

Photoluminescence of ytterbium-doped porous silicon

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Yb³⁺-related photoluminescence is observed at room temperature from Yb-doped porous silicon layers prepared by the electro-chemical method developed by our group for Er doping of porous silicon layers. After rapid thermal annealing in a pure argon atmosphere at high temperatures (above ~ 900 °C), samples show a sharp photoluminescence band at around 1.0 μm which is assigned to the intrashell 4*f*-4*f* transitions ²F_{5/2} → ²F_{7/2} of Yb³⁺. The enlarged energy bandgap of silicon as a result of anodization makes possible the excitation of Yb³⁺ 4*f*-electrons with the recombination energy of photocarriers generated in the host porous silicon layers. © 1995 American Institute of Physics.

Luminescence of rare earth (RE) doped semiconductors has been intensively studied due to their potentialities for optical devices.^{1,2} The successful observations of both photo- and electro-luminescence of Er-doped silicon at 1.54 μm^{3,4} have aroused special interests in the developments of silicon-based optoelectronic devices, since the emission wavelength corresponds to the lowest loss of the optical fibers. However, because the luminescence energy of RE ions is limited below the bandgap of crystalline silicon (1.1 eV at room temperature), very few studies have been reported on the luminescence of RE-doped Si other than Er-doped Si, for instance, the luminescence of Tm-implanted Si at 6 K in the 0.95 to 1.01 eV region.⁵ Very recently, luminescence of Yb-implanted Si at around 1.0 μm at 77 K has been reported.⁶ However, the spectra are very broad (~200 nm) and no explanation for the excitation mechanism in relation with the emission energy (centered at ~1.24 eV) and the bandgap of silicon (~1.18 eV at 77 K) has been made.

In the case of Er-doped silicon, the small difference between the bandgap of host silicon and the luminescence energy of Er³⁺ results in a large thermal quenching and an extremely low luminescence efficiency at room temperature. Co-implantation of oxygen,⁷ use of O-rich liquid encapsulated Czochralski silicon substrates⁷ or semi-insulating polycrystalline silicon (SIPOS)⁸ with high content oxygen as host materials has been found to reduce the thermal quenching of the Er³⁺-related 1.54 μm luminescence and to increase the luminescence intensity at room temperature. We have recently reported on the electro-chemical Er incorporation into porous silicon layers (PSLs) and a strong room temperature Er³⁺-related 1.54 μm luminescence.⁹ The very small thermal quenching up to room temperature has been ascribed to the enlarged bandgap of PSLs. In this study, we report on the luminescence of Yb³⁺ ions which are incorporated into PSLs with the above electro-chemical method.

PSLs are made by anodically etching Czochralski-grown p-type Si (100) (several Ω-cm) substrates in a room-temperature 46% HF/H₂O solution for one hour at a current density of 6 mA/cm². The thickness of the PSLs formed is around 10 μm. The PSLs formed under this condition show a luminescence band centered at ~800 nm with a full width at half maximum (FWHM) of about 100 nm. After rinse in deionized water, PSLs are immersed in an YbCl₃/ethanol solution and are negatively biased relative to a counter platinum electrode to draw Yb³⁺ ions into pores of PSLs by the electric field. The total charge of 0.21 C/cm² which corresponds to 4.4 × 10¹⁷ Yb³⁺/cm² is introduced into the PSLs at a constant current density of 0.14 mA/cm². Thereafter, samples are annealed at high temperatures (900–1300 °C) in a pure Ar (99.9998%) atmosphere using a lamp furnace. Photoluminescence (PL) measurements are carried out by exciting samples with an Ar-ion laser 514.5 nm line. The PL signal is monitored using a single-grating monochromator (Jobin-Yvon HR320) and a cooled germanium pin photodiode.

Figure 1 shows the isochronal annealing temperature dependence of the PL spectra of Yb-doped PSLs for the annealing time of 30 s. A sharp luminescence band at about 1.0 μm is observed above 900 °C. Its intensity becomes maximum at about 1100 °C and then decreases at higher annealing temperatures. This luminescence band is not observed either after annealing in Ar/20%O₂ nor from undoped PSLs. The broad band centered at ~0.8 μm is the luminescence of the host PSLs and the other broad band with a small fine structure ranging from 1.0 to 1.4 μm is considered to be related with defects in PSLs. The latter two bands are also observed in undoped PSLs and unannealed Yb-doped PSLs. Note that the peak at ~1.0 μm is still clearly observed after annealing at 1200 °C, when the photoluminescence from the host PSLs almost disappears.

