

Enhanced Yb³⁺-related 0.98 μm emission in porous silicon and its time decay characteristics

Tadamasa Kimura, Yasuhiro Nishida, Akinori Yokoi, and Riichiro Saito
University of Electro-Communications, 1-5-1 Chofugaoka, Chofu-shi, Tokyo 182, Japan

(Received 14 July 1997; accepted for publication 8 October 1997)

A strong enhancement in the intensity of the ~0.98 μm emission ($^2F_{5/2} \rightarrow ^2F_{7/2}$) of Yb³⁺-ions in porous silicon is obtained by adding a pre-annealing process to host porous silicon in O₂ or H₂ prior to Yb³⁺-ion incorporation and subsequent post-dope annealing. The luminescence intensity shows a small temperature quenching, decreasing from 20 K to 300 K by a factor of ~10. The time decay measurements show that there are two major Yb³⁺-related luminescence centers in Yb-doped porous silicon. One is a fast decaying center with a decay time of ~30 μs at 20 K which decreases rapidly with increasing temperature. The other is a slowly decaying center with an almost temperature independent decay time of ~400 μs. The latter is responsible for the small temperature quenching of Yb³⁺-related 0.98 μm emission. © 1998 American Institute of Physics. [S0021-8979(98)02702-9]

I. INTRODUCTION

A strong temperature quenching of the decay time of the Yb³⁺-related emission for Yb-doped crystalline semiconductors has been reported,^{1,2} and has been successfully explained in terms of the energy back flow mechanisms via an Yb³⁺-related trap level.³ However, we have recently reported that Yb³⁺-ions incorporated in porous silicon (PS) shows emission at ~0.98 μm with a small temperature quenching.⁴ In the photoluminescence of Yb³⁺-doped semiconductors, Yb³⁺ 4f-electrons of the spin orbit split $^2F_{5/2}$ and $^2F_{7/2}$ energy levels are excited by the recombination of electrons and holes generated when the samples are excited with an above bandgap energy laser line. Therefore, the Yb³⁺-related emission intensity is related to the density of the generated electrons and holes, energy transfer rate, and the fluorescence decay time of the Yb³⁺ luminescence centers.

This paper deals with improved material processes to increase the emission intensity of Yb³⁺ ions in porous silicon by more than ten times. It also deals with the time decay characteristics of the emission intensity of both Yb³⁺- and PS-related bands for these improved Yb-doped porous silicon (Yb:PS) samples in the temperature range from 20 K to room temperature. The causes of the small temperature quenching have also been studied.

II. EXPERIMENTAL PROCEDURE

Porous silicon is made by anodic etching of Czochralski-grown p-type Si (100) (6~12 Ω-cm) substrates in a 46% HF/H₂O solution for one hour at a current density of 6 mA/cm². The PS layers formed under this condition have a thickness of around 10 μm and show a luminescence band centered at 750~770 nm with a full width at half maximum (FWHM) of about 120 nm. Some of the PS samples are then pre-annealed in an Ar/O₂(20%) or pure H₂ ambient at 900 °C for 3 min prior to Yb³⁺ incorporation. This treatment should stabilize the PS hosts against post-dope high temperature annealing in a pure H₂ ambient (see below) by terminating dangling bonds with O or H atoms.

Incorporation of Yb³⁺ ions into PS hosts is carried out by dipping the PS in an YbCl₃/ethanol saturated solution for two hours. Electrochemical incorporation of Yb³⁺ ions is also used for PS samples which undergo no pre-annealing. A typical Yb concentration measured by secondary ion mass spectrometry (SIMS) is 3~4 × 10¹⁹/cm³. After the Yb³⁺-ion incorporation processes, samples are annealed in a pure Ar (99.9999%), pure H₂(99.9999%) or Ar/O₂(20%) ambient at high temperatures (1000~1100 °C) for 30 sec to 50 min using a lamp furnace in order to optically activate Yb³⁺ ions.

Photoluminescence (PL) measurements are carried out by exciting samples with the 514.5 nm line of an Ar ion laser. The PL signal is monitored using a single-grating monochromator (Jobin-Yvon HR320) and a cooled germanium pin photodiode (North-Coast EO-817L) for the luminescence measurements or a photomultiplier (Hamamatsu Photonics R1767) for the time decay measurements.

