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Stabilized electronic state and its luminescence at the surface of oxygen-passivated porous silicon

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Photoluminescence (PL) spectra of as-made porous Si samples were obtained in a wide peak-wavelength range. After exposure to air or coupling with C_{60} molecules, the PL peak shifts to a pinning wavelength within the range of 610–630 nm. This pinning wavelength is almost independent of the size of the original porous Si nanocrystallites and both redshifting and blueshifting can occur for different sizes. A self-consistent effective-mass calculation shows that the Si═O binding states are responsible for the radiation of this pinning wavelength and the blueshift for the large nanocrystallites is due to the additional potential modulation within the Si nanocrystallite by the long-range Coulomb interaction of oxygen ions.

Porous Si (PS) has attracted considerable interest over the past nine years because of its applications in optoelectronic integration.[1–4] Its photoluminescence (PL) mechanism has been the subject of numerous experimental and theoretical investigations and intense controversy has appeared.[3] Several models have been proposed to describe the origin of PL spectra, mainly involving quantum confinement,[1,5] surface states,[6,7] and interfacial oxide-related defects.[8] However, the microscopic details of PS are complicated and the obtained results usually depend on the experimental conditions. Thus it seems difficult to contrive a unified model that can explain all the experimental results. So far, the commonly accepted theory is that the band gap is widened as a result of the quantum confinement of Si nanocrystallites, which pushes the PL peaks into the visible range for crystallite sizes below 5 nm. For naturally oxidized PS, it has been reported[9–14] that the PL peak in the red regime is gradually blueshifted with increasing the storage time in air and finally stays at about 620 nm (2.0 eV). The corresponding PL intensity was reported to decrease in some cases and increases in others.

Recently, Wolkin *et al.*[15] reported that after PS samples with initially blue-to-orange emission were stored in air for 24 h, the PL peak was redshifted to about 590 nm (2.1 eV). No PL shift was observed for the samples with initial emission in the red (the crystallite sizes being 3 nm) whether the samples were stored in Ar or aged in air. This observation is not in agreement with those reported previously. A model with new energy level, which appears in the gap of smaller (3 nm) crystallites and is attributed to the Si═O bond states at the surface of nanocrystallites, is proposed in Ref. 15. It can explain very well the redshift of samples with initially blue-to-orange PL. However, for samples with initially red PL, this model cannot predict the blueshift of PL peaks, because the spacing of levels corresponding to Si═O bond states is larger than the gap.[15] Similarly, this model can only explain the huge Stokes shift observed for the smaller (2 nm) nanocrystallites. In fact, similar phenomenon was observed for the larger (3 nm) nanocrystallites.[11,16,17] Therefore, it is necessary to further examine the shift of PL spectra from experiments and to seek a more comprehensive explanation for its origin. In this paper, we present the results of PL measurements in PS samples with different porosities both stored in air and coupled with C_{60} molecules. The experimental results indicate that the oxygen-related surface states play an important role in the recombination mechanism. A self-consistent effective-mass calculation shows that the Si═O binding states are responsible for the radiation at the pinning wavelength and the blueshift for the large nanocrystallites is due to the additional potential modulation within the Si nanocrystallite by the long-range Coulomb interaction of oxygen ions.

The PS samples were prepared from ⟨100⟩-oriented *p*-type Si ($\sim 5\,\Omega\,\mathrm{cm}$) wafers by anodization in a $C_2H_5OH{:}HF = 1{:}2$ solution with a current density of 15–25 $\mathrm{mA/cm^2}$. The PS layers with different porosities were obtained under an anodization time of 15–40 min. To change the surface chemistry, some samples were exposed to air for more than three months and the others were chemically coupled with C_{60} molecules through a coupling agent $[(CH_3O)_3Si(CH_2)_3NH_2]$. One end of the coupling agent is NH_2, which easily combines with the C_{60} molecule by nucleophilic addition reaction, and the other end is $Si(OCH_3)_3$, which has an affinity for hydrolysis treated Si. The coupling experiments were as follows: The as-made PS samples were first immersed in ethanol for 24 h to prevent the samples from oxidization in air followed by the application of the coupling agent (3–4 drops) dropping onto the sample surface, so the coupling agent molecules were combined with the PS through Si═O bonds. Second, the remaining uncombined coupling was washed away by toluene and the treated samples were then immersed in a solution of $2\times 10^{-2}\,\mathrm{mg/ml}\ C_{60}$/toluene for 24 h. In this process, some carbon-carbon double bonds in the C_{60} molecules were broken and combined with NH_2 groups [see Fig. 1(a)]; Finally, the free uncombined C_{60} molecules in the pores of PS were fully washed away by toluene.

