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Light-emitting mechanism conversion in C₆₀-coupled porous Si systems

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Abstract

We reveal two kinds of light-emitting origins in two typical porous Si (PS) samples by carefully examining the photoluminescence (PL) and PL excitation (PLE) spectra. The interfacial oxygen-related defect states and Si=O binding states at the surfaces of the two samples are considered to be responsible for the two emissions, which is useful in clarifying some problems in controversy related to the emission mechanisms of PS. After the two kinds of PS samples were coupled with C₆₀ molecules, the PL from the surface states is replaced by the emission associated with the oxygen-related defects. The coupling process plays an important role in conversion of the light-emitting mechanism. We suggest that this PL conversion is due to destruction of original Si=O binding states caused by C₆₀ coupling and therefore the PL from the interfacial defect states becomes main emission process. © 2002 Elsevier Science B.V. All rights reserved.

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Silicon-based light-emitting materials have been studied extensively because of their potential applications to optoelectronics [1]. Among these materials, porous Si (PS) attracted considerable interest for its room temperature visible luminescence [2–4]. In the studies of the luminescence of PS, many researchers have proposed several models for its mechanism, mainly involving quantum confinement [2], surface state [5,6], and interfacial oxygen-related defects [7]. Although the obtained results usually depend on the experimental conditions and thus it seems diffi-

cult to contrive a unified model to explain all the experimental results, these models provide a real basis for explaining the emission mechanisms of other Si-based light-emitting materials. Therefore, it is still necessary to pay attention to the PL origins. On the other hand, C₆₀ is well-known as a promising molecule material with a highly symmetrical structure and unique physical and chemical properties [8]. If C₆₀ molecules are placed in certain environments, the PL at room temperature related to C₆₀ can be expected [9]. Based on this idea, much interest has recently been focused on the interaction of C₆₀ molecules with PS [10–12]. Such studies would improve the understanding of both PS light-emitting mechanism and interaction process between the two nano-materials.

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In this Letter, we report two types of PS samples whose emissions were identified to be from interfacial oxygen-related defects and Si=O double bond surface states [13], respectively. After they are coupled with C₆₀ molecules through a kind of coupling agents [14], we found that the luminescence from the surface states become an emission from the interfacial oxygen-related defect states by examining the photoluminescence (PL) and PL excitation (PLE) spectra. Fourier-transform infrared (FTIR) absorption spectra strongly suggest that the essence of this PL mechanism conversion is due to destruction of the Si=O double bond states on the surface of PS in process of C₆₀ coupling. The present work will be useful in clarifying some problems in controversy related to the emission mechanisms of some Si-based nano-materials.

The PS samples used in our experiments were made from (100)-oriented *p*-type Si wafers (10–20 Ω cm). The etching solution was selected to be 1 : 3 dilution of 40 wt% aqueous HF in ethyl alcohol. Two typical samples (marked as A and B) were obtained with the etching current densities of 40 and 25 mA/cm², respectively, under an etching time of 20 min. To identify the influence of various post-treated conditions on the samples, each sample was cut into four pieces. The first one was considered as fresh PS (samples A1 and B1). The second one was annealed in a diluted oxygen (10% in N₂) at 300 °C for 1 min (samples A2 and B2). The third one was chemically coupled with C₆₀ molecules through a kind of coupling agents [(CH₃O)₃Si(CH₂)₃NH₂] (samples A3 and B3). The last piece was annealed at 300 °C for 1 min and then coupled with C₆₀ molecules (samples A4 and B4). The coupling experiments have been described in Ref. [12]. The PL and PLE data in our experiments were obtained on a Hitachi 850 fluorescence spectrophotometer and the FTIR spectra were measured at a Nicolet 170SX spectrometer.

