Effects of hydrogen plasma treatment on the 1.54 μm luminescence of erbium-doped porous silicon

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Well resolved, sharp photoluminescence (PL) peaks of Er^{3+} ($4f^{11}$) ions at $\sim$1.54 μm are obtained from Er-doped porous silicon (PS:Er) on which a hydrogen plasma treatment is carried out after electrochemical incorporation of Er^{3+} ions into porous silicon. The full width at half maximum (FWHM) of the 1.538 μm main peak at 20 K is less than 1 nm, which is much smaller than that obtained from PS:Er samples annealed in a H_2 or O_2 flow (FWHM 7–10 nm), and is comparable to that of Er-doped crystalline silicon. The thermal quenching of the PL intensity is, however, relatively small, the PL intensity decreasing only by a factor of 10 from 20 to 300 K. © *1998 American Institute of Physics.* [S0021-8979(98)03114-4]

I. INTRODUCTION

Er-doped silicon which illuminates at $\sim$1.54 μm has been attracting much attention as a light source for silicon based optoelectronic devices.[1,2] However, Er-doped crystalline Si shows a large thermal quenching of the luminescence intensity, which leads to almost no luminescence intensity at room temperature. Co doping of Er and O ions, for example, by ion implantation[3,4] or by chemical vapor deposition,[5] has been found to reduce the thermal quenching. Formation of Er–O complexes is thought to reduce the energy backflow from Er^{3+} ions to Er related traps or to free carriers in the host materials.[6]

Recently, we have shown a strong Er related 1.54 μm luminescence at room temperature, using Er-doped porous silicon (PS:Er),[7] in which Er^{3+} ions are electrochemically incorporated and the subsequent annealing is performed in an O_2(20%)/Ar(80%) gas flow at temperatures above 1000 °C. Widening of the band gap of Si due to the quantum size effect[8] as well as the formation of Er–O complexes[3,4,9,10] is speculated to reduce the thermal quenching.[11] A small thermal quenching has also been obtained in PS:Er, in which Er is incorporated by Er spin coating,[12] by Er-ion implantation,[13,14] or by immersing PS into an $ErCl_3$/C_2H_5OH saturated solution,[15] followed by annealing in an O_2 or N_2 gas flow at high temperatures. Er implanted semi-insulating polycrystalline silicon, Er-doped amorphous silicon (*a*-Si) with a high content of oxygen[16] and Er-doped *a*-Si:H[17] have also shown a strong Er related 1.54 μm luminescence at room temperature. However, the luminescence is generally broad, which may be relevant to various crystal fields for Er^{3+} ions incorporated in noncrystalline samples. Recently, very sharp peaks at 1.539 and 1.548 μm have been reported by Stepikhova *et al.*[18] in Er-doped PS at 4.2 K. However, they are observed only at low temperatures.

In this paper, we show a breakthrough technique which uses a high-temperature hydrogen plasma treatment as an annealing method which is needed to obtain the Er related luminescence after electrochemical incorporation of Er ions into porous silicon. The hydrogen plasma treatment is adopted first with an intention of plasma etching of amorphous as well as oxidized silicon around silicon nanocrystals with an oxygen-free atmosphere. Second, passivation of the dangling bonds, which appear after plasma etching, with activated hydrogen atoms is also expected. As a result, sharp Er related luminescence peaks with a small thermal quenching have been obtained. These results are shown and the effects of hydrogen plasma treatment are discussed.

II. EXPERIMENTS

PS samples are obtained from Czochralski-grown *p*-type Si(100) wafers (resistivity: ρ=6–12 Ω cm) which are anodically etched in a 1:1 HF(46%)/ethanol solution at 40 °C for 10 min at a constant current density of 20 mA/cm². The thickness of the PS layers obtained is estimated around 17 μm by scanning electron microscope (SEM). The photoluminescence (PL) of as-anodized PS shows a broad peak at 0.8 μm with a FWHM of $\sim$0.2 μm at room temperature. After rinsed with ethanol, the as-anodized PS samples are dipped in a saturated $ErCl_3$/ethanol solution and doped with Er^{3+} ions by applying a negative bias to the PS at a constant current density of 0.14 mA/cm². A total charge of 0.21 C/cm² is introduced into the PS. The density of the Er ions, measured by secondary ion mass spectroscopy (SIMS), is almost uniform in the whole PS layers at a density of 7 $\times 10^{19}$/cm³, which is smaller than that simply estimated from the total charge (3×10^{20}/cm³).

