Nondegrading Photoluminescence in Porous Silicon

Yu Heng Zhang,[1,2] Xin Jian Li,[1–3] Lei Zheng,[1,2] and Qian Wang Chen[1,2]
[1]*Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China*
[2]*Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China*
[3]*Department of Physics, Zhengzhou University, Zhengzhou 450052, People's Republic of China*

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Porous silicon (PS) with nondegrading photoluminescence (PL) was prepared by a novel method. For fresh samples, the PL peak intensity is 2–2.5 times stronger than that in normal PS. Upon exposing PS to ambient air, the PL intensity increases during the first four months and then saturates. No PL degradation is observed for eight months, and the peak position remains unchanged. The same effect can also be achieved by annealing treatments. This PL stability is attributed to the formation of stable Fe-Si bonds on the surface of PS. Exploration of the mechanism provides strong proof of the quantum confinement model of the luminescence of PS. [S0031-9007(98)06914-2]

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The discovery of light-emitting porous silicon (normal PS) [1] has made it possible to develop Si-based optoelectronic devices. In recent years, most of the research has been directed at understanding the origin of the luminescence [1–8] and fabricating PS-based light emitters [9–12]; but the problems of the degradation [2,13,14] and the relatively low efficiency [15] of the photoluminescence (PL) remain unsolved. The PL degradation subsequent to normal PS preparation, accompanied with a blueshift of the peak position, is generally believed to originate from the chemical instability of the PS surface [2,13,14]. Under the attack of oxygen, the Si-H bonds on the surfaces of the Si nanocrystallites will be broken and the quantity of the Si dangling bonds will increase. This variation will ultimately lead to the degradation of the PL intensity [13,14]. On the other hand, deep oxidation will reduce the sizes of the Si nanocrystallites and result in the blueshift of the PL peak position [13,14]. The motivation of this research is to try to construct a stable Fe-Si bond on PS surface to substitute the easily broken Si-H bond and thereby realize the stabilization of the intensity as well as the peak position of the PL of PS.

The PS samples reported here were prepared by a hydrothermal method which was first adopted by Chen *et al.* in preparing normal PS [16], but with a different solution. The initial materials were P/P^+-type boron-doped single crystal Si wafers with (111) orientation and $\sim 1.5–2.0\ \Omega\,\mathrm{cm}$ resistivity. The solution for hydrothermal treatment was composed of 40% (weight) hydrofluoric acid and 0.3 mol/l ferric nitrate aqueous solution according to 7:6 (volume) and the treatment was performed at 140 °C for 50 minutes. We name as-prepared PS samples as iron-passivated PS. For comparison, normal PS samples were also prepared by the hydrothermal method, but here the Si wafers were treated at 170 °C for 4 hours in a solution of 15 mol/l hydrofluoric acid.

The PL spectra of all these samples were measured with an 850-type visible-ultraviolet spectrophotometer (Hitatchi, Japan) at room temperature, and these results were corrected for the system response. Here the most efficient wavelengths for excitation were adopted as the excitation wavelengths, 320 nm for iron-passivated PS and 280 nm for normal PS. For both freshly prepared samples, it was found that the PL peak intensity of iron-passivated PS is typically ~2–2.5 times stronger than that of normal PS. This conclusion was arrived by comparing their relative intensities recorded by the spectrophotometer. The time evolution of the PL spectra for a typical iron-passivated PS sample exposed to ambient air at room temperature is presented in Fig. 1. Obviously, during the first 4 months subsequent to preparation, the peak intensity of the PL under identical excitation wavelength (320 nm) increases monotonically with time. At the end of the fourth month, the intensity reaches a saturation (~3 times stronger than that measured immediately after preparation) and then remains constant. It should be noted that the peak position (~670 nm) of the PL keeps unchanged all through the eight months. The inset in Fig. 1 shows the normalized PL peak intensities of the same sample measured at different exposing time based on the intensity measured immediately after preparation. One-hour annealing treatments at different temperatures (below 250 °C) were also carried out for the samples fabricated under the same conditions, and the results are shown in Fig. 2. Here, each spectrum in the main figure is normalized based on the peak intensity of the corresponding freshly prepared sample. It is easy to find that the PL peak intensity for the annealed samples have the same evolution trend with that for exposed samples, but the saturating process is greatly accelerated. The inset of Fig. 2 shows the evolution of the peak intensities of the samples annealed for 1 hour at different annealing temperatures. For comparison, the PL from normal PS was also examined. Figure 3 exhibits the time evolution of the PL spectra of a typical normal PS sample exposed also to ambient air, and the inset shows the degradation of the PL peak intensity with exposing time; these results qualitatively agree with those reported for anodically prepared PS [13,14].