The PL and PLE spectra of as-made PS samples (stored in air for more than 1 h) are shown in Fig. 1. The PL peak of sample A1 shows a broad band at 590 nm and its PLE peak has a pinning wavelength at about 367 nm when monitored at different emission wavelengths (Fig. 1(a)). Shown in Fig. 1(b) are the PL and PLE spectra of sample B1. The PL peak is at 610 nm and the PLE peak shows a blueshift with decreasing the monitored wavelength. From the difference in the PLE spectra of the two kinds of samples,

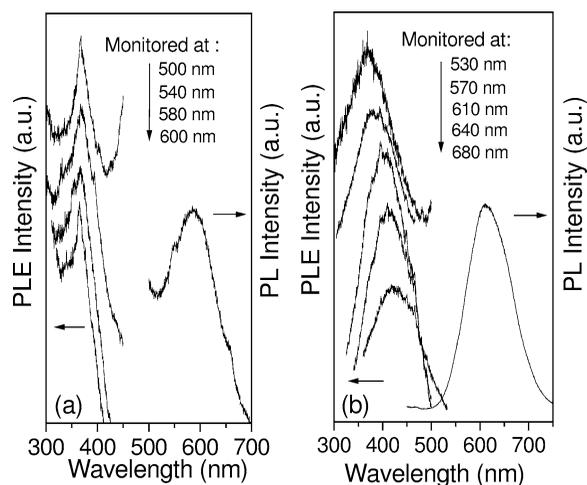


Fig. 1. PL and PLE spectra of two typical as-made PS (40 wt% aqueous HF : ethyl alcohol = 1 : 3, 20 min). (a) Sample A1, with an etching current density of 40 mA/cm² and (b) sample B1, with an etching current density of 25 mA/cm².

we can infer that their light-emitting mechanisms are different. In view of the commonly accepted models discussed below, we believe that the light-emitting origin of sample A1 is related to the interfacial oxygen-related defects [7], while the luminescence of sample B1 is from the Si=O double bond states on the surface of PS [12,13].

Now we pay our attention to the PL origins of the two kinds of PS samples. The quantum confinement (QC) model claims that the PS luminescence originates from band-to-band radiative recombination of electron–hole pairs in *c*-Si cores whose band gaps are widened by the QC effect [2]. According to the QC model, after *c*-Si core sizes are reduced due to oxidation, the PL spectra should blueshift, but for our samples, the positions of the PL peaks have no noticeable change after low temperature oxidation (Fig. 2). Therefore, we can rule out the possibility for the two observed PL to be owing to band-to-band recombination in the QC *c*-Si cores. For the interfacial oxygen-related defect model, since the energies of photoexcited carriers have no dependence on special partial size [7,15], the PLE peaks should not show any shift with various monitored wavelengths. From our experimental results shown in Figs. 1(a) and 2(a), it can be inferred that the PL peaks from samples A1 and A2 arise from optical transitions in the oxygen-related defect states. The presence of these oxygen-related de-

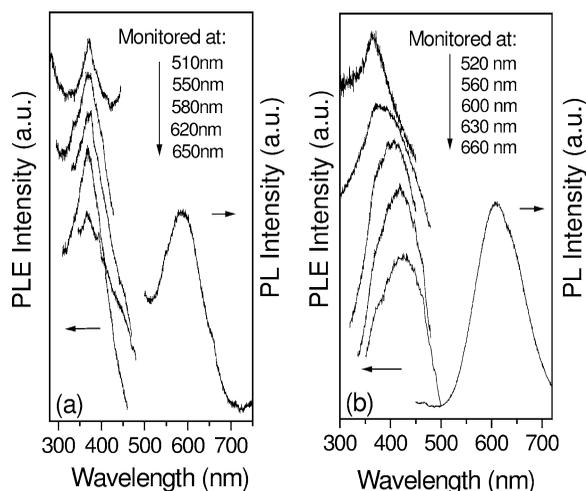


Fig. 2. PL and PLE spectra of PS samples annealed at a low temperature. (a) Sample A2 and (b) sample B2.

