

Optical emission from annealed coupled-C₆₀ porous Si systems

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 L739

(<http://iopscience.iop.org/0953-8984/14/49/101>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 19:18

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Optical emission from annealed coupled-C₆₀ porous Si systems

S S Deng, X L Wu¹, J Li, C Tan, X Yang, Y Gu and X M Bao

National Laboratory of Solid State Microstructures and Department of Physics,
Nanjing University, Nanjing 210093, People's Republic of China

E-mail: hkxluwu@nju.edu.cn

Received 24 September 2002

Published 29 November 2002

Online at stacks.iop.org/JPhysCM/14/L739

Abstract

C₆₀ molecules were chemically coupled on porous silicon by means of a kind of silane coupling agent, (CH₃O)₃Si(CH₂)₃NH₂. After annealing in N₂ at 900 °C, three photoluminescence (PL) peaks were observed, at 384, 440, and 465 nm, under an excitation with the 310 nm line of a Xe lamp. The 440 and 465 nm PL peaks were attributed to optical transitions in hydrogenated amorphous silicon carbide (a-Si_{1-x}C_x:H). Upon excitation at 345 nm, three PL peaks appear, at 384, 400, and 480 nm. Spectral analyses suggest that radiative recombination of carriers occurs in the states at the surface of the β-SiC nanocrystal formed during annealing, whereas their photogeneration takes place in the β-SiC core. After further annealing at 1100 °C, two new PL peaks were observed, at 417 and 436 nm. Spectral examinations reveal that the two blue PL peaks arise from excess Si defect centres at the β-SiC surface, while the photoexcited carriers still come from the β-SiC core. Our experiments and results provide a good understanding of light-emitting mechanisms related to SiC materials.

Silicon carbide (SiC) shows promise as a blue-emitting material in applications in optoelectronic devices because of its notable properties: wide band gap, thermal stability, and chemical inertness [1–4]. Since bulk SiC only exhibits weak blue photoluminescence (PL) at room temperature [5], various fabrication techniques have been explored in efforts to improve its luminescence efficiency. Matsumoto *et al* [2] fabricated porous SiC on 6H-SiC substrates by anodization and obtained a strong blue emission in the wavelength range of 460–480 nm. This work shows that nanoscale SiC has a new optical property. Subsequently, β-SiC nanocrystals with diameters less than 5 nm were fabricated by annealing a-Si_{1-x}C_x alloy deposited onto oxidized Si [3]. This kind of SiC material also displays a blue emission. An exciting finding of Liao *et al* [4] was the observation of a strong blue emission at 445 nm from C⁺-implanted Si wafers. This blue emission was considered to be due to the quantum confinement on the β-SiC nanocrystals. However, fabrications of such light-emitting β-SiC films are complicated

¹ Author to whom any correspondence should be addressed.

and still based on electrochemical etching, incompatible with traditional Si planar techniques. Recently, a simple and efficient technique for forming SiC film or nanocrystals, carbonization of C₆₀ on Si wafer, was presented [6, 7]. This novel method has some advantages such as providing a low-temperature carbon source, only involving pure carbon and silicon to protect the SiC formed from impurities, and easily forming SiC nanocrystals at the interface between Si wafer and C₆₀ molecules. If Si wafer is replaced by porous silicon (PS), smaller β -SiC nanocrystals can be formed through pore confinement under high-temperature annealing and therefore efficient light emission can be expected.

In this work, we first fabricate coupled-C₆₀ PS systems and then investigate the light-emitting properties of coupling systems of this kind after high-temperature annealing. Spectral analyses show that the β -SiC nanocrystals are formed in a-Si_{1-x}C_x:H matrix after annealing at 900 °C. Radiative recombination of carriers was disclosed to take place in the states at the surfaces of β -SiC nanocrystals, whereas the photogeneration of carriers occurs in the cores of β -SiC nanocrystals. The samples subjected to annealing at different temperatures show different light-emitting properties, which is due to changes in both the surface (defect) states and β -SiC nanocrystal sizes. This work provides a good understanding of light-emitting mechanisms related to SiC materials.