Annealing at a high temperature is needed after the Er incorporation into PS to obtain the Er related 1.54 μm luminescence. We have employed the following three annealing ambients: (1) O_2(20%)/Ar(80%) gas flow, (2) pure H_2 gas flow, and (3) hydrogen plasma. The annealing in an O_2/Ar or H_2 flow is carried out at 1300 °C for 30 s with a flow rate of 500 cc/min at the atmospheric pressure. This condition is found to result in the maximum intensity for the Er related 1.54 μm luminescence by this gas flow method. The hydro-
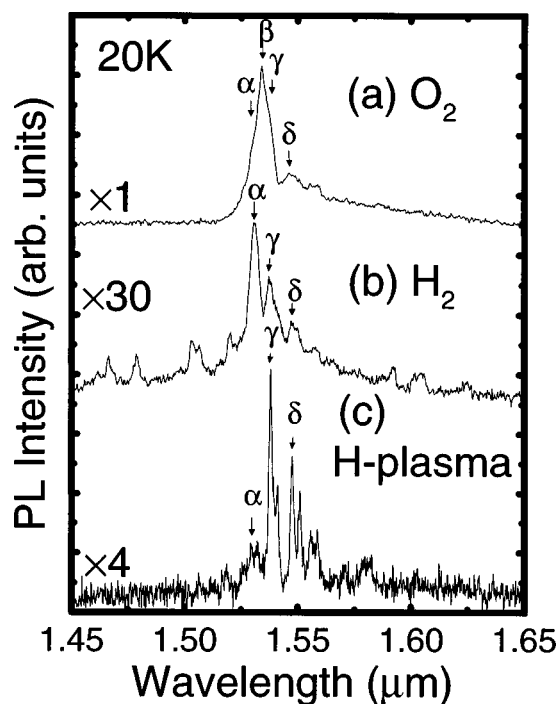
FIG. 1. Photoluminescence spectra at 20 K of Er-doped porous silicon samples annealed (a) in $O_2(20\%)/Ar(80\%)$ at 1300 °C, (b) in H_2 at 1300 °C, and (c) in hydrogen plasma at 1000 °C. The duration times are (a) 30 sec, (b) 30 sec, and (c) 30 min. The values of wavelength are α:1.530 μm, β:1.534 μm, γ:1.538 μm, and δ:1.547 μm.

gen plasma is obtained by applying 2.54 GHz, 600 W microwave power to the H_2 gas which is flown at a rate of 350 cc/min. Under this condition, the pressure of the H_2 gas is 30 Torr and the samples are heated to 1000 °C. The treatment time is 30 min.

Photoluminescence measurements are carried out using the 514.5 nm line of an argon ion laser. The luminescence signal is monitored by using a single grating monochromator (Jobin-Yvon HR320) and a cooled germanium pin photodiode. In order to investigate the chemical bond structure of samples, Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer FTIR spectrometer SPECTRUM-2000) is used in a resolution of 0.2 cm^{-1}.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the photoluminescence spectra at 20 K of the Er-doped porous silicon samples annealed (a) in $O_2(20\%)/Ar(80\%)$ at 1300 °C for 30 s (PS:Er/O_2), (b) in H_2 at 1300 °C for 30 s (PS:Er/H_2), and (c) in hydrogen plasma at 1000 °C for 30 min (PS:Er/H plasma). Samples annealed in $O_2(20\%)/Ar(80\%)$ show a strong but broad luminescence centered at 1.534 μm (indicated with β) with a FWHM of 10 nm [Fig. 1(a)]. As discussed in Sec. I, the strong luminescence is thought due to the formation of Er–O complexes.[3] The large value for the FWHM obtained is consistent with the values of previous reports.[12–15] It should be noted that two shoulders are observed at 1.530 μm (α) and 1.538 μm (γ) around the peak. Annealing of PS:Er samples in a pure H_2 gas flow results in narrower luminescence peaks as shown

