

Strong Red Photoluminescence from Nano-porous Silicon Formed on Fe-Contaminated Silicon Substrate

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The influences of the deep-level concentration of p-type Si substrates on the optical properties of nano-porous silicon (PS) are investigated by deep level transient spectroscopy (DLTS) and photoluminescence (PL). Utilizing a Si substrate with Fe contaminations significantly enhanced the PL intensity of PS. All the PS samples formed on Fe-contaminated silicon substrates had stronger PL yield than that of reference PS without any intentional Fe contamination but the emission peak is not significantly changed. For the PS1000 sample with Fe contamination of 1,000 ppb, the maximum PL intensity showed about ten times stronger PL than that of the reference PS sample. From PL and DLTS results, the PL efficiency strongly depends on the Fe-related trap concentration in Si substrates.

Keywords : Porous silicon, Fe contamination, Deep level transient spectroscopy

1. INTRODUCTION

Since the discovery of strong visible photoluminescence (PL)[1] and electroluminescence (EL)[2] from porous silicon (PS) at room temperature, luminescent PS has gained much attention in recent years due to their potential applications for electronic[3] and optoelectronic[4] devices. Especially, PS with visible wavelength is intensively studied in terms of the realization of strong and stable emission for optical devices such as PS-based optoelectronics and full color displays, but there is still some problem on the luminescent inefficiency[5] and instability[6] for the use of these kinds of device applications. Recently, in order to improve the PL efficiency and the stability in emission wavelength of PS, lots of research efforts have been made by using the various formation conditions for PS[7], that is, e.g., using the HF aqueous solution containing Fe ions[8], the metal passivation of silicon surface such as Au/Si[9] or Pt/Si[10], and the impurity incorporation through a doping[11] or ion implantation[12] on PS layer, respectively. But it was not easy to achieve simultaneously both the high PL efficiency and the invariable PL wavelength of PS obtained by the reported process above.

In this work, we report the strong red PL of PS formed on Fe-contaminated Si substrates, where the PS samples

are prepared by a conventional chemical anodization of Si substrates. In order to investigate the effects of the Fe-related trap caused by the Fe contamination on the optical properties such as PL intensity and emission peak position, the amount of the Fe contamination is systematically changed. Based on the results of deep level transient spectroscopy (DLTS) and PL, the PL efficiency of PS can be drastically improved without any significant degradation in the PS properties.

2. EXPERIMENTAL PROCEDURE

The samples investigated in this work are formed by using a boron-doped Si (100) substrate with a resistivity of 5~10 Ω -cm. Using the spin coating method[13], the front surface of Si substrates is intentionally contaminated by Fe with a different concentration of 100, 1,000, and 10,000 ppb noted as PS100, PS1000, and PS10000, respectively. The Fe-contaminated Si substrates are annealed at 900 °C for 1 hour in a dry N₂ ambient to diffuse Fe ions into the Si substrate. After thermal annealing treatment, the Fe-contaminated Si substrates are normally cooled down from 900 °C to room temperature. An electrochemical etching is proceeded to form PS layer on the Fe-contaminated Si substrate in the solution of HF:H₂O:C₂H₅OH (1:1:2)

under the illumination of halogen lamp with 250 W. The anodization current density is a 60 mA/cm^2 and the etching time is 5 minutes for all Fe-contaminated Si substrates. The reference PS sample was also prepared through the same process without the Fe contamination. Following the anodization, the samples are rinsed in ethanol.

DLTS measurement is performed to identify the trap level and trap concentration of Fe, which is caused by the diffusion of Fe into Si substrates, before the formation of PS layer on Si substrates. In PL measurement, He-Cd laser with a wavelength of 442 nm is used, as an excitation source. The luminescence light from the samples is focused with collection lenses, dispersed by a 0.75 m SPEX single grating monochromator and detected by a water-cooled photomultiplier tube using lock-in technique.

3. RESULTS AND DISCUSSION

Figure 1 shows the summary on the Fe-related trap concentration for the PS samples with Fe contamination obtained from DLTS measurements. The Fe-related trap concentration is increased with an increase in the Fe contamination up to 1000 ppb and then, decreased with a further increase in the Fe contamination. That is, Fe-related trap concentrations for PS100, PS1000, and PS10000 are 1×10^{14} , 9×10^{14} , and $3 \times 10^{13} \text{ cm}^{-3}$, respectively. The formation of Fe-related trap levels can be largely attributed to the incorporation of Fe into Si crystalline phase by the remaining Fe in the gettered region from the Fe precipitations. The Fe precipitations are occurred during the normal cooling at the end of high-temperature thermal annealing, resulting from supersaturation of Fe.

