

# Photoluminescence Enhancement of Porous Silicon by Organic Cyano Compounds

Feng Yin, Xu Rui Xiao,\* Xue Ping Li, Zhen Zong Zhang, Bao Wen Zhang, and Yi Cao

*Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China*

Guo Hua Li and Zao Pin Wang

*National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China*

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A pronounced photoluminescence enhancement on chemically oxidized porous silicon was induced by a series of organic cyano compounds including 1,2-dicyanoethylene (CE), 1,3-dicyanobenzene (1,3-CB), 1,4-dicyanobenzene (1,4-CB), 1-cyanonaphthalene (1-CN), and 9-cyanoanthracene (9-CA). Photoluminescence enhancement effects were reversible for all compounds studied in this work. A dependence of photoluminescence enhancement on the steric effect and the electronic characteristics of these compounds and the structure of the porous silicon substrates were analyzed in terms of the photoluminescence enhancing factors. Surface chemical composition examined by Fourier transform infrared (FTIR) spectra demonstrated that the surface Si–H bonds were not changed and no new luminescent compounds were formed on porous silicon surface during adsorption of cyano compounds. A mechanism based on induced surface states acting as radiative recombination centers by cyano compounds adsorption was suggested.

## Introduction

The room-temperature visible photoluminescence (PL) from porous silicon (PS) has both theoretical and technological importance in optoelectronics.<sup>1–3</sup> Photoluminescence of PS has been shown to be quite sensitive to the surface adsorption of molecules. Much attention has been attracted in the studies of the effects of surface adsorption on photoluminescence of PS. Recent reports showed that the PL of porous silicon can be quenched by a number of chemicals including organic solvents, amines, metal salts, hydroxide ions, etc.<sup>4–22</sup> Our interest was centered on the studies of photoluminescence enhancement induced by chemical adsorption, which may provide a simple way to improve photoluminescence efficiency of PS and gain an insight into surface reactivity of luminescent porous silicon.

Recent investigations in our laboratory have showed that the PL of porous silicon can be enhanced by chemical adsorption of organic compounds with cyano substituents on the chemically oxidized porous silicon surface. In this paper, we report a series of organic cyano compounds induced an enhancement of the PL intensity and the influence of PS substrates on the PL enhancing behaviors.

## Experimental Section

Organic cyano compounds including 1,2-dicyanoethylene (CE), 1,3-dicyanobenzene (1,3-CB), 1,4-dicyanobenzene (1,4-CB), 1-cyanonaphthalene (1-CN), and 9-cyanoanthracene (9-CA) were reagent-grade (Aldrich chemical Co.) and were used as received.

The PS samples were prepared by anodically etching p-Si (B-doped, (100), 1.0–3.5  $\Omega$  cm) at a current density of 30 mA/cm<sup>2</sup> for 10 min in a 1:1 solution of HF (40 wt %)/ethanol, followed by chemical oxidation in 20% (wt %) HNO<sub>3</sub> solution

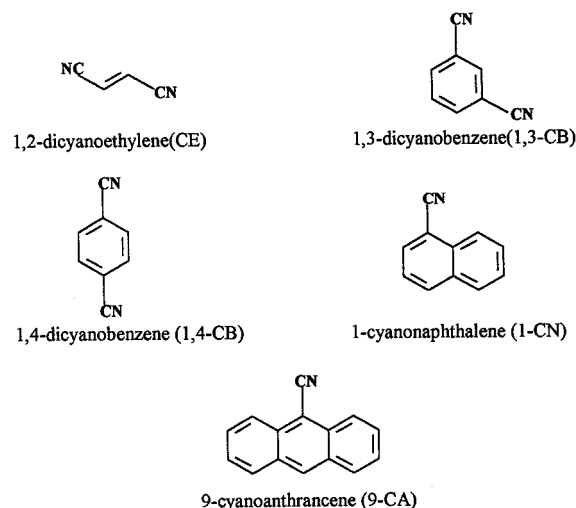
for 30 min at room temperature. The oxidized samples were rinsed sequentially with distilled water and ethanol and then dried in air. The porosity of PS samples was measured by a gravimetric method. PL measurements were performed with a microscopic spectral system. The 488.0 nm line of an Ar<sup>+</sup> laser was used as excitation source. The fluorescent light collected with a microscope (BH-2) and fed into a double-grating monochromator (JY-HPD-2) was detected by a photomultiplier (GaAs cathode) and a photocounter. During the measurements, PS samples with and without adsorbates fixed in a measuring tube were excited at the same point, monitoring with the microscope. After PL spectra of blank samples (without adsorbates) were measured, surface adsorption of organic molecules was carried out by immersing the sample in 5 mL of  $5 \times 10^{-3}$  mol/L acetone solution of each cyano compound for 5 min, followed by withdrawing the solution and drying under air. The amount of adsorbed cyano compound was determined by dissolving the cyano compound into acetone or ethanol solutions and measuring its absorption spectra. The absorption spectra of cyano compounds in acetone or ethanol solutions were measured by Hitachi 557 UV–visible spectrometer. Fourier transform infrared (FTIR) spectra were taken by a Nicolet Magna IR 750 spectrometer. All the measurements were performed at room temperature and in the air.

