Japanese Journal of Applied Physics, **31** (8) (1992) 2470-2471

Time-Resolved Luminescence Spectra of Porous Si

Tadaki Miyoshi, Kyu-Seok Lee[1] and Yoshinobu Aoyagi[1]

Department of Electrical and Electronic Engineering, Yamaguchi University, Tokiwadai, Ube 755

[1]*RIKEN, Wako, Saitama 351-01*

(Received April 7, 1992; accepted May 16, 1992)

Time-resolved luminescence spectra of porous Si were measured under an N_2 laser excitation. The luminescence shows a nonexponential decay with an initial time constant of less than 5 ns and more than 200 ns for the secondary decay. The luminescence is considered to be associated with localized states, which are probably conduction and valence sublevels in Si microstructures.

KEYWORDS: porous Si, photoluminescence, time-resolved spectrum

Recently, Canham observed visible photoluminescence from porous Si formed by anodization of crystalline Si in fluoric acid (HF) solution.[1)] The visible luminescence has been interpreted as arising from quantum confinement of carriers in Si quantum wires or dots. However, the optical properties of porous Si are not thoroughly understood yet, and more experimental evidence is necessary to clarify the mechanism of the luminescence. Here, we report time-resolved luminescence spectra of porous Si, which may provide insight into the physics underlying the luminescence.

Si wafers ($p = 1.7 \times 10^{15}$ cm^{-3}) with a resistivity of 9.8 Ωcm were anodized at 10 mA/cm^2 for 5 min in HF solution (47% HF:ethanol:water =2:1:1), and then etched in the HF solution. The excitation source for luminescence was an N_2 laser (Laser Photonics LN120, wavelength = 337.1 nm, pulse duration = 0.3 ns). The peak intensity of the laser light on the sample was about 50 kW/cm^2. Time-resolved luminescence spectra were measured at 300 K using an optical multichannel analyzer (Princeton Instruments D/SIDA-700) with a minimum gate time of 5 ns.

Figure 1 shows time-resolved luminescence spectra of porous Si after 30-min etching. A broad band is observed. The shorter wavelength side of the luminescence spectrum decays rapidly. Figure 2 shows peak wavelength as a function of time. The peak wavelength shifts to a longer wavelength with time. Figure 3 shows luminescence intensities at 500 nm and 650 nm as a function of time. The luminescence shows a nonexponential decay with an initial time constant of less than 5 ns and a secondary decay constant of more than 200 ns.

Gardelis et al.[2)] have measured transient characteristics of luminescence from porous Si at a fixed wavelength. They observed a nonexponential decay and discussed the results in the context of amorphous Si:H. The luminescence properties of porous Si are similar to those associated with band tail states in amorphous Si:H.[3)] Thus the luminescence from porous Si is associated with localized states, which probably originate from conduction and valence sublevels in Si microstructures. The energy difference between the lowest conduction sublevel and the highest valence sublevel has been calculated for a Si island in SiO_2.[4)] For instance, the energy gap is 2.78 eV for Si islands with a diameter of 1.5 nm, and 1.64 eV for islands of 2.0 nm diameter. Sublevels

are thought to be distributed according to the size distribution of the microstructures. The broad luminescence band probably arises from the distributed states.

The time-resolved shift of the luminescence peak is explained by carrier thermalization. The inset in Fig. 4 shows a schematic of the luminescence. It is expected that thermalization in bulk semiconductors occurs within 10^{-12} s. However, thermalization in porous Si is slow since it may be incorporated by tunneling between sublevels. Hence the nonexponential decay in the luminescence intensity in Fig. 3 is understood in terms of the tunneling. A fraction of the carriers may tunnel to sublevels with lower energy, and other carriers may recombine radiatively. The former phenomenon is considered to be related to the initial decay of luminescence and the latter to the secondary decay.

Luminescence spectra were measured for samples with various etching times. The peak wavelength shifts to a shorter wavelength and the initial decay speeds up with an increase in etching time. Figure 4 shows luminescence intensities at 650 nm as a function of time for samples (a) before etching and (b) after 15-min etching. Increasing the etching time increases the luminescing sublevels and enhances the tunneling between sublevels. The inset in Fig. 4 shows a schematic of the luminescence for samples with (a) short and (b) long etching times.

