

Ultrafast Luminescence Decay in Porous Silicon

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Ultrafast decay dynamics of luminescent porous Si has been studied by picosecond spectroscopic technique. Picosecond luminescence decay becomes faster and the luminescence red shift in initial picosecond decay stage disappear on increasing the proportion of silicon hydride. These results indicate the existence of two luminescent states in porous Si: a quantum confinement state and a localized state in the near-surface region.

Porous silicon fabricated by electrochemical anodization has been reported to exhibit visible luminescence at room temperature¹⁾. The structure of this material is like condensed nanometer order Si microcrystals²⁾ and the quantum confinement effect is suggested to be the origin of this strong luminescence¹⁾. However other mechanisms such as the amorphous effect or the siloxene effect³⁾ are proposed and the luminescent mechanism still remains unknown.

In this work we have studied the picosecond decay dynamics⁴⁾ in porous Si using the second harmonic of a cw mode-locked YLF laser ($\lambda = 527$ nm) and a synchroscan streak camera. The substrates were (100) - oriented 3.5 ~ 4.5 Ω cm resistivity p-type Si. Thin Au 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 : H₂O : C₂H₅OH = 1 : 1 : 2) at constant current density in the range of 10mA/cm² for 5 minutes. During the anodization, the sample was illuminated with a tungsten light source to increase the luminescence intensity of the porous Si layer. Then it was etched under open circuit conditions for 0 (as-anodized), 1, 3, and 5 minutes. After the etching, the samples were rinsed in deionized water for several minutes.

FTIR measurements show that etching

treatments increase the proportion of silicon hydride in porous Si. Figure 1 shows the peak luminescence wavelength as a function of the etching time. The luminescence peak shifts to the higher energy side as this proportion increases. However a peak wavelength beyond 550 nm can not be obtained by further etching. Figure 2 shows the picosecond luminescence intensity decay curves at an emission wavelength of 600 nm

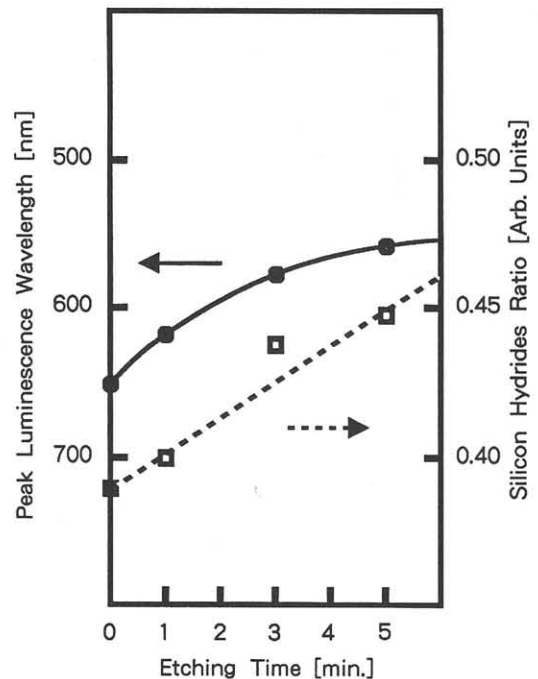


Fig. 1. Peak luminescence wavelength vs. etching time and silicon hydride ratio vs. etching time.

for various etching times. The picosecond luminescence decay becomes faster with increasing proportion of silicon hydride. Figure 3 shows the semilog plots of these curves. Especially the initial decay becomes faster. To understand the carrier dynamics versus etching effect more clearly, we performed the time-resolved luminescence measurements in the picosecond region. Figure 4 shows the picosecond time-resolved luminescence spectra for 1 min. etched porous Si. These are taken every 129 ps. The luminescence peak position rapidly shifts from 600 nm to 620 nm within 500 ps. The peak luminescence wavelength of this sample by cw laser excitation is 620 nm. This red shift gradually disappears on increasing the proportion of silicon hydride. These results indicate that there are two luminescent states in porous Si and the excited carriers move to the lower energy state within 500 ps in this sample. However as the hydrogen termination increases on the surface of porous Si, this carrier movement becomes suppressed.