C_{60} introduction into the surface of PS should not lead to a reduction of the Si crystallite sizes but change the surface

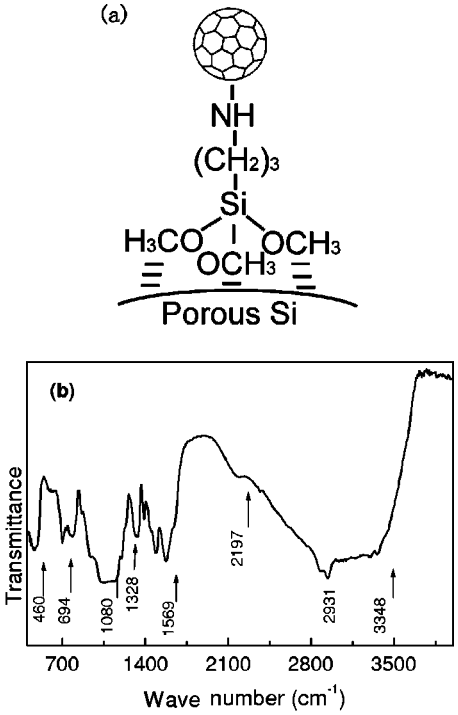

FIG. 1. (a) Schematic diagram and (b) a typical FTIR spectrum of the PS/C_{60} coupling system.

structure. A typical Fourier-transform infrared (FTIR) absorption spectrum of the C_{60}-coupled samples, taken from a Nicolet 170SX spectrometer, is shown in Fig. 1(b). This spectrum mainly displays the following vibrational bands:[18] The 694 and 779 cm^{-1} bands are connected with polysiloxanes and the 1328, 1358, 1486, and 1569 cm^{-1} bands with a resin containing $-\mathrm{NH}_3{}^{+}\,{}^{-}\mathrm{HCO}_3$. The 2871 and 2931 cm^{-1} bands correspond to CH_n $(n=1\text{–}3)$ symmetric and asymmetric stretching vibrations and the 3292 cm^{-1} band is from the NH_2 group. The 3348 cm^{-1} band comes from O—H stretching vibration and the 460 and 1080 cm^{-1} bands from the Si—O—Si vibrations. A sharp feature of this spectrum is that the Si—O—Si vibrations are largely strengthened after C_{60} molecules are coupled, similar to the situation in the naturally oxidized samples.[11,15] In addition, the Si—H_n $(n=1\text{–}3)$ vibrations at 2000–2200 cm^{-1} are weak, implying that the originally hydrogen-terminated surface has completely been modified due to the coupling with C_{60}.

Figure 2(a) shows the PL spectra of a series of as-made PS samples, taken from a Hitachi 820 fluorescence photospectrometer. The peak positions are at 590, 630, 660, 685, and 710 nm, respectively. After these samples were stored in air, the 590-nm peak redshifts, while the others gradually blueshift. These peaks finally saturate at about 620 nm (2.0 eV) after air exposure for more than three months [see Fig. 2(b)], and in the meantime their intensities slightly decrease. The greater the deviation from this saturating wavelength, the greater the shift. In view of the present results and the previous reports,[9–15] we conclude that the PL from the samples exposed to air has a pinning wavelength at about 620 nm.