in Fig. 1(b). The main peak is located at 1.530 μm (α) with a FWHM of 7 nm together with subpeaks at 1.538 μm (γ), 1.547 μm (δ) and so on. The different wavelengths for the main peak between Figs. 1(a) and 1(b) indicate that the Er^{3+} ions in different crystal fields are responsible for these two luminescence peaks. It is of interest that the main peak at 1.534 μm (β) for PS:Er/O_2 [Fig. 1(a)] corresponds to the local minimum of the intensity for PS:Er/H_2 [Fig. 1(b)], whereas the main peak at 1.530 μm (α) for PS:Er/H_2 corresponds to one of the shoulder peaks for PS:Er/O_2. The luminescence intensity of the main peak for PS:Er/H_2 is however only 1/30 that of the main peak for PS:Er/O_2.

As shown in Fig. 1(c), the hydrogen plasma treatment is found not only to bring about a very sharp luminescence structure, but also to give a PL intensity comparable to that of PS:Er annealed in $O_2(20\%)/Ar(80\%)$. At least, six sharp peaks are clearly observed in the luminescence of PS:Er/H plasma. The main peak which is located at 1.538 μm (γ) has a FWHM less than 1 nm. This value is by one order smaller than that of PS:Er/O_2. The wavelength of the main peak corresponds to that of the second maximum peak in PS:Er/H_2, whereas the 1.530 μm (α) main peak in PS:Er/H_2 is very small in PS:Er/H plasma. The intensity of the main peak in PS:Er/H plasma (γ at 1.538 μm) amounts to one-third that of the main peak of the PS:Er/O_2 samples (β at 1.534 μm), and is about 10 times as strong as the intensity of the main peak of the PS:Er/H_2 samples (α at 1.530 μm).

Two effects are speculated for the hydrogen plasma treatment: one is the plasma etching of the amorphous and/or oxidized surface layers around Si nanocrystallites in the PS
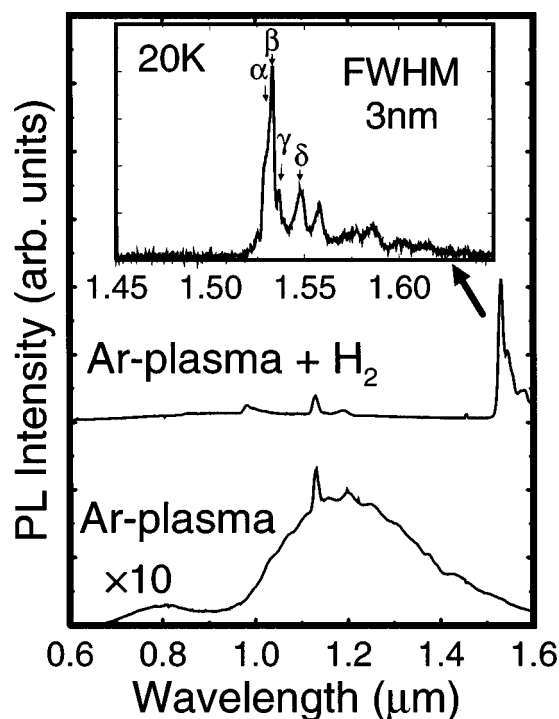