The substrates used in this work were (100)-oriented p-type Si wafers ($\sim 5 \Omega \text{ cm}$). The anodization was conducted in a solution of C₂H₅OH:HF = 3:1 with a current density of 20 mA cm⁻² for 20 min. The as-made PS samples were chemically coupled with C₆₀ molecules through a kind of silane coupling agent, (CH₃O)₃Si(CH₂)₃NH₂. The coupling experiments have been described in the literature [8]. To prevent C₆₀ molecules from escaping from the surface of PS during high-temperature annealing, a cleaned Si wafer was used to cover the coupled-C₆₀ PS sample. Subsequent thermal treatment was performed in N₂ at 900 and 1100 °C for 30 min. High-temperature annealing makes C₆₀ molecules decompose to produce active C atoms. They react with neighbouring Si atoms to form SiC [7]. In our experiments, PL and photoluminescence excitation (PLE) spectral measurements were carried out on a Hitachi 850 fluorescence spectrophotometer. Fourier transform infrared (FTIR) absorption spectra were obtained on a Nicolet 170SX spectrometer. All the measurements were run at room temperature.

Figure 1(a) shows the PL spectrum of a typical coupled-C₆₀ PS sample annealed at 900 °C, taken under excitation with the 310 nm line of a Xe lamp. This spectrum exhibits three well-resolved PL peaks, at 384, 440, 465 nm. To identify their origins, the PLE spectra were examined and the corresponding results monitored at 440 and 465 nm are shown in figure 1(b). Obviously, the two PLE spectra are similar, showing three well-resolved peaks at 280, 310, and 345 nm. This result indicates that the 440 and 465 nm PL peaks have the same origin. The inset of figure 1(b) shows the corresponding FTIR absorption spectrum in the range of 680–910 cm⁻¹, which is associated with Si–C stretching vibrations. The 814 cm⁻¹ vibration band is connected with TO phonon of β -SiC [4, 9]. The 740 cm⁻¹ band correlates with the a-Si_{1-x}C_x:H component when $x \approx 0.6$ [10]. The 793 cm⁻¹ shoulder arises from the a-Si_{1-x}C_x content, also when $x \approx 0.6$ [11]. Therefore, we can conclude from this FTIR spectrum that some β -SiC particles have been formed at the annealing temperature of 900 °C. They should be surrounded by a-Si_{1-x}C_x:H and a-Si_{1-x}C_x composite. For carbon-rich a-Si_{1-x}C_x:H films, previous investigations have indicated that there is a blue emission at $\sim 2.65 \text{ eV}$ (468 nm), when $x \approx 0.6$ [12]. Thus, we can infer that the 440 and 465 nm PL peaks are closely related to the a-Si_{1-x}C_x:H component in the film.

For the 384 nm PL peak, the PLE spectrum is inconsistent with the luminescent band monitored at 440 or 465 nm, showing three peaks at 250, 280, and 345 nm, as shown in figure 2(a). The 280 and 345 nm PLE peaks have relatively large intensities, but the 310 nm

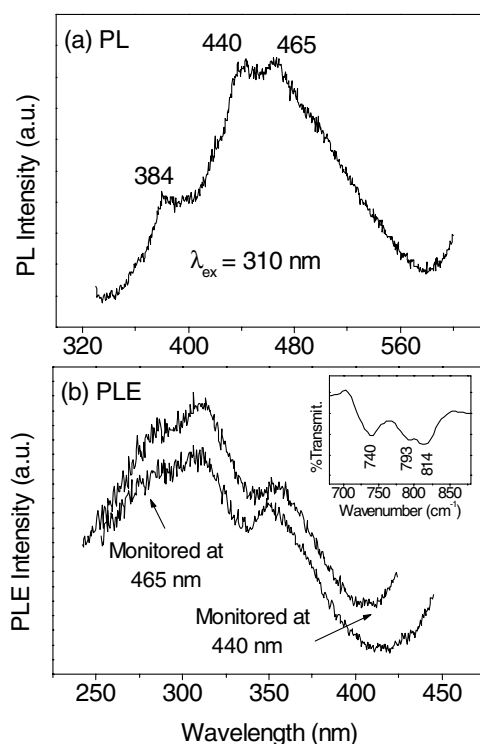


Figure 1. (a) PL spectra of a coupled-C₆₀ PS sample annealed in N₂ at 900 °C for 30 min, taken under excitation with the 310 nm line of a Xe lamp. (b) The corresponding PLE spectra monitored at 440 and 465 nm. The inset shows the corresponding FTIR spectrum in the range of 680–910 cm⁻¹.