Figure 2 shows the photoluminescence spectra of Yb-doped PSLs annealed at 1300 °C for 3 min measured at various temperatures. A narrow emission band is observed at

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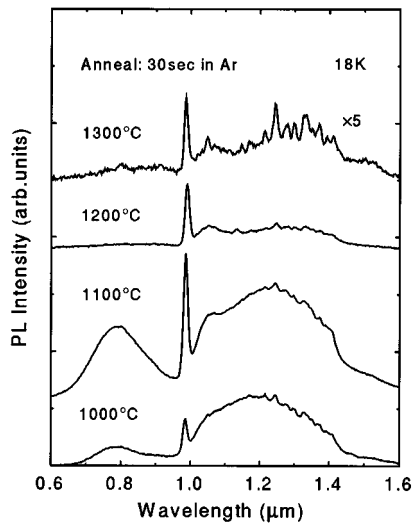


FIG. 1. Isochronal annealing dependence of the photoluminescence spectra of Yb-doped PSLs. Annealing time is 30 s in pure Ar.

0.985 μm with a FWHM of 10 nm. The peak energy is found almost constant with changing measuring temperature from 18 K to room temperature, and we assign this peak to the Yb^{3+} intrashell $4f$ - $4f$ transition ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$. In contrast, many small peaks observed on the lower energy side are found to shift to lower energies with increasing temperatures, indicating that they are presumably related with crystal defects of PSLs.

In most intensively studied Yb-doped InP, the major Yb^{3+} -related luminescence peaks are located at ~ 1002 nm (strongest) and ~ 1007 nm (second strongest) with weak phonon side bands in the lower energy range and hot lines in the higher energy range.¹⁰ Strong Yb^{3+} -related emission bands in the energy range higher than 1.24 eV, as in the present study, have been observed for Yb incorporated in wide bandgap semiconductors; for instance, in ZnS,¹¹ GaP,^{10,12} and GaAs.¹⁰

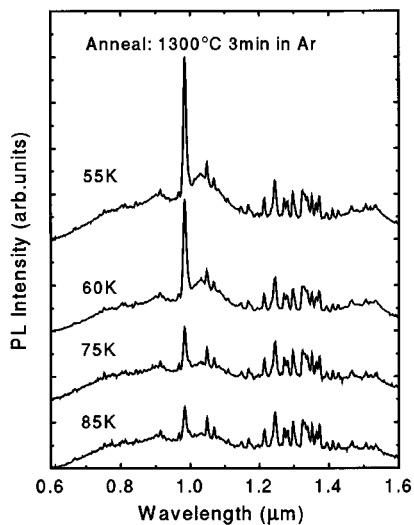


FIG. 2. Temperature dependence of the photoluminescence spectra of Yb-doped PSLs annealed at 1300 $^{\circ}\text{C}$ for 3 min.

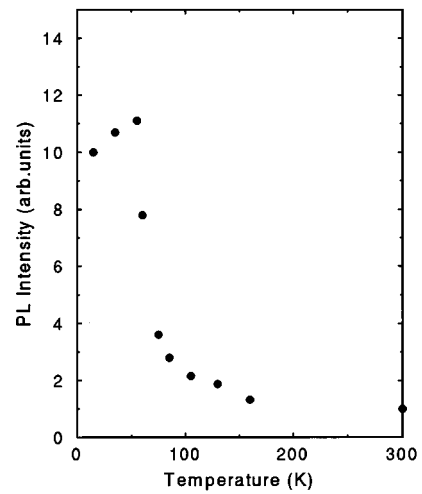


FIG. 3. Temperature dependence of the Yb-related luminescence intensity of Yb-doped PSLs.

