Effective passivation on Si nanocrystal surface by peroxide

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Received 30 June 2006; received in revised form 27 January 2007; accepted 16 February 2007
Communicated by H. Fujoka
Available online 1 March 2007

Abstract

Using ultrasonic vibration of as-made porous silicon in water, the suspension of Si nanocrystals is prepared for exploring light-emitting properties of Si nanocrystals. By analyzing the photoluminescence (PL) property of the as-made suspension, we conclude that the observed red PL band arises from radiative recombination of carriers in the interface layer full of Si–H\(_x\) (\(x = 1, 2\)) and Si–O bonds. To effectively passivate the Si nanocrystal surface, we mixed the suspension with peroxide and then heated it. Spectral examinations show that the PL and PL excitation spectra all shift under different excitation wavelengths and at different monitoring wavelengths, respectively. This result illuminates clear evidence for the quantum confine effect of the Si nanocrystals. We suggest that the surfaces of the Si nanocrystals are covered by SiO\(_2\) after treated by peroxide, which leads to the currently observed blue PL phenomenon.

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PACS: 78.67.--n; 73.22.--f; 33.50.--j

Keywords: A1. Characterization; A1. Etching; B1. Nanomaterials

1. Introduction

Since the discovery of porous silicon (PS) with strong room-temperature visible photoluminescence (PL) in 1990 [1,2], many models have been proposed to explain its PL mechanism, mainly including quantum confinement [1–3], surface states [4], defects in the oxide [5], and specific chemical species [6]. Presently, it is usually accepted that the band gap opens as a result of quantum confinement, which pushes the corresponding PL band into the visible range for Si crystallites sized below 5 nm [3]. However, many groups have reported that when the crystallite size decreases to a few nanometers, the PL in air does not increase much beyond 2.1 eV even when the crystallite size drops well below 3 nm [7,8]. To reveal light emission mechanism of small crystallites, Wolkin et al. [9] proposed a model in which new electronic states appear in the band gap of the smaller quantum dots when a Si–O bond is formed on the surface of Si nanocrystal. Introduction of the complicated surface states makes it rather difficult to observe the band-to-band recombination of photoexcited carriers in Si core. Thus, dispersion of the material into ultrasmall particles allows the isolation of single particle effects and opens the way for direct examination of quantum confine theory [10]. To achieve uniform distribution, Si nanocrystals crumbled from PS are usually mixed into a polar solvent such as water [11,12].

In this work, we have carefully investigated the PL spectra of as-made and peroxide-treated suspensions of Si nanocrystals crumbled from fresh PS in water. Our experimental results clearly exhibit the quantum confine effect of Si nanocrystals in the treated suspension, in which the average crystallite size is \(\sim 2\) nm. On the basis of the PL behavior of Si nanocrystals in the suspension, we propose that SiO\(_2\) may be formed on the Si nanocrystal surfaces.

2. Experiments and samples

Cleaned p-type, B-doped silicon (1 0 0) (1–10 \(\Omega\) cm) wafer was first immersed in a HF solution for oxide removal and surface passivation, and then etched in a mixture of...
methanol:HF = 2:1 (98% CH3OH:40% HF) by volume at a current density of 40 mA cm⁻² for 20 min under room light illumination [10]. After drying by a stream of N₂, the PS was then immersed in an ultrasonic water bath, in which the top layer of the as-made PS, a weakly interconnected nanostructure network, was crumbled into ultrasmall particles to form a suspension of Si nanocrystals. After mixing with some peroxide whose volume was ½ similar to the suspensions', the suspension of Si nanocrystals was heated at 100 °C for 10 min.

The morphology of Si nanocrystals was characterized with a JEOL JEM-200CX transmission electron microscopy (TEM) and a JEOL JEM-4000EX high-resolution transmission electron microscopy (HRTEM) equipments. In the process of preparation of the TEM samples, Si nanocrystals in water were treated with ultrasonic vibration and then a drop of suspension was applied to a copper mesh coated with a layer of carbon film. Excess water was then removed with a paper tip. Mean dimension of Si nanocrystals was examined by means of TEM images and Raman spectroscopy (on a T64000 triple Raman system of Jobin-Yvon Company). PL measurements were carried out on a Jobin-Yvon FluoroMax-2 spectrophotometer with a 150 W Xe lamp as light source. All the measurements were performed at room temperature.