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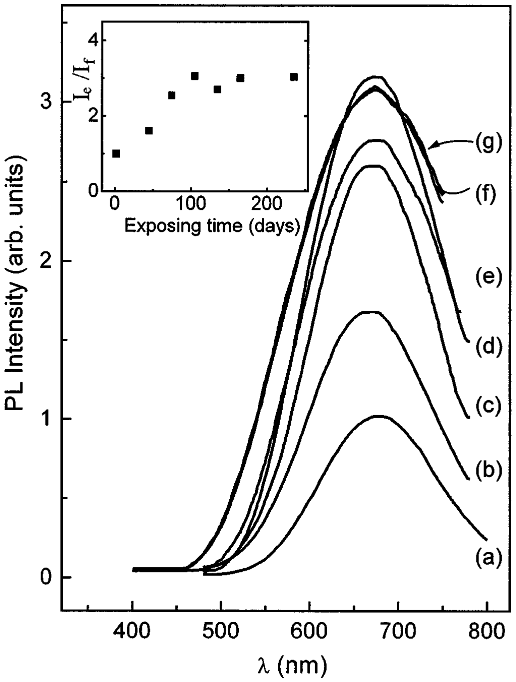

FIG. 1. The time evolution of the PL spectra for an iron-passivated PS sample exposed to ambient air at room temperature. These spectra were measured (*a*) immediately after preparation, and (*b*) 45, (*c*) 75, (*d*) 110, (*e*) 140, (*f*) 170, (*g*) 235 days after preparation. The excitation wavelength is 320 nm and the adopted filter is #430. Inset: The evolution of the PL peak intensity ratio I_e/I_f (the PL intensity for the exposed sample to that for the freshly prepared sample) with exposing time.

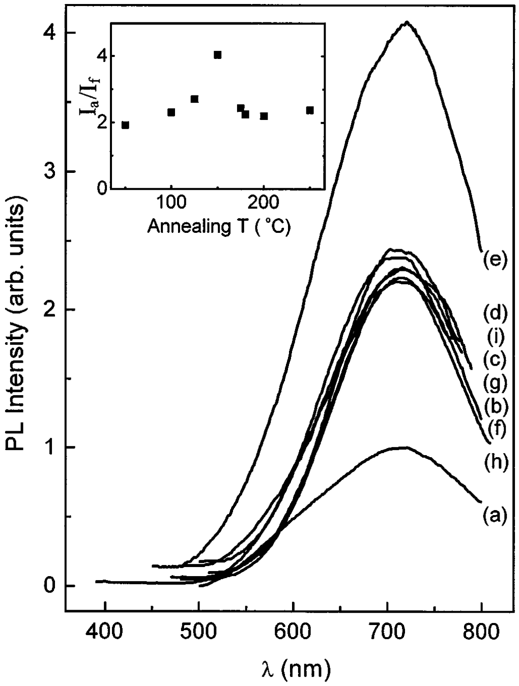

FIG. 2. The evolution of the PL spectra for iron-passivated PS samples annealed at different temperatures for 1 hour. These spectra were measured (*a*) immediately after preparation and after annealing at (*b*) 50 °C, (*c*) 100 °C, (*d*) 125 °C, (*e*) 150 °C, (*f*) 175 °C, (*g*) 180 °C, (*h*) 200 °C, and (*i*) 250 °C. The excitation wavelength is 320 nm and the adopted filter is #430. Inset: The evolution of the peak intensity ratio I_a/I_f with different annealing temperatures.