Figure 3 shows the temperature dependence of the intensity of the Yb^{3+} -related peak of an Yb-doped PSL annealed at 1300 $^{\circ}\text{C}$ for 3 min from 18 K to room temperature. With increasing temperature, the intensity begins to increase slightly at first, then decreases above 50 K. The decrease is not, however, rapid. The PL intensity activation energy obtained from Fig. 3 is about 15 meV.

For Yb-doped InP, the PL intensity of the Yb^{3+} peak begins to decrease rapidly above ~ 80 K. The activation energy relevant to this rapid thermal quenching ranges from 115 meV¹³ to 150 meV.¹⁴ In the low temperature range before the rapid thermal quenching takes place, however, the PL intensity shows sometimes a slight decrease with increasing temperature with a small activation energy (for instance, 10.8 meV¹³). The Er^{3+} -related 1.54 μm peak in InP also shows a small and a large activation energy (40 meV and 150 meV, respectively).¹⁵

The activation energy for the rapid thermal quenching corresponds to the binding energy of an electron to the RE trapping center.^{16,17} Accordingly, the larger the bandgap of host semiconductors, the larger the activation energy, and the higher the temperature for the rapid thermal quenching to take place. Our PSLs with a PL spectrum centered at around 1.55 eV may show a rapid thermal quenching much above the room temperature. Similar small thermal quenching with a small activation energy for below room temperature measurements were also reported for Yb/ZnS,¹¹ Er/GaP,¹⁸ etc. This small activation energy was explained in terms of a mechanism similar to the charge-transfer mechanism via RE-bond exciton.¹¹ The 15 meV activation energy of our Yb/PSL may also be related to a de-excitation process between the $4f$ -shell of Yb^{3+} and an Yb-related center, but we have at present no definite idea about the center.

Because of the simple two level scheme of the Yb^{3+} $4f$ -electron energy states with a separation of ~ 1.24 eV, the $4f$ -electrons are undoubtedly excited through a photocarrier-mediated process. Electron-hole pairs are first generated in silicon nanocrystallites by the 514.5 nm laser light excitation and then their recombination energy is transferred to Yb^{3+}

ions. This is, in principle, impossible in the case of Yb-doped bulk crystalline Si because of its smaller bandgap relative to the Yb^{3+} luminescence energy. The enlarged bandgap of host PSLs makes possible the excitation of Yb^{3+} 4f-electrons with the electron-hole recombination energy.

As is shown in Fig. 1, the Yb^{3+} -related luminescence is not directly related with the luminescence of host PSLs (the spectra of the samples annealed at 1200 °C and 1300 °C). This result indicates two important facts. First, the possibility of the excitation of Yb^{3+} ions with the light emitted from the host PSLs is excluded. Second, disappearance of the photoluminescence from PSLs does not directly mean the disruption of the porous structure. The decrease in the PL intensity of porous silicon by high temperature annealing in Ar is due to desorption of hydrogen atoms which passivate the surface of nanocrystallines, resulting in increased nonradiative centers. The radiative lifetime of porous silicon similar to our samples (*p*-type substrate, $\sim 20 \Omega\text{-cm}$, luminescence peak at 1.55–1.8 eV) is $\sim 1\text{--}10$ ms at low temperatures and on the order of $\sim 100 \mu\text{s}$ at room temperature.¹⁹ On the other hand, our preliminary measurement shows that the decay time of the Yb^{3+} -related peak in PSLs lies in the microsecond range at low temperatures, which is consistent with that observed for Yb-doped InP.^{13,20} Therefore, even if the luminescence of porous silicon at low temperatures is killed due to increased nonradiative centers, we can expect a situation in which the energy transfer process from the photocarriers generated in silicon nanocrystallites to Yb^{3+} centers can still be competitive with the nonradiative decay processes via surface states.

In conclusion, Yb^{3+} ions are incorporated into porous silicon layers by the electro-chemical method and a strong Yb^{3+} -related photoluminescence at $\sim 1.0 \mu\text{m}$ is observed at room temperature. These results suggest that the luminescence of various rare earth ions with energies larger than the energy bandgap of crystalline silicon will be obtained by using porous silicon layers as host materials. This will open the way to the RE-doped silicon based optical devices in a wide luminescence energy range.

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