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Carrier dynamics in porous silicon studied with a near-field heterodyne transient grating method

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Abstract

The dynamics of excited carriers in porous silicon were investigated using the near-field heterodyne transient grating method, and the fundamental processes related to light emission were determined. The processes include trapping to surface states and two-body recombination of excited carriers, with trapping being the dominant source of light emission. Since nonlinear processes, namely two-body recombination, are included, it is necessary to measure the pump intensity dependence of the transient responses and to analyze them with a nonlinear differential equation in order to obtain accurate decay times.

1. Introduction

Since Canham [1] reported on the light emission of porous silicon at room temperature, considerable attention has been given to the emission mechanism; however, the mechanism remains unclear. Canham explained it on the basis of the effect of the quantum confinement of nano-sized silicon particles, where light is emitted via the quantitized energy state. Koch et al. [2] extended Canham's explanation and proposed that light is emitted from photo-excited carriers that are transferred to defect states when they are eliminated due to recombination, while light absorption itself occurs due to the quantitized energy state.

To elucidate the mechanism, the dynamics of the photo-excited carriers has been investigated by time-resolved measurements [3–11]. The studies indicated that surface states are involved in the emission mechanism. Matsumoto et al. [6,7] studied the correlation between the fluorescence decay time and the number of hydrogen-terminations on sample surfaces and reported that weak emission with a decay time of several hundreds of picoseconds comes from excited carriers at a quantitized state and that strong emission with a lifetime of nanoseconds occurs due to excited carriers at surface states. Others also reported, using time-resolved fluorescence and transient absorption measurements, that fluorescence with a faster decay time is due to the recombination of photo-excited carriers in the core of silicon nano-crystals and that fluorescence with a slower decay time is due to the recombination of carriers localized in surface states [8–11].

However, two difficulties are encountered when time-resolved measurements are made for porous silicon. The first comes from the nonlinear recombination processes of excited carriers. Porous silicon has a low-intensity threshold of pump intensity where nonlinear processes start, and the ratio between nonlinear and linear recombination processes then changes according to the experimental pump intensity used, which causes a change in the apparent decay time. Furthermore, since the threshold value changes depending on the sample preparation conditions, it is difficult to get

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reproducible data for different samples [12]. The second difficulty lies in sample damage. The sample is subject to physical property changes under light illumination, especially by pulse light sources with high peak intensity. The damage is often seen by the naked eye after experiments. Thus, it has been difficult to clarify the linear and nonlinear processes and surface-related processes, and a conclusive description of the light-emitting processes has not been obtained.

A new type of time-resolved measurement method, the near-field heterodyne transient grating (NF-HD-TG) method, has been developed, [13,14] which features a very simple optical design, high sensitivity using heterodyne detection, and negligible photo-induced damage because focused light is not used. Furthermore, this method can be applied to samples with surface roughness on the order of microns [15]. These features ensure that the method is suitable for the measurement of porous silicon because photo-induced damage can be prevented, nonlinear processes can be excluded by measuring at low pump intensity, and rough surfaces present no problem. In this Letter, the pump intensity dependence of the responses of excited carriers is clarified using the NF-HD-TG method, and the responses are then analyzed to obtain accurate relaxation dynamics.

2. Experiment

Porous silicon (PSi) layers were formed on p-type, boron-doped, (100)-oriented Si substrates (thickness: 525 μm) with 5–15 Ω cm resistivity by electrochemical anodic etching in an HF(47%)-water solution at room temperature in darkness [16]. A Pt film with a thickness of 150 nm was sputtered onto the unpolished surface of the Si for use as an electrode. The anodization current density was 1.4 mA/cm^2, and the anodization time was 30 min. Three PSi samples were prepared, with or without chemical post-etching after anodization. The etching was carried out in a solution of HF: C_2H_5OH: $H_2O = 1$: 3: 8 [16] for different times (S_1:0 min, S_2:2 min, and S_3:6 min). The thicknesses of the PSi layers were measured using scanning electronic microscope (SEM) images at almost 4 μm for all of the samples. The porosities of samples S_1, S_2, and S_3 were determined to be about 50%, 60%, and 70%, respectively, by measuring the weight changes of each Si wafer before and after electrochemical anodic etching. Pictures of the three samples when they were irradiated by 365 nm are shown in Fig. 1. The emission intensity increased with an increase of the etching time, as reported previously [1,16].