Luminescence under intense excitation was also measured. The luminescence intensity is almost proportional to the excitation intensity. The spectral shape is the same as that under weak excitation. On the other hand, the initial decay speeds up with an increase in the excitation intensity, as shown in curve (c) in Fig. 4. The intensity dependence of the decay time has been observed in amorphous Si:H and explained by bimolecular recombination since the mean distance between electron-hole pairs becomes less than the electron-hole separation of a pair under intense excitation.[3)] The intensity dependence for porous Si may be explained by the same recombination process.

In summary, time-resolved luminescence spectra of porous Si are reported. The luminescence shows a red shift of the time-resolved spectra, a nonexponential decay, and an excitation-intensity-dependent decay. These properties are similar to those

associated with band tail states in amorphous Si:H. Thus the luminescence is associated with localized states, which are probably conduction and valence sublevels in Si microstructures.

References

1) L. T. Canham: Appl. Phys. Lett. **57** (1990) 1046.
2) S. Gardelis, J. S. Rimmer, P. Dawson, B. Hamilton, R. A. Kubiak, T. E. Whall and E. H. C. Parker: Appl. Phys. Lett. **59** (1991) 2118.
3) C. Tsang and R. A. Street: Phys. Rev. B **19** (1979) 3027.
4) D. J. DiMaria, J. R. Kirtley, E. J. Pakulis, D. W. Done, T. S. Kuan, F. L. Pasavento, T. N. Theis, J. A. Cutro and S. D. Brorson: J. Appl. Phys. **56** (1984) 401.

Figure captions

Fig. 1. Time-resolved luminescence spectra of porous Si after 30-min etching. The peak intensity of the laser light on the sample is about 50 kW/cm^2.

Fig. 2. Peak wavelength of luminescence from porous Si after 30-min etching as a function of time. Open circles represent the data and a solid curve was drawn through data points as a visual guide.

Fig. 3. Luminescence intensities at 500 nm and 650 nm of porous Si after 30-min etching as a function of time. Circles represent the data and solid curves were drawn through data points as visual guides.

Fig. 4. Luminescence intensities at 650 nm of porous Si as a function of time: (a) before etching, (b) after 15-min etching, and (c) after 15-min etching. The excitation intensity for curve (c) is about ten times as high as the others. Luminescence intensities at t = 0 ns are normalized. The inset shows a schematic of the luminescence: (a) short etching time, (b) long etching time.