PLE peak vanishes. An interesting feature is that under excitation with the 345 nm line, a strong PL spectrum can be observed. This spectrum shows three PL peaks, at 384, 400, and 480 nm (see figure 2(b)). For the 400 nm PL peak, its PLE spectrum is similar to that monitored at 384 nm, indicating that the 384 and 400 nm PL peaks have similar origins. When we take the 250 or 280 nm line as the excitation source, the 384 and 400 nm PL peaks still exist, but their intensities have been substantially reduced, as shown in the inset of figure 2(b). The 250 and 280 nm PLE peaks have previously been reported to be associated with oxygen-deficient defects in Si oxide materials [13–16]. Therefore, for the 384 and 400 nm PL peaks, radiative recombination of carriers occurs in oxygen-related defect centres, but the photogeneration of carriers mainly takes place in the states associated with the absorption band at ~345 nm. For the 480 nm PL peak, it appears only under excitation with the 345 nm line. This result indicates that the 480 nm PL has a light-emitting mechanism different to those for the 384 and 400 nm PL peaks, but the photoexcited carriers also arise from the states related to the 345 nm PLE band.

To clarify the nature of the PLE peak at ~345 nm, we direct our attention to the origin of the 480 nm PL peak. This blue PL peak cannot be from an a-Si_{1-x}C_x:H component in our material, because its PLE spectrum was found to be completely different from those of the 440 and 465 nm PL peaks. For PS samples, a blue emission was observed at 2.6 eV (480 nm) and considered to correlate with Si–H bonds [17]. However, in our current samples no obvious Si–H_x ($x = 1-3$) bond-related vibration bands (2000–2200 cm⁻¹) were observed in the FTIR spectrum (see the inset of figure 2(a)). This indicates that the luminescent centre associated with Si–H bonds is not a source of the 480 nm PL. In many investigations on Si oxide, a blue

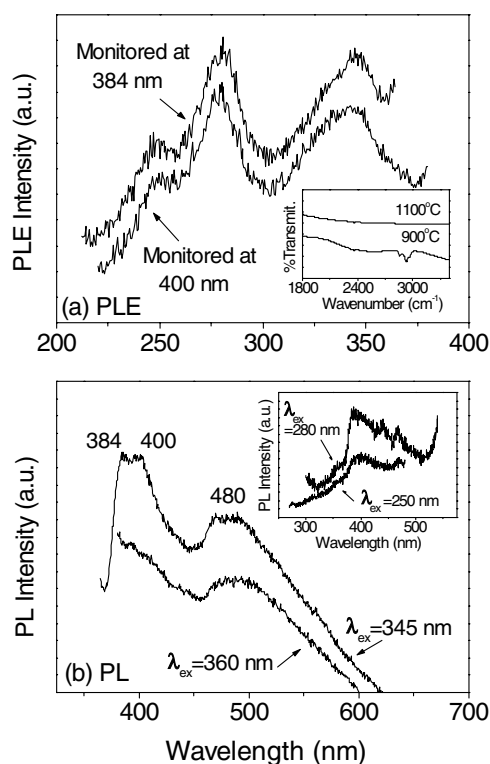


Figure 2. (a) PLE spectra monitored at 384 and 400 nm. The inset shows the FTIR spectra of the samples annealed at 900 and 1100 °C in the vibration range of C–H bonds. (b) PL spectra taken with 345 and 360 nm excitation lines. The inset shows the PL spectra with 250 and 280 nm excitation lines.

emission was frequently reported at ~ 480 nm and assigned to optical transitions in the neutral oxygen vacancy ($O_3\equiv Si-Si\equiv O_3$) [14, 15]. The blue PL peak has a strong PLE band at 250 nm. For our samples, no obvious PL peak appears at 480 nm under excitation at 250 nm (see the inset of figure 2(b)). Here, we should mention that although the PL measurement was limited by the 480 nm cut-off wavelength, there is no noticeable tendency for the 480 nm PL peak to appear. This clearly indicates that the process of recombination of the blue PL does not take place in the neutral oxygen vacancy. Finally, we can also rule out the possibility of the 480 nm PL being from band-to-band recombination in the quantum-confined β -SiC nanocrystals [4], because the 480 nm PL peak shows no shift when excited at a different wavelength (see figure 2(b)) [18, 19]. If the PL was from band-to-band recombination in nanocrystals, the excitation and recombination energies would be closely related to the sizes of the nanocrystals. When excited at 360 nm, the photoexcitation mainly takes place at those nanocrystals with larger sizes and thus the PL peak has lower energy. Under 345 nm excitation, the PL peak would have higher energy. This would be inconsistent with our experimental observations.