The principle of the NF-HD-TG method has been described elsewhere [13,14]. The method offers versatile applications for various samples, such as transparent and non-transparent solids, liquids, polymers, and particles, as well as samples with rough surfaces [15,17]. The light source was a regenerative amplified Ti:Sapphire laser (CPA2010, Clark-MXR), and the conditions were as follows: center wavelength, 775 nm; pulse width, 150 fs; repetition rate, 1 kHz; and output power, 900 mW. The light was separated into two beams: one was used to generate the second harmonic, which was used as the pump beam (388 nm), and the other was used as the probe beam. The pump and probe beams were set co-axially and sent to the samples after passing through a transmission grating (grating spacing, 9.1 μm; thickness, 3 mm). Both pump and probe beams were 3 mm in diameter, and the pump intensity was adjusted by an ND filter for the range from 2.4 to 10 μJ/pulse. The pump intensity corresponds to 34–140 mW/cm^2, which is around the threshold pump intensity of nonlinear processes for the photoluminescence of porous silicon [18], and the used pump intensity is suitable for investigating the nonlinear processes of carriers.

3. Results and discussion

The dependences of the transient responses on pump intensity for the three samples are shown in Fig. 2a,b,c where all the responses are normalized. Since the signal intensities easily changed depending on the detection position, all the responses were normalized by the intensity at the origin. In spite of the signal intensity change, the waveforms of the responses, that is, the decay times, were not changed; the decay times and the ratio between decay components are discussed. A prominent feature of the signals is that the pump intensity dependence becomes smaller as the etching time increases, and no dependence is observed for sample S_3. For samples S_1 and S_2, the lifetime becomes shorter with increasing the pump intensity.

In general, excited carriers in semiconductors have several kinds of decay processes depending on what power of the carrier density the decay rate is proportional to.

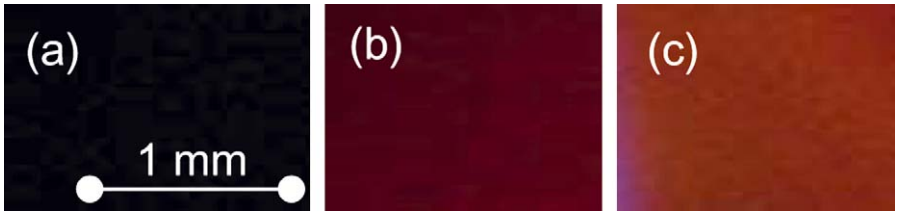

Fig. 1. Pictures of three samples being irradiated by a 365 nm light. They have different porosities as a result of post-etching for different lengths of time: (a) 0 min, (b) 3 min,and (c) 6 min.