In the time decay measurements, the 514.5 nm line from a 100 mW Ar ion laser is chopped with an acousto-optic modulator (AOM). The duty ratio is 1:1 and the period is 10~100 msec. The time decay signal is monitored and recorded with a digital oscilloscope. The time constant of the measuring system is 0.18 μs.

III. RESULTS AND DISCUSSION

Fig. 1 shows the photoluminescence spectra of PS:Yb samples (no pre-annealing, electrochemical doping) at 20 K for different post-dope annealing atmospheres just after the Yb³⁺-ion incorporation. The post-dope annealing is carried out at 1000 °C for 20 min. As already mentioned in our previous paper,⁴ the Yb³⁺-related luminescence at ~0.98 μm is observed after post-dope annealing in a pure Ar ambient (middle curve) but not in an O₂ containing ambient (bottom curve). It is newly found in this study that when post-dope annealing is carried out in pure H₂, the Yb³⁺-related emission is increased by a factor of about four compared to annealing in pure Ar (top curve). The broad luminescence band on the higher energy side of the Yb³⁺

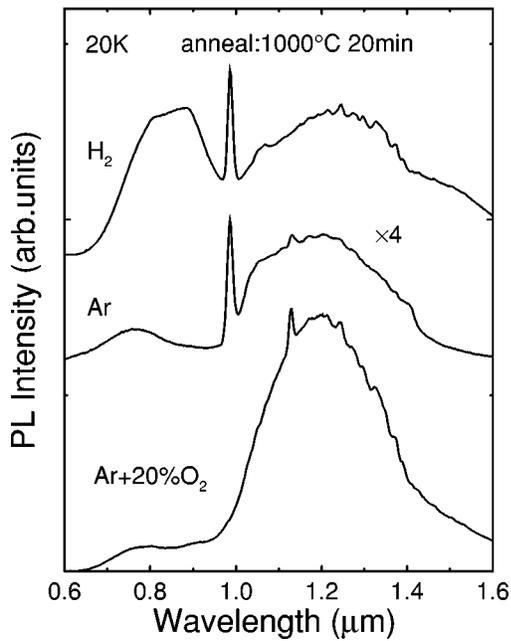


FIG. 1. Photoluminescence spectra of ytterbium doped porous silicon (PS:Yb) samples at 20 K for different post-dope annealing ambient just after the Yb³⁺-ion incorporation. The samples have no pre-annealing, and Yb³⁺ ions are electrochemically incorporated into PS. The annealing is carried out at 1000 °C for 20 min.

band in Fig. 1 is the band-to-band emission of the host PS which is modified by the annealing process. The band on the lower energy side may be related with defects in PS. (Note that the intensity on the low energy side is enhanced due to the spectral response of the germanium detector.)

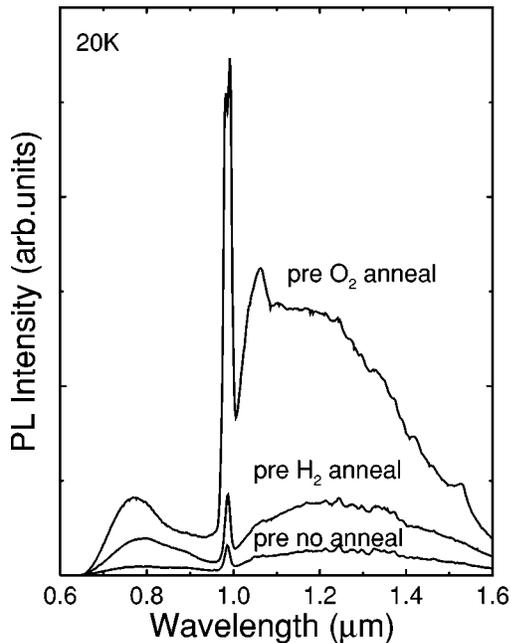


FIG. 2. Effects of pre-annealing of PS hosts in H₂ or Ar/O₂ (900 °C, 3 min) before Yb³⁺ incorporation on the photoluminescence spectra at 20 K. Here, the Yb³⁺ ions are incorporated by the dipping method, since the PS hosts become high resistive after pre-annealing in Ar/O₂(20%). The post-dope annealing is carried out in H₂ at 1100 °C for 30 sec.