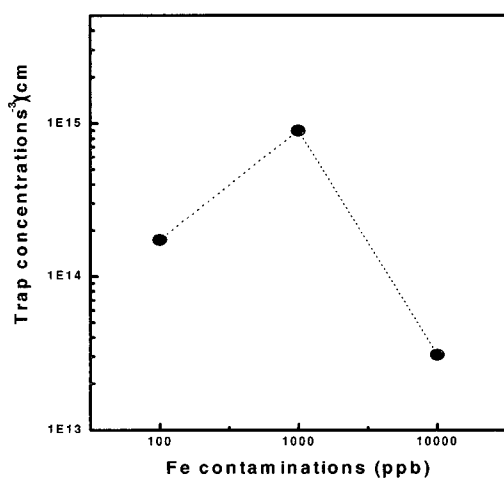


Fig. 1. Summary on the Fe-related trap concentration for the PS samples with Fe contamination obtained from DLTS measurements. The dashed lines are only guides for the eyes.

Figure 2 shows the DLTS spectra for the reference PS sample and three PS samples contaminated by Fe with a different concentration of 100, 1,000, and 10,000 ppb noted as PS100, PS1000, and PS10000. As shown in Fig. 2, two traps, T_1 and T_2 , related to Fe are observed from the PS samples with Fe contamination. These trap peaks are strongly affected to Fe interstitial (Fe_i) and Fe-O pair[14]. DLTS signal of the Si substrate with Fe contamination of 1,000 ppb is the stronger than the other samples. This strong signal indicated that the re-emission of gettered Fe could be occurred from the Si substrate by Fe contamination. The drastic decrease in DLTS intensity for the Si substrate with Fe contamination of 10,000 ppb is probably caused by an abrupt increase of Fe precipitation. In other words, an excess Fe contamination in Si may act as the defect in Si substrate rather than as the factor of internal gettering.

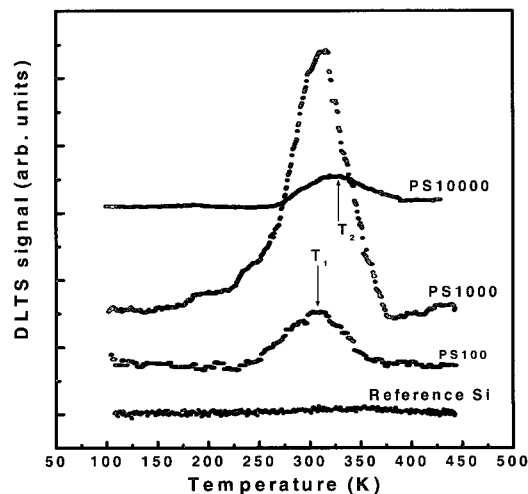


Fig. 2. DLTS spectra of Si substrates with different Fe contaminations.

Figure 3 shows (a) the room-temperature PL spectra, and the summary on (b) the integrated PL intensity and (c) the emission peak (solid circles) and full width at half maximum (FWHM) (solid squares) from the PS samples formed on Si substrates with different Fe contaminations and the reference PS sample. The reference PS sample exhibits a broad red PL centered at 756 nm. The broad red PL from PS are possibly due to the size distribution of nanocrystalline Si ($nc\text{-Si}$) along the depth of PS layers and originated from the localized exciton at the interface region between $nc\text{-Si}$ and SiO_2 layer of surface[15]. This indicates the efficient localization of charge carriers into the surface-localized states of $nc\text{-Si}$, even though no intended confining layer for carriers is introduced. All the PS samples with Fe contaminations have stronger PL compared to that of the reference PS sample as shown in Fig. 3(b). The enhancement in the PL intensity can be

closely related to trap concentrations produced by Fe contaminations of Si substrate. In particular, the PL intensity for the PS1000 sample shows almost ten times stronger compared to that of the reference PS sample.