3. Results and discussions

Fig. 1 shows the PL spectrum of the as-made water suspension of Si nanocrystals. One can see that the as-made suspension shows a red PL band which can frequently be observed in PS film. The PL spectrum has a broad full-width at half-maximum (FWHM) of ~140 nm and shows obvious double-peak structure. So the PL spectrum is Gaussian divided into two subbands, one being at 590 nm and the other at 645 nm. To investigate the origin of the red PL band, we excited the red PL band under different wavelengths and found that the red PL band does not shift with increasing excitation wavelength and the shape of the double-peak structure remains unchanged. To go deeper into the photoexcitation process of carriers, we examined the PLE spectra of the suspension by monitoring at different emission wavelengths. The obtained PLE spectra are demonstrated in the inset in Fig. 1, which shows a fixed PLE peak at 330 nm. According to the quantum confinement theory, if the sizes of Si nanocrystals are inhomogeneous, the PL and PLE spectra will redshift with increasing excitation and monitored wavelengths, respectively [1–3]. Therefore, we can rule out the possibility of the red PL band being connected with the band-to-band recombination based on our PL and PLE results. Furthermore, the PLE results also illustrate that the excitation of carriers cannot take place in the interior Si core. Thus, we suggest that the photoexcitation and recombination processes of carriers should be tightly linked with surface defects of Si crystallite. According to the studies on PS fabrication mechanisms [14–17], it is known that there is a significant concentration of Si–H and Si–H₂ bonds on the surface of the as-made PS. By analyzing the Fourier transform infrared spectra (FTIR) and PL spectra of the PS aging in air, the Si–Hₓ (x = 1, 2) bonds can be the origin of the red PL of the PS [14]. Consequently, we attribute the origin of the 645 nm subband to the Si–H₂ (x = 1, 2) in the present experiment. In addition, it is well-known that after a PS sample is stored in air for only 3 min, the surface Si=O–Si bonds have started to form [9]. Later, the Si=O double bonds will form on the surface of Si nanocrystal due to the fracture of Si=O–Si bonds caused by large stress at the Si/SiO₂. The Si=O binding states at the surface of Si nanocrystal have previously been assigned to the source for the 590 nm radiation in oxygen-passivated PS [9,13].

Here we should discuss the influence of water on the PL property of Si nanocrystals. When the Si nanocrystals are crumbled from the skeleton of PS, the surfaces of nanocrystals are full of active Si dangling bonds that act as nonradiative recombination centers. On the other hand, the ionization action in water, H₂O→H⁺+OH⁻, can provide the H and OH ions, so active surface of the Si nanocrystals can easily be passivated by H⁺ and OH⁻. Since the ionization action is feeble, the Si=O–H bands on the Si nanocrystal surface can be ignored for their low concentration. The O₂ dissolved in water acts as it is in air atmosphere, so the Si nanocrystals in water can be passivated by Si=O bonds [14]. We examined the PL and PLE spectra of the as-made PS, the obtained features were just like those of the suspension. This means that water does not provide new defects that can change the red PL band, and it can be an indirect evidence to support the conclusion that Si–Hₓ (x = 1, 2) bonds and Si=O bonds are the origin of the broad red PL band. Water is a kind of effective solvent, because it can keep individual Si nanocrystals apart and provide a high potential barrier for carriers (electrons and holes) [11,12]. Moreover, little difference between the PL and PLE spectra of the as-made
PS and Si nanocrystal suspension demonstrates that the surrounding water has little influence on luminescence property of the Si nanocrystals.

To determine the size of Si nanocrystals, we have examined the micro-Raman spectra of the interconnected nanostructure network in the as-etched PS sample and present a typical result in Fig. 2. It can be seen that a Raman peak associated with Si nanocrystals appears at 500 cm\(^{-1}\). According to the following formula [18]:

\[
d = 2\pi \sqrt{\frac{B}{\Delta \omega_{\text{TO}}}}
\]

