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Influence of electron beam and ultraviolet ozone irradiation on blue-emission properties of C_{60}-coupled porous silicon

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Abstract

Electron beam irradiation was carried out to change the surface structure of Si nanocrystals in C_{60}-coupled porous silicon with blue light emission at 460 nm. It was found that the photoluminescence (PL) intensities of the coupled system irradiated with an electron dose of 10^{15} cm^{-2} and energy of 0.5 MeV more than doubled compared to the untreated materials and then the intensities diminished with storage time in air. After 13 days, the PL intensities reached stable values that were higher than those observed from the untreated sample. Spectral analysis and ultraviolet ozone irradiation experiments on the coupled systems suggest that the formation of self-trapped excitons at the surfaces of the silicon nanocrystals with a higher density is responsible for the enhanced blue PL. Our technique provides an efficient way to improve the efficiency of blue light emission from these silicon nanostructures.

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Keywords: Porous silicon; C_{60}; Electron beam irradiation; Photoluminescence

1. Introduction

In the past years, the origins of blue light emission from many silicon nanostructures have been extensively investigated [1,2] because blue emission is of great importance in full-color all-Si optoelectronics. Hou et al. [3] studied the PL spectral shift from red to blue from porous silicon (PS) treated with boiling water. They attributed the short-lifetime blue emission to the quantum confinement effect of the very thin Si skeleton resulting from the etching of boiling water. Subsequently, Tsybeskov et al. [4] observed blue emission at 460 nm from thermally and chemically oxidized PS layers and correlated it with oxygen-related defects. However, due to the complex microscopic details, they did not provide the exact defect structure to theoretically describe the origin of the observed blue emission. Since then, many researchers have explored strong blue emission from various Si nanostructures, including oxidized nanocrystalline silicon films [5–9], Si-implanted SiO_2 films [10,11], $Pb(Zr_x,Ti_{1-x})O_3$-embedded PS [12], and C_{60}-coupled PS systems [13]. These Si nanostructures can generally luminesce in two distinct bands that include the blue band at ∼460 nm discovered earlier and a newly identified higher energy blue band at 417–437 nm. Although the blue-emitting mechanism of the former is still unclear and more work is required, a possible origin of the latter is believed to be the Si vacancy defects in the Si nanocrystals [2]. However, the 460 nm blue photoluminescence (PL) from Si nanostructures is not always observed from many Si nanostructures. This is particular true for PS samples that have undergone various steps of post-processing. Many investigators have attempted to attain blue emission by direct oxidization of PS but had little success. Recently, we fabricated C_{60}-coupled PS and found that this type of nanocomposite material exhibited obvious blue PL at ∼460 nm even after storage in air for more than 1 year [13]. Using primary spectroscopic characterization and neutron irradiation experiments with low dosage (10^6 cm^{-2}), we postulated that the blue PL arose from radiative recombination of the self-trapped excitons in the SiO_x layer at the surface of Si nanocrystals. However, experimental evidence to support the model has been lacking.

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In this work, we utilize electron beam irradiation to change the surface structure of Si nanocrystals in the C_{60}-coupled PS system and investigated the change in the blue PL property. The C_{60}-coupled PS materials after electron beam irradiation show large enhancement in the blue PL intensity. Spectral analysis and subsequent ultraviolet ozone (UVO) irradiation experiments suggest that the formation of the self-trapped excitons at the surfaces of silicon nanocrystals with a higher density is responsible for the enhanced blue PL. Our experimental work not only provides a useful way to fabricate blue-emitting Si nanostructures but also deepens our understanding on the origin of the 460 nm blue PL emission from PS-related nanomaterials.

2. Experimental details

The preparation procedures of the PS and C_{60}-coupled PS samples have been reported previously [13,14]. We selected a silane coupling agent $[(CH_3O)_3Si(CH_2)_3NH_2]$ to chemically incorporate C_{60} molecules onto the PS sample surface for 24 h. One end of the coupling agent is $-NH_2$, which easily combines with the C_{60} molecule by nucleophilic addition reactions, and the other end is $-Si(OCH_3)_3$, which has affinity to hydrolysis-treated Si.

