PHYSICAL REVIEW B VOLUME 47, NUMBER 20 15 MAY 1993-II

Ultrafast decay dynamics of luminescence in porous silicon

Takahiro Matsumoto, Toshiro Futagi, and Hidenori Mimura
Electronics Research Laboratories, Nippon Steel Corporation, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229, Japan

Yoshihiko Kanemitsu
Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
(Received 30 December 1992)

Ultrafast decay dynamics of luminescent porous silicon has been studied with a picosecond-spectroscopic technique. We have observed that the surface structure of the Si microcrystals changes the picosecond carrier dynamics: picosecond luminescence decay becomes faster with increasing hydrogen termination on the surface of a Si microcrystal. We have also observed the redshift of the luminescence peak in the initial decay stage. This shift disappears with increasing hydrogen termination. These results suggest that there are two luminescent states in Si microcrystals: a weak luminescent quantum-confinement state (Si microcrystal core) and a strong luminescent surface state. Surface treatment by hydrogen termination on Si microcrystals influences the transfer rate between the two states and changes the origin of luminescence from the surface state to the quantum-confinement state.

Porous silicon (Si) fabricated by electrochemical anodization has attracted much interest because it exhibits strong luminescence at room temperature.[1] The structure of this material is similar to a condensed state of nanometer-size Si microcrystals.[2,3] The luminescence peak[1] and the absorption edge[4] shift to higher-energy with increasing chemical dissolution. For these reasons, the quantum-confinement effect[1-4] is suggested as the origin of the strong luminescence. However, other mechanisms, such as an amorphous effect or siloxene effect,[5] are proposed, and the luminescence mechanism still remains unknown. The difficulty of this problem mainly arises for two reasons: there are few theoretical studies that probe the quantum-confinement effect of the indirect band-gap semiconductor microcrystals. The surface effect becomes more enhanced than the volume effect (confinement effect) on decreasing the microcrystal size and it becomes difficult to confine excited carriers.

Our methods for clarifying the above problems are picosecond[6] and femtosecond spectroscopies. The excited carriers are influenced by scattering, thermalization, or recombination. These are expected to be very fast, especially for nanometer-order semiconductor microcrystals,[7-11] and the ultrafast spectroscopic technique becomes a powerful tool for probing the transient decay dynamics.

In this paper, we elucidate the picosecond carrier dynamics in porous Si. We report that the surface structure of a Si microcrystal changes the picosecond carrier dynamics: the picosecond luminescence decay becomes faster on increasing the proportion of hydrogen termination on the surface of a Si microcrystal. We also observe the redshift of the luminescence peak in the initial picosecond decay stage. This picosecond redshift gradually disappears with increasing hydrogen termination. On the basis of these observations, we present a model that elucidates the luminescent mechanism in porous Si. This model shows that there are two luminescent states in Si microcrystals: a weak luminescence quantum-confinement state (Si microcrystal core) and a strong luminescent surface state (molecularlike Si cluster on the surface of a Si microcrystal core). Surface treatment by hydrogen termination on Si microcrystal cores influences the transfer rate between the two states and changes the origin of the luminescence from the surface state to the quantum-confinement state.

The porous Si layers were formed by electrochemical anodization. The substrates were (100) oriented 3.5–4.5 Ω cm resistivity *p*-type silicon. Thin Al films were evaporated on the back of the wafers to form a good Ohmic contact. The anodizations were carried out in HF-ethanol solution ($HF:H_2O:C_2H_5OH=1:1:2$) at constant current density in the range of 10 mA/cm^2 for 5 min. During the anodization, the sample was illuminated with a tungsten light source to increase the luminescence intensity of the porous Si layer. This layer was then photochemically dissolved under open circuit conditions for 0 (as anodized), 1, 3, and 5 min. After the dissolution, the samples were rinsed in deionized water for several minutes. These porous Si layers are known to have a huge surface area (200–600 m^2/cm^3) (Refs. 12 and 13) terminated with hydrogen.[14] To confirm the structure of these samples, we have performed transmission-electron microscope (TEM) analysis, Fourier-transform infrared (FTIR) spectroscopy, and the photoluminescence excitation spectrum (PLES) measurements. FTIR spectroscopy indicates that photochemical dissolution increases the proportion of silicon hydride, as shown in Fig. 1. Five-minutes photochemical dissolution produces an almost 20% increase. This proportion is estimated from the scissor mode of the SiH_2 species at the peak wave number 907 cm^{-1} (the absorbance of the stretching modes of the SiH and SiH_2 at the peak around 2100 cm^{-1} is also correlated with the dissolution time).[15,16] However, TEM analysis and PLES measurements do not show any significant change of the microcrystal size on dissolution.