To analyze these experimental results, we employ the three-level model as shown in Figure 5. We assume that the higher energy state represents the microcrystalline state and the other represents the localized state in the near-surface region. As the hydrogen termination on the surface increases, the confinement becomes stronger. This phenomenon can be expressed quantitatively by varying the tunneling rate β in the following equations.

$$N_m = N_0 \exp[-(\alpha + \beta)t] \quad (1)$$

and

$$N_l = \frac{\beta}{\alpha + \beta - \gamma} N_0 \{ \exp(-\gamma t) - \exp[-(\alpha + \beta)t] \} \quad (2)$$

where N_0 is the initial population generated by laser excitation, N_m and N_l are the populations in the microcrystalline state and the localized state, and α and γ are the decay rates of the microcrystalline state and the localized state. In the case of $\beta \gg \alpha$,

almost all the carriers flow into the localized state and the nonexponential slow decay begins to occur from this state. In the case of $\alpha \gg \beta$, almost all the carriers are

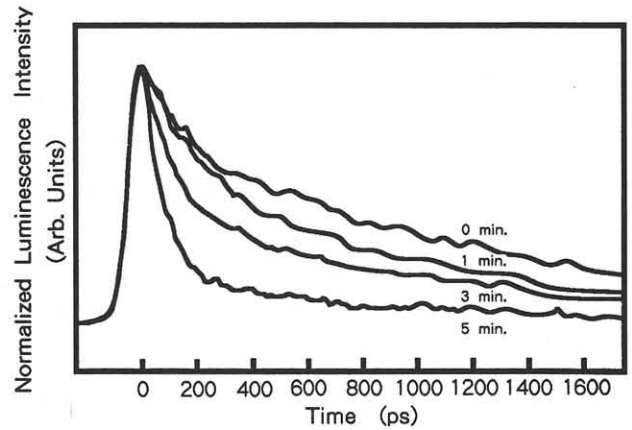


Fig. 2. Picosecond luminescence intensity decay curves at emission wavelength of 600 nm for 0, 1, 3, and 5 minutes photochemically etched porous Si samples.

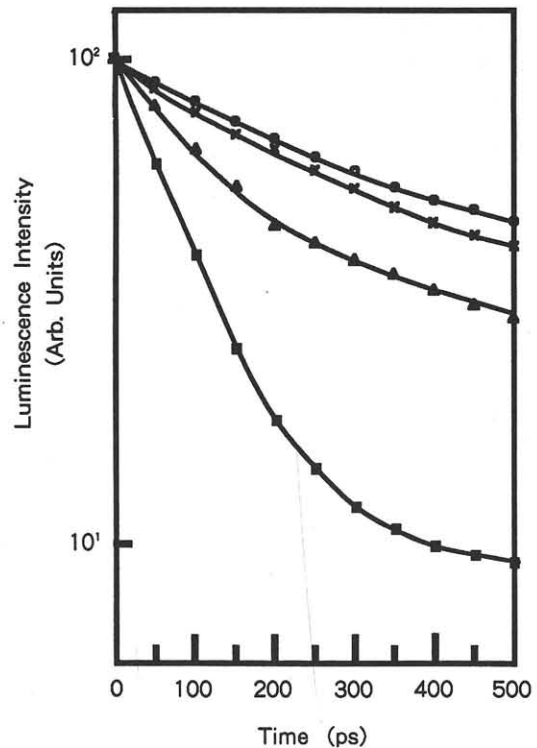


Fig. 3. Semilog plot of the picosecond luminescence intensity vs. time at emission wavelength of 600 nm for 0, 1, 3, and 5 minutes photochemically etched porous Si samples.

confined in Si microcrystals and the picosecond luminescence red shift will disappear. It is the case of $\alpha \approx \beta$ that the rapid red shift from the microcrystalline state to the localized state can be observed as shown in Figure 4.