FIG. 2. PL spectra at 20 K for Er-doped porous silicon sample annealed in Ar-plasma at 1000 °C for 30 min (lower), and sample annealed in Ar plasma at 1000 °C for 30 min and subsequent H_2 gas flow at 1300 °C for 30 s (upper). The inset shows enlarged section near 1.54 μm for the case of Ar plasma and H_2 gas flow. The values of wavelength are α:1.530 μm, β:1.533 μm, γ:1.537 μm, and δ:1.547 μm.
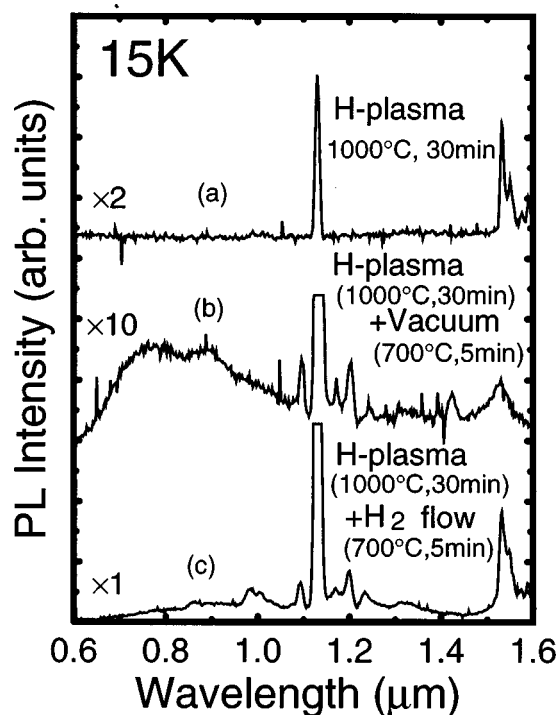
FIG. 3. PL spectra at 15 K for Er-doped porous silicon samples annealed (a) in hydrogen plasma at 1000 °C for 30 min, (b) in hydrogen plasma and subsequent vacuum anneal at 700 °C for 5 min, and (c) in hydrogen plasma and subsequent H_2 gas flow at 700 °C for 5 min.

layer due to enhanced supply of hydrogen radicals, and the other is the passivation of dangling bonds, which may be formed on the surface of the nanocrystals due to plasma etching, with hydrogen atoms during the hydrogen plasma treatment and/or in the cooling process with a H_2 gas flow.

In order to estimate the effects of plasma etching, PS:Er samples are treated in an argon plasma under the same plasma conditions as those of the hydrogen plasma treatment. The argon plasma is expected to have a similar etching effect as the hydrogen plasma, even though the etching rate may be different. The obtained PL spectra is shown in Fig. 2. As shown in the bottom line of Fig. 2, no Er related 1.54 μm luminescence is observed after the argon plasma treatment. However, when these Ar plasma treated samples are subjected to an annealing in a H_2 gas flow at 1300 °C for 30 s, the Er related luminescence appears as shown in the upper line in Fig. 2. The inset shows that this luminescence consists of sharp peaks. The main peak at 1.533 μm (β) has a FWHM of 3 nm and its intensity is comparable to that of PS:Er samples which are treated in the hydrogen plasma. A shoulder observed on the shorter wavelength side is located at 1.530 μm (α) and a subpeak observed on the longer wavelength side is at 1.536–1.537 μm (γ).

The above result indicates that the plasma etching is the cause for the sharply structured Er related luminescence and that hydrogen plays an important role for the appearance of the Er related luminescence. The importance of hydrogen for the Er related luminescence is also confirmed by the following experimental results. When the hydrogen plasma treated PS:Er samples are annealed in a vacuum at 700 °C for 5 min, the Er related 1.54 μm luminescence almost disappears [see

Fig. 3(b)]. This result is explained in terms of the hydrogen dissociation from dangling bonds due to high-temperature annealing in a vacuum. However, when the hydrogen plasma treated PS:Er samples are annealed in H_2 gas under the same conditions, the Er^{3+}-related 1.54 μm luminescence is found to keep its intensity or to increase the intensity slightly as shown in Fig. 3(c). We speculate that hydrogen atoms may passivate the dangling bonds on the surface of the Si nanocrystals. Due to the plasma etching of amorphous and/or oxidized layers, a lot of dangling bonds which may act as strong nonradiative centers may be formed. Photoexcited electrons and holes may recombine via these dangling bonds and the energy transfer to the Er^{3+} $4f$ electrons may be greatly reduced. However, hydrogen atoms as well as oxygen atoms may passivate these Si dangling bonds, and the nonradiative electron hole recombination via dangling bonds may be reduced. This passivation effect has been confirmed from the fact that the decay of the PL intensity of PS becomes slower when PS is annealed in an O_2/Ar atmosphere.[19]