## Results and Discussion

**PL Enhancement by Adsorption of Organic Cyano Compounds.** A series of organic cyano compounds shown in Chart 1 have been employed as adsorbates attached on the surface of chemically oxidized PS samples. Cyano compounds were chosen because cyano groups are nonreactive with silicon hydrides, inhibiting the destruction of Si–H bonds and the formation of new compounds onto the PS surface, and because of their good photostabilities. Cyano-substituted aliphatic hydrocarbon compounds and a series of aromatic compounds

\* To whom correspondence should be addressed.

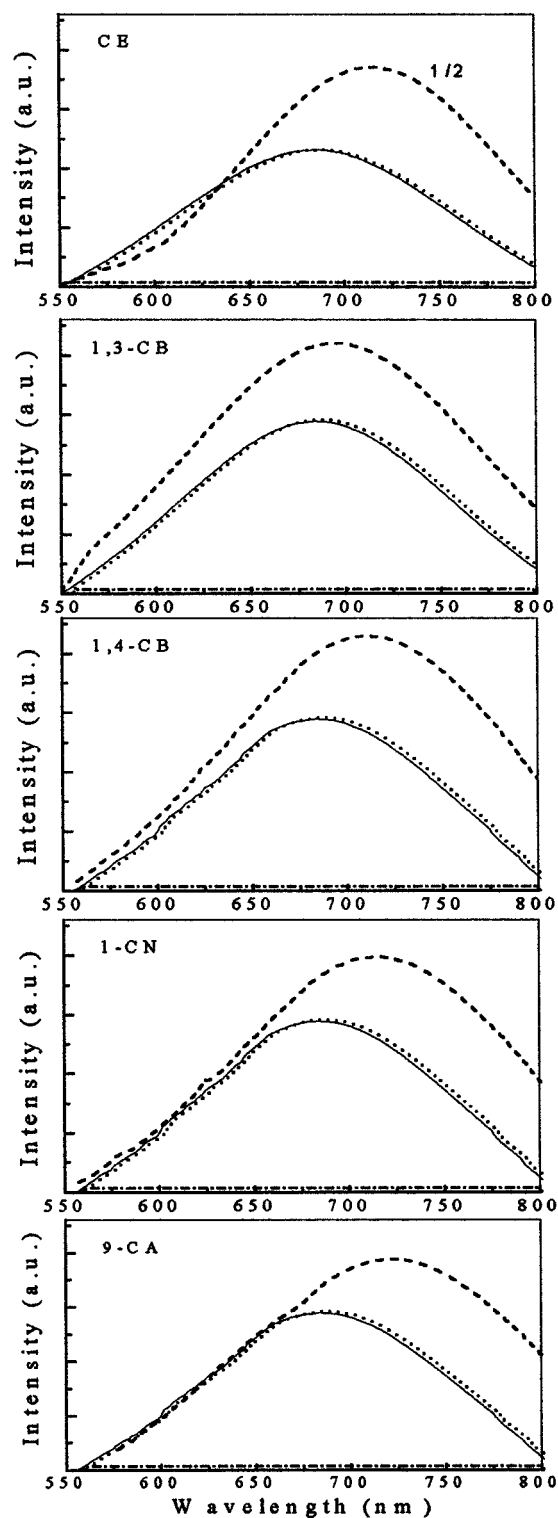
## CHART 1



were also selected for comparing the abilities of different kinds of cyano compounds to enhance the PL intensity and clarifying the structural effects of these compounds.