The luminescence was measured using Ar-ion laser excitation ($\lambda=457.9$ nm) at room temperature. The sample

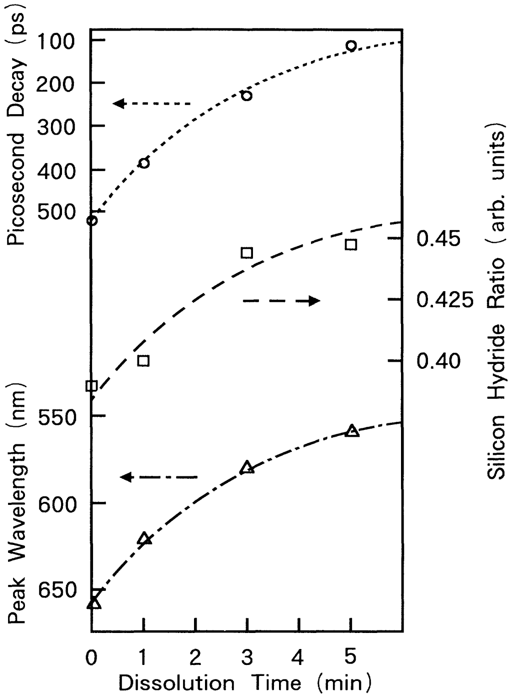

FIG. 1. Peak luminescence wavelength vs dissolution time, silicon hydride ratio vs dissolution time, and picosecond luminescence decay vs dissolution time.

was purged in nitrogen gas to avoid the luminescence degradation.[17] The luminescence peak was found to be the same using the second harmonic (SH) of a cw mode-locked neodymium-doped yttrium lithium fluoride (Nd:YLF) laser excitation ($\lambda = 527$ nm). Figure 1 shows the peak luminescence wavelength as a function of photochemical dissolution time. The luminescence peak shifts to higher-energy on increasing the proportion of silicon hydride. However, a peak wavelength beyond 550 nm could not be obtained by further dissolution.

The picosecond luminescence decay measurements were performed using the SH of a cw mode-locked Nd:YLF laser and a synchroscan streak camera through a spectrometer. The SH pulse duration was 40 ps, the repetition rate was 76 MHz, and the excitation power on the sample, was 100 mW/cm^2. The wavelength range for detection was 450–900 nm, and the time resolution was 10 ps. Figure 2 shows the picosecond luminescence intensity decay curves and the semilogarithmic plots of these curves at 600-nm emission wavelength for 0-, 1-, 3-, and 5-min dissolution times. The decay becomes faster with increasing proportion of silicon hydride. In particular, initial decay that has a single exponential component becomes faster with dissolution time: 520 ps for 0-min, 385 ps for 1-min, 240 ps for 3-min, and 110 ps for 5-min dissolved samples. We could not see any luminescence saturation and picosecond decay change by making the excitation intensity about ten times stronger. These picosecond luminescence decays as a function of dissolution time are plotted in Fig. 1. The luminescence peaks and the picosecond decays are correlated with the proportion of silicon hydride.

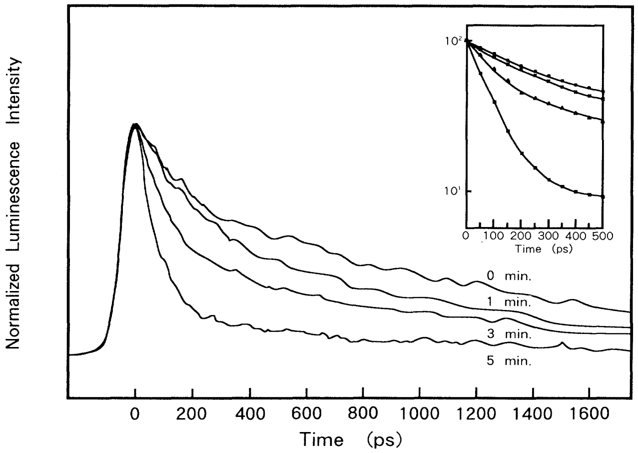

FIG. 2. Picosecond luminescence intensity decay curves and semilogarithmic plots of these curves at 600-nm emission wavelength for 0-, 1-, 3-, and 5-min photochemically dissolved porous Si samples.