Fourier-transformed infrared (FTIR) absorption measurement is performed to observe the etching effect. The result is shown in Fig. 4. The absorption peak at 1100 cm^{-1} due to the Si–O–Si stretching mode is clearly observed in the unannealed PS:Er sample (d), in the PS:Er sample annealed in $O_2(20\%)/Ar(80\%)$(c), and in H_2 (b). However, this mode totally disappears after the hydrogen plasma treatment as shown in Fig. 4(a). This result indicates that oxidized silicon inside the PS layers as well as on the PS surface is almost removed by the hydrogen plasma treatment (within the detection limit of FTIR).
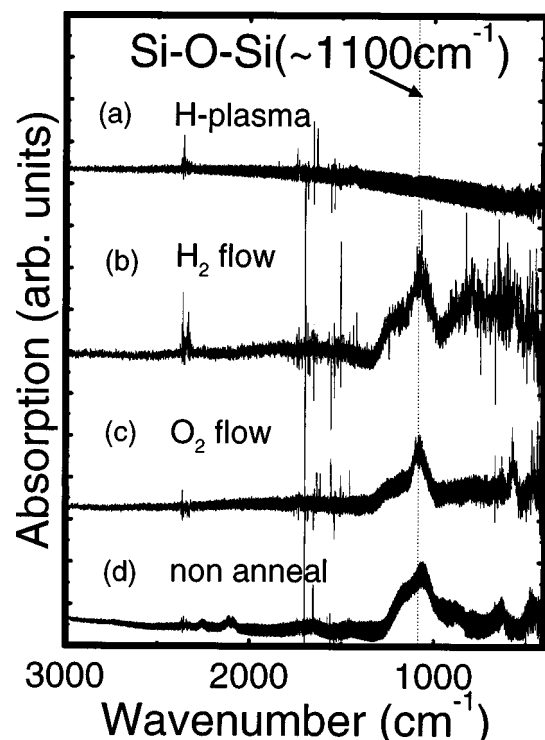

FIG. 4. FT-IR spectra for Er-doped porous silicon samples annealed (a) in hydrogen plasma at 1000 °C for 30 min, (b) in H_2 gas flow at 1300 °C for 30 s, (c) in O_2 gas flow at 1300 °C for 30 s, and (d) nonannealing. A dotted line corresponds to the Si–O–Si vibration mode.
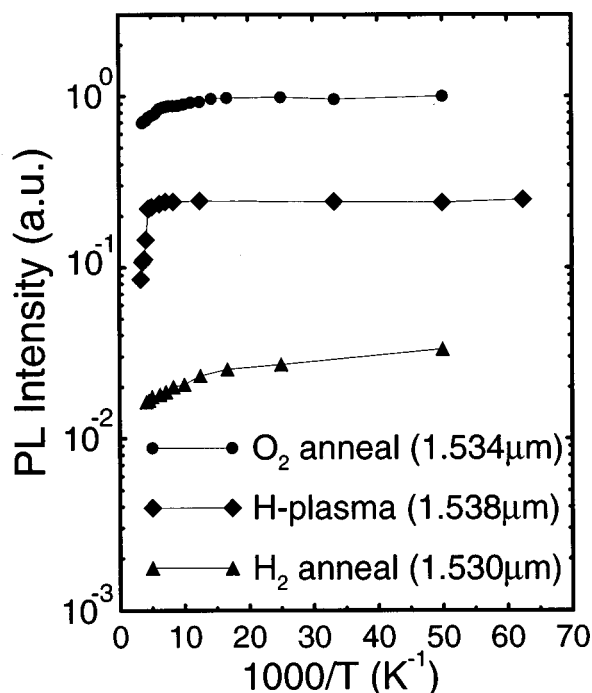
FIG. 5. Temperature dependence of the photoluminescence intensity of the emission peak 1.538 μm in PS:Er annealed in hydrogen plasma at 1000 °C for 30 min, the emission peak 1.534 μm in PS:Er annealed in O_2(20%)/Ar(80%) at 1300 °C for 30 s, and the emission peak 1.530 μm in PS:Er annealed in H_2 gas flow at 1300 °C for 30 s between 20 K and room temperature (300 K).