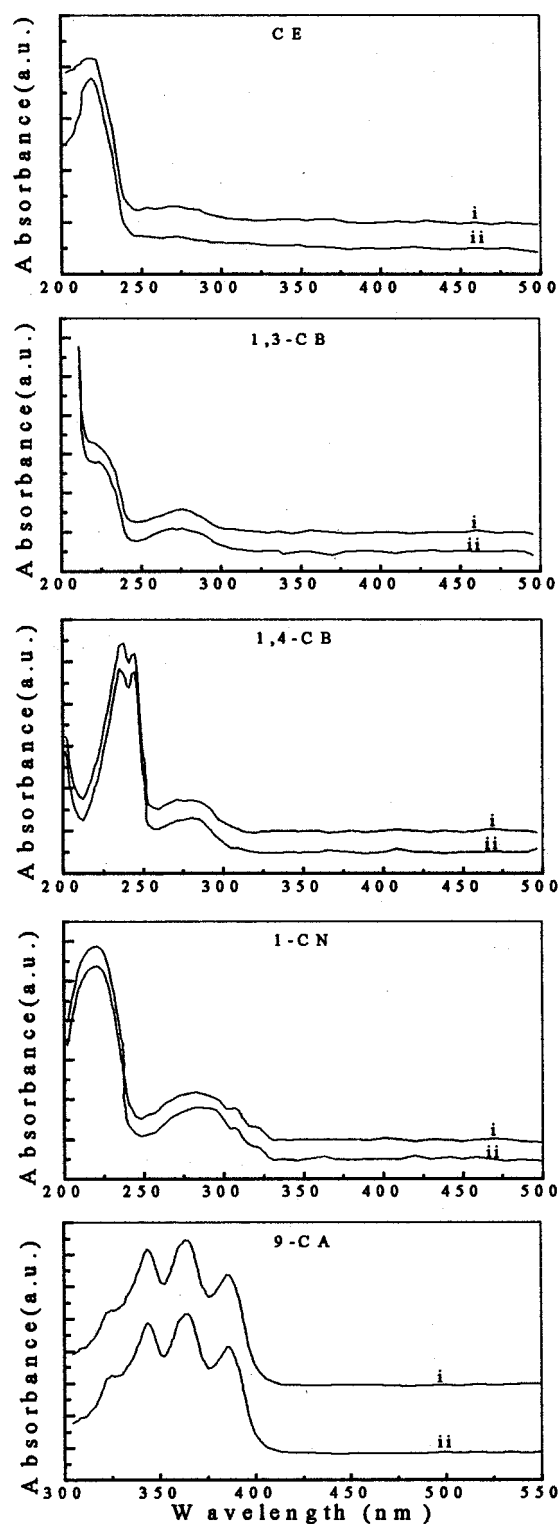
PL spectra of PS samples with and without surface adsorbates are compared in Figure 1. A strong photoluminescence with  $\lambda_{\max}$  at about 680 nm was present in the chemically oxidized PS samples (blanks). Increases in PL intensity and red shifts of  $\lambda_{\max}$  were observed in these samples after adsorption of CE, 1-CN, 1,3-CB, 1,4-CB, and 9-CA. It was found that PL intensity and  $\lambda_{\max}$  of organic molecules adsorbed to PS samples can be restored to the original values of the respective PS blank samples upon careful rinsing with acetone or ethanol solvent, indicating that PL enhancement effects were reversible. This results can also be reproduced and repeated on the other PS samples. Figure 2 illustrates the absorption spectra of the rinsing solutions and a comparison of the absorption spectra of CE, 1-CN, 1,3-CB, 1,4-CB, and 9-CA; the good correspondence between two spectra demonstrated that these molecules adsorbed on the PS surface. No light absorption in the wavelength region longer than 420 nm was observed, implying that the adsorbed molecules cannot be excited by an excitation wavelength of 488.0 nm. Furthermore, there was no PL response of single-crystal samples adsorbed with these molecules as shown in Figure 1. These results indicated that the increases of PL intensity were not attributed to the light emission of organic molecules themselves.