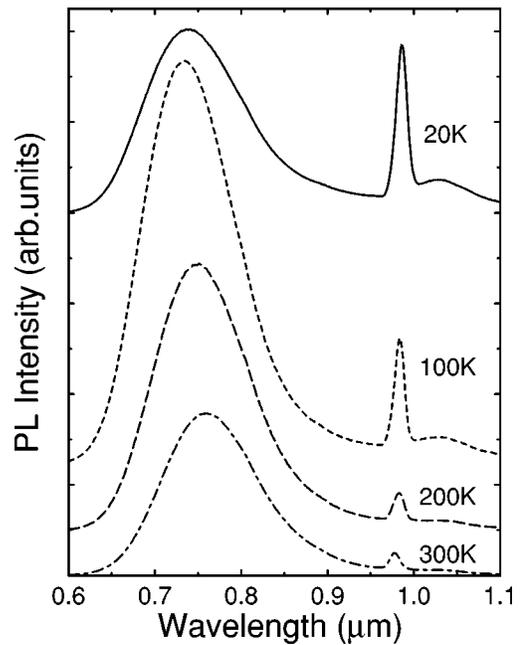


FIG. 3. Temperature dependence of the photoluminescence spectra of a PS:Yb sample. A photomultiplier tube is used for the detection. The PS host is pre-annealed in Ar/O₂(20%) at 900 °C for 3 min, doped with Yb³⁺ ions by dipping in YbCl₃/ethanol, and then post-dope annealed in H₂ at 1100 °C for 30 sec.

Fig. 2 shows the effects of pre-annealing of PS hosts in H₂ or Ar/O₂ before Yb³⁺ incorporation on the photoluminescence spectra at 20 K. Here, the Yb³⁺ ions are incorporated by the dipping method, since the PS hosts become highly resistive after pre-annealing in Ar/O₂(20%) and, hence, the electrochemical technique cannot be used. The post-dope annealing is carried out in H₂ at 1100 °C for 30 sec. It is found that pre-annealing in both H₂ and Ar/O₂ increases the intensity of Yb³⁺-related luminescence (top and middle). The enhancement is especially large after pre-annealing in Ar/O₂(20%) (more than ten times). We observe that the ~0.8 μm luminescence band of the PS hosts retains its original strong luminescence intensity as well as its spectral shape after the 1100 °C, 30 sec post-dope annealing in H₂ (compare with the spectrum shown at the top of Fig. 1). This indicates that the pre-annealing produces the PS hosts stable against the post-dope high temperature annealing in H₂, and that the stable and strong luminescence of the PS hosts results in a strong Yb³⁺-related emission. Note, however, that the Yb³⁺-related luminescence is not obtained even for the pre-annealed PS:Yb samples, when the post-dope annealing is carried out in Ar/O₂(20%).

Fig. 3 shows the temperature dependence of the photoluminescence spectra of a PS:Yb sample. Here a photomultiplier tube is used for the detection. The PS host is pre-annealed in Ar/O₂(20%) at 900 °C for 3 min, doped with Yb³⁺ ions by dipping in YbCl₃/ethanol, and then post-dope annealed in H₂ at 1100 °C for 30 sec. The temperature dependence of the intensity of the Yb³⁺-related ~0.98 μm emission is nearly the same as reported in reference 4. The intensity decrease from 20 K to 300 K is a factor of ~10. Contrary to the Yb³⁺-related peak, the peak intensity of the