We have previously found that after the C_{60}-coupled PS materials are stored in air for more than 1 year, they generally show blue emission at ~460 nm [13]. Fig. 1 displays the representative PL results. It can be seen that the as-prepared PS sample shows a PL peak at 710 nm that shifts to 590 nm when coupled with C_{60} molecules for 24 h [see Fig. 1(a)]. Our PL and PLE spectral investigations indicate that the 710 nm PL originates from band-to-band recombination in the quantum confined Si nanocrystals, whereas the 590 nm PL arises from radiative recombination of carriers photoexcited from the Si crystallite core in the Si=O double bonding states at the surfaces of the Si nanocrystals [14,15]. After the C_{60}-coupled PS system has been stored in air for more than 1 year, the 590 nm PL intensity diminishes significantly and a blue PL band appears as shown in Fig. 1(b). The blue PL intensity decreases further with increased storage time. Our spectral measurements and analyses suggest that the origin of the 590 nm PL has not changed and the intensity reduction is a result of the decease in the Si=O bonding state density. With regard to the 460 nm blue PL, we have found that it is still related to the quantum confinement effect of Si nanocrystal, but radiative recombination of carriers takes place in the interface (or surface) between the Si nanocrystal and the coupled C_{60} molecule [13]. Since the interface is very complicated, we can only postulate that the blue luminescent center is an oxygen vacancy and an interstitial oxygen atom [16,17]. The interstitial oxygen atom also forms a peroxy linkage with a neighboring lattice oxygen atom. The blue PL from such a luminescent center depends on the co-existence of both oxygen vacancy and interstitial oxygen in a SiO_2 lattice structure. However, most Si oxide materials are oxygen deficient, and so it is difficult to observe the blue emission at ~460 nm in many experiments.

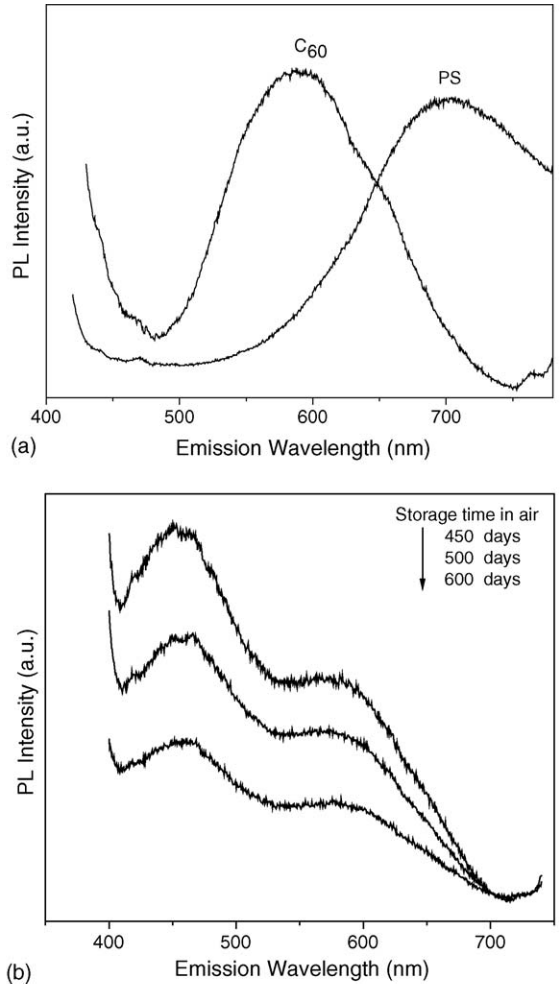

Fig. 1. (a) PL spectra acquired from the as-prepared and C_{60}-coupled PS samples. (b) PL spectra of the C_{60}-coupled PS samples after storage times of 450, 500, and 600 days in air. These PL spectra were taken under excitation with the 370 nm line of a Xe lamp.