PL enhancement of PS samples by adsorption of different cyano compounds were evaluated quantitatively in terms of the magnitude of PL enhancing factors and red shifts of  $\lambda_{\max}$ . The red shifts of  $\lambda_{\max}$  obtained from the PL spectra given in Figure 1 were  $22 \pm 7$  nm and the magnitudes of PL enhancing factors are listed in Table 1. From this table, it is found that a higher PL enhancing factor was obtained for the PS sample adsorbed with CE. Cyanoaromatic compounds induced PL enhancement with lower enhancing factors following the trend cyanobenzene > cyanonaphthalene > cyanoanthracene. The appreciable different PL enhancing factors of cyano compounds were corresponding to the trends of the changes of adsorbed amount, indicating a pronounced steric effect. An increase of steric hindrance of these molecules from CE, 1,3-CB (1,4-CB), 1-CN, and 9-CA led to a diminution of adsorbed amount and resulted in a sequential declination of enhancing factors. The redox potentials shown in Table 1 displayed the different electronic characteristics of these cyano compounds. As the electron acceptors, these cyano compounds having different electron-



**Figure 1.** PL enhancing behaviors of porous silicon induced by organic cyano compounds (—) before adsorption, (---) after adsorption, (...) desorption, and (-.-) adsorption on single-crystal Si samples. Power density was 200 mW/cm<sup>2</sup>.

withdrawing abilities may give rise to the different contributions to PL enhancement. This can be seen from Table 1: the effects of electronic characteristics on the PL enhancing factors were pronounced in the cases of CE and 9-CA due to the stronger electron-withdrawing abilities than the other cyano compounds. The different effects between one and two cyano functional groups on the PL enhancing behavior cannot be distinguished in the PS substrates due to the steric hindrance of the porous



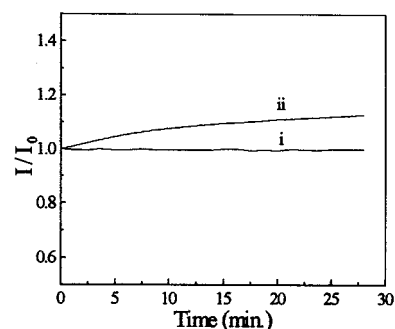
**Figure 2.** Absorption spectra of organic cyano compounds: (i) rinsing solution; (ii) acetone or ethanol solutions containing respective cyano compounds.

matrix, which was discussed in the recent work of Coffey and co-workers.<sup>23</sup> Figure 3 shows the dependence of the PL intensity of chemically oxidized PS sample before and after adsorption of CE on photoexcitation time. The PL intensity of chemically oxidized PS (blank) was very stable during the excitation time range: after adsorption of CE, the PL intensity was slightly increased in the initial 10 min and then turned to a constant with excitation time, exhibiting a stabilized PL enhancing behavior of PS induced by CE adsorption. Similar

**TABLE 1: PL Enhancing Behaviors of Porous Silicon Induced by Cyano Compounds**

cyano compounds	amount of adsorption (mol/cm <sup>2</sup> )	redox potential (V vs SCE)	PL enhancing factor <sup>a</sup> (%)
CE	$1.6 \times 10^{-7}$	-1.36[30]	$204 \pm 17$
1,3-CB	$8.3 \times 10^{-8}$	-2.03[30]	$30 \pm 2$
1,4-CB	$7.5 \times 10^{-8}$	-1.83[30]	$34 \pm 2$
1-CN	$3.3 \times 10^{-8}$	-1.98[31]	$24 \pm 2$
9-CA	$7.2 \times 10^{-9}$	-1.39[31]	$20 \pm 2$

<sup>a</sup> Enhancing factor defined as  $(PL_a - PL_0)/PL_0 \times 100$ .  $PL_a$  and  $PL_0$  are the PL intensity of the PS samples with and without adsorbates, respectively.



**Figure 3.** PL intensity of porous silicon with and without CE as a function of illumination times. Power density was 200 mW/cm<sup>2</sup>.

