

Improvement in photoluminescence efficiency of SiO₂ films containing Si nanocrystals by P doping: An electron spin resonance study

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SiO₂ and phosphosilicate glass (PSG) films containing Si nanocrystals (nc-Si) as small as a few nanometers were studied by electron spin resonance (ESR) and photoluminescence (PL), and the correlation between the two measurements was examined. It is shown that the incorporation of nc-Si in SiO₂ results in the drastic increase in the ESR signal; the signal is assigned to the Si dangling bonds at the interfaces between nc-Si and matrices (P_b centers). The ESR signal becomes weaker by doping P into SiO₂ matrices, i.e., by using PSG as matrices. By increasing the P concentration, the ESR signal decreases further. By decreasing the ESR signal, the low-energy PL peak at 0.9 eV decreases, while the band-edge PL at 1.4 eV increases. These results suggest that the 0.9 eV peak is related to P_b centers, and that the decrease in the density of the P_b centers by P doping brings about an improvement in the band-edge PL efficiency of nc-Si. © 2000 American Institute of Physics. [S0021-8979(00)07104-8]

I. INTRODUCTION

Light emission in the near-infrared and visible regions has been observed for a variety of Si nanostructures.^{1–5} Owing to the large surface area of Si nanostructures, proper surface passivation is essential in obtaining efficient luminescence. Surface passivation controls the luminescence intensity through the elimination of competing nonradiative carrier relaxation pathways.⁶ Passivation by hydrogen and oxygen is reported to be effective in improving the luminescence efficiency.⁶ However, the hydrogen passivation is impractical for the device application, because hydrogen is easily dissociated from the surface by a low-temperature heat treatment.

Oxygen-passivated Si nanocrystals (nc-Si), i.e., oxidized nc-Si, have been prepared by the oxidation of porous Si,^{6–8} and by plasma chemical deposition,¹ cosputtering^{4,5,9} and ion implantation^{10,11} methods. These oxidized nc-Si are reported to exhibit strong luminescence, and the surface passivation by oxygen is considered to play an important role in the strong luminescence. However, it is also reported that oxygen passivation induces some kinds of new defects.^{6–8} One of the well-known defects in oxidized nc-Si is the Si dangling bonds at the interface between nc-Si and SiO₂ matrices (P_b center).^{6–8} At room temperature, the P_b center acts as a nonradiative recombination center, thereby decreasing the band-edge luminescence efficiency. Therefore, by decreasing the density of the P_b center, further improvement in the band-edge luminescence efficiency of oxidized nc-Si is expected.

In our previous work, we have prepared nc-Si as small as a few nanometers embedded in SiO₂ matrices by a cosputtering method, and studied the photoluminescence (PL) properties.^{4,5} At room temperature, the nc-Si exhibited a PL at around 1.4 eV. From the observed size dependence of the PL peak, we attributed the PL to the recombination of free electron–hole pairs in nc-Si (band-edge PL).^{4,5} In addition to the band-edge PL, an additional PL peak was observed at 0.9 eV at low temperatures (typically less than 100 K). At 5 K, the intensity of the low-energy peak was comparable to that of the band-edge PL. The low energy peak is observed also for porous Si and is generally attributed to the recombination of photoexcited carriers via the P_b centers.^{5,7,8}

In a previous paper,⁹ we reported a new method in improving the band-edge PL efficiency of oxidized nc-Si. We employed phosphosilicate glass (PSG), which is the mixture of SiO₂ and P₂O₅, instead of pure SiO₂ as surrounding matrices of nc-Si. It was shown that, as the P concentration increases, the intensity of the band-edge PL increases drastically, while the P_b center-related PL decreases. These results suggest that the density of the P_b centers decreases by P doping and that this decrease results in improvement in the band-edge PL efficiency.

Although the optical data suggest a decrease in the P_b centers, direct evidence was not shown in the previous work. Defects in Si nanostructures have been studied by electron spin resonance (ESR).^{6–8,10,11} The large surface area of Si nanostructures allows the ESR study of surface and interface defects under highly improved conditions compared with bulk samples. In this article, we will show the results of ESR studies of the PSG films containing nc-Si. We will discuss the effects of P doping on the density of paramagnetic de-

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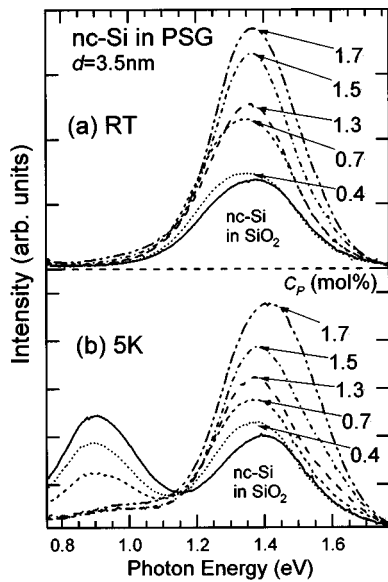


FIG. 1. Photoluminescence from nc-Si dispersed in PSG thin films (a) at room temperature and (b) at 5 K. P concentration (C_P) is changed from 0 to 1.7 mol %.

facts and reveal the mechanism of the improvement in the band-edge PL efficiency.