It is well known that when Si oxide is irradiated by neutrons, vacancies V_o and interstitials O_i are produced in pairs by the knock-on, kick-out events [18,19]. The density of the pairs depends on the irradiation dosage. We have performed neutron irradiation experiments to change the surface structure of the C_{60}-coupled PS system. Due to the low irradiation dosage of $10^6\ cm^{-2}$, the blue PL intensity enhancement is not very evident [13]. Since electron irradiation may produce a similar effect, here we use electron irradiation instead to change the surface structure of the C_{60}-coupled PS materials to produce a large density of the defect pairs. In our experiments, the coupled samples were irradiated with an electron energy of 0.5 MeV and an electron dose of $10^{15}\ cm^{-2}$. To possibly increase the density of oxygen interstitials, UVO irradiation experiments were also carried out in an ultraviolet ozone cleaner (Model No. 144A-220 equipped with Model 1000 ozone generator) with 60 min [20].

PL and PL excitation (PLE) spectral measurements were conducted on a Hitachi 850 fluorescence spectrometer. Fourier-transform infrared (FTIR) absorption spectra were taken on a

Nicolet 170SX spectrometer. All the measurements were performed at room temperature.

3. Results and discussions

To clearly show the influence of electron beam irradiation on the blue PL intensity, we select a C_{60}-coupled PS system with initially low blue PL intensity. Fig. 2 shows the corresponding PL spectra of the coupled system before and after electron irradiation, taken under excitation of the 370 nm line of a Xe lamp. It can be seen that the blue PL intensity is enhanced more than twice in comparison with that from the original system and subsequently attenuates with increasing storage time. After a storage time of 13 days, the PL intensity reaches a stable value, which is still higher than that of the original system. In addition, the PL peak shape remains unchanged in spite of the intensity variation. This indicates that the mechanism of the blue emission is the same before and after irradiation. The PL intensity enhancement should be a result of the increase in the defect pair and/or photoexcited carrier densities. For verification, we examine the PLE spectra of the coupled systems before and after electron irradiation and the results are shown in Fig. 3. For the original coupling system with a low blue intensity, its PLE spectrum shows slight redshift with increasing monitoring emission wavelength [see Fig. 3(a)], indicating that a small amount of photoexcited carriers from a quantum confined band, that is, from the Si nanocrystal cores, contribute to the blue PL. Most of the photoexcited carriers from the Si cores recombine in some nonradiative centers at the surfaces of the Si nanocrystals introduced during sample storage in air. Considering the smaller defect pair density at the crystallite surface (this depends upon the fabrication process and storage environment of the sample), the low blue PL intensity from the original coupling system is understandable. For the irradiated coupled system, its PLE spectrum shows an obvious redshift with increasing monitoring emission wavelength [see Fig. 3(b)], indicating that the photoexcited carriers responsible for the enhanced blue PL partially come from the Si crystallite cores [21]. This result clearly demonstrates that electron irradiation has caused a large change in the surface electron structure of the coupled system, possibly removing many nonradiative centers from the sample surface leading to radiative recombination of the photoexcited carriers in the blue luminescent centers of the surface. As a result, the blue PL intensity is largely enhanced. For the irradiated and stored samples, we have found that the PLE spectral redshift gradually decreases with increasing monitoring mission wavelength. After the sample has been stored for more than 13 days, the PLE spectra are almost pinned at ~380 nm, indicating the introduction of some nonradiative centers. Thus, the blue PL intensity enhancement in the stored (13 days) sample implies that the density of the blue luminescent centers is still higher than that of the initial sample. It can thus be inferred that electron irradiation which has a large influence on the formation of the blue defect pairs is a useful way to improve the blue PL properties.

