{-2} for 30 min (#2) and 50 mA cm^{-2} for 10 min (#36). The PS layers separated from the substrate were clamped between two quartz slides. The thicknesses of the samples were $26 \mu\text{m}$ (#2) and $23 \mu\text{m}$ (#36). The dynamics of differential absorption was measured by a standard pump and probe technique [3]. The pump pulses were obtained by frequency doubling of the 1064 nm Nd:YAG laser output in a KDP crystal (532 nm, 33 ps, energy $\approx 100 \text{ mJ cm}^{-2}$). The tunable probe pulses (532–1064 nm, 40 ps, energy $< 0.1 \text{ mJ cm}^{-2}$) were spectrally selected from a picosecond continuum. The dynamics of integral PL excited by 532 nm pump pulses was measured using a Hadland streak camera (time resolution of 3 ps). Continuous wave (CW) PL was excited by the 488 nm line from an Ar-ion laser. All experiments were performed at room temperature.

3. Results and discussion

Fig. 1 shows the absorption and CW PL spectra of the two representative samples. The onset of absorption of sample #36 is blue shifted compared with that of sample #2, but the maxima of PL spectra are located at the same photon energy, as observed also by others

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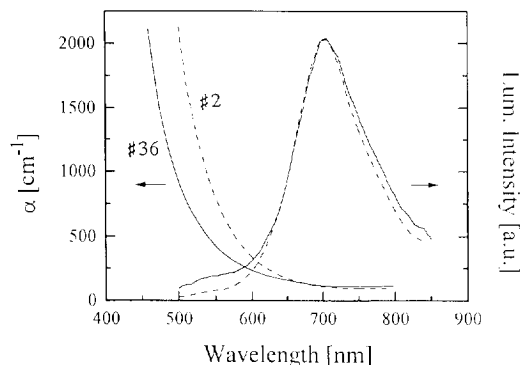


Fig. 1. Conventional absorption and photoluminescence spectra of free-standing PS layers #2 (broken curve) and #36 (full curve) at $T = 300$ K.

[4]. The differential absorbance A_D (i.e. difference between excited and unexcited absorbances) vs. time delay of both samples at the probe wavelength of 1064 nm is shown in Fig. 2, while the dynamics of the PL intensity is plotted for the same samples in Fig. 3. The full curves in Fig. 2 are theoretical fits which will be discussed later. The important observations from Figs. 2 and 3 are the following.

(i) The dynamics of both A_D and PL intensity follow approximately the same time course, i.e. transmission and emission measurements monitor identical excited states.

(ii) The dynamics of both A_D and PL have a fast and a slow component. The fast component has a decay time of the order of hundreds of picoseconds, while the slow component decay time is longer than tens of

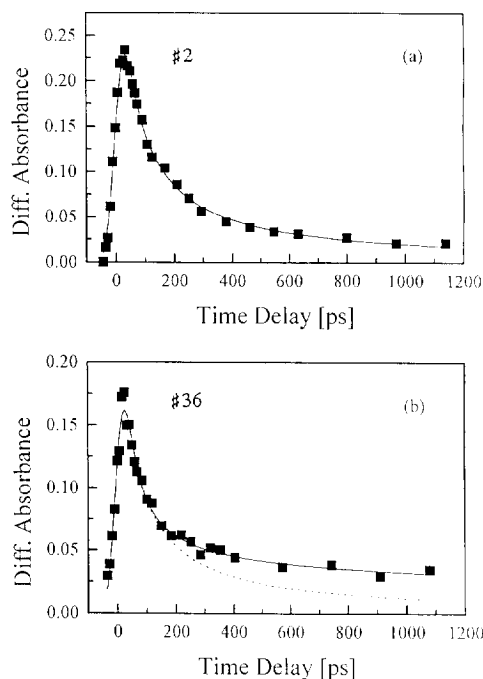


Fig. 2. Differential absorbance vs. time delay for samples (a) #2 and (b) #36. The full and broken curves are theoretical fits (see text).

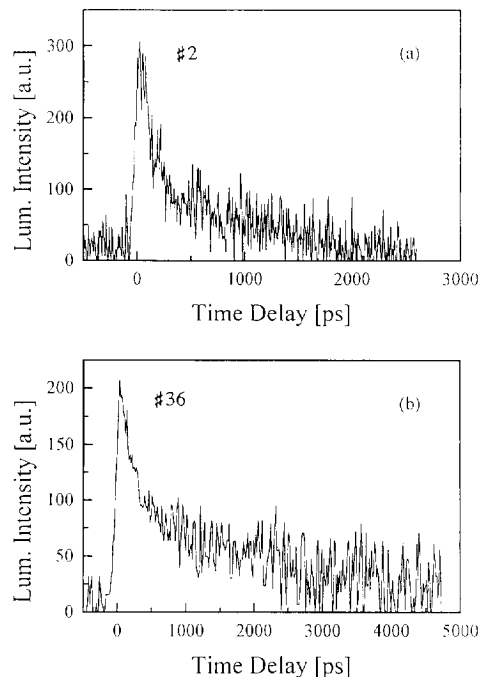


Fig. 3. Photoluminescence dynamics of samples (a) #2 and (b) #36.

nanoseconds and its detailed investigation goes beyond the time scale of our apparatus.

The relative weight of these components is sample dependent. Sample #2 is an example of a practically negligible amplitude of the slow component [3] (Figs. 2(a) and 3(a)), while sample #36 is a typical representative of a comparatively intense slow component (Figs. 2(b) and 3(b)).