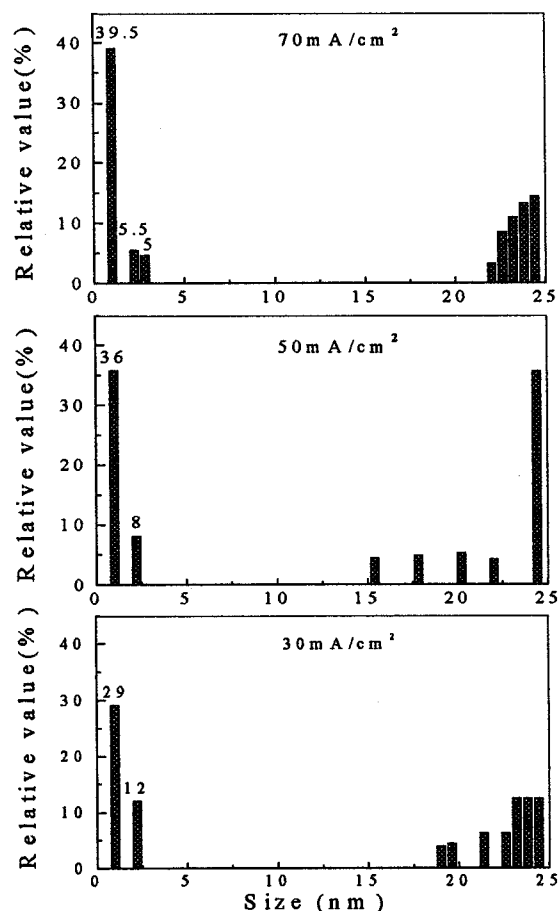
**TABLE 2: PL Enhancement Induced by CE on Different PS Substrates**

current density (mA/cm <sup>2</sup> )	porosity (%)	amount of adsorption (mol/cm <sup>2</sup> )	enhancing factor (%)
30	78	$1.6 \times 10^{-7}$	$204 \pm 17$
50	81	$7.6 \times 10^{-8}$	$287 \pm 17$
70	84	$4.8 \times 10^{-8}$	$378 \pm 18$

behavior can also be obtained in PL enhancement induced by the other cyano compounds.

**Dependence of PL Enhancement on PS Substrates.** Previous studies on the photoluminescence quenching of PS by organoamine revealed that the PL quenching behavior was strongly affected by the structures of PS substrates.<sup>24</sup> To examine the effect of PS substrates on PS enhancing behavior by cyano compounds studied in this work, different PS substrates were prepared by anodic etching of p-Si (100) at different current densities of 30, 50, and 70 mA/cm<sup>2</sup>, resulting in porosities of 78%, 81%, and 84%, respectively. PL enhancing behavior of the different PS substrates was evaluated by surface adsorption of CE; the results are listed in Table 2. By increasing the porosity of PS substrates with larger etching current density, PL enhancing factors were increased pronouncedly, accompanying a  $\lambda_{\text{max}}$  red shift of  $22 \pm 10$  nm. However, the amount of CE adsorbed was decreased with increased porosity of PS. The pronounced changes of PL enhancing factors for CE-adsorbed PS substrates with different porosities revealed the dependence of PL enhancing behavior on the structures of PS substrates. Further characterization of the structures of PS substrates was carried out to interpret the large changes in the PL enhancing behavior induced by CE.

For a better understanding of the nanocrystalline structure of these PS substrates with different porosities, silicon nanocrystals present at the porous layer of PS substrates were studied by Raman spectra. In this studies Raman scattering intensity was calculated in terms of wave functions of phonon in nanocrystals, the theoretical correlation between the frequency

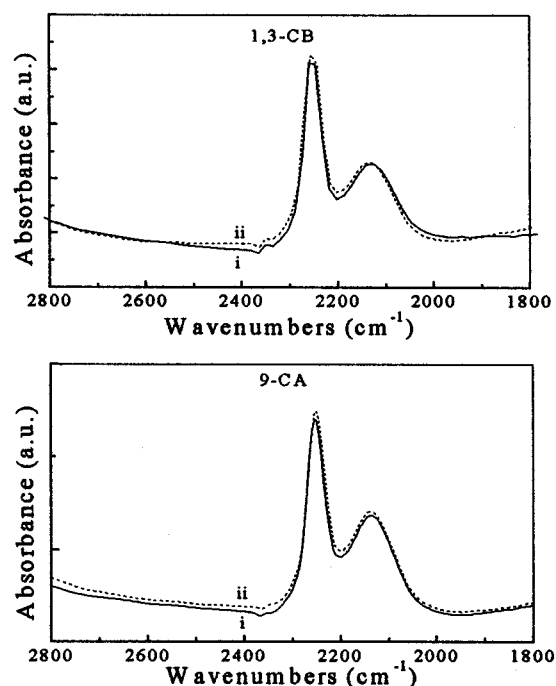


**Figure 4.** Nanocrystal size distribution of PS substrates with porosity 78%, 81%, and 84%, prepared by anodic etching current density of 30, 50, and 70 mA/cm<sup>2</sup>, respectively.