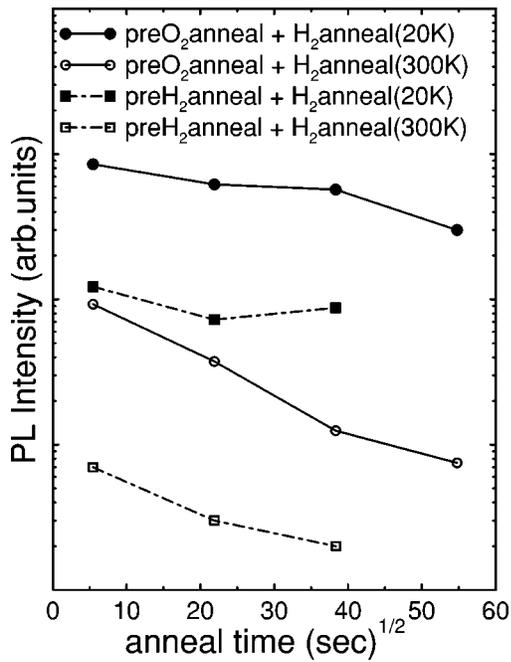


FIG. 4. Dependence of the 0.98 μm intensity at 20 K and 300 K on the post-dope annealing time at 1100 $^{\circ}\text{C}$ for PS:Yb samples which are pre-annealed in $\text{Ar}/\text{O}_2(20\%)$ or in H_2 at 900 $^{\circ}\text{C}$ for 3 min.

luminescence band of the PS host increases at first, reaches a maximum and then decreases again with increasing temperature.

Fig. 4 shows the dependence of the 0.98 μm intensity at 20 K and 300 K on the post-dope annealing time at 1100 $^{\circ}\text{C}$ for PS:Yb samples which are pre-annealed at 900 $^{\circ}\text{C}$ in $\text{Ar}/\text{O}_2(20\%)$ or in H_2 for 3 min. The intensity decreases slowly with increasing post-dope annealing time, and the temperature quenching of the intensity becomes a little bit larger.

The role of the post-dope annealing ambient is very important. In the case of Er^{3+} ions in porous silicon, oxygen is found to be more effective for the optical activation than hydrogen, nitrogen or vacuum as a post-dope annealing ambient.⁵ This means that the ligand atoms or the environment of the rare earth ions is strongly related to the optical activation. It is not yet clear why a hydrogen atmosphere is effective and an oxygen atmosphere is ineffective for the optical activation of Yb^{3+} ions in the post-dope annealing, although the pre-annealing in $\text{Ar}/\text{O}_2(20\%)$ enhances the Yb^{3+} -related emission greatly. SIMS data does not show any marked decrease in the oxygen content in the porous silicon layer ($5 \times 10^{22}/\text{cm}^3 \sim 1 \times 10^{23}/\text{cm}^3$) nor marked increase in the H_2 content ($\sim 5 \times 10^{20}/\text{cm}^3$) after post-dope annealing in H_2 . It is speculated that the formation of Yb-H complexes may be responsible for the intense luminescence of Yb^{3+} -related 0.98 μm emission.

The time decay measurements are carried out for the enhanced Yb^{3+} -related 0.98 μm emission in the temperature range from 20 K to room temperature and the results are shown in Fig. 5. At 20 K, the decay curve is expressed approximately by two (fast and slow) time constants. The initial intensity decays down to less than 1/10 with a time con-

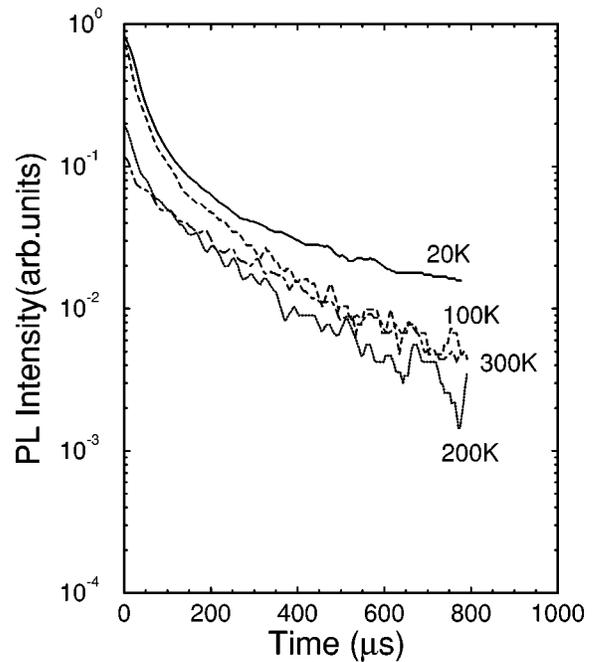


FIG. 5. Time decay of Yb:PS samples for the enhanced Yb^{3+} -related 0.98 μm emission in the temperature range from 20 K to room temperature. The sample processes are the same as in Fig. 4.

stant of $\sim 30 \mu\text{s}$, which is then followed by a slow decay with a decay time of $\sim 470 \mu\text{s}$. With increasing temperature, the fast decay component decreases and, the decay curve is approximately described by one slow decay time at 300 K (the fitted value is $\sim 390 \mu\text{s}$).