To understand the origin of the characteristics in PL spectra, the PL excitation (PLE) spectra of as-made and the oxidized samples were examined and a large Stokes shift (~1.1 eV) was observed [see Fig. 3(a)]. If one sample was used and the data were taken with different air storage history, the PL peaks obviously shift toward the pinning wavelength with storage time, but no noticeable peak shift was observed for the corresponding PLE spectra, as shown previously.[11,16,17] These observations suggest that the absorption peak is from a special excitation in the band with quantum confinement (~3.1 eV), while the radiative recombination occurs via relaxed electronic states, possibly oxygen-related surface states.[15,16] Koch *et al.*[6] and Kanemitsu *et al.*[7] have suggested such surface state models. In their models, the photogeneration of carriers takes place in the quantum confined *c*-Si core, but the radiative recombination occurs in states localized at the surface of PS, or in a interfacial region between the Si and an oxide. These models can easily ex-

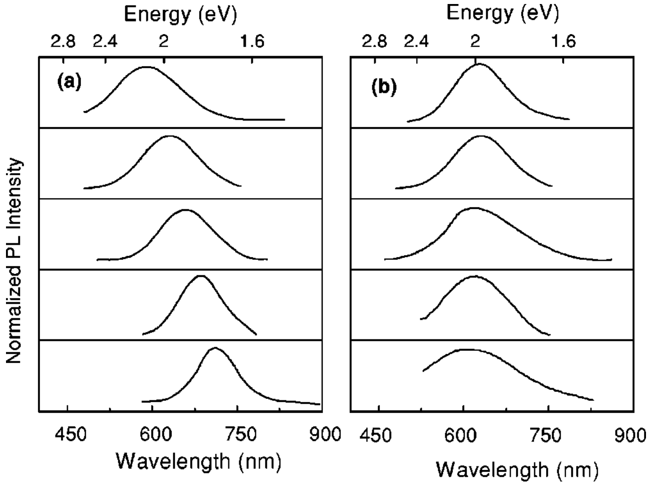

FIG. 2. PL spectra of (a) as-made and (b) naturally oxidized (more than three months) PS samples.

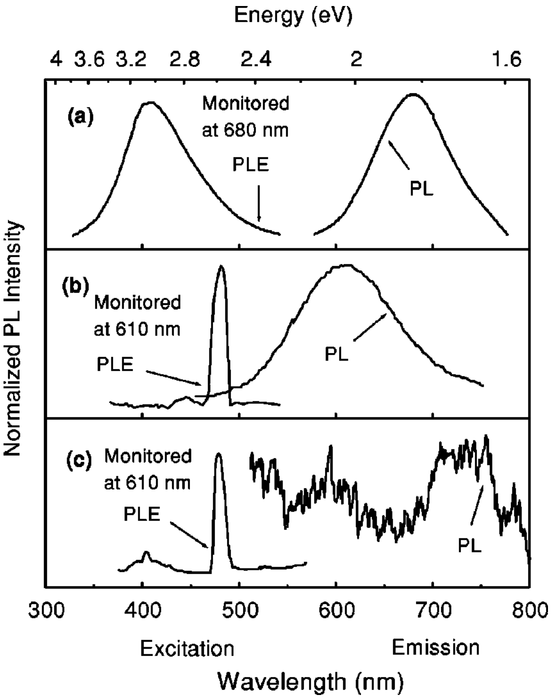

FIG. 3. PL and PLE spectra of (a) as-made PS sample, (b) C60-coupled PS sample, and (c) C_{60}-coupled *c*-Si wafer.

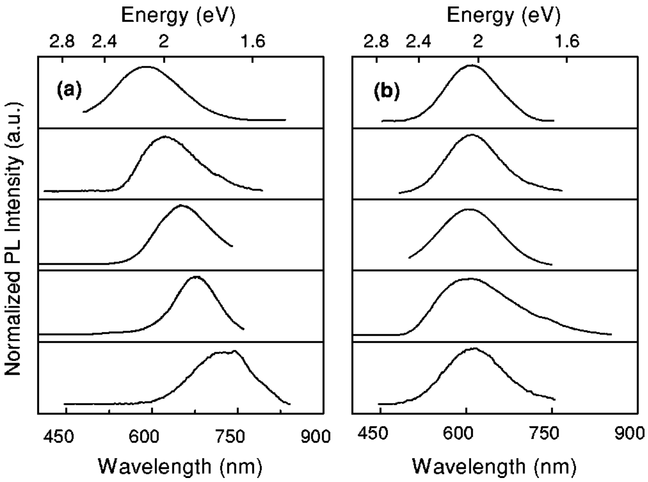

FIG. 4. PL spectra of (a) as-made and (b) C_{60}-coupled PS samples.

plain the redshift of blue-to-orange PL in small crystallite samples and the blueshift of red PL in the large crystallite ones, because the PL peak energy is not dependent upon the size of the c-Si core but the surface passivation.[19] Therefore, the surface state mechanism is a suitable candidate for the PL origin.