Fig. 1

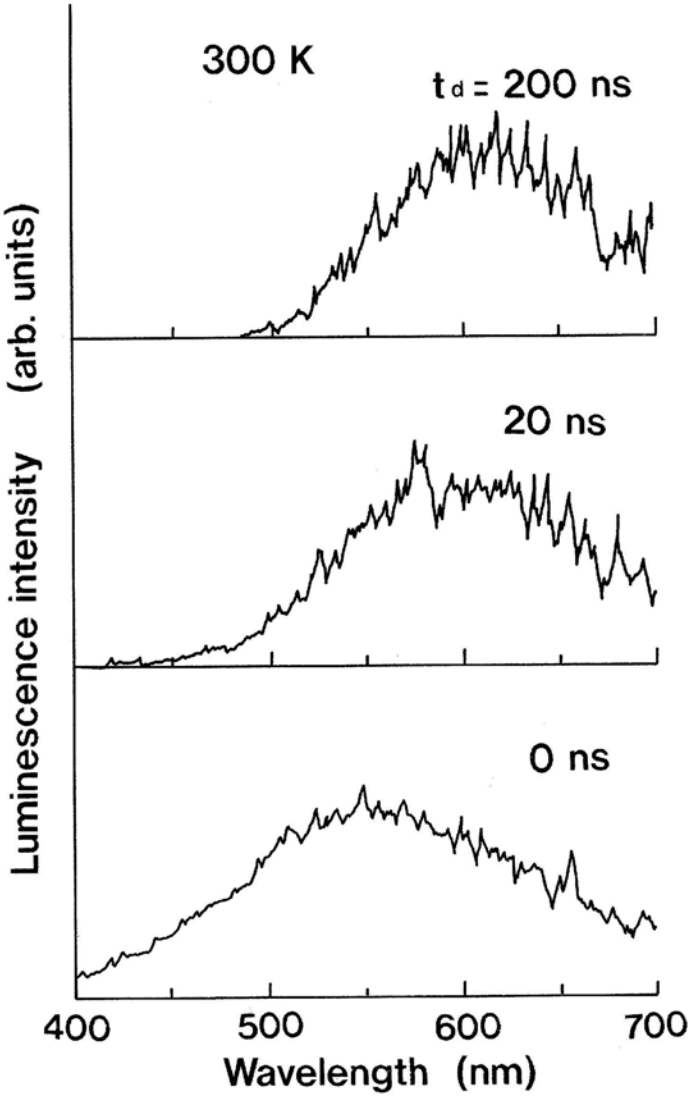

300 K
t_d = 200 ns
20 ns
0 ns
Luminescence intensity (arb. units)
400
500
600
700
Wavelength (nm)

Fig. 2

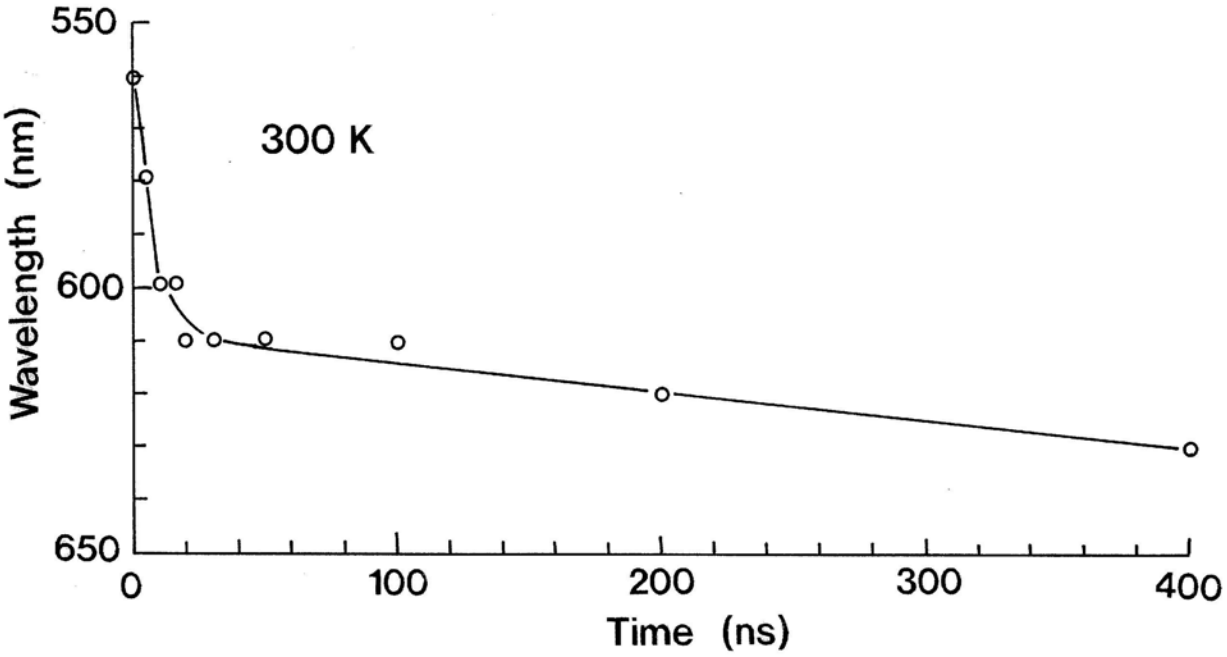

550
600
650
Wavelength (nm)
300 K
0
100
200
300
400
Time (ns)