We also performed time-resolved luminescence spectrum measurements in the picosecond region. Figures 3(a) and 3(b) show the picosecond time-resolved luminescence spectra for 1- and 5-min photochemically dissolved porous Si. The time-resolved luminescence spectra are taken every 130 ps. Figure 3(a) shows the rapid redshift of the luminescence peak from 600 to 620 nm within 500 ps. (The peak luminescence wavelength of this sample by cw Ar-ion laser excitation is 620 nm.) However, this redshift gradually disappears with increasing proportion of silicon hydride as shown in Fig. 3(b). From the results in Figs. 2 and 3, the picosecond luminescence decay behaviors are affected by the proportion of silicon hydride.

The structure of porous Si is similar to a condensed state of nanometer-order Si microcrystal core[3,4] and the surface of a Si microcrystal core is terminated with hydrogen.[14] Hydrogen termination on the surface causes a reduction of the nonradiative recombination of the surface state and the structurally relaxed Si surface.[18] Therefore, we can assume the existence of the microcrystalline core state and the surface state in porous Si. Figure 4 shows the model in which there are two excited states, one representing the microcrystalline core state (quantum-confinement state) and the other representing the surface state on a Si microcrystal core. It is well known that molecularlike small Si clusters show strong luminescence and their optical properties (absorption or emission) depend on their size and shape.[7,19] We consider that the strong luminescent surface state exhibits molecularlike character[20] whereas a Si microcrystal core exhibits solidlike character. The increase of hydrogen termination on the surface makes the molecularlike Si cluster smaller and its band gap become wider.[21] The band-gap widening of the surface state by hydrogen termination changes the relative energy level of the microcrystalline core state and the surface state. Thus the transfer rate between both states is affected by this hydrogen termination.

The carrier dynamics of the microcrystalline core state and the surface state are discussed below by changing the transfer rate between two states. We consider a three-level model. The rate equations that describe the population in the microcrystalline core state N_m and the surface state N_s become

$$\frac{dN_m}{dt} = -(\alpha+\beta)N_m \,, \tag{1}$$

$$\frac{dN_s}{dt} = \beta N_m - \gamma N_s \,, \tag{2}$$

where α and γ are the decay rates of the microcrystalline core state and the surface state, and β is the transfer rate from the microcrystalline core state to the surface state. Using Eqs. (1) and (2), we can solve the time evolution of the populations in both states as

$$N_m = N_0 \exp[-(\alpha+\beta)t] \tag{3}$$

and

$$N_s = \frac{\beta}{\alpha+\beta-\gamma} N_0 \{\exp(-\gamma t) - \exp[-(\alpha+\beta)t]\} \,, \tag{4}$$

where N_0 is the initial population generated by laser excitation. Here we consider two limiting cases. In the case $\beta \gg \alpha$ (the case in which the surface hydrogen concentration is lower), using Eqs. (3) and (4), $N_m \approx N_0 \exp(-\beta t)$ and $N_s \approx N_0\{\exp(-\gamma t) - \exp(-\beta t)\}$. Almost all the carriers flow into the surface state within the excitation duration; the rising (β^{-1}) of the luminescence is much faster than the value α given below, so we cannot measure this with our time resolution. The strong luminescence begins to occur from this state. The picosecond decay rate γ depends on the emission energy because of the inhomogeneity of the surface state and this is the origin of the rapid luminescence redshift in the initial decay stage. In the case $\alpha \gg \beta$ (the case in which the surface hydrogen concentration is higher), $N_m \approx N_0 \exp(-\alpha t)$ and $N_s \approx \beta/\alpha N_0\{\exp(-\gamma t) - \exp(-\alpha t)\} \cong 0$. Almost all the carriers become confined in Si microcrystal cores. We can determine the decay rate α to be approximately equal to $10^{10}\ \mathrm{s}^{-1}$ from the semilogarithmic plots of Fig. 2. The integrated luminescence intensity of this state is weak compared with that of the surface state (the luminescence intensity of the 5-min sample is about ten times weaker than that of 1-min sample). The recombination in a Si microcrystal is largely affected by the nonradiative decay process. This explains why the picosecond redshift of the luminescence peak disappears as shown in Fig. 3(b). To fit the picosecond time-resolved luminescence spectra shown in Figs. 3(a) and 3(b), we need to take account of the inhomogeneous broadening and the nonradiative decay in both states. Theoretical fits including these effects are now under investigation.