facts in PS has previously been reported by Prokes et al. [7]. These defects are considered to be some non-bridge oxygen hole centers. They are stable under thermal annealing at low temperature. Another model, the surface (or interface) state model proposed by Koch et al. [5] (or Kanemitsu et al. [6]), suggests that the photogeneration of carriers takes place in the quantum confined *c*-Si cores, whereas the radiative recombination occurs in states localized at the surface (or interface) of PS. This model can easily explain the PL and PLE spectra of samples B1 and B2 (Figs. 1(b) and 2(b)). The blueshift of the PLE spectra with decreasing the monitored wavelengths is due to the dependence of the energies of photoexcited carriers on the sizes of *c*-Si cores [16], whereas the PL spectra only depend on the surface states and thus no shift is observed in the oxidized PS. To identify the 610 nm PL mechanism, we examined the FTIR spectrum of sample B1 and the corresponding result is presented in Fig. 3(a). It can be seen that the Si–O–Si stretching vibration band at 1070 cm^{-1} shows a large intensity, indicating that the surface of the as-made sample has been passivated well by oxygen. Previously, we have known that oxygen passivation at the surface of PS can result in the formation of Si=O double bond states [12,13], which introduces a new energy state in the gap of small Si nanocrystallites. The corresponding PL shows a pinning wavelength at about 620 nm. Therefore, the 610 nm PL mechanism is closely re-

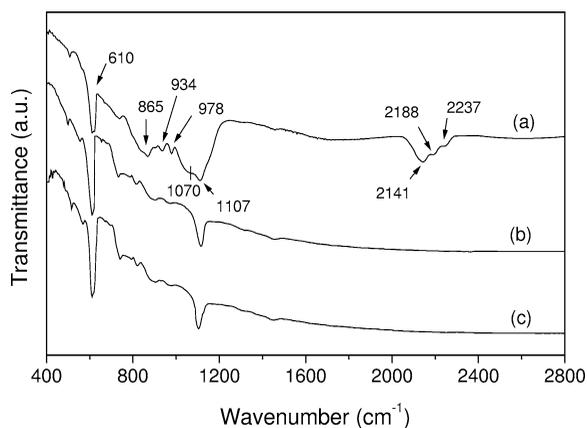


Fig. 3. Typical FTIR spectra of (a) as-made PS (sample B1), (b) as-made PS with C_{60} coupling (sample B3), and (c) the annealed PS with C_{60} coupling (sample B4).

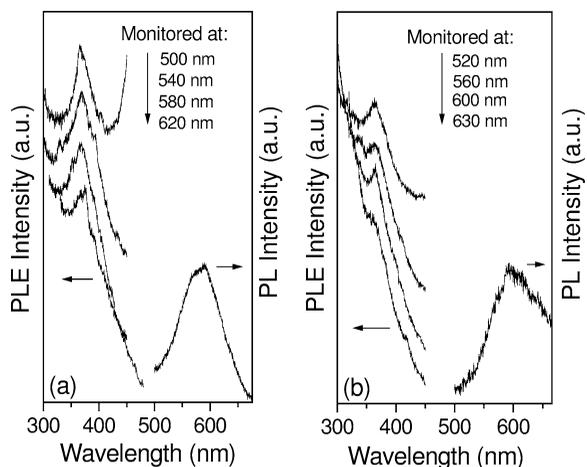


Fig. 4. PL and PLE spectra of as-made PS samples with C_{60} coupling. (a) Sample A3 and (b) sample B3.

lated to the existence of some Si=O bonds at the surface of the as-made PS sample. Subsequent annealing under low temperature keeps these surface Si=O binding states not to be changed. As a result, the PL spectrum still shows a peak at 610 nm.