In order to decide about the origins of the two components, further experiments have been done. In Fig. 4 the dynamics of A_D at wavelengths of 570 and 760 nm under the same experimental conditions are shown. At short time delays the magnitudes of the two dynamics differ considerably, while their slow components are of the same amplitude. This behaviour is also illustrated in Fig. 5, where the spectral dependence of the differential absorbance is shown. From these results

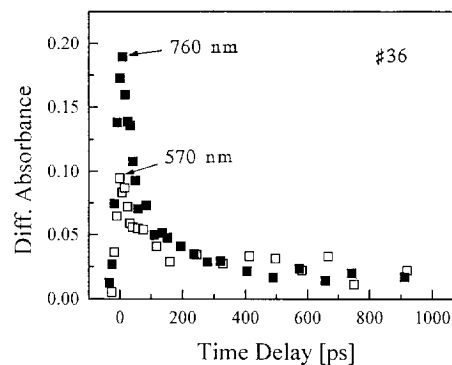


Fig. 4. Differential absorbance vs. time delay for probe wavelengths of 760 nm (full squares) and 570 nm (open squares).

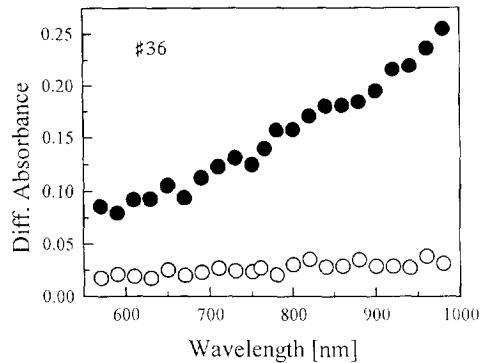


Fig. 5. Spectral dependence of differential absorbance at maximum (full circles) and at a time delay of 500 ps (open circles).

we conclude that the fast and slow components are of different origin.

In general A_D is composed of (i) a positive contribution connected with the excited state absorption and (ii) a negative contribution due to saturation of the absorption from unexcited states. In our case A_D is positive in the spectral interval studied. The conventional absorption is vanishingly small above 650 nm (Fig. 1) and therefore A_D has only a positive contribution. The spectral shape of A_D is thus given by the excited state absorption spectrum over practically the whole spectral interval studied. A simple description of the free-carrier absorption by the Drude model gives a cross-section proportional to the squared wavelength, which our data do not seem to follow. The curve in Fig. 5 should rather follow the joint density of states at relevant energies, which reflects the distribution of dimensions of silicon nanostructures.

We propose a simple model to analyse the fast dynamics of the absorption [3]. We assume that the differential absorbance is directly proportional to the instantaneous density of photoexcited carriers, $N(t)$, and is given by $A_D = CN(t)$ with $C = L\sigma$, where σ is the excited carrier cross-section and L is the length of the excited region. We further assume that carriers are excited by a gaussian pulse $P(t)$ and that they recombine by a bimolecular process with the rate constant B . The dynamics of photoexcited carriers can then be described by

$$\frac{dN(t)}{dt} = P(t) - BN(t)^2 \quad (1)$$

The solution of Eq. (1) is convoluted with the probe pulse profile and fitted by a least-squares method to the measured data. The fitting parameters are B and C . The fit of the data in Fig. 2(a) (full curve) gives $B = 4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $\sigma = 9 \times 10^{-18} \text{ cm}^2$. The same equation gives a very good fit to the data in Fig. 2(b) for small time delays (dotted curve), with the same value of B and with $\sigma = 2 \times 10^{-18} \text{ cm}^2$. The value for B corresponds well with the radiative recombination constant for direct gap semiconductors (e.g. $B = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for GaAs). However, the bimolecular

type of recombination of PS could also be of non-radiative origin as reported very recently for amorphous silicon [5], where values of the coefficient B of $(1-7) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ were found.

To discuss the origin of the slow component, let us return to Fig. 2(b). The (dotted) theoretical curve of A_D according to Eq. (1) with any value of B cannot fit the experimental data of the slow component. However, very good agreement with the experimental data can be obtained by adding a term N/τ with $\tau > 5 \text{ ns}$ into Eq. (1) (full curve in Fig. 2(b)). This underlines again the different origins of the fast and slow components. To be more specific, we recall the blue shift of the absorption edge of sample #36 in Fig. 1. This indicates a smaller average dimension of Si crystallites in sample #36 compared with sample #2, which reflects the general effect of increasing anodization current density in shifting the crystallite size distribution to smaller mean crystallite size. In crystallites of smaller dimension the surface obviously plays a more important role. Sample #36 exhibits a higher relative weight of the slow component as seen from Figs. 2 and 3. This is a clear indication of the involvement of surface states [6] in the slow emission component, though further experiments are needed to verify this assumption.

In conclusion, after photoexcitation of PS by fairly strong picosecond pulses the photocarriers recombine first on a picosecond time scale by a bimolecular process. This recombination takes place most probably in nanodimensional Si crystallites with a quasi-direct gap energy structure. The recombination process then continues on a slower time scale ($> 5 \text{ ns}$), its nature is monomolecular rather than bimolecular and it is probably related to photocarrier diffusion from the crystallite bulk to the surface.

Acknowledgements

This work was supported in part by EC Grant No. CIPA 3510CT92 7839, by Charles University Grant No. 287 and by Grant no. 202/93/0383 of the Grant Agency of the Czech Republic. The authors thank Dr. J. Kočka for valuable discussions.

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