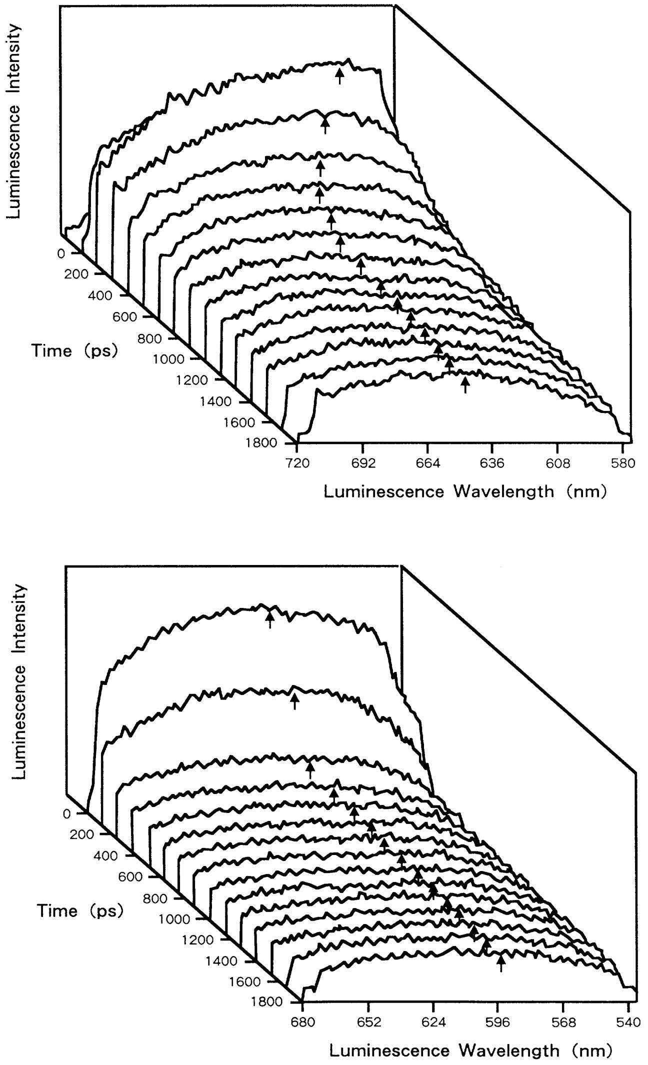

FIG. 3. Picosecond time-resolved luminescence spectra for (a) 1-min and (b) 5-min photochemically dissolved porous Si samples. Each spectrum is taken every 130 ps.

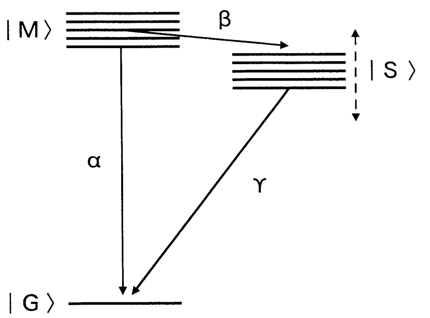

FIG. 4. Three-level luminescent states model in porous Si.

The luminescence from porous Si is subjected to both the charge transfer (denoted in β) and the recombination (denoted in α) mechanisms. Strong luminescence occurs when the charge transfer is larger than the recombination. Luminescence from this surface state shows slow decay in the range of 1 ns or more. However, besides this luminescence, we have observed a rapid luminescence decay in the 100-ps range. This luminescence appears only when the charge transfer rate is much smaller than the recombination rate. Slow decay components in the range of nanoseconds to microseconds[22] may be attributed to the recombination at the surface state and/or the carrier tunneling between these states. The luminescence from the quantum-confinement effect is weaker and has faster decay components on the order of 100 ps. The luminescence from the quantum-confinement effect can be clearly observed in the picosecond time region.

In conclusion, we have observed the picosecond luminescence decay and the picosecond luminescence redshift in porous Si. Hydrogen termination on the surface of a Si microcrystal core changes these picosecond carrier dynamics. We present a three-level model that concerns the microcrystalline core state and the surface state. We show in this model that the surface treatment by hydrogen termination influences the transfer rate between the two states and changes the origin of luminescence from the surface state to the quantum-confinement state. The luminescence occurs from both states. However, the strong luminescence originates from the molecularlike surface Si clusters. The luminescence from the confinement state is weak compared with that from the surface state. The weak luminescence originating from the quantum-confinement effect is found to have fast decay components on the order of 100 ps. Picosecond spectroscopy reveals the carrier dynamics related to the quantum-confinement effect which is hidden in the luminescence of porous silicon.

We are grateful to Professor Y. Masumoto of University of Tsukuba for his valuable advice.

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