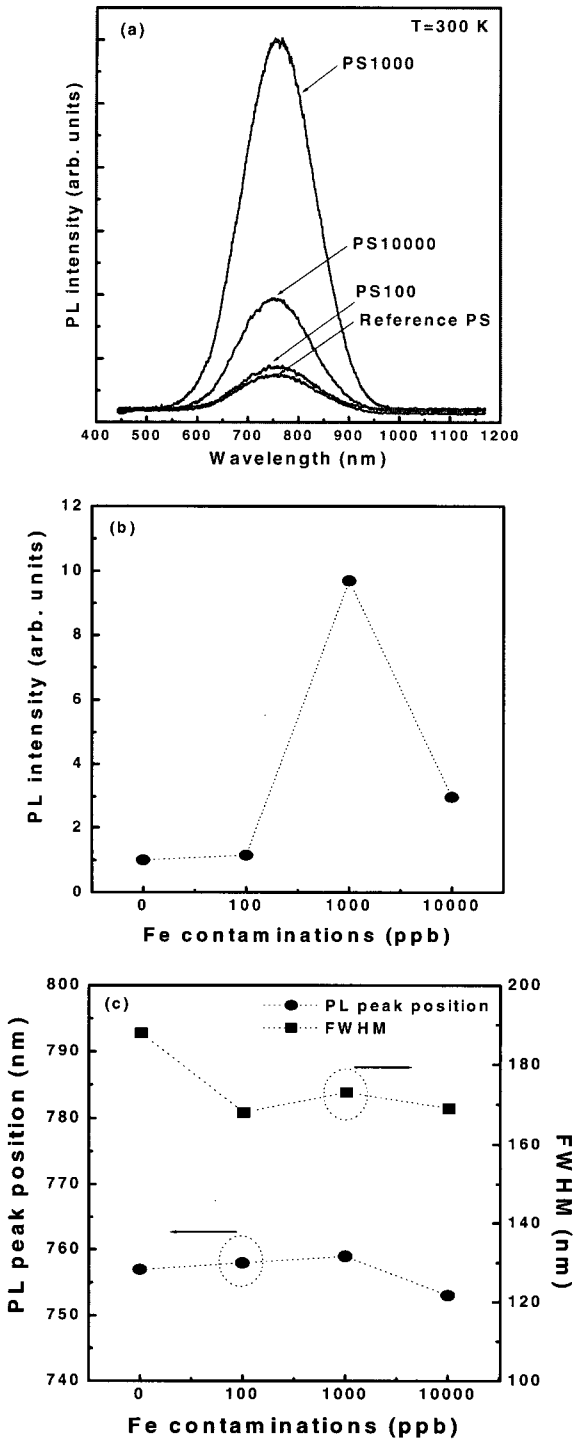


Fig. 3. (a) Room-temperature PL spectra, and the summary on (b) the integrated PL intensity and (c) the emission peak (solid circles) and FWHM (solid squares) from the PS samples.

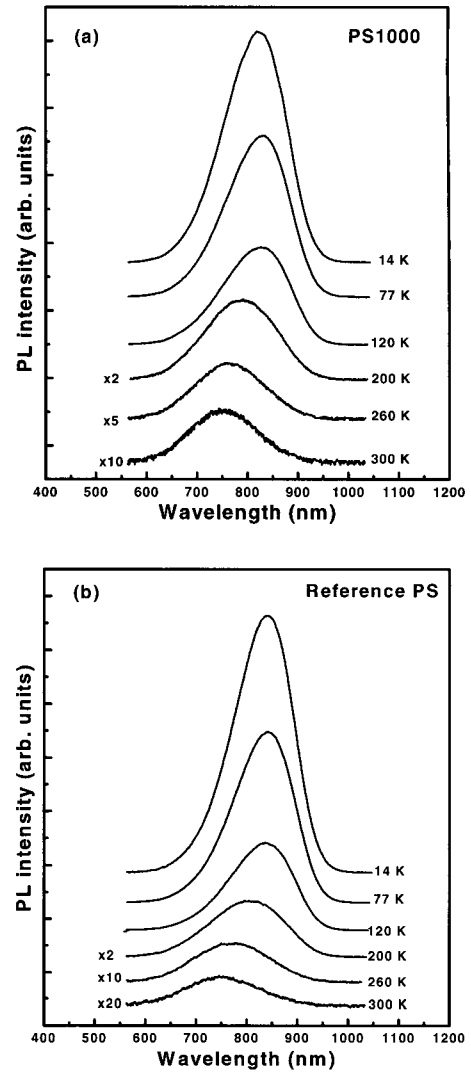


Fig. 4. Temperature-dependent PL spectra of (a) the PS1000 sample and (b) the reference PS sample.