II. EXPERIMENT

The samples were prepared by the same method as used in our previous work.⁹ Small pieces of Si chips were placed on a PSG sputtering target and they were cosputtered in Ar gas. The substrates were fused quartz. After the sputtering, the films were annealed in an N_2 gas atmosphere for 30 min at 1100 °C. P concentration in the films was controlled by changing the P concentration in the PSG target. The average P concentration in a whole film, i.e., the mol concentration of P_2O_5 [C_P (mol%)] was determined by an electron probe microanalysis [JXA8900 (JEOL)]. The size of nc-Si was determined by cross-sectional high-resolution transmission electron microscopic (HRTEM) observations [JEM-2010 (JEOL)]. The HRTEM observations revealed that each nc-Si was isolated from the others by PSG barriers several nanometers in thickness. The size of nc-Si was found to be not affected by P doping. In this work, the diameter of nc-Si was fixed to about 3.5 nm, and only C_P was changed from 0 to 1.8 mol %.

PL spectra were measured using a Jobin Yvon HR-320 monochromator equipped with a Ge detector [EO-817 (North Coast)]. The excitation source was a 488.0 nm line of an Ar ion laser. The spectra were measured in the temperature range between 5 and 300 K in a continuous-flow He cryostat [Optistat (Oxford Instruments)]. X-band ESR was measured by a conventional ESR spectrometer [EMX 8/2.7 (Bruker)] at room temperature. A nuclear magnetic resonance Gauss meter with 10^{-6} resolution was used for field monitoring.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the room temperature PL spectra for the samples with different C_P . The spectra are the same as

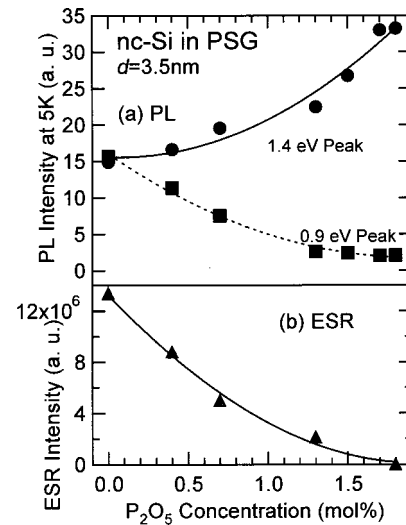


FIG. 2. (a) PL intensities of the 1.4 and 0.9 eV peaks at 5 K, and (b) integrated ESR signal as a function of C_P .

those shown in Ref. 9. A peak can be observed at about 1.4 eV. Although not shown here, the 1.4 eV peak shifted to a higher energy and became intense with decreasing the size of nc-Si. The peak energy versus size relation was in good agreement with those reported for porous Si and nc-Si,^{1,2,4,5} suggesting that the PL arises from the recombination of electron-hole pairs confined in nc-Si (band-edge PL). In Fig. 1, we can see that as C_P increases, the PL intensity increases.

Figure 1(b) shows the PL spectra at 5 K. For the samples with C_P smaller than 1.3 mol %, a broad peak appears at around 0.9 eV in addition to the 1.4 eV peak. The 0.9 eV peak is generally assigned to the recombination of electron-hole pairs via P_b centers. Detailed studies on the size dependence of the 0.9 eV peak were made in our previous work.⁵ In Fig. 2, we can see that the 0.9 eV peak becomes weaker as C_P increases and almost disappears for $C_P=1.3$ mol %. The integrated intensities of the 0.9 and 1.4 eV peaks at 5 K are shown in Fig. 2(a) as a function of C_P . The 1.4 eV peak increases with C_P , while the 0.9 eV peak decreases monotonously. The C_P dependence of the 1.4 eV peak at room temperature was very similar to that at 5 K.

