第 17 卷 第 12 期 光 学 学 报 Vol. 17, No. 12
1997 年 12 月 ACTA OPTICA SINICA December, 1997

Photoluminescence from Porous Silicon by Plane-Polarized Light Excitation

Wu Jiada[1] Xie Guowei[2] Zheng Wanhua[2]

1, Department of Physics, Fudan University, Shanghai 200433
2, Department of Physics, Hong Kong Baptist University, Kowloon, Hong Kong

Abstract Luminescence from porous silicon is studied with plane-polarized light excitation under grazing incidence. The experiments show that the incident angle of light almost has no influence on the luminescence behavior of porous silicon. However, the luminescence with z -polarization excitation is found to be higher in intensity than that with x -polarization excitation. The different orientations of the electric field of the exciting light with respect to the sample surface result in the difference in the excited luminescence, which reveals the anisotropy of the optical properties of porous silicon and rules out the assembly of pure quantum silicon dots as the structure of porous silicon.

Key words photoluminescence, porous silicon, quantum size effect, polarized-light excitation.

Because of both fundamental physics and potential applications in optoelectronics technology, the discovery of visible light emission from porous silicon (PS) by Canham[1] has attracted great attention of many researchers. There have been a great deal of investigations devoted to the preparation and characterization of PS and to the mechanism responsible for the strong visible photoluminescence (PL) from PS. However, the latter still remains unclear. Several proposals have been given to explain the large blue shift of the PL spectra from PS compared to that from bulk crystalline silicon. They can basically be classified as three entirely different groups, namely quantum confinement effects[1, 2], surface-localized states effects[3, 4] and surface species present in PS such as siloxene[5, 6]. But it is now almost commonly agreed that porous silicon and surface species are two different kinds of luminescent materials. A variety of evidences illustrate that the quantum confinement is real. Meanwhile, the surface states and surface species are also found to contribute to the luminescence process. Canham[1] has suggested the silicon-wire nanocrystal as a porous silicon structure to explain the visible light emission by bandgap widening and relaxation of the momentum selection rule due to quantum confinement. Cullis and Canham[7] later observed a structure of chained ball-like nanocrystallines rather than pillar-like crystals. It is more acceptable to

Received 19 June 1996; revised 27 February 1997

suggest that the structure of porous silicon be a mixture of nanosize silicon wires and silicon dots[8]. Calculations of the band structure and optical properties have been made for silicon quantum wires[9~12] and quantum dots[13, 14]. Xia and Cheah[15] have also developed a theoretical model of the surface state effect for PS in the framework of effective-mass theory, from which the temperature effect on the photoluminescence spectrum for pillar and spherical structures was considered.

Many of the investigations on PS have concentrated on PL spectrum, which has been of importance to the studies on both the materials characteristics and light-emitting mechanism. For an assembly of quantum silicon wires[10] or a mixture of silicon wires and dots, the optical properties are very anisotropic, and the PL spectrum should be dependent on the polarization of the exciting light, as contrasted with those of an assembly of silicon dots or bulk silicon which are independent of polarization. However, the influences of polarization have not been considered in PL measurements of PS reported so far. In the present work, we investigated luminescence from porous silicon by exciting PS with polarized laser light. Two samples have been subjected to the polarized light excited PL measurements at room temperature and reduced temperatures. It is found that the variation of the PL over the temperature range 10~ 300K does not differ too much for different polarized light excitation. However, more interesting is the finding that overall the PL intensities of both samples by z-polarized light excitation (with the electric field of the exciting light perpendicular to the sample surface, i. e. oriented along the wire axis) are higher than those by x-polarized light excitation (with the electric field of the light parallel to the sample surface) when other conditions remained the same. The results obtained seem to support the assumption that the PS samples examined consist of nanosize silicon wires or a mixture of silicon wires and silicon dots, rather than consist purely of nanosize silicon dots.