To investigate the origin of the difference of the PL behaviors between iron-passivated PS and normal PS, room-temperature Mössbauer spectroscopy for iron-passivated PS was studied. Figure 4(a) represents the experimental Mössbauer spectrum of a freshly prepared iron-passivated PS sample, as well as the fitting results which were obtained by using the Gauss-Newton method. It is found that the main spectrum *A* can be decomposed into three sets of subspectra, indicating that there exist three different iron bonding states. Further data analyses disclose that the sextet *B* represents iron atoms in nanosized α-Fe_2O_3. The stronger doublet *C*, with an isomer shift (IS) of $\sim$0.25 mm/s and a quadruple splitting (QS) of $\sim$0.42 mm/s, represents a kind of Fe-Si bond with the iron atoms in Fe^{3+} valence state; while the weaker doublet *D*, with an IS of $\sim$0.27 mm/s and a QS of $\sim$0.64 mm/s, represents another kind of Fe-Si bond with the iron atoms in Fe^{2+} valence state. The above parameters for Fe^{2+} valence state agree well with those of iron-silicon alloy [17,18]; while the QS for the Fe^{3+} valence state shows a little deviation. This deviation may be caused by the difference of the surroundings between the iron ions in the two cases. Figure 4(b) shows the Mössbauer spectroscopic results for the same sample after having exposed it to ambient air for $1\frac{1}{2}$ months. What should be especially noted is that the shapes and the peak positions of the two doublets (*C* and *D*), which represent the two kinds of the Fe-Si bonds, remain almost unchanged; although the shape of the main spectra *A* has changed obviously. This phenomenon indicates that the Fe-Si bonds formed on the surfaces of the Si nanocrystallites in iron-passivated PS are stable. The newly appeared sextet *E* represents the iron atoms in bulk α-Fe_2O_3. This might result from the crystal growth of the nanosized α-Fe_2O_3. Furthermore, the portions of the iron atoms of different iron states change from about 41.5:32:26.5 (nanosized α-Fe_2O_3:Fe^{3+}-Si:Fe^{2+}-Si) for the freshly prepared sample to about 14:36:27:23 (nanosized α-Fe_2O_3:α-Fe_2O_3:Fe^{3+}-Si:Fe^{2+}-Si) for the sample exposed to ambient air for $1\frac{1}{2}$ months. Considering the fact that both the spectra in Figs. 4(a) and 4(b) were measured with the same amount of time under the identical condition, it is easy to find that both the total amounts of the two Fe-Si bonds and that of α-Fe_2O_3 increase $1\frac{1}{2}$ months later. By integrating the areas of these subspectra, we found that the quantities of the bonds of Fe^{3+}-Si and Fe^{2+}-Si given in Fig. 4(b) increased about 16% and 20%, respectively, compared with those given in Fig. 4(a). These data infer that there are extra iron atoms to be combined with silicon atoms during this period. Individual iron atoms were found in freshly prepared iron-passivated PS by the energy spectra analysis of high resolution transmission electron

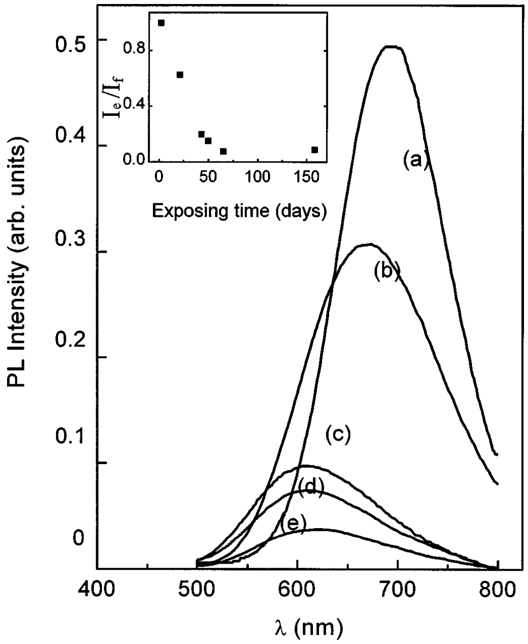

FIG. 3. The time evolution of the PL spectra for a hydrothermally prepared normal PS sample exposed to ambient air at room temperature. These spectra were measured (*a*) immediately after preparation and (*b*) 17, (*c*) 39, (*d*) 50, and (*e*) 65 days after preparation. The excitation wavelength is 280 nm and the adopted filter is #430. Inset: The evolution of the peak intensity ratio I_e/I_f with exposing time.