From the DLTS and PL results above, we carefully suggest that the improved PL efficiency of the PS samples must be related to an intrinsic mechanism, that is, the increase in trap concentrations from the Fe-related deep traps rather than the variation in size and shape, and surface chemistry of *nc*-Si during the formation procedure of PS by using Fe contaminations. As the amount of Fe contamination is increased, the integrated PL intensity increases until 1,000 ppb, and then decreases for Fe contamination of 10,000 ppb. As shown in Fig. 3(b), the integrated PL intensity of the PS samples depends on Fe contaminations and it shows the direct correlations between the integrated PL intensity of PS formed on Fe-contaminated Si substrates and Fe-related trap concentrations of Si substrates. These correlations indicate that the distinct increase of PL efficiency can be attributed to the increase of trap con-

centrations produced by the Fe contaminations, and it seems that the remarkable enhancement of PL intensity is due to the increase of carrier localization in the *nc*-Si via trap levels induced by the incorporation of Fe into Si crystalline phase. For Si substrate and the PS10000 sample with the same Fe contamination of 10,000 ppb, the decrease in both trap concentration and PL intensity may be due to the generation of crystallographic defects as a non-radiative recombination center in Si caused by an abrupt increase of Fe precipitation. As shown in Fig. 3(c), it is noticeable that the PL peak of the PS samples is almost the same as that of the reference PS sample. As well as the PL peak, a remarkable variation in FWHM is not observed in the PL spectra of Fe contaminated PS. These results indicated that there is no significant variation in the size and size distribution of *nc*-Si in the PS samples. Therefore, the optical properties of PS can be significantly improved without any degradation in the structural properties by using Si substrates with an adequate Fe contamination.

In order to verify the strong localization effect of carriers with regard to the enhanced PL efficiency in the PS samples, temperature-dependent PL spectra, which are shown in Figs. 4(a) and 4(b) for the PS1000 and the reference PS sample respectively, are investigated. The peak and the line shape for both the PS1000 sample and the reference PS sample show no significant changes up to ~120 K, even though the PL intensity is decreased slightly. This indicates that the excitons are comparatively well localized in a certain potential minimum, until the localized carriers in *nc*-Si have been to be a thermally activated. However, the peak of the PS1000 sample and reference PS are blueshifted by 75 and 91 nm with the drastic decrease of PL intensity in the temperature range from 120 to 300 K. From this result, the peak position of the PS1000 sample is less sensitive to the temperature than that of the reference PS sample.

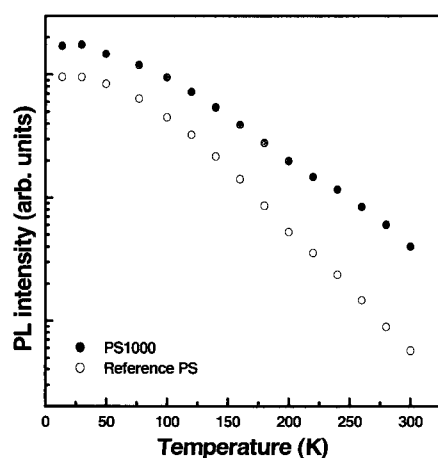


Fig. 5. Temperature dependence of the integrated PL intensity for PS1000 and reference PS.

In order to obtain further evidence of the enhanced exciton localization for PS1000 sample, the temperature dependence of integrated PL intensity for PS1000 and reference PS sample is indicated in Fig. 5. In Fig. 5, as the temperature increases, the PL intensity decreases gradually with temperature. The decrease of PL intensity is associated with exciton dissociation due to the increase in the thermal activation of localized excitons. As shown in Fig. 5, the PL intensity of the PS1000 is more thermally stable with temperature than that of the reference PS. Especially, the PL intensity of the PS1000 is ~2 times higher than that of reference PS at 14 K. Then, this difference increases still more at the high temperature above ~200 K. This result indicate that the PS1000 has a higher thermal stability than the reference PS considerably.

4. CONCLUSIONS

We report on the strong and thermally stable red PL of nano-porous silicon (PS) formed on Fe contaminated Si substrates. Regardless of Fe contamination concentrations, all the PS samples exhibited the similar PL peak position, 750 nm at 300 K. Especially, the PS1000 sample shows ten times stronger red PL than that of the reference PS sample, and this sample also shows the less sensitive dependence of the emission peak position on the temperature compared with the reference PS sample. Based on the results of PL and DLTS, the strong and thermally stable red PL is reasonably due to the enhanced localization of excitons in the interface region between nanocrystalline Si and SiO₂ layer of surface via trap levels induced by the incorporation of Fe into a Si crystalline phase.

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