FIG. 6. PL spectra at 20 and 300 K for an Er-doped porous silicon sample treated in hydrogen plasma at 1000 °C for 30 min. Luminescence peaks at 1.538 μm and 0.98 μm correspond to the Er^{3+} intra $4f$ transition $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^4I_{11/2} \rightarrow ^4I_{15/2}$, respectively. The inset shows temperature dependence of the photoluminescence intensity of the emission peaks 1.538 and 0.98 μm in PS:Er annealed in hydrogen plasma at 1000 °C for 30 min.

The above FTIR results show that the hydrogen plasma effectively etches the oxidized region of the PS layers. When we compare the three PL spectra in Fig. 1, the 1.534 μm peak (β) (which is the main peak for the PS:Er samples annealed in O_2/Ar) and the 1.530 μm peak (α) (the main peak for the PS:Er samples annealed in H_2) may be more or less related with oxygen, whereas the 1.538 μm peak (γ) (the main peak for the PS:Er samples annealed in the hydrogen plasma) is much less related with oxygen. We speculate that the 1.538 μm peak (γ) comes from Er^{3+} ions in Si nanocrystals, whereas the former two originate from Er^{3+} ions in the oxidized surface of the Si nanocrystals or in the amorphous silicon layers among the nanocrystals. The 1.538 μm main peak (γ) has been observed in Er-doped crystalline silicon[20–25] in which the amount of oxygen is $\sim 10^{20}$/cm^3 at most, whereas the 1.534 μm main peak (β) is observed in Er-doped silica glass,[26] Er-implanted SIPOS,[16] Er-doped SiO_2 glass[27] etc. where the host silicon is greatly oxidized. The present discussion is consistent with these reports. It is shown from the spectra in the inset of Fig. 2 that the Ar plasma treatment does not etch the oxidized layer so perfectly as the hydrogen plasma.

Figure 5 shows the temperature dependence of the PL peak intensity of the main peaks for the three annealing atmospheres. The PL intensity of the main peaks for PS:Er samples annealed in O_2/Ar and H_2 shows both a very small thermal quenching, the former being smaller than the latter. The 1.538 μm main peak for PS:Er samples annealed in hydrogen plasma shows a larger thermal quenching, but only about by a factor of 10 from 20 to 300 K, which is extremely smaller than that of Er-doped crystalline silicon without O
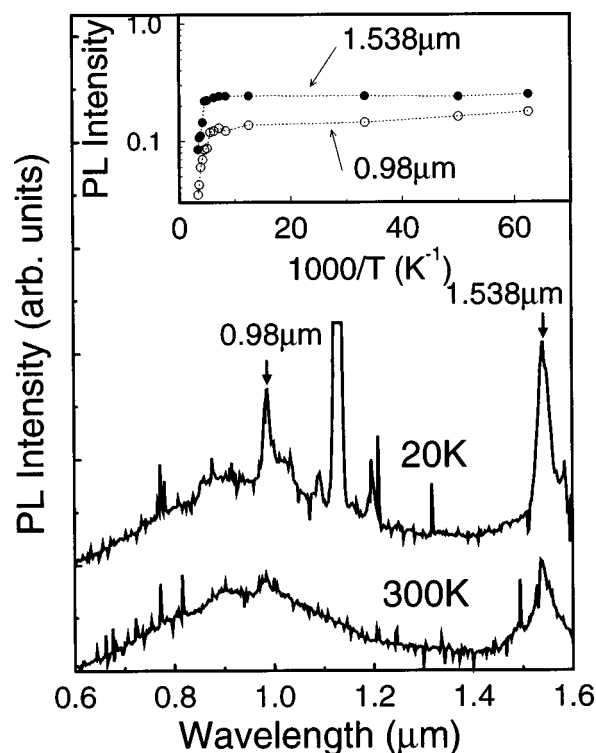
ion co-implantation which shows a thermal quenching of two or three orders of magnitude. The smaller thermal quenching is due to the larger bandgap of the host silicon nanocrystals.