The time decay of the luminescence intensity at 0.98 μm of undoped PS samples which undergo the same processes as those of the PS:Yb is also measured in order to eliminate the base luminescence of the PS hosts. The results are shown in Fig. 6, where the scale of the ordinate is adjusted to that of Fig. 5. At 20 K, the intensity decreases quickly ($\tau \sim 49 \mu\text{s}$) at the initial stage down to about a half, and thereafter decreases slowly with a time constant of 4 ms. The decay becomes faster with increasing temperature, and it shows a time constant of $\sim 40 \mu\text{s}$, followed with a slowly decaying tail with a time constant of $\sim 240 \mu\text{s}$ at 300 K. The decay characteristics of the band-to-band emission of the PS hosts at 0.75 μm are similar to those at 0.98 μm . The slow tail of the PS luminescence at 20 K is caused by the pre-annealing in an $\text{Ar}/\text{O}_2(20\%)$ ambient. The band-to-band luminescence of the PS:Yb samples which are not annealed in the $\text{Ar}/\text{O}_2(20\%)$ ambient decays much faster with the initial decay time of $\sim 40 \mu\text{s}$ and the tail decay time of ~ 0.8 ms. Comparing Fig. 5 with Fig. 6, the slowly decaying tail observed for PS:Yb at 20 K in Fig. 5 is due to the slowly decaying background luminescence of the PS hosts, and the real tail of the Yb^{3+} -related emission at 20 K is speculated to have a faster decay time. Above 200 K, on the other hand, the background luminescence due to the PS host in Fig. 6 decays much faster than the Yb^{3+} -related luminescence in Fig. 5, and therefore, the slow decay observed above 200 K in Fig. 5 is characteristic of the Yb^{3+} -related 0.98 μm luminescence.

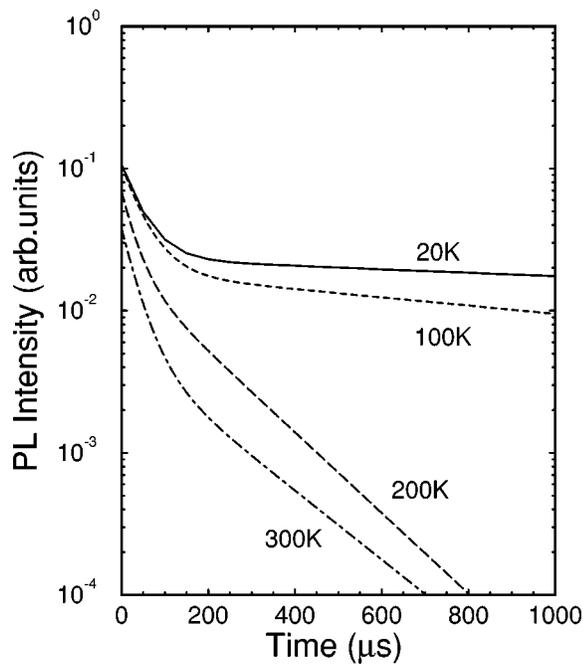


FIG. 6. Time decay of the luminescence intensity at $0.98 \mu\text{m}$ of undoped PS samples which undergo the same processes as those of the PS:Yb in Fig. 4. The scale of the ordinate is the same as that of Fig. 4.