In previous work [3, 8, 20–22], it was proposed that surface states are important in the blue PL from nanoscale SiC materials. Therefore, we believe that the 480 nm PL should be from a kind of surface state at the surfaces of some quantum-confined nanocrystals which can exhibit a strong PLE peak at ~ 345 nm. For our samples, there exist two kinds of nanocrystal [22], one being silicon and the other β -SiC. Since the energy level of the absorption band for Si nanocrystals with the quantum confinement effect was observed to be less than 3.4 eV

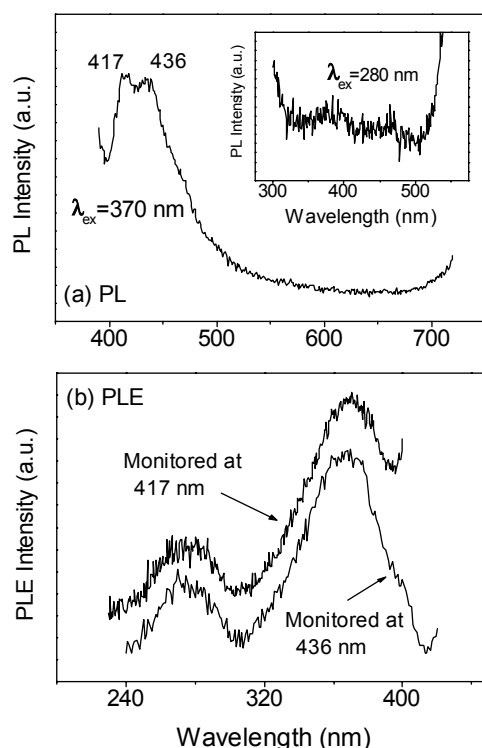


Figure 3. (a) The PL spectrum of the sample annealed in N_2 at $1100^\circ C$, taken under excitation with the 370 nm line of a Xe lamp. The inset shows the PL spectrum under excitation with the 280 nm line. (b) The corresponding PLE spectra monitored at 417 and 436 nm.

(365 nm) [23, 24], the nanocrystals with the 345 nm PLE band should be β -SiC. The quantum confinement effect is responsible for the widening of the band gap of β -SiC nanocrystals [25]. Therefore, we can derive such a physical picture for the 480 nm PL origin: the photogenerated carriers are produced in the cores of the quantum-confined β -SiC nanocrystals and then transfer to the surfaces to radiatively recombine. Similar conclusions can be obtained for the 384 and 400 nm PL peaks.

To identify the feature of the surface state producing the 480 nm PL, the sample was further annealed in N_2 at $1100^\circ C$ for 30 min. We can see from the corresponding PL spectrum in figure 3(a) that the 480 nm PL peak vanishes, and this is accompanied with the appearance of two new strong PL peaks at 417 and 436 nm. The FTIR spectral examinations show disappearance of the vibration bands related to C–H bonds ($2800\text{--}3000\text{ cm}^{-1}$; see the inset of figure 2(a)). This result implies that the 480 nm PL should be connected with a C–H bond-related surface state at the surface of β -SiC nanocrystal.

The two strong blue PL peaks at 417 and 436 nm are noteworthy as regards their light-emitting mechanisms. The PLE spectra monitored at 417 and 436 nm are identical and show two peaks at 280 and ~ 370 nm (see figure 3(b)). The 280 nm peak has a weak intensity. When taking the 280 nm line as the excitation source, no blue PL peaks were observed at 417 and 436 nm, as shown in the inset of figure 3(a). This result indicates that the two peaks are intimately related to the 370 nm excitation band. Since the 345 nm PLE peak for the sample annealed at $900^\circ C$ has been assigned to an excitation band in the quantum-confined β -SiC nanocrystals, the ~ 370 nm PLE peak should have the same origin. The reduction of its band gap results from the increase of the sizes of β -SiC nanocrystals after high-temperature

annealing. In Si⁺-implanted SiO₂ films, the two blue PL bands have been observed and assigned to optical transition in excess Si defect centres [26]. Our investigation on the growth mechanism of β -SiC nanocrystals in the current samples indicates that the formation of β -SiC nanocrystals starts at the interface between the substrate and C₆₀ molecules and continues by diffusion of Si through the already formed β -SiC. This implies that excess Si atoms will exist at the surface of β -SiC nanocrystal. Therefore, we can describe the mechanism of the two blue emissions as follows: radiative recombination of carriers occurs in excess Si defect centres at the surface of β -SiC nanocrystal, whereas the photogeneration of carriers takes place in the quantum-confined β -SiC core.