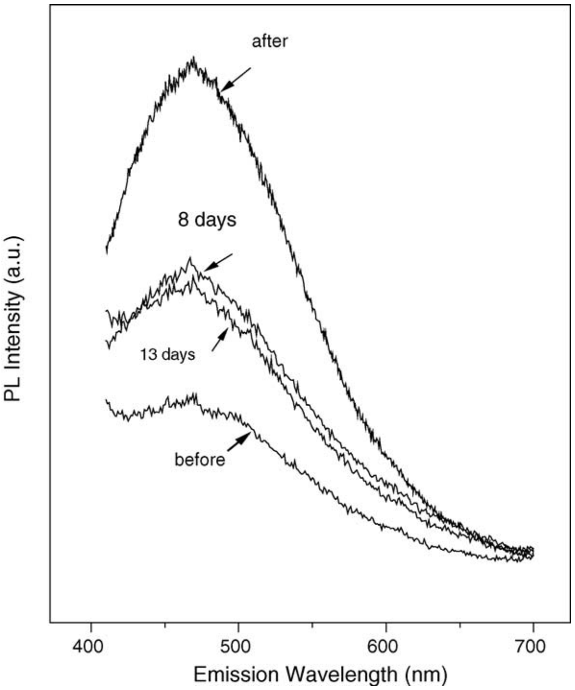

Fig. 2. PL spectra of the C_{60}-coupled sample exhibiting the 460 nm blue emission before and after electron beam irradiation. The PL intensities stabilize after storage in air for 13 days. These PL spectra were taken under excitation with the 370 nm line of a Xe lamp.

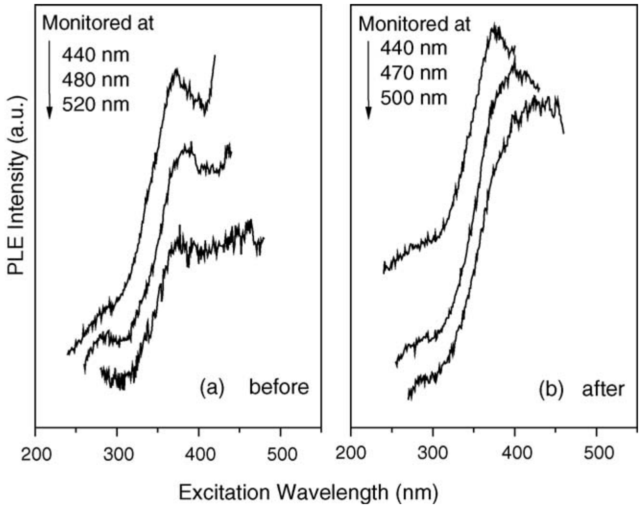

Fig. 3. PLE spectra of the C_{60}-coupled PS sample with the 460 nm blue emission: (a) before and (b) after electron beam irradiation, taken under three different monitoring emission wavelengths.

Here, we examine the influence of UVO irradiation on the blue PL. We have previously known that UVO irradiation will increase the density of oxygen interstitials at the surface of Si nanocrystals by oxygen diffusion from the environment [20]. For a sample with a number of oxygen vacancies, this may increase the defect pair density (oxygen vacancies and interstitials). Fig. 4(a) and (b) shows the PL spectra of a C_{60}-coupled PS sample before and after UVO irradiation, respectively. Comparing the two spectra, we can see that the sample with UVO irradiation has the PL intensity enhanced, but the PL spectral shape hardly changes. Since oxygen diffusion mainly occurs in the surface layer of the Si nanocrystal, two processes may

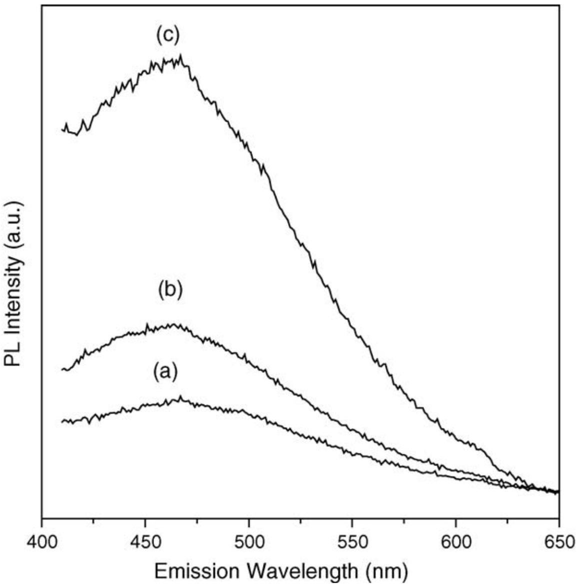

Fig. 4. PL spectra of the electron-irradiated C_{60}-coupled sample: (a) before and (b) after UVO irradiation. (c) PL spectrum of the UVO-irradiated sample after electron beam irradiation for the second time. These spectra were taken under excitation with the 370 nm line of a Xe lamp.