The temperature dependence of the time decay of the Yb^{3+} -related $0.98 \mu\text{m}$ emission is completely different from that of the Yb^{3+} emission reported for Yb-doped crystalline semiconductors, for example, Yb-doped InP, where the decay becomes faster with increasing temperature.^{1,2} The strong temperature quenching of Yb-doped InP is explained in terms of the energy backflow to the host via Yb^{3+} -related traps.³ We speculate that the temperature dependence of the decay curve of Yb:PS measured in this study may be explained in terms of two different Yb^{3+} -related luminescence centers, as has been discussed for Er:InP in reference 6. One of these is a center which dominates the low temperature luminescence, with a fluorescent lifetime, and therefore intensity, which decreases rapidly with increasing temperature. The other center has a slow decay time which is less dependent on temperature. Since the host porous silicon is considered very varied in its crystal structure, we can expect various Yb^{3+} centers which are in different crystal fields or those which form different types of complexes with various impurities. Moreover, the emission band of the host porous silicon is very broad, and there may be various paths, via which the e-h recombination energy is transferred from the host to the Yb^{3+} ions. The large thermal quenching of the fast decaying component may be due to centers which show a strong coupling with the host porous silicon, leading to an increased energy backflow with increasing temperature. The centers which shows a slow decay with almost no temperature quenching may have a loose coupling with the host, leading

to little energy backflow even at room temperature. The centers which have a loose coupling with the host have been observed in rare-earth doped wide gap semiconductors or even in Er-doped InP and Er-doped Si when they are pumped by impact excitation.^{7,8} These centers become dominant at high temperatures, since the centers with a faster decay time shows a large temperature quenching. We observe a slight difference in the wavelength (energy) of the Yb^{3+} -related emission peak between 20 K and room temperature. The peak is located at $0.986 \mu\text{m}$ (1.258 eV) at 20 K, whereas it is at $0.982 \mu\text{m}$ (1.263 eV) at room temperature. This may support the idea of the presence of two Yb^{3+} optically active centers in Yb:PS.

A more detailed study in relation with the crystalline and optical parameters of the host porous silicon (e.g., luminescent energy, annealing conditions etc.) is necessary to give a deeper insight into the decay mechanisms of the Yb^{3+} -related centers in porous silicon.

IV. CONCLUSION

Very strong luminescence at $0.98 \mu\text{m}$ due to the intra $4f$ transition of Yb^{3+} ions is obtained from Yb^{3+} -ion doped porous silicon, when the host porous silicon is pre-annealed at 900°C for 3 min in an $\text{Ar}/\text{O}_2(20\%)$ or H_2 atmosphere prior to Yb^{3+} ion incorporation and post-dope anneal in H_2 at 1100°C for 30 sec. The intensity of the luminescence decreases slowly from 20 K to 300 K by a factor of about 10. The temperature dependence of the time decay shows two major Yb^{3+} luminescence centers. One has a decay time of $\sim 30 \mu\text{s}$ at 20 K which decreases rapidly with increasing temperature and the other has a decay time of around $400 \mu\text{s}$ which is almost independent of temperature and responsible for the room temperature emission.

ACKNOWLEDGMENTS

This work is partly supported by the grant in aid (No. 07555135) by the Ministry of Education, Science, Sports, and Culture. We thank Dr. T. Ikoma of TI Japan, Dr. H. Isshiki, Dr. S. Yugo, and Mr. H. Horiguchi for valuable discussions and technical supports. We also thank Dr. H. Yasuhara and Dr. A. Sato of Fujikura Co. Ltd. for their support of this research.

¹P. B. Klein, *Solid State Commun.* **65**, 1097 (1988).

²K. Takahei, A. Taguchi, H. Nakagome, K. Uwai, and P. S. Whiteny, *J. Appl. Phys.* **66**, 4941 (1989).

³A. Taguchi, H. Nakagome, and K. Takahei, *J. Appl. Phys.* **70**, 5604 (1991).

⁴T. Kimura, A. Yokoi, Y. Nishida, R. Saito, S. Yugo, and T. Ikoma, *Appl. Phys. Lett.* **67**, 2687 (1995).

⁵T. Kimura, A. Yokoi, H. Horiguchi, R. Saito, T. Ikoma, and A. Sato, *Appl. Phys. Lett.* **65**, 983 (1994).

⁶T. Kimura, H. Isshiki, H. Ishida, S. Yugo, R. Saito, and T. Ikoma, *J. Appl. Phys.* **76**, 3714 (1994).

⁷H. Isshiki, R. Saito, T. Kimura, and T. Ikoma, *J. Appl. Phys.* **70**, 6993 (1991).

⁸G. Franzó, F. Priolo, S. Coffa, A. Polman, and A. Carnera, *Appl. Phys. Lett.* **64**, 2235 (1994).