In conclusion, we have revealed that coupled-C₆₀ PS samples annealed in N₂ at different temperatures can exhibit multiple PL peaks. Spectral investigations indicate that they generally arise from the defect states at the surface of β -SiC nanocrystal, but the photogeneration of carriers for producing these radiations takes place in the core of the β -SiC nanocrystal. Our experiments and results provide a good understanding of light-emitting mechanisms related to SiC materials.

This work was supported by Grants (Nos 60076007 and 60178036) from the National Natural Science Foundation of China. Partial support was from the National Outstanding Youth Foundation of China.

References

- [1] Ikeda M, Hayakawa T, Yamagiwa S, Matsunami H and Tanaka T 1979 *J. Appl. Phys.* **50** 8215
- [2] Wang H, Ma Z, Allen L H and Rigsbee J M 1993 *Silicon-Based Optoelectronic Materials (MRS Symp. Proc. vol 298)* (Pittsburgh, PA: Materials Research Society) p 235
- [3] Matsumoto T, Takahashi J, Tamaki T and Futagi T 1994 *Appl. Phys. Lett.* **64** 226
- [4] Liao L S, Bao X M, Yang Z F and Min N B 1995 *Appl. Phys. Lett.* **66** 2382
- [5] Choyke W J and Patrick L 1970 *Phys. Rev. B* **2** 4959
- [6] Chen D, Workman R and Sarid D 1995 *Surf. Sci.* **344** 23
- [7] Moro L, Paul A, Lorents D C, Malhotra R, Ruoff R S, Lazzeri P, Vanzetti L, Lui A and Subramoney S 1997 *J. Appl. Phys.* **81** 6141
- [8] Wu X L, Xiong S J, Fan D L, Gu Y, Bao X M, Siu G G and Stokes M J 2000 *Phys. Rev. B* **62** R7759
- [9] Borders J A, Picraux S T and Beezhold W 1971 *Appl. Phys. Lett.* **18** 509
- [10] Rubel H, Schroder B, Fuhs W, Krauskopf J, Rupp T and Bethge K 1987 *Phys. Status Solidi b* **139** 131
- [11] Suzuki Y, Inoue S, Hasegawa I, Yoshii K and Kawabe H 1989 *Thin Solid Films* **173** 235
- [12] Nevin W A, Yamagishi H, Yamaguchi M and Tawada Y 1994 *Nature* **368** 529
- [13] Song H Z and Bao X M 1997 *Phys. Rev. B* **55** 6988
- [14] Nishikawa H, Shiroyama T, Nakamura R, Ohki Y, Nagasawa K and Hama Y 1992 *Phys. Rev. B* **45** 586
- [15] Liao L S, Bao X M, Zheng X Q, Li N S and Min N B 1996 *Appl. Phys. Lett.* **68** 850
- [16] Siu G G, Wu X L, Gu Y and Bao X M 1999 *Appl. Phys. Lett.* **74** 1812
- [17] Tsybeskov L, Vandyshev J V and Fauchet P M 1994 *Phys. Rev. B* **49** 7821
- [18] Zheng X Q, Liu C E, Bao X M, Yan F and Yang H C 1993 *Solid State Commun.* **87** 1005
- [19] Bao X M, Wu X W, Zheng X Q and Yan F 1994 *Phys. Status Solidi* **141** K63
- [20] Koch K and Petrova-Koch V 1994 *Porous Silicon* ed Z C Feng and R Tsu (Singapore: World Scientific) p 133
- [21] Kanemitsu Y, Uto H and Masumoto Y 1993 *Phys. Rev. B* **48** 2827
- Kanemitsu Y, Uto H and Masumoto Y 1994 *Phys. Rev. B* **48** 2238
- [22] Wu X L, Siu G G, Stokes M J, Fan D L, Gu Y and Bao X M 2000 *Appl. Phys. Lett.* **77** 1292
- [23] Filippov V V, Pershukovich P P, Kuznetsova V V, Khomenko V X and Dolgii L N 2000 *J. Appl. Spectrosc.* **67** 5
- [24] Deng S S, Wu X L, Zhang Z Y, Mei Y F, Yang Y, Chen H and Bao X M 2002 *Phys. Lett. A* **299** 299
- [25] Cullis A G, Canham L T and Calcott P D J 1997 *J. Appl. Phys.* **82** 909
- [26] Skorupa W, Yankov R A, Rebohle L, Frob H, Bohme T, Leo K, Tyschenko I E and Kachurin G A 1996 *Nucl. Instrum. Methods B* **120** 106