where \(\Delta \omega_{\text{TO}}\) is the shift of Raman peak for nanocrystal as compared with that of the c-Si and \(B = 2.0 \text{ nm}^2 \text{ cm}^{-1}\), we can roughly estimate the mean crystallite size to be \(\sim 2\) nm. Top left inset in Fig. 2 shows a TEM image of the Si nanocrystals. It can be seen that Si nanocrystals have been dispersed well. The nanocrystal sizes vary between 1 and 10 nm. Though there are some Si nanocrystals with sizes larger than 5 nm, the majority of Si nanocrystals are smaller than 2 nm in diameter. Moreover, top right inset in Fig. 2 displays the HRTEM image of a nanoparticle with diameter of \(\sim 5\) nm. We can see that the particle has lattice fringes corresponding to the \(\{2 2 0\}\) plane of Si, indicating that the Si nanocrystals are still of diamond structure. The three-region structure presented by Kanemitsu et al. [19] can describe the spatial structure of a Si nanocrystal. The Si nanocrystal consists of a Si core, an interfacial layer, and an outer space. When the size of Si nanocrystal is \(\sim 2\) nm, the band gap of Si nanocrystal enlarged by quantum confine effect is 2.6 eV [9]. The electronic states of the Si–H\(_x\) \((x = 1, 2)\) bonds and Si=O bonds locate at the enlarged band gap. The excited carriers would relax to energy levels of these defect centers and then recombine to emit a red PL, making band-to-band recombination undetectable [9]. Therefore, if we can remove the Si–H\(_x\) \((x = 1, 2)\) bonds and Si=O bonds in the interface layer, a blue PL band that originates from band-to-band recombination of excited carriers in the Si core will be observed.

To demonstrate this assumption, we heated up the suspension mixed with peroxide. Fig. 3(a) shows the PL spectra of this post-treated suspension. The sharp rising in the left side of the PL spectra taken under excitation of the 350 nm line of a Xe lamp is the Raman scattering signal of water. One can see that the red PL band vanishes and a new PL band appears at 430 nm whose peak position shifts with increasing excitation wavelength. The different PL behavior suggests that the origin of the 430 nm PL band should be different from that of the aforementioned red PL band. According to the quantum confinement theory for Si nanocrystals, the 430 nm PL peak can be inferred to be from the band-to-band recombination in quantum confined Si nanocrystals with size of 1.8 nm [9]. This is basically consistent with our TEM result. Therefore, we believe that the 430 nm PL band arises from the band-to-band recombination in the quantum-confined Si nanocrystals. To explore the photoexcitation process of carriers, we examined the PLE spectra of the suspension by monitoring at different emission wavelengths. The obtained results are displayed in Fig. 3(b). In each PLE spectrum, a sharp peak arises from the Raman scattering signals of water. It can be seen that the PLE spectra show an evident redshift with increasing the monitored wavelength. This redshift reflects the dimension distribution of Si nanocrystals. Thus, we reach a conclusion that the PL and PLE spectra should originate from optical transitions between valence and conduction bands of the Si core in Si nanocrystal. Quantum confinement effect is evident in Si nanocrystals in the treated suspension. We may infer that peroxide should play an important role in the post-treatment. Peroxide in water will decompose, releasing active O atom: \(\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}\). The H atom in Si–H\(_x\) bonds can thus be
replaced by the O atom, while the Si–O bond should be saturated to form SiO$_2$. The calefaction condition enhances activity of oxygen atom, accelerating the oxidization process to reconstruct the interface layer. As a result, Si core is surrounded by a stoichiometric SiO$_2$ layer in the post-treated suspension. This Si nanocrystal can exhibit quantum confinement effect, since the defect energy levels in enlarged band gap have been eliminated.

4. Conclusions

We have fabricated the suspension of Si nanocrystals to explore the light-emitting properties of Si nanocrystals by using ultrasonic vibration treatment of the as-made porous silicon in water. The Si–H$_x$ ($x = 1, 2$) and Si–O bonds in interface layer are considered to be responsible for the observed red PL band by analyzing the PL of the as-made suspension. To change the interface layer, the suspension was heated after mixed with peroxide. PL spectra of the treated suspension show an evident quantum confinement effect of the Si nanocrystals. We suggest that the surfaces of the Si nanocrystals are surrounded by SiO$_2$ after treated by peroxide, which eliminates the defect luminescent centers.

Acknowledgments

This work was supported by the grants (nos. 60576061, 60476038, and BK2006715) from the National and Jiangsu Natural Science Foundations and the LAPEM. Partial support was also from the State Key Program for Basic Research of China under Grant no. 2006CB921803 and City University of Hong Kong Direct Allocation Grant No. 9360110.

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