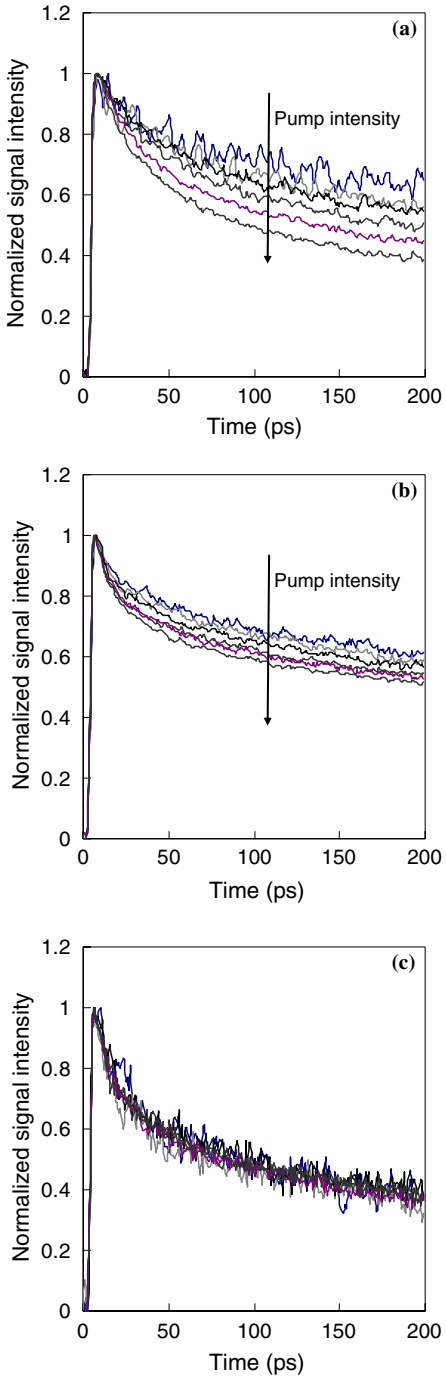

Fig. 2. Pump intensity dependences of the transient responses of porous silicon measured using the near-field heterodyne transient grating technique. Three samples with different porosities were prepared by post-etching for different lengths of time. The post-etching times were 0, 3, and 6 min, corresponding to (a), (b), and (c). The decreasing pump intensity is indicated with arrows in (a) and (b), but no arrow is shown in (c) because no dependence was observed.

Typical three decay channels are called one-body, two-body, and three-body recombination processes, which mean that one, two, and three excited carriers are involved in the elimination processes of excited carriers. For porous silicon, the first two are the main decay processes. In the one-body relaxation, trapping of excited carriers to surface or defect states and normal decays of carriers are included. In the two-body relaxation, pairs consisting of an electron and a hole disappear. If the relaxation mechanism includes only one-body processes, the response time does not depend on the pump intensity, but it does depend on the intensity if two-body processes are involved. For the typical pump intensity used in the NF-HD-TG method, no dependence has been observed for semiconductor wafers [19]. The dependence of the pump intensity in Fig. 2a,b indicates a low-intensity threshold for the two-body relaxation processes of porous silicon.

For sample S_3, the responses do not show any dependence on the pump intensity, and they include two exponential decays. The responses of sample S_3 can be modeled by a sum of exponential curves in the following:

$$S(t) = C_1 \times \exp\left(\frac{-t}{\tau_1}\right) + C_2 \times \exp\left(\frac{-t}{\tau_2}\right) + C_3, \quad (1)$$

where τ_1 and τ_2 are the decay times, and C_n (n: integer) is a coefficient of each component. C_3 is assumed to be caused by a longer decay component than the time range we could measure (300 ps). This is assumed to be due to a sample's temperature rise because another possible effect of a signal is carrier decay, which is not related to surface states; however, this was not usually observed for porous silicon since most carriers were trapped by the surface states.[3–11]

The fitting result is shown in Fig. 3; the τ_1 and τ_2 values are 8.2 and 70 ps, respectively. The C_1 and C_2 components have shorter decay times than a time window range, and the decay times can be obtained precisely, although it appears they do not decay in the window due to the C_3 component (constant signal). Since the typical carrier decay times of semiconductors are on the temporal order of nanoseconds, the first component corresponds to the trapping, and the trapped energy states would be the surface states for porous silicon [6–11]. The observed trap time is reasonable and agrees with reports [6,7] that trapping to surface states takes about 5 ps, even though it is supposed that the trapping time depends on the sample preparation

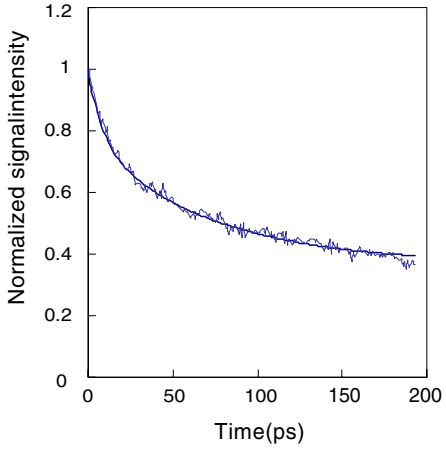

Fig. 3. Fitted curves of the transient responses in Fig. 2c using a double-exponential plus constant function.

conditions. Since the second component also has a shorter relaxation time than the typical carrier decay times and the temporal order is close to the fluorescence decay of surface states, [6–11] the second component corresponds to the decay of the trapped carriers to the lower states.