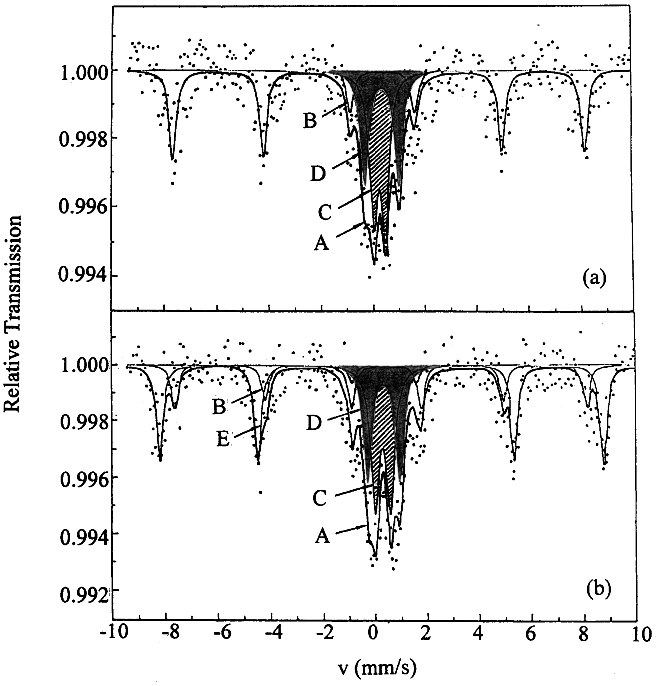

FIG. 4. The room-temperature Mössbauer spectra and the corresponding fitting results for a typical iron-passivated PS measured (a) immediately after preparation and (b) after being exposed to ambient air at room temperature for $1\frac{1}{2}$ months.

microscopy (Li *et al.*, unpublished data); but it is not clear at present how these individual iron atoms were formed in the hydrothermal process. When iron-passivated PS samples are exposed to ambient air, some individual iron atoms go to passivate the residual silicon dangling bonds which are formed in the hydrothermal process, while the others are oxidized by oxygen and form Fe_2O_3. By combining these Mössbauer spectroscopic results with those of PL spectroscopy, the physical configuration of iron-passivated PS can be illustrated in Fig. 5(a). The inner part is the silicon nanocrystallite and the outer part is Fe_2O_3. The Fe-Si bonds are formed on the surface of the silicon nanocrystallite and located between these two parts. Under this configuration, the two essential effects of iron passivation are obvious: (1) The formation of Fe-Si bonds decreases the number of the Si dangling bonds, and therefore results in strong PL; (2) the formed stable Fe-Si together with the outer α-Fe_2O_3 coat protected the inner Si nanocrystallite from being further oxidized and therefore keeps its size undiminished and guarantees the peak position unchanged. Further iron passivation decreases the number of the residual Si dangling bonds on PS surface and thereby leads to the increase of the PL intensity. These experimental results of Mössbauer spectroscopy well explain the PL behavior of iron-passivated PS.

On the other hand, normal PS exhibits PL degradation subsequent to preparation, accompanied with a blueshift of the peak energy [2,13,14]. As has been reported [14,19,20], strong Si-H vibrational absorption peak was observed in the Fourier transform infrared (FTIR) experiments for fresh PS. With time going on, this peak decreased gradually and disappeared finally. At the same time, an absorption peak for Si-O-Si vibrational mode gradually enhanced. These results indicate that the Si-H bonds were broken under the attack of oxygen and the hydrogen atoms in Si-H bonds were substituted by oxygen atoms, as illustrated in Fig. 5(b). During this process, Si dangling bonds were formed and the size of those silicon nanocrystallites was decreased. These structural changes finally resulted in the degradation of the PL and the blueshift of the peak energy.