shifts, full width at half-maximum (fwhm) of phonon Raman peak, and the diameter of PS nanocrystals were obtained.<sup>25,26</sup> By fitting the measured Raman spectra of PS with the calculated correlation, the distributions of the diameters of silicon nanocrystals were determined. The detailed line shape analysis of the phonon Raman peak was described by Mündler et al.<sup>27,28</sup> Figure 4 illustrates the size distribution of silicon nanocrystals for different PS substrates. It was found that the porous layers of these different PS substrates were composed of two kinds of silicon nanocrystals with diameters <3 nm and >15 nm. With increasing porosity, the percentage of small-size nanocrystals (diameters <3 nm) increased. Since only silicon nanocrystals of small size (diameters <3 nm) were responsible to the photoluminescence of PS,<sup>29</sup> the increase of small-size nanocrystals (diameters <3 nm) in the porous layer of PS substrates was rationalized to improve the PL enhancing behavior due to CE adsorption.

PL enhancement was also presented reversibly in the chemically oxidized PS substrates prepared by anodic etching of n-doped Si [n (100), 5~8 Ω cm, 30 mA/cm<sup>2</sup>, 15 min under light]. The PL enhancing factor induced by CE was evaluated to be 25% and the  $\lambda_{\text{max}}$  red shift was 8 nm. The difference in PL enhancing factors and red shifts of  $\lambda_{\text{max}}$  between both PS substrates prepared from n- and p-doped Si for CE adsorption can be considered to arise from the anodic etching of n- and p-doped Si, resulting in different nanocrystalline structures.

**FTIR Spectral Studies of Surface Composition of PS.** Examination of the surface chemical composition of the PS samples with adsorption of cyano compounds was important for analyzing the mechanism of PL enhancement. By compar-



**Figure 5.** FTIR spectra of PS before and after adsorption of 1,3-CB and 9-CA: (i) before adsorption; (ii) after adsorption.

ing the FTIR spectra of PS samples before and after adsorption of cyano compounds, the changes of surface composition were studied. Figure 5 illustrates FTIR spectra of PS samples before and after adsorption of 1,3-CB and 9-CA in the region of 2400–2000 cm<sup>-1</sup>. From this figure, a noticeable change in Si–H absorption band between 2000 and 2300 cm<sup>-1</sup> cannot be found, indicating the Si–H bonds at the PS surface were not affected by 1,3-CB and 9-CA adsorption. The C≡N absorption band of 1,3-CB and 9-CA at 2200~2210 cm<sup>-1</sup> was probably overlapped with the Si–H absorption band and cannot be distinguished in Figure 5 due to the low amount of these adsorbates. PS samples with surface adsorption of the other cyano compounds such as CE, 1,4-CB, and 1-CN showed similar behavior of FTIR spectra as that shown in Figure 5. The FTIR spectra of PS samples with adsorption of these cyano compounds measured in the region of 400–4000 cm<sup>-1</sup> were identical to those of PS samples without adsorption. These results imply that formation of new luminescent compounds on the PS surface was excluded from consideration.

PL enhancement of PS can be interpreted presumably by an increase of surface states that acted to trap electrons on the PS surface, acting as radiative recombination center due to adsorption of cyano compounds. The increase of radiative recombination centers was pronounced in the case of CE adsorption compared to the other cyano compounds and in the PS substrates with larger porosity and large percentage of small-size (diameter <3 nm) Si nanocrystals, leading to increases of PL enhancing factors in both cases as stated above. The mechanism for the adsorbate-induced PL red shifts is not clear at the present stage; probably, the adsorption favors emission from the subset of Si nanocrystals that emit at lower energy.

## Conclusion

Photoluminescence enhancement by surface adsorption of a series of organic cyano compounds on chemically oxidized porous silicon was studied in this work. The pronounced changes in PL enhancing factors of porous silicon adsorbed with different cyano compounds were obtained due to steric effects

and the electronic characteristics of these compounds. PL enhancing behavior was significantly improved by increasing the porosity and the percentage of small-size (diameter <3 nm) Si nanocrystals of PS substrates. The results of PL enhancing behavior were suggested to be correlated with induced surface states by organic cyano compounds that acted as radiative recombination centers and led to enhanced PL intensity.