It is widely known that surface recombination shows a weak luminescence in a-Si:H because of the small diffusion length owing to the presence of band-tail states⁶. The diffusion length is reported to be in the range of 50–100 Å. However in porous Si, both the microcrystalline phase and the amorphous phase are mixed and the characteristic size of both phases is in the above range. In this case the carriers are not trapped in the band-tail states but reach the near-surface region. Then many carriers can condense and recombine radiatively in these localized states.

The experimental results showing that the picosecond luminescence decay at each emission wavelength becomes constant with increasing proportion of silicon hydride seem to originate from the individual confinement⁵ of the electrons and holes. However we need further theoretical and experimental investigations to understand the carrier dynamics in the microcrystalline state.

In conclusion we have observed the picosecond time evolution of the luminescence spectra as a function of hydrogen termination on the surface in porous Si. We have discussed the origin of the luminescence by varying the tunneling rate β that connects the two luminescent states. The quantum mechanical calculation of this rate seems to be very interesting problem.

REFERENCES

- 1) L. T. Canham, Appl. Phys. Lett. 57 (1990) 1046.
- 2) M. W. Cole et al., Appl. Phys. Lett. 60 (1992) 2800.
- 3) M. S. Brandt et al., Solid State Commun. 81 (1992) 307.

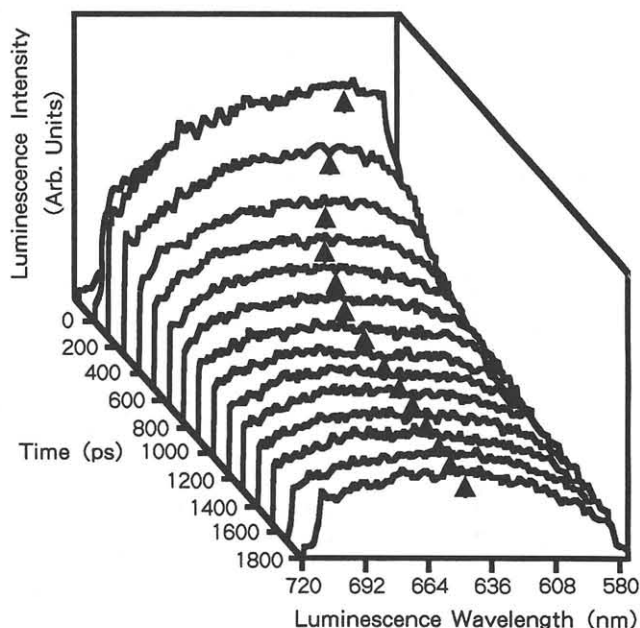


Fig. 4. Picosecond time-resolved luminescence spectra for 1 minute photochemically etched porous Si sample. Each spectrum is taken every 129 ps.

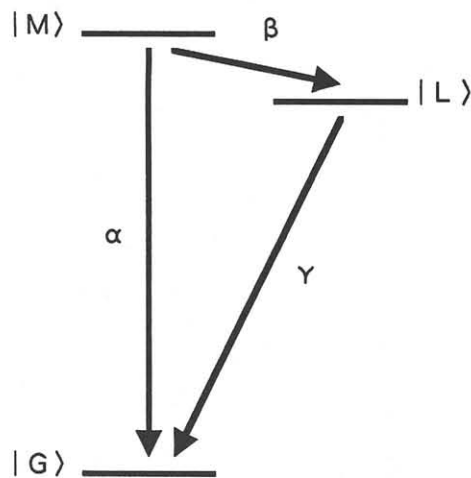


Fig. 5. Three-level model of porous Si.

- 4) T. Matsumoto et al., Jpn. J. Appl. Phys. 31 (1992) L619.
- 5) Y. Kayanuma, Phys. Rev. B38 (1988) 9797.
- 6) R. A. Street: Semiconductors and Semimetals edited by J. A. Pankove (Academic, London, 1984) vol. 21, Part B, p. 197.