Figure 3 shows the ESR derivative spectra of a SiO_2 film (A), and SiO_2 (B) and PSG (C–F) films containing nc-Si; C_P is changed from 0 to 1.8 mol %. A factor of 10 is multiplied to the spectra A, E and F. All the samples are annealed at 1100 °C for 30 min. For the SiO_2 film (A), a weak ESR signal is seen; the g factor and the linewidth are 2.0044 and 7 G, respectively. The ESR signal becomes much stronger by incorporating nc-Si in the SiO_2 film (B), although the g factor (2.0059) and the linewidth (7.9 G) are not largely affected. The drastic increase in the ESR signal indicates that the signal arises from the defects induced by the incorporation of nc-Si in SiO_2 . By doping P into samples, the ESR signal changes gradually (C–F). As C_P increases, the signal becomes weaker and for the sample with $C_P=1.8$ mol % (F), no ESR signals were detected. The integrated intensity of the ESR signal is plotted in Fig. 2(b). The intensity is calibrated by simultaneously measuring the signal from a fixed amount

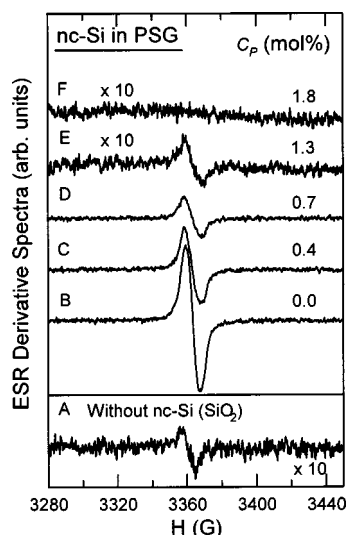


FIG. 3. ESR derivative spectra of a SiO_2 film (A), and SiO_2 (B) and PSG (C)–(F) films containing nc-Si. For the samples containing nc-Si, the size and concentration of nc-Si are fixed to almost the same and C_P is changed from 0 to 1.8 mol %.

of CuSO_4 powder. We can see that the intensity decreases drastically with C_P . In Fig. 4, the g factor and the linewidth are plotted as a function of C_P . The g factor is almost independent of C_P , while the linewidth increases with C_P . The reason for the increase in the linewidth is not known at present.

In the present samples, nc-Si are dispersed in SiO_2 films. Very similar films have been prepared by implanting Si in SiO_2 and postannealing.^{10,11} For the samples prepared by Si implantation, the presence of three kinds of paramagnetic defects is reported. These defects are Si E' centers, non-bridging oxygen hole centers (NBOHCs) and P_b centers. Among three types of defects, the NBOHC- and E' -type defects are annealed out above 500 °C, and only the P_b centers remain in the samples annealed above 500 °C.^{10,11} Since the present samples are annealed at 1100 °C, the NBOHC- and E' -type defects are considered to be annealed out. We can thus attribute the observed ESR signal to P_b centers. Therefore, Fig. 2 indicates that the number of P_b centers decreases by P doping.

In Fig. 2, we can see a clear correlation between the intensities of the ESR signal and those of the two PL peaks. The 0.9 eV PL becomes weaker as the ESR signal becomes weaker, i.e., as the number of P_b centers decreases, while the 1.4 eV PL becomes intense. These results clearly demonstrate that the 0.9 eV peak is related to P_b centers as has been suggested so far. Furthermore, the results suggest that the decrease in density of the P_b centers by P doping brings about an improvement in the band-edge PL efficiency of nc-Si.

Although our results clearly demonstrate that the density of P_b centers decreases by P doping, its mechanism is not clear. One of the possible explanations is that the incorporation of P atoms in matrices reduces the stress at the interfaces

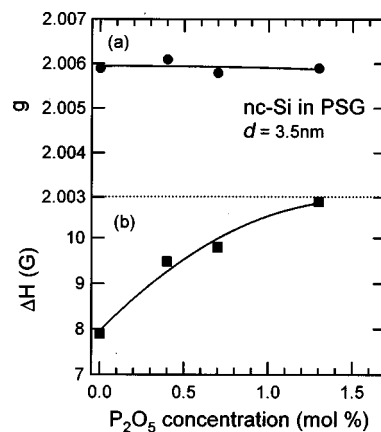


FIG. 4. g factor and linewidth of ESR signal as a function of C_P .

between nc-Si and the matrices, and that the reduction of the stress results in a decrease in the defect density.⁹

IV. CONCLUSION

SiO_2 and PSG films containing nc-Si as small as a few nanometers were studied by ESR and PL. It was found that the incorporation of nc-Si in SiO_2 results in the drastic increase in the intensity of the ESR signal, which is assigned to the P_b centers. The ESR signal was found to be weak by doping P and almost disappears for $C_P=1.8$ mol %. As the ESR signal became weak, the intensity of the low-energy PL at 0.9 eV decreased, while that of the band-edge PL at 1.4 eV increased. These results suggest that the 0.9 eV peak is related to P_b centers, and that the decrease in density of the P_b centers brings about a drastic improvement in the band-edge PL efficiency of nc-Si.

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