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## References and Notes

- (1) Canham, L. T. *Appl. Phys. Lett.* **1990**, 57, 1046.
- (2) Koshida, N.; Koyama, H. *Appl. Phys. Lett.* **1992**, 60, 347.
- (3) Zheng, J. P.; Jiao, K. L.; Shen, W. P.; Anderson, W. A.; Kwok, H. *S. Appl. Phys. Lett.* **1992**, 61, 459.
- (4) Lauerhaas, J. M.; Credo, G. M.; Heinrich, J. L.; Sailor, M. J. *J. Am. Chem. Soc.* **1992**, 114, 1911.
- (5) Lauerhaas, J. M.; Sailor, M. J. *Science* **1993**, 261, 1567.
- (6) Chun, J. K. M.; Bocarsly, A. B.; Cottrell, T. R.; Benziger, J. B.; Yee, J. C. *J. Am. Chem. Soc.* **1993**, 115, 3024.
- (7) Coffey, J. L.; Lilley, S. C.; Martin, R. A.; Files-Sesler, L. A. *J. Appl. Phys.* **1993**, 74, 2094.
- (8) Canham, L. T. *Appl. Phys. Lett.* **1993**, 63, 337.
- (9) Fisher, D. L.; Harper, J.; Sailor, M. J. *J. Am. Chem. Soc.* **1995**, 117, 7846.
- (10) Ko, M. C.; Meyer, G. J. *Chem. Mater.* **1995**, 7, 12.
- (11) Dittrich, Th.; Kashkarov, P. K.; Kostantinova, E. A.; Timoshenko, V. Yu. *Thin Solid Films* **1995**, 255, 74.
- (12) Hory, M. A.; Hérino, R.; Ligeon, M.; Muller, F.; Mihalcescu, I.; Vial, J. C. *Thin Solid Films* **1995**, 225, 200.
- (13) Konstantinova, E. A.; Dittrich, Th.; Timoshenko, V. Yu.; Kashkarov, P. K. *Thin Solid Films* **1996**, 276, 265.
- (14) Kelly, M. T.; Chun, J. K. M.; Bocarsly, A. B. *Nature* **1996**, 382, 214.
- (15) Harper, J.; Sailor, M. J. *Anal. Chem.* **1996**, 68, 3713.
- (16) Coffey, J. L. *J. Luminesc.* **1996**, 70, 343.
- (17) Rehm, J. M.; McLendon, G. L.; Fauchet, P. M. *J. Am. Chem. Soc.* **1996**, 118, 4490.
- (18) Ko, M. C.; Meyer, G. J. *Chem. Mater.* **1996**, 8, 2686.
- (19) Lin, V. S.-Y.; Moteshare, K.; Dancil, K.-P. S.; Sailor, M. J.; Ghadiri, M. R. *Science* **1997**, 278, 840.
- (20) Harper, T. F.; Sailor, M. J. *J. Am. Chem. Soc.* **1997**, 119, 6943.
- (21) Song, J. H.; Sailor, M. J. *J. Am. Chem. Soc.* **1997**, 119, 7381.
- (22) Buriak, J. M.; Allen, M. J. *J. Am. Chem. Soc.* **1998**, 120, 1339.
- (23) Sweryda-Krawiec, B.; Chandler-Henderson, R. R.; Coffey, J. L. *J. Phys. Chem.* **1996**, 100, 13776.
- (24) Chandler-Henderson, R. R.; Sweryda-Krawiec, B.; Coffey, J. L. *J. Phys. Chem.* **1995**, 99, 8851.
- (25) Richter, H.; Wang, Z. P.; Ley, L. *Solid State Commun.* **1981**, 39, 625.
- (26) Campbell, I. H.; Fauchet, P. M. *Solid State Commun.* **1986**, 58, 731.
- (27) Münder, H.; Andrzejak, C.; Bergen, M. G.; Klemeradt, U.; Luth, H.; Herino, R.; Ligeon, M. *Thin Solid Films* **1992**, 221, 27.
- (28) Münder, H.; Berger, M. G.; Frohnhoff, S.; Thonissen, M.; Lüth, H. *J. Luminesc.* **1993**, 57, 5.
- (29) Cullis, A. G.; Canham, L. T. *Nature* **1991**, 353, 335.
- (30) Meites, L.; Zuman, P.; Rupp, E. B.; Fenner, T. L.; Narayanan, A. *Handbook Series in Organic Electrochemistry*; CRC Press, Inc.: Boca Raton, FL, 1982; Vol. 5.
- (31) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York and Basel, Switzerland, 1983; Vol. 6, p 237.