Both samples used were made from p-type silicon wafers with a resistivity of 5 Ω·cm and fabricated by electrochemical anodization, but with different etching conditions: for sample A, the anodic etching was carried out in a HF∶ethanol= 1∶1 solution at a constant current density of 15 mA/cm^2 for 30 min; for sample B, the anodization was carried out in 2∶1 mixture of HF and ethanol at a current density of 20 mA/cm^2 for 60 min. Each of the as-prepared samples was placed in a closed-cycle cryostat which was evacuated in order to prevent thermally induced oxidation of PS during the measurements.

The experimental setup used was somewhat different from conventional one. The 488 nm line from an Ar-ion laser, after passing two polarizers and a focusing lens, was used as an excitation source. The combination of the two polarizers determined the polarization and power of the laser light fallen on the sample. The focused light beam had a spot diameter of ~ 0.5 mm and excited the sample with grazing incidence (> 85° from the normal of the sample surface). By adjusting the polarizers, x-polarized or z-polarized laser light with a constant power density was chosen to excite the samples. Throughout the measurements of each sample, the excited spot on the sample remained unchanged, so that any changes due to variation in local sample structure could be avoided. The excitation power density was kept low enough so that any irradiation-induced degradation would also be avoided. The luminescent emission was collected in a direction perpendicular to the sample surface and the PL signal was detected using a cooled photomultiplier tube (PMT) through an Oriel monochromater.

For comparison, conventional PL measurement, near-normal incidence excitation, was also carried out on these two samples. Also by taking measurements as described in our previous paper[8], namely by comparing two room-temperature PL taken at the beginning and at the end of the measurements respectively, it was confirmed that neither thermally induced changes nor degradation due to the laser irradiation occurred in the two samples after each set of temperature PL measurements.

For each sample two sets of temperature-dependent PL measurements were taken, one excited by x -polarized laser light and one by z -polarized light. Typical photoluminescence spectra from sample A at different temperatures are shown in Fig. 1, which were obtained by exciting the sample with x or z -polarized laser light of equal power density ($\sim 0.5\ \mathrm{W/cm^2}$). During each measurement, the samples were maintained at constant temperature in the cryostat equipped with quartz windows. Sample B behaves similarly in its PL spectra, although there are differences in the temperature-dependent PL and on the whole the PL intensities are approximately one order lower than those of sample A under the same conditions. As usually, the PL spectra show a strong dependence on temperature. In Fig. 2 the obtained PL peak intensities of the samples were plotted as a function of temperature. From Fig. 1 and Fig. 2, one notices that irrespective of x or z -polarization there is a general trend of PL intensity decreasing with increase in temperature, which is similar to the result obtained by exciting porous silicon with near-normal light incidence[8]. The PL peak wavelengths were plotted against temperature in Fig. 3, from which one could observe that for both samples there is a general tendency for the PL to red-shift as the sample temperature is decreased, also just as the same observation obtained in the conventional PL measurements in our previous work[8].