The research on iron-passivated PS can also provide new insights for clarifying the mechanism of the luminescence of PS. The problem about the luminescent mechanism of PS has been debated for a long time among several models [1,20–22]. Considering the facts of our experiments, the models which attribute the light emission to the surface-related states [20–22] seem incorrect. Because the silicon nanocrystallites with iron passivation should possess a surface electronic structure which is different from that with hydrogen passivation or oxygen passivation; and this difference should be reflected in their PL spectra. But the similarity of the luminescent properties between normal PS and iron-passivated PS denied those hypotheses. Therefore our experiments support the quantum confinement model [1] and it seems that the luminescent process has no relation with those surface-related states.

In conclusion, PS samples with strong and stable red PL were prepared by hydrothermally treating single crystal

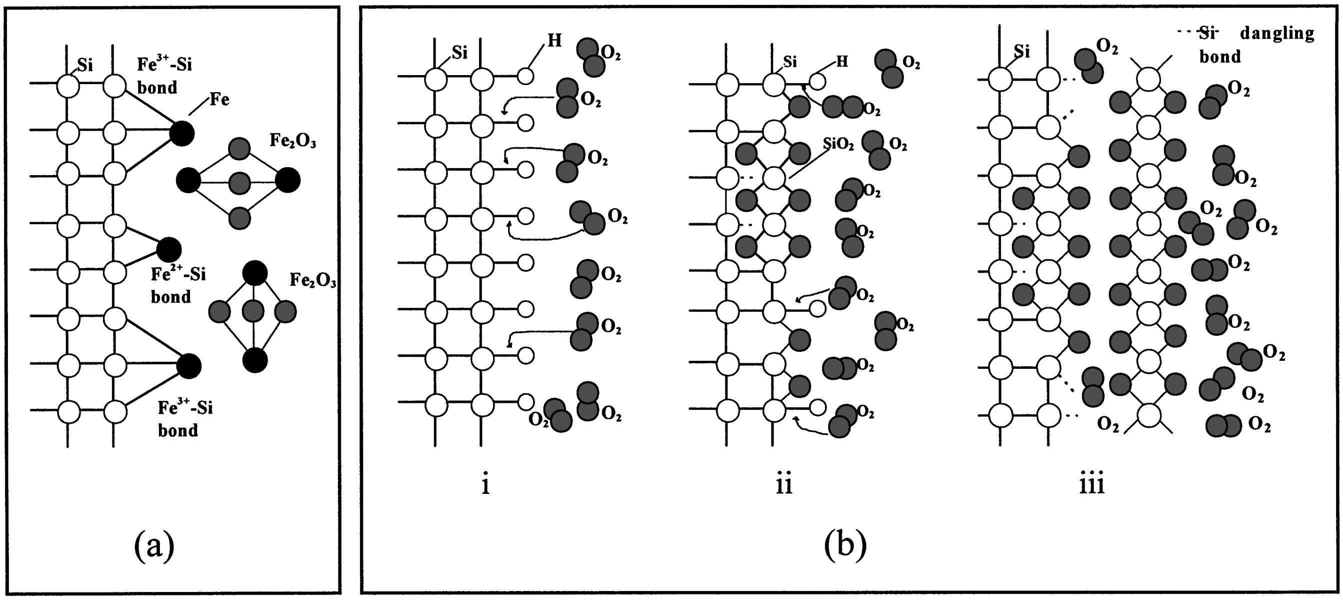

FIG. 5. Schematic diagrams of (a) the iron passivation formed on the surface of the silicon nanocrystallite and the outer Fe_2O_3 layer in the iron-passivated PS and (b) the oxidation process happened in normal PS: (i) Fresh silicon nanocrystallite surface; (ii) slightly oxidized surface; (iii) deeply oxidized surface.

Si wafers in a solution of hydrofluoric acid containing ferric nitrate. The peak intensity of the PL from freshly as-prepared PS is typically $\sim 2-2.5$ times stronger than that from normal PS. Spectroscopic studies for the samples exposed to ambient air and annealed at different temperatures show that this PL doesn't degrade with time and the peak position remains unchanged. Room-temperature Mössbauer spectroscopic analysis proved that the stability of the PL comes from the stable Fe-Si bonds formed on the surface of PS. Our results support the quantum confinement model.

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