We also show that a luminescence peak at 0.98 μm is observed from PS:Er samples which are subjected to the hydrogen plasma treatment as shown in Fig. 6. Since its wavelength does not depend on temperature, we assign this peak to the intra $4f$ transition from $^4I_{11/2}$ to $^4I_{15/2}$ of Er^{3+}. The observation of this peak becomes possible due to the enlarged band gap energy ($\sim$1.55 eV) of the host PS. The temperature dependence of its intensity (shown in Fig. 6) is nearly similar to the 1.538 μm main peak.

Summarizing the results obtained above, we can speculate the effects of the annealing atmosphere on the Er related luminescence of PS:Er samples as follows. As-anodized porous silicon is considered to be composed of silicon nanocrystals, oxidized silicon and/or amorphous silicon. The surface of the nanocrystals is greatly damaged due to the electrochemical etching process. A part of the dangling bonds of Si atoms on the surface of the nanocrystallites may be terminated with H, OH, or O atoms. The Er^{3+} ions which are incorporated into PS pores may either stick on the surface of the Si nanocrystals or remain in the amorphous Si layers just after the Er^{3+} ion incorporation, and thus the Er^{3+} ions are not excited by the recombination energy of electrons and holes generated in the nanocrystals. When the Er-doped PS (PS:Er) is annealed at high temperatures, Er^{3+} ions may diffuse into silicon nanocrystals by several nanometers which are roughly estimated from the diffusion coefficient of

10^{-14} cm^2/s for Er ions in bulk silicon at 1000 °C.

When samples are annealed in O$_2$/Ar or in H$_2$, a part of the dangling bonds may be terminated with O or H atoms, respectively (note that the hydrogen is flown during the cooling process). When samples are annealed in the hydrogen plasma, almost all the oxidized and amorphous silicon layers are etched, and the clean surface of the Si nanocrystals with dangling bonds may appear. These dangling bonds may be terminated with H atoms during the plasma treatment or during the cooling process. When the PS:Er samples are annealed in a vacuum, a large part of H, OH, or O atoms may dissociate from the dangling bonds of silicon nanocrystals and the nonradiative recombination may increase extremely.

The present result shows that the small thermal quenching of the Er related luminescence is possible when Er^{3+} ions are incorporated in silicon nanocrystals whose surface is well passivated with hydrogen atoms. Because of the uniform crystal fields for these Er^{3+} ions, well resolved sharply structured Er^{3+} related luminescence peaks are obtained.

IV. CONCLUSION

In conclusion, a strong and very sharply structured luminescence is obtained from Er-doped porous silicon samples which are treated in a hydrogen plasma. The main peak at 1.538 μm shows a FWHM less than 1 nm at 20 K. Its peak intensity attains 1/3 that of PS:Er samples annealed in O$_2$(20%)/Ar(80%), and shows only a thermal quenching of a factor of 10 from 20 K to room temperature. Plasma etching of the oxidized and amorphous silicon layers with hydrogen radicals and the passivation of dangling bonds with hydrogen are speculated to increase the energy transfer of the recombination energy of electron and holes to Er^{3+} ions which are diffused into silicon nanocrystals. The wide band gap of the silicon nanocrystals and uniform crystal fields are the reasons for the sharp peaks with a small thermal quenching.

ACKNOWLEDGMENTS

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