For samples S_1 and S_2, the responses depend on the pump intensity, which means the decay processes include nonlinear (two-body) recombination. In this case, the excited carrier density decreases according to the following equation:

$$\frac{dN}{dt} = -AN - BN^2, \tag{2}$$

where N is the carrier density, and A and B are physical constants. The first and second terms on the right side correspond to the one-body and two-body recombination terms, respectively, and, from the above discussion, the first term comes from the trapping to surface states:

$$N(t) = \frac{A\exp(KA)}{\exp(At) - B\exp(KA)}, \tag{3}$$

where $K = \frac{1}{A}\ln\left(\frac{N_0}{A+BN_0}\right)$ and N_0 is the initially excited carrier density. Since the response includes the decay of trapped carriers 2nd term in Eq. (1)), the responses are modeled with the following equation,

$$S(t) = D_1 \times N(t) + D_2 \times \exp\left(\frac{-t}{\tau_2}\right) + D_3, \tag{4}$$

where D_n (n: integer) is the coefficient of each component and the second component corresponds to the decay of trapped carriers, which have the same decay time τ_2 as that in Eq. (1), and the third component is due to a temperature rise. Therefore, only the first term, that is, the initial carrier decay, was revised to have a nonlinear response from Eq. (1). Since A and B are physical property values, they should be constants for each sample. For the fitting, first, the A and B values are obtained by fitting with the response taken at the maximum pump intensity (10 μJ/pulse), and the other responses are then fitted using the same A and B values with the N_0 value as a parameter. These two steps are repeated until all the responses are well fitted. For samples S_1 and S_2, a two-body recombination becomes dominant, and the trapping component becomes relatively smaller. The first term in Eq. (2) and the second term in Eq. (4) usually had a minor influence on the responses.

The fitted results for sample S_1 are shown in Fig. 4. The responses can be well fitted by Eq. (4). It was impossible to fit the responses with exponential functions, especially around the initial decay part, which indicates that the initial decay part includes a functional form different from an exponential function. Since only the first component in Eq. (4) was revised on the basis of a physical model and the fitting results were considerably improved, this model was considered to be physically correct. The obtained N_0 values decreased as the pump intensity decreased; this is shown in Table 1. This means that the proposed model gives a good description of the physical

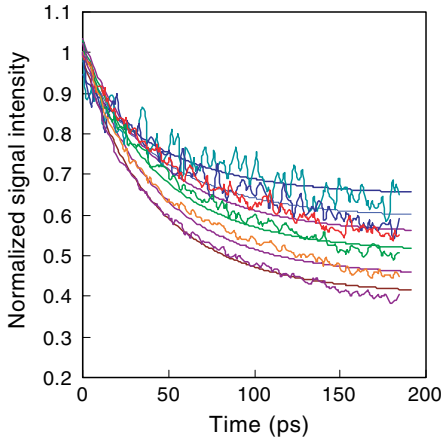

Fig. 4. Fitted curves of the transient responses in Fig. 2a using the model based on the nonlinear differential equation corresponding to nonlinear recombination processes.

Table 1
Fitting parameters used in the fitting procedures for the transient responses of the sample that was post-etched for 0 min

Pump intensity (μJ/pulse)	N_0 (relative value)
2.4	0.295
3.3	0.388
4.5	0.480
5.9	0.521
7.8	0.576
10	0.588

processes. As the pump intensity increased, the N_0 value appeared to be saturated. It is assumed that the optical absorption was saturated. The same procedure was taken for sample S_2, and the responses could be well fitted as well. A summary of the energy diagram is shown in Fig. 5.

From these analyses, it was concluded that there are two main decay processes for excited carriers, namely, two-body recombination and trapping to surface states. These are competing processes depending on the pump intensity and porosity. When the porosity is increased, the trapping

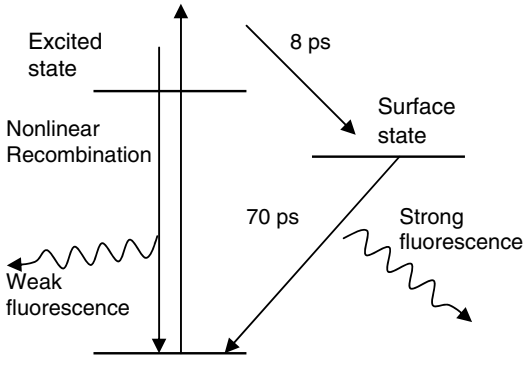

Fig. 5. Energy diagram of the porous silicon. The decay processes of excited carriers are shown in the figure.

becomes dominant; on the other hand, two-body recombination is important when the porosity is small. It is noteworthy that the ratio between two-body recombination and trapping changes depending on the pump intensity.