Fig. 3

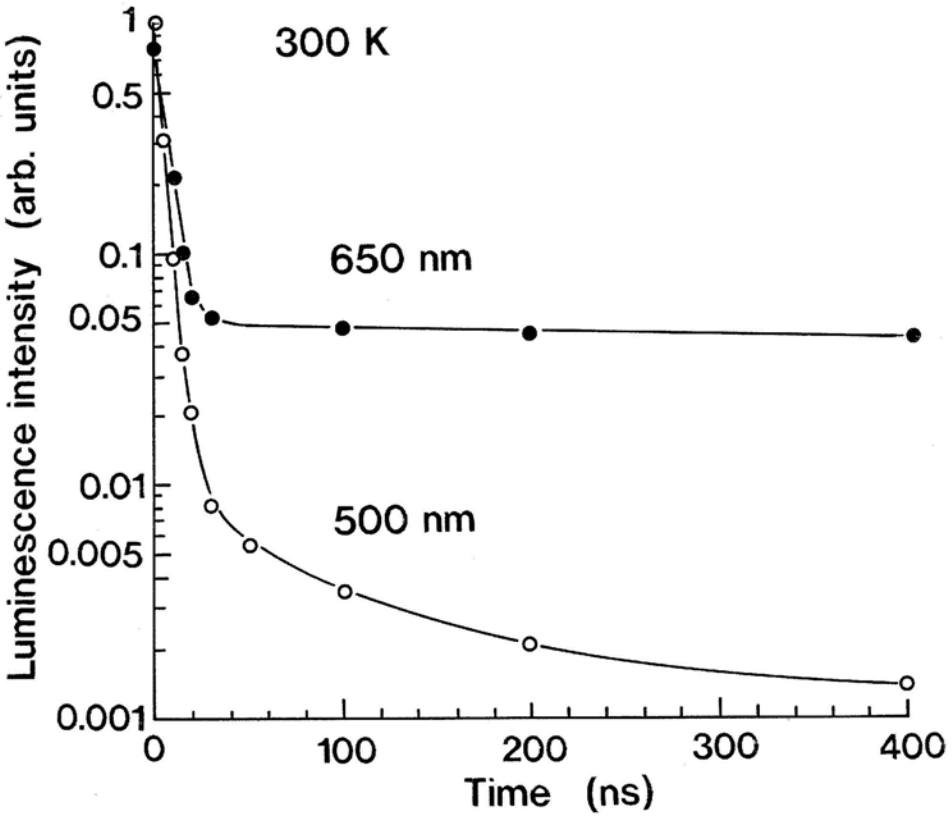
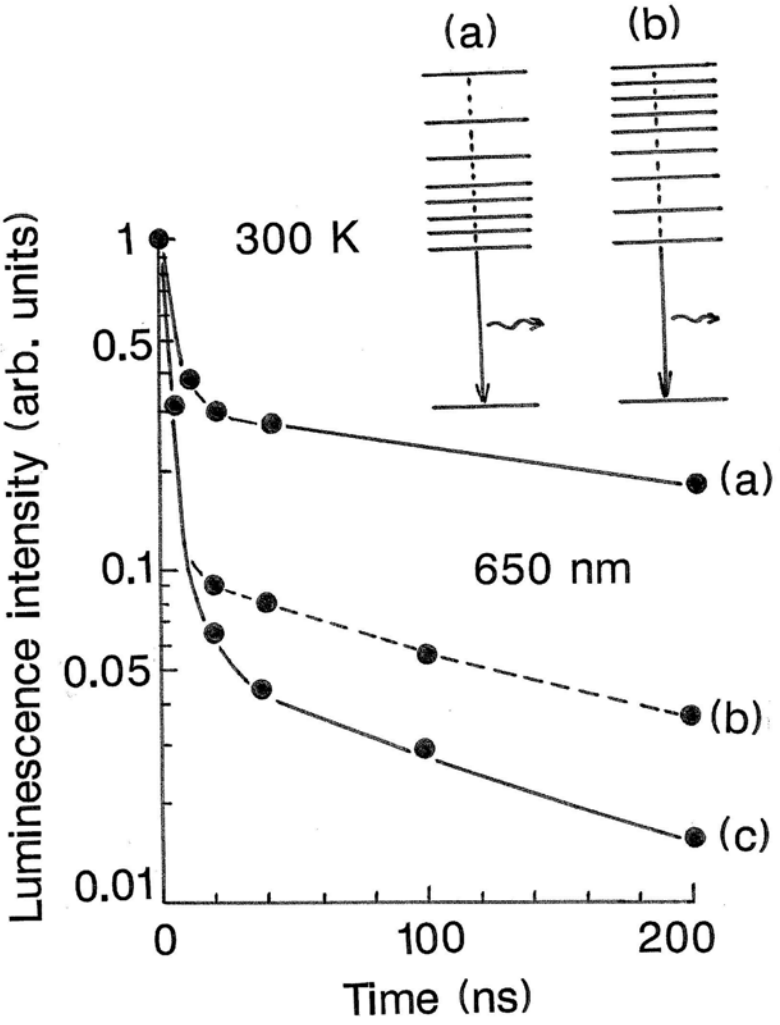

300 K
650 nm
500 nm
Luminescence intensity (arb. units)
1
0.5
0.1
0.05
0.01
0.005
0.001
0
100
200
300
400
Time (ns)

Fig. 4


(a)
(b)
300 K
650 nm
(a)
(b)
(c)
Luminescence intensity (arb. units)
1
0.5
0.1
0.05
0.01
0
100
200
Time (ns)