To disclose the influence of the surface passivation on the PL, we further investigate the PL spectra of C_{60}-coupled PS samples, as shown in Figs. 4(a) and 4(b). For as-made samples, the PL peaks are observed at 590, 620, 650, 680, and 730 nm, respectively. After they are chemically coupled with C_{60} molecules for 24 h, the 590-nm PL peak redshifts and the others consistently blueshift to $\sim 610\,\mathrm{nm}$, almost at the pinning wavelength for the naturally oxidized samples, and their intensities are slightly increased. Obviously, the coupling of C_{60} molecules only modifies the surface chemistry of the PS samples. To explore the origin of the photoexcited carriers in this kind of C_{60}-coupled sample, the PLE spectra monitored at 610 nm were examined and a typical result is shown on the left side of Fig. 3(b) [the right side of Fig. 3(b) shows the corresponding PL spectrum]. The PLE spectrum clearly shows an excitation peak at 480 nm ($\sim 2.58\,\mathrm{eV}$) with large intensity. Since it has a narrow line shape compared to the 400-nm PLE peak observed in the naturally oxidized samples, it should not be from the c-Si core but the coupling agent/C_{60} system. The coupling system is a source of the photoexcited carriers.

To verify the origin of the carriers, we used a c-Si wafer to replace the PS sample for fabricating a C_{60}/c-Si coupling system. The PLE measurements found that the 480 nm peak still has a large intensity, but in the meantime another PLE peak with low intensity can be observed at about 400 nm, as shown in Fig. 3(c). The corresponding PL spectrum only displays a noisy signal. Further, we dropped the coupling agent into a C_{60}/toluene solution and then measured the PL and PLE spectra. The results obtained are similar to those from the C_{60}/c-Si coupling system. These experimental results indicate that the photoexcited carriers are from the coupling agent/C_{60} system, while the radiative recombination occurs at the PS surface modified by the C_{60} coupling. The carrier transfer from the C_{60} system to the PS surface can be further examined by measuring the corresponding Raman spectra. The most characteristic C_{60} Raman mode related to the carrier transfer is the $A_g(2)$ pentagonal pinch mode at $1464\,\mathrm{cm}^{-1}$.[20] In the Raman results, the mode shifts up to $1478\,\mathrm{cm}^{-1}$ in our samples, indicating a charge transfer of at least two electrons per C_{60} molecule to the surface. Thus for the naturally oxidized and C_{60}-coupled PS samples, although the photoexcited carriers come from different part, the PL has a similar origin related to the surface states. Moreover, we also dipped the PS samples for 15–30 s in the NH_4OH solution which acts as an oxidant and found that the PL peak also shifts to the similar wavelength range.[21] Meanwhile the Si—O—Si vibration at $1070\,\mathrm{cm}^{-1}$ in the FTIR spectra also shows large intensity. This result further confirms that surface oxygen passivation plays an important role in the recombination mechanism.

According to the consistency of the FTIR feature and the pinning wavelength in naturally oxidized, C_{60}-coupled, and NH_4OH-treated PS samples, we believe that the PL peak is closely related to oxygen-related surface states. When Si nanocrystallites are oxidized in air or by an oxidant, surface Si—Si or Si—O—Si bonds are likely to weaken or break to form a Si═O double bond because of the large stress at the Si/SiO2 interface and thus stabilize the interface.[15]