take place for oxygen introduction, one to occupy the oxygen vacancy and the other to become interstitial oxygen. For the untreated and stored PS sample, the Si crystallite surface is generally oxygen deficient and there exists few oxygen interstitials. Thus, it is difficult to observe the 460 nm blue emission, which arises from the defect pairs. After oxygen diffuses into the surface layer to produce the defect pairs, the blue PL may appear in the case with few nonradiative recombination centers at the surface of the Si nanocrystal. Our experiments indicate that UVO irradiation indeed changes the surface structure and leads to the increase in the defect pair density. To investigate the surface structure, we acquire FTIR spectra from the electron-irradiated samples before and after UVO irradiation that are displayed in Fig. 5(a) and (b). With the exception that a vibration mode at 1220 cm^{-1} becomes a shoulder of the 1064 cm^{-1} mode, all the IR vibration modes are at the same peak positions. Their relative intensities also remain unchanged. With regard to the 1220 cm^{-1} IR vibration mode, some theoretical studies have indicated that it corresponds to the vibration of Si=O double bonds [13,22]. Hence, a reduction in the relative intensity is a result of the decomposition of Si=O bonds induced by oxygen diffusion into the surface of the Si nanocrystal. The formation of Si=O bonds is due to an accumulation of the surface stress, which splits the Si–O–Si vibration bond [15]. The stress will be relaxed when the surface chemistry is changed [23], and so the defect pairs form as a result of the splitting of the Si=O bonds. The IR results further confirm that the formation of oxygen vacancies and interstitials is responsible for the 460 nm blue emission. Interestingly, using the same electron energy and dosage, we have carried out electron beam irradiation for the second time on the sample after UVO irradiation and found that the blue PL intensity is afresh enhanced more than one time, as shown in Fig. 4(c). This result provides useful information that the blue defect pairs can be controlled by electron beam irradiation. This technique has high potential in applications involving the 460 nm blue emission from Si oxide nanostructures.

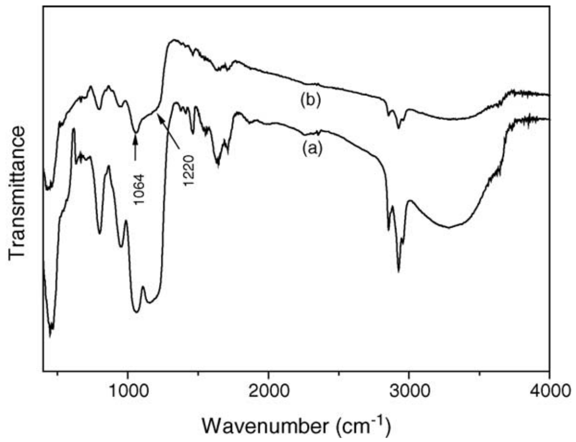

Fig. 5. FTIR spectra of the electron-irradiated C_{60}-coupled sample: (a) before and (b) after UVO irradiation.

4. Conclusion

We have used electron beam irradiation to change the surface structure of the C_{60}-coupled PS materials. It is found that the PL intensities of the coupled systems irradiated with an electron dose of 10^{15} cm^{-2} and energy of 0.5 MeV are enhanced more than twice compared to the untreated materials. The PL intensities diminished with storage time and after 13 days, the PL intensities reached stable values that were still higher than those of the untreated materials. Spectral analysis and subsequent ultraviolet ozone irradiation experiments on the coupling systems suggest that the formation of the self-trapped excitons at the surfaces of silicon nanocrystals with a higher density is responsible for the enhanced blue PL. Our experiments provide an efficient way to improve the blue-emission intensity from silicon nanostructures.

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