RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 16 15 APRIL 1995-II

Two-peak photoluminescence and light-emitting mechanism of porous silicon

S. L. Zhang,* F. M. Huang, K. S. Ho, L. Jia, and C. L. Yang
Department of Physics, Peking University, Beijing 100871, China

J. J. Li, T. Zhu, Y. Chen, S. M. Cai, A. Fujishima,† and Z. F. Liu
College of Chemistry and Molecule Engineering, Peking University, Beijing 100871, China

(Received 6 September 1994; revised manuscript received 7 February 1995)

A two-peak photoluminescence (PL) spectrum of p^--type porous silicon (PS) has been observed in atmospheric stored samples. According to different spectral characteristics, especially linewidth, and different effects induced by storage and illumination of samples, the low- and high-energy peaks are identified as due to emission caused by quantum confinement effects of remnant Si walls of PS and siloxene and/or SiO_2 on PS surfaces, respectively. A light-emitting mechanism accounting for the two-peak PL spectrum is discussed.

In the past few years, much of the investigation on porous silicon (PS) has concentrated on photoluminescence (PL) measurements, which has played an important role in studies on either its material characteristics or its light-emitting mechanisms. The PL spectra of PS reported so far, generally, exhibit a single broad peak structure with a linewidth of about 0.3 eV. Nishitani *et al.*[1] mentioned a two-peak PL spectrum at room temperature and thought that the origin of PL is the disordered material attached to the surface of Si pillars, which is similar to the surface light-emitting model proposed by Koch *et al.*[2] and Qin and Jia.[3] Afterwards, Cheah *et al.*[4] reported on a four-peak PL spectrum of PS at 10 K and, following the Canham model,[5] suggested that the PL is derived from quantum confinement in silicon crystallites. Wang[6] presented a two-peak PL spectrum at 77 K on a PS sample treated by dry oxidation and found that the two excitation states in Si nanostructures and sufaces of PS are responsible for the green and red PL, respectively. Very recently, Kontkiewicz *et al.*[7] showed a red and blue two-peak PL from the PS samples annealed in a rapid thermal processor with dry oxygen ambient but only pointed out the blue PL originating from the emission of SiO_2 film rather than the silicon nanocrystals, which is opposite to the above finding of Wang. In this paper we report on an investigation of a two-peak PL spectrum, at room temperature, induced by atmospheric storage, for p^--type PS and a quantum well light-emitting model, of which the well and barrier, respectively, correspond to the volume and surface regions of remnant Si and emit the light of the low and high energies.

The PS samples used were formed on p^--type silicon wafers (100), with a resistivity of 10–15 Ω cm, by anodic oxidation with HF aqueous solution containing ethanol. The values of the anodic parameters, i.e., HF concentration C_{HF} (wt %), current density J (mA/cm^2), and forming time t (min), will be given in parentheses ($C_{\mathrm{HF}}/J/t$) after the sample batch number. After the samples were taken out of the HF solution, they were first cleaned with deionized water, then dried by blowing, and finally stored in an atmospheric environment at room temperature. The PL spectra were excited by a 457.9 nm Ar^+ laser line, and measured by a Spex-1403 double monochromator with a cooled photomultiplier tube and conventional photon counting electronics at room temperature. The Fourier transform infrared (FTIR) spectra were measured by a Perkin Elmer 2000 FT-IR spectrometer.

All the PL spectra in the figures have been corrected using the dispersion curve of the instrument transmissivity, and the corrected PL spectra energy should be a direct measurement of the radiative energy. A method of least-square fitting with a Gaussian line shape was used to fit the single-peak spectrum or resolve the spectrum of overlapping peaks. The fitting spectra in the figures are given by dotted lines. Table I lists the fitting values of peak energy, full linewidth at half

TABLE I. Fitting values of peak energies $E_{p,S}$ and $E_{p,Q}$, full linewidth at half maximum $W_{F,S}$ and $W_{F,Q}$, and peak intensities $I_{p,S}$ and $I_{p,Q}$ for the S peak and Q peak in PL spectra, in terms of a method of least-square fitting with Gaussian line shape.

	S peak			Q peak		
Spectra	$E_{P,S}$ (eV)	$W_{F,S}$ (eV)	$I_{P,S}$ (arb. units)	$E_{P,Q}$ (eV)	$W_{F,Q}$ (eV)	$I_{P,Q}$ (arb. units)
1(a)			~ 0	1.77	0.35	
1(b)	2.33	0.90	23	1.71	0.30	85
1(c)	2.20	0.73	10	1.71	0.26	86
1(d)			~ 0	1.71	0.27	92
2(a)			~ 0	1.97	0.30	
2(b)	2.48	0.64	1112	1.96	0.27	904
2(c)	2.34	0.47	394	1.95	0.27	643

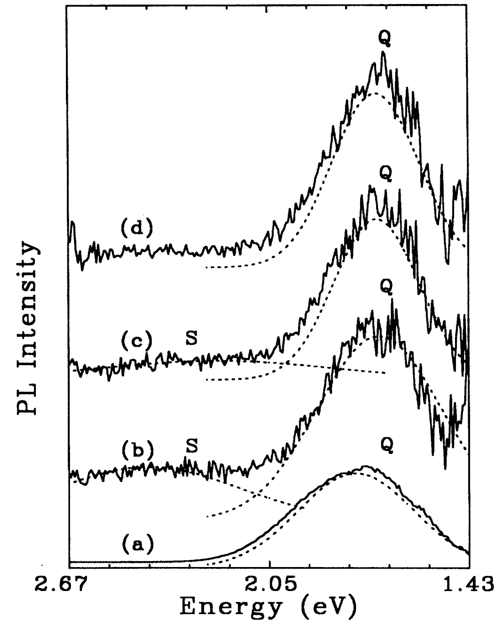

FIG. 1. Micro-PL spectra of PS film sample 595 (35/50/55) separated from its Si substrate, for (a) as-prepared; (b) atmospheric stored for one week; (c) illuminated by 457.9 nm laser (50 W/cm^2) for 30 min after one week storage; (d) illuminated by 457.9 nm laser (50 W/cm^2) for 60 min after one week storage.

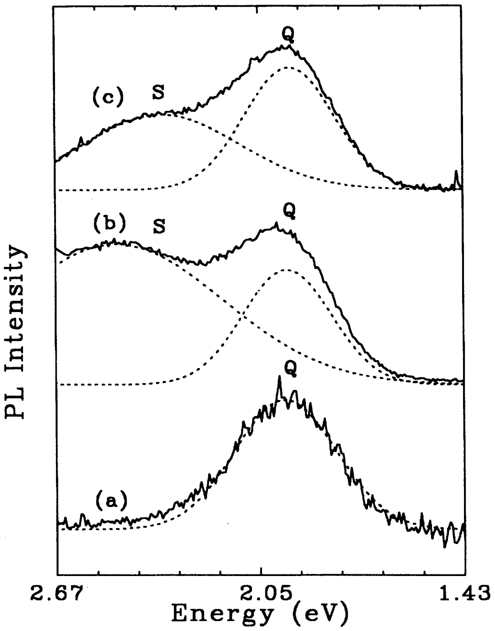

FIG. 2. PL spectra of sample 208 (12/50/8) for (a) as-prepared; (b) exposed to the atmosphere for one year; (c) illuminated by 457.9 nm laser (25 W/cm^2) for 30 min after one year storage.

maximum, and peak intensity. In Table I the intensities of as-prepared samples are not listed since the measurement conditions for as-prepared samples are different from those for stored samples so an exact comparison of intensity between them cannot be made.

Figures 1(a)–(d) show the micro-PL spectra of a PS film sample 595 (35/50/55) which has been separated from its Si substrate by the electrochemical polishing method. From Fig. 1(a) and Table I, we see that the spectrum of the as-prepared sample is a typical Gaussian single-peak spectrum with peak energy $E_{p,Q}$ at 1.77 eV and linewidth $W_{F,Q}$, of 0.35 eV. After the sample was exposed to the atmosphere for one week, the spectrum shown in Fig. 1(b) had changed to a two-peak spectrum: Besides the one corresponding to the peak of Fig. 1(a), which is slightly redshifted and has a narrower $W_{F,Q}$, a new peak at 2.33 eV occurs. It should be noticed that the linewidth of the new peak, $W_{F,S}$, is about 0.90 eV which is much wider than the linewidth of about 0.3 eV of a conventional PL peak of PS. We refer to the low- and high-energy peaks as the Q and S peaks, respectively. Thus Figs. 1(a) and (b) show that a two-peak spectral structure is obtained for an atmospheric stored PS sample. Moreover, the results clearly indicate that the two-peak PL spectrum is due to the PS layer since the sample has been separated from its Si substrate, and also since the same spectrum has been obtained, by the microspectral method with a laser spot about 1 μm in diameter, on different positions of the sample; it is not due to spatial inhomogeneity.

Figures 1(c) and 1(d) show the *in situ* PL spectra of stored sample 595 illuminated by 457.9 nm laser with power density of about 50 W/cm^2 for 30 and 60 min, respectively. From Fig. 1(c) and Table I, we see that after 30 min illumination the $E_{p,Q}$, $W_{F,Q}$, and $I_{p,Q}$ of the Q peak have not essentially changed while the S peak has changed significantly: $E_{p,S}$ has redshifted, $W_{F,S}$ has narrowed, and $I_{p,S}$ is reduced. After illumination for 60 min the Q peak persists as before whereas the S peak has disappeared completely, clearly showing that strong illumination has a degrading effect on the S peak.

To demonstrate further that atmospheric storage induces a two-peak PL spectrum, the PL spectra of a sample formed under other conditions, i.e., a 208 (12/50/8) sample, were measured for the as-prepared case and after exposure to ambient air for one year and then after illumination with power density of about 25 W/cm^2 for 30 min, and are shown in Fig. 2. The effect of storage is similar to that for sample 595. Comparing Fig. 2(b) with Fig. 2(a), and Fig. 1(b) with Fig. 1(a) the ratio of $I_{p,S}$ to $I_{p,Q}$ is 1.25 for sample 208 and 0.25 for sample 595, which may reflect the simple fact that the storage time of sample 208 is longer than that of sample 595. Comparing Fig. 2(c) with Fig. 2(b) we see variation in the spectral features similar to those found by comparing Fig. 1(c) with Fig. 1(b). These results confirm that atmospheric storage induces two peaks and illumination has a degrading effect on the S peak and this might be an intrinsic phenomenon.

Figures 3(a) and (b) show the FTIR spectra of a 208 (12/50/8) sample for as-prepared and atmospheric stored for two years, respectively. Owing to the limited output of the laser source we were not able to obtain the FTIR spectra after illumination. On comparing these two spectra we see some prominent features: (i) the most intense, the next intense, and

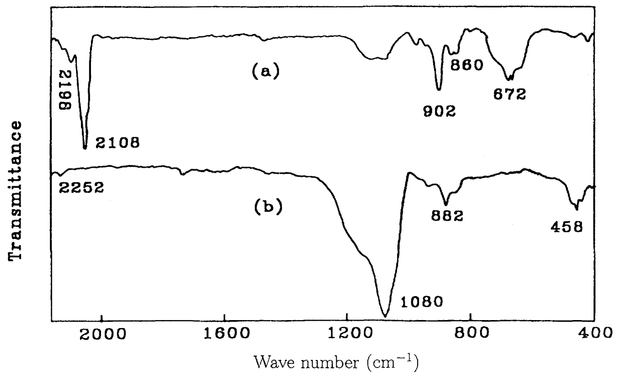

FIG. 3. Fourier transform infrared (FTIR) absorption spectra of sample 208 for (a) as-prepared; (b) atmospheric stored for two years.

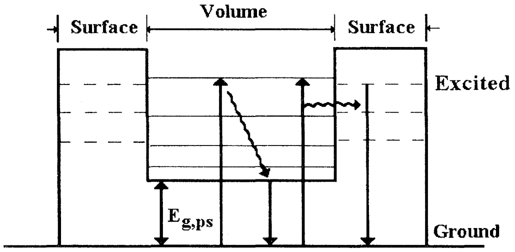

FIG. 4. Schematic picture of the two-peak light-emitting mechanism. The solid horizontal lines in the well and dashed horizontal lines in the barrier represent the confinement induced subbands of Si electrons and the electron states of silicides, respectively. The wavy lines indicate the electron relaxation in the well or the electron penetration in the barrier.

the third intense peak at 2108, 902, and 672 cm^{-1} in the as-prepared sample, which are, in turn, assigned to the Si-H stretching, Si-H_2 scissors, and Si-H bending modes, disappear in the stored sample; (ii) in the stored sample, the most intense peak at 1080 cm^{-1} and the second intense peak at 458 cm^{-1}, which are the stretching and bending modes, respectively, of Si-O-Si in SiO_2, are not seen in the as-prepared sample; (iii) after storage the two O-Si-H stretching modes at 2198 and 860 cm^{-1} shift up to 2252 and 882 cm^{-1}, respectively, and in addition increase in intensity, which is considered to be due to increase in the oxygen component in O-Si-H species.[8] These results clearly reflect that atmospheric storage induces, on the one hand, a loss of Si-H and Si-H_2, and, on the other hand, an increase in the oxygen in siloxene or/and the production of silicide (e.g., SiO_2). The above FTIR results coincide well with the changes in chemical composition of the PS surface induced by atmospheric storage at room temperature as measured by secondary ion mass spectroscopy, i.e., storage converts the hydride surface of as-prepared PS samples to that of a contaminated native oxide.[9] Comparing with a report on siloxene PL (Ref. 10) regarding its wide linewidth, with our PL and FTIR results, it is more reasonable to associate the *S* peak, and not the *Q* peak, with emission from siloxene and its derivatives or from SiO_2 on the PS surface.

For as-prepared samples we have reported a steplike behavior of PL peak energies,[11] that is, with HF concentration variation the PL peak energies shift in a steplike manner as shown in Fig. 1 of Ref. 11. It has also been found that atmospheric storage does not alter the steplike behavior, thus implying that the light-emitting, with steplike behavior, originates from the quantum confinement effect of remnant Si walls.[12] The features of *Q* peaks from as-prepared and stored samples 595 and 208 coincide well with the steplike behavior, that is, the *Q*-peak energies of samples 208 and 595 both fit the step energies corresponding to the respective forming conditions. This fact further indicates that the *Q* peak is due to emission arising from quantum confinement effects of remnant Si in PS.

Based on the above results a reasonable mechanism for PS visible light emission may include the following two points.

(1) The emission is not limited to only one origin. There are, at least, emissions from carrier recombinations in the Si gap of the inner region of PS widened by the quantum confinement effect and from chemical species of silicide (e.g., SiO_2 and siloxene and its derivatives with "rich" oxygen components) on areas of the PS surface.

(2) Accounting for the description of the PS constitution mentioned above, the electronic structure of PS may be like a quantum well structure shown schematically in Fig. 4: the well and barrier correspond to the volume region consisting of remnant Si walls and the Si surface region consisting of silicides of PS, respectively. Once the electrons are excited to the conduction bands of remnant Si the following relaxation process may proceed along two channels. Some of the excited electrons penetrate into the barrier where they induce light emission from the siloxene and SiO_2. Other excited electrons, which do not enter barriers, will relax down the band side by nonradiative transitions and then recombine back to the valence band, accompanying the emission of light. Since the higher the excited electron energy the greater the penetration depth,[13] and the siloxene and SiO_2 usually have higher emitting energies, the emitted energy from siloxene and SiO_2 in the barrier should be higher than that from the gap recombination. Moreover, since the surface of the as-prepared samples is short of the siloxene of the "rich" oxygen component and SiO_2 as shown in Fig. 3, the emission of the high-energy peaks from the barriers should be impossible for the as-prepared samples. Thus we can explain the appearance of the two peaks in terms of the quantum well model.

To summarize, we have observed a two-peak PL spectrum at room temperature in atmospheric stored p^--type PS samples. Based on the experimental results, a model of the PS light-emission mechanism is proposed. More experimental and theoretical work is needed and is under way to confirm this model.

This work was supported by National Science Foundation of China (NSFC).

[*] Also at the Surface Physics Laboratory, Fu Dan University, Shanghai 200433, China.

[†] Also at Department of Synthetic Chemistry, University of Tokyo, Tokyo 113, Japan.

[1] H. Nishitani, H. Nakata, T. Ohyama, and Y. Fujiwa, in *Proceedings of 21st International Conference on Semiconductors, Beijing, China, 1992*, edited by J. Jing and H. Z. Zhang (World Science, Singapore, 19xx), Vol. 2, p. 1455.

[2] F. Koch, V. Petrova-Koch, and T. Muschik, J. Lumin. **57**, 271 (1993).

[3] G. G. Qin and Y. Q. Jia, Solid State Commun. **86**, 559 (1993).

[4] K. W. Cheah, T. Chan, W. L. Lee, D. Teng, W. H. Zang, and Q. M. Wang, Appl. Phys. Lett. **63**, 3464 (1993).

[5] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1992).

[6] X. Wang, Mod. Phys. Lett. B **8**, 69 (1994).

[7] A. J. Kontkiewicz, A. M. Kontkiewicz, J Siejka, S. Sen, G. Nowak, A. M. Hoff, P. Sakthivel, K. Ahmed, P. Mukherjee, S. Witannachhchi, and J. Lagowski, Appl. Phys. Lett. **65**, 1436 (1994).

[8] R. A. Jeshkumar, Appl. Phys. Lett. **63**, 3032 (1992).

[9] L. T. Canham, M. R. Houlton, W. Y. Leong, C. Pickering, and J. M. Ken, J. Appl. Phys. **70**, 422 (1991).

[10] M. S. Brandt, H. D. Fuchs, M. Stutzmamn, J. Weber, and M. Cardona, Solid State Commun. **81**, 307 (1992).

[11] S. L. Zhang, K. S. Ho, Y. T. Hou, B. D. Qian, P. Diao, and S. M. Cai, Appl. Phys. Lett. **62**, 642 (1993).

[12] S. L. Zhang (unpublished).

[13] S. L. Zhang, Y. T. Hou, K. S. Ho, Z. L. Peng, J. Li, and S. X. Yuan, Phys. Lett. A **186**, 433 (1994).