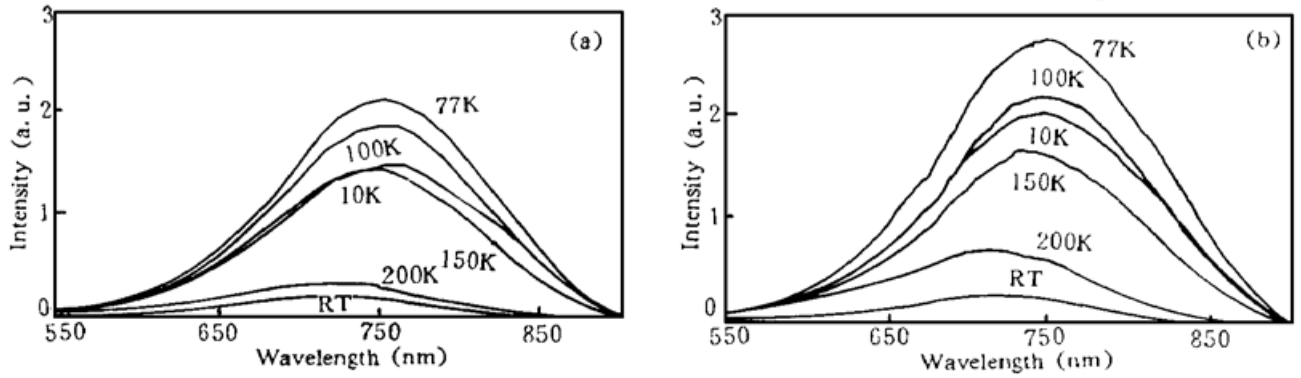

Fig. 1 PL from sample A at various temperatures: (a) x -polarization; (b) z -polarization

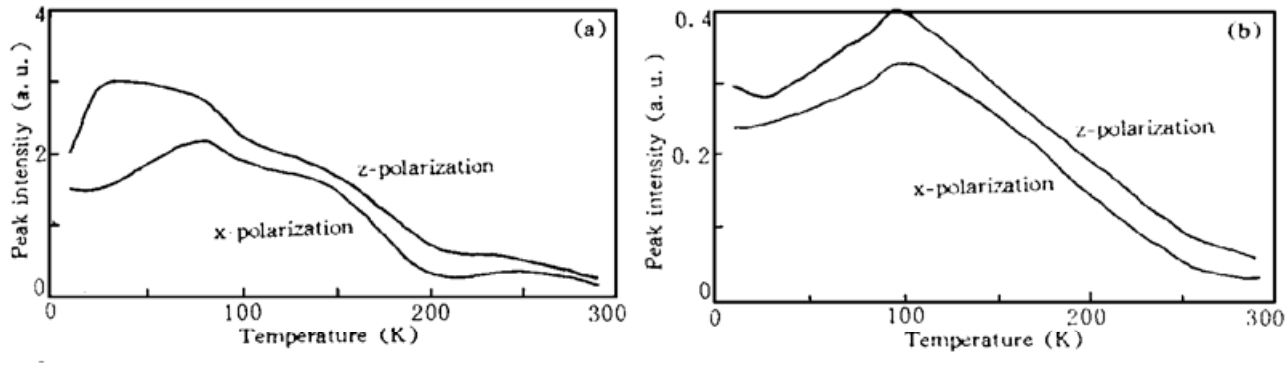

Fig. 2 PL peak intensities with x and z -polarization excitation, plotted against temperature: (a) sample A; (b) sample B

By comparing the PL intensities from PS excited by different polarized light, it is found that for both samples all the PL by z -polarized light excitation is stronger than that by x -polarized excitation with all other conditions being equal, an interesting observation never reported before. Just as shown in Fig. 1 for sample A, although the PL spectra are strongly dependent on temperature, the large differences between the x and z -polarized light excited PL intensities are obvious. Especially from Fig. 2 (a) for sample A, one notices the strong increase in the PL peak intensity by z polarization excitation with the temperature increasing to about 30 K, whereas the x polarization excited PL increases little in its PL intensity. And in a wider wavelength range the PL excited by z -polarized light is almost twice as strong as that excited by x -polarized light (Fig. 4) with sample A setting at that temperature.

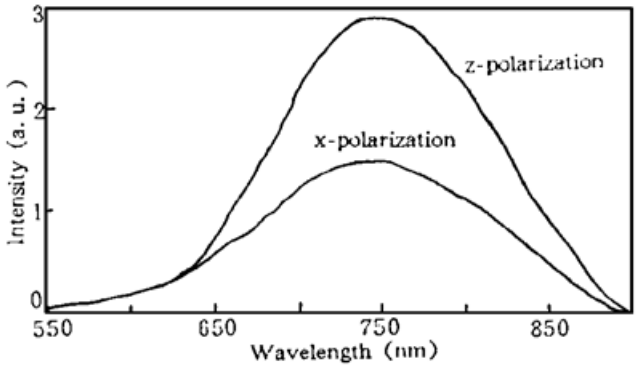

Fig. 3 PL peak wavelengths versus temperature: curve a, sample A, x -polarization; curve b, sample A, z -polarization; curve c, sample B, x -polarization; curve d, sample B, z -polarization