In the following, we consider the PL of C_{60} -coupled PS systems. For samples A3 and A4, their PL and PLE spectra exhibit no obvious change compared to those of samples A1 and A2 (Figs. 4(a) and 5(a)). This result is understandable, because C_{60} coupling on the surface of PS is difficult to change the structures of the interfacial defect states and therefore optical

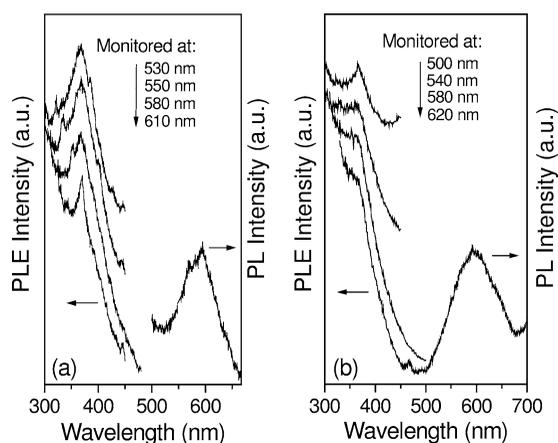


Fig. 5. PL and PLE spectra of the annealed PS sample with C_{60} coupling. (a) Sample A4 and (b) sample B4.

transitions in these defect states will still contribute to the PL. For samples B3 and B4, the PL and PLE peaks shift to a pinning wavelength at 590 and 367 nm, respectively, as in the case of sample A. Meanwhile, the PL intensities are strongly reduced (Figs. 4(b) and 5(b)). According to these PL and PLE results, we can infer that the luminescence of the two kinds of coupling samples has same origin. However, a problem arises: how does the PL from the surface states become the emission from the defect states in C_{60} -coupled samples?

To disclose this conversion, we present the FTIR absorption spectrum of samples B after C_{60} coupling in Fig. 3(b) and (c). For the FTIR spectrum of sample B1 (Fig. 3(a)), it mainly displays the following vibration bands [17–19]: the 865, 934, 978, and 2000–2300 cm^{-1} bands are related to Si-H_x ($x = 1-3$) vibrations and the 610 cm^{-1} band comes from Si–Si stretching vibration. The dominant bands at 1070 and 1107 cm^{-1} are due to Si–O–Si symmetric and asymmetric stretching vibrations in SiO_x ($x \leq 2$), respectively. For the FTIR spectrum of sample B3 (Fig. 3(b)), three sharp features can be identified in comparison with those of Fig. 3(a). First, the hydrogen-related vibrations cannot be observed; second, the 1070 cm^{-1} vibration band disappears and the 1107 cm^{-1} vibration intensity decreases; third, the Si–Si vibration intensity at 610 cm^{-1} has a large increase. To obtain a general FTIR result, we have measured a number of C_{60} -coupled samples. A typical spectrum from sample B4 is shown in Fig. 3(c). Obviously, spectra (b) and (c)

are very similar, indicating that originally hydrogen- and oxygen-terminated surface has completely been modified after C_{60} coupling. Therefore, it is evident that the coupling process plays a key role in the conversion of light-emitting mechanism from the surface states to the oxygen-related defect states. According to the above FTIR result, we can infer that after C_{60} is coupled on PS, some characteristic bonds on the surface, Si-H_x ($x = 1-3$), Si=O , and partial Si–O–Si bonds, are broken. The increase of the 610 cm^{-1} band in intensity indicates that more Si–Si bonds have been formed in this coupling process. This may lead to the introduction of some oxygen-related defect centers at the surface. Once the surface states connected with Si=O double bonds vanish and meantime the oxygen-related defect states form, the luminescence from the surface states become the emission from the interfacial oxygen-related defects.

In conclusion, we have observed two kinds of light-emitting mechanisms in different PS samples. From their PL and PLE spectra, the interfacial oxygen-related defects and Si=O surface binding states are considered to be the sources of their luminescence. The obtained results indicate that different fabrication conditions of PS may lead to different PL mechanisms. Thus, it is not necessary to pursue an exact mechanism for PS emission. For C_{60} -coupled PS samples, we have observed a conversion of the PL mechanism from the surface state to the oxygen-related defect state, which further reveals that light-emitting mechanism can transfer each other through surface passivation. The present work improves the understanding of light-emitting mechanisms of PS and its composite materials.

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