The emission intensity became stronger with the porosity, as shown in Fig. 1 [16], and the sample with the largest porosity had a relaxation that was only due to the trapping to surface states. This is confirmed by the fact that the response does not depend on the pump intensity. This is direct evidence that most of the emission is due to the surface states.

There are three important points to properly deduce the rates of trapping and recombination and the ratio between them. First, measurements should be made under low pump intensity; otherwise, trapping processes cannot be observed because nonlinear recombination processes are too dominant. Second, the pump intensity dependence of the responses should be measured because nonlinear recombination depends on the pump intensity. Third, proper physical modeling is necessary to model nonlinear processes.

In summary, transient responses of porous silicon were measured by the NF-HD-TG method, and the physical processes related to emission were analyzed. The main two mechanisms were trapping to surface states and two-body recombination. It is concluded that the physical processes need to be clarified by investigating the dependences of the pump intensity and porosity.

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References

[1] L.T. Canham, Appl. Phys. Lett. 57 (1990) 1046.
[2] V. Petrova-Koch, T. Muschik, D.I. Kovalev, F. Koch, V. Lehmann, in: P.M. Fauchet, C.C. Tsai, L.T. Canham, I. Shimizu, Y. Aoyagi (Eds.), Microcrystalline Semiconductors: Materials Science & Devices, MRS Symposia Proceedings, vol. 283, Materials Research Society, Pittsburgh, 1993, p. 179.
[3] J.C. Owrutsky, J.K. Rice, S. Guha, P. Steiner, W. Lang, Appl. Phys. Lett. 67 (1996) 1966.
[4] R. Tomasiunas et al., Thin Solid Films 276 (1996) 55.
[5] R. Tomasiunas, J. Moniatte, I. Pelant, P. Gilliot, B. Honerlage, Appl. Phys. Lett. 68 (1996) 3296.
[6] T. Matsumoto, O.B. Wright, T. Futagai, H. Mimura, Y. Kanemitsu, J. Non-Cryst. Solids 164–166 (1993) 953.
[7] T. Matsumoto, T. Futagai, H. Mimura, Y. Kanemitsu, Phys. Rev. B 47 (1993) 13876.
[8] F. Trojanek, P. Maly, I. Pelant, A. Hospodkova, V. Kohlova, J. Valenta, Thin Solid Films 255 (1995) 77.
[9] J. Kudrna, F. Trojanek, I. Pelant, S. Banas, V. Kohlova, P. Maly, Thin Solid Films 276 (1996) 58.
[10] P. Maly et al., Phys. Rev. B 54 (1996) 7929.
[11] P. Maly, J. Kudrna, F. Trojyanek, A. Hospodkova, Thin Solid Films 276 (1996) 84.
[12] D. Kovalev, H. Heckler, G. Polisski, F. Koch, Phys. Stat. Sol (b) 215 (1999) 871.
[13] M. Yamaguchi, K. Katayama, T. Sawada, Chem. Phys. Lett. 377 (2003) 589.
[14] K. Katayama, M. Yamaguchi, T. Sawada, Appl. Phys. Lett. 82 (2003) 2775.
[15] K. Katayama, Q. Shen, T. Toyoda, M. Yamaguchi, T. Sawada, J. of . Phys. 125 (2005) 349.
[16] T. Toyoda, T. Takahashi, Q. Shen, J. Appl. Phys. 88 (2000) 6444.
[17] Q. Shen, K. Katayama, M. Yamaguchi, T. Sawada, T. Toyoda, Thin Solid Films 486 (1–2) (2005) 15.
[18] A.L. Efros, M. Rosen, B. Averboukh, D. Kovalev, M. Ben-Chorin, F. Koch, Phys. Rev. B 56 (1997) 3875.
[19] K. Katayama, M. Yamaguchi, T. Sawada, J. Appl. Phys. 94 (2003) 4904.