In the calculations of Ref. 15, it is found that the radiation at energy near 2.0 eV in the Si nanocrystallite passivated by oxygen arises from a stabilized electronic state formed on the Si═O covalent bond. The peak in PL spectrum before the oxygen passivation comes from the free electron in the nanocrystallite, which is determined from the model of quantum confinement. As the nanocrystallite size decreases, the PL energy increases, as predicted by the calculation of the energy gap from the quantum confinement. Thus if the nanocrystallite size is smaller (shown in zone III of Fig. 3 in Ref. 15), the energy of the free exciton is larger than the excitation energy of the Si═O state, a redshift of the PL peak occurs from the oxygen passivation. However, if the size of nanocrystallites is larger (zone I of Fig. 3 in Ref. 15), the Si═O state is outside the gap which cannot be shown in the PL spectrum. As a result, the blueshift of the PL peak for larger nanocrystallites due to the oxygen passivation cannot be explained from this theory. In the present experiments, we observe a clear blueshift of the PL peak from the oxygen passivation for larger nanocrystallites. This can be explained as follows: When the oxygen passivation is deeper, not only one or two silicon atoms on the surface of one nanocrystallite, but a finite fraction of the surface Si atoms, are attached by oxygen ions to form a dilute shell of oxygen. Due to the negative charge of this oxygen shell, the electrons in a Si shell near the surface feel a strong increase of the electrostatic potential. The thickness of this Si shell is determined by the screening effect of the electrons in this composite system. This reduces the effective size of the Si nanocrystallites and enlarges the gap for the free excitons. Therefore, the blueshift of the larger nanocrystallites due to the oxygen passivation becomes possible. By the effective-mass approximation[22] the eigenenergies E and eigenstates ψ in a spherical nanocrystallite can be solved from the Schrödinger equation

$$-\frac{\hbar^2\nabla^2}{2m_{e(h)}}\psi+V(\mathbf{r})\psi=E\psi,$$

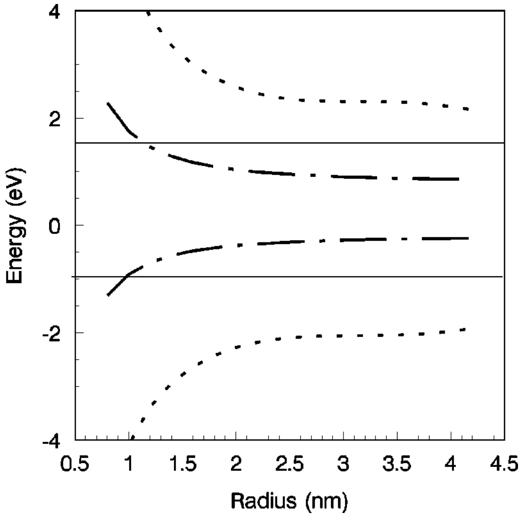

FIG. 5. The gap edges of Si nanocrystallites as functions of the nanocrystallite size from a self-consistent effective-mass calculation. Dashed-dotted and dotted lines are for the situations before and after oxygen passivation, respectively. In the passivation, 40 Si surface atoms are attached by the oxygen ions. The two solid lines are for the energy levels of the Si═O bound states.

with $m_{e(h)}$ being the electron (hole) effective mass and $V(\mathbf{r})$ the spherical potential produced by the charge. $V(\mathbf{r})$ can be self-consistently determined from the charge density obtained from the occupied hole eigenstates by using the Poisson equation. At the same time, since the Si═O bonds are isolated from each other the Si═O bond states can be regarded as the local ones with a weak coupling to the crystallite, like the bound states on a dot weakly coupled to the leads.[23] Thus the excitation energy of the local Si═O bond states is almost unchanged by the variation of the crystallite size and the degree of the oxygen passivation. We show the results of the self-consistent effective-mass calculation in Fig. 5 for the electronic states of Si nanocrystallites of different sizes before and after oxygen passivation, respectively. There are 40 surface Si atoms being attached by the oxygen ions in the passivation. It can be seen that both the redshift for the smaller nanocrystallites and the blueshift for the larger nanocrystallites can occur. If the passivation is too light, that is, the number of the oxygen ions is too small, the blueshift cannot occur because the screening potential in the crystallites is too weak.

In conclusion, the PL spectra of as-made PS, naturally oxidized PS, and C_{60}-coupled PS were examined. For the oxidized and coupled samples, the PL peak shifts to a pinning wavelength in the range of 610–630 nm. This pinning wavelength is almost independent of the size of the original porous Si nanocrystallites and both the redshift and blueshift can occur for different sizes of the nanocrystallites. A self-consistent effective-mass calculation shows that the Si═O binding states are responsible for the radiation of this pinning wavelength and the blueshift for the large nanocrystallites is due to the additional potential modulation within the Si nanocrystallite by the long-range Coulomb interaction of the oxygen ions.

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