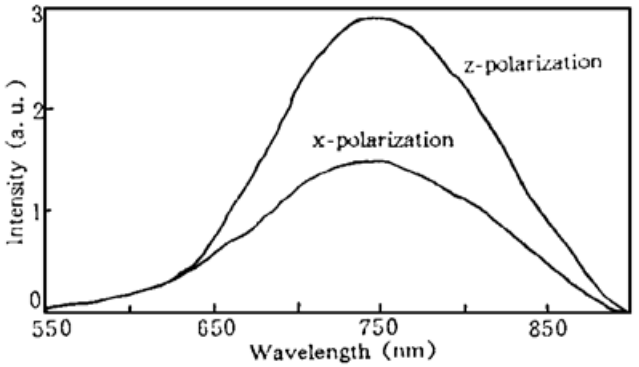

Fig. 4 PL from sample A with x and z -polarization at 30 K

To examine the influence of the incident angle of the exciting light on luminescence, these two samples were also subjected to conventional PL observation with normally incident 488 nm laser light of the same power density as before. The samples were also excited at the same spots on the surface as with polarization excitation. Some of the temperature PL spectra were chosen for comparison. No distinct differences were observed. However, the PL spectra appear more similar to the x -polarized light excited PL spectra than to the z -polarized light excited ones while setting the samples at the same temperature. In particular, the PL intensities with normal incidence excitation are found to be much closer to those with x -polarization excitation.

From the results shown above, we could come to the conclusion that light incident angle alone does not change the PL behavior of PS drastically. As for the large difference in intensity between x and z -polarized light excited luminescence, it could only be due to different orientations of the electric field of the exciting light, which reveals the anisotropic optical properties of the samples. Sanders and Chang[10] pointed out that the quantum-wire optical spectra are very anisotropic, and that this anisotropy is enhanced as the quantum wire becomes narrower. Because porous silicon is a complex mixture of Si nanostructures, and because PL from PS also strongly depends on the size of the Si crystallites, it is difficult to compare our experimental results with an ideal model quantitatively. However, our results show convincingly evidence on structural asymmetry of the samples along and perpendicular

to the surface, and disprove the assumption that porous silicon prepared by anodic etching consist purely of quantum silicon dots.

The microscopic structure of porous silicon is dependent on preparation conditions. We notice that PL of sample A differs somewhat from PL of sample B, which could arise from difference in their structure. Since porous silicon is a nanostructured material, and difference in the nanoscaled structure is even smaller, it is difficult to determine structural difference between PS samples merely from their PL. In fact, the exact structure of porous silicon and the accurate mechanism of strong photoluminescence from porous silicon are currently under debate.

In conclusion, we have studied the luminescence from porous silicon excited by plane-polarized light with electric fields parallel and perpendicular to the sample surface. The PL variation against temperature shows similar trend, however, the luminescence with z -polarization excitation observed is much higher in intensity than that with x -polarization excitation. This indicates that the optical properties of porous silicon are anisotropic, excluding the possibility of the samples used in this work being an assembly of pure nanosize silicon dots. Our experiments also show that the incident angle of the exciting light does not change the PL behavior of porous silicon. Further theoretical and experimental work is required for details of correlation between the photoluminescence and nanostructure of porous silicon.

This work was supported by Faculty Research Grant of Hong Kong Baptist University.

References

[1] L. T. Canham, Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. *Appl. Phys. Lett.*, 1990, **57**(10) : 1046~ 1048

[2] P. D. J. Calcott, K. J. Nash, L. T. Canham *et al.*, Identification of radiative transitions in highly porous silicon. *J. Phys.: Condens. Matter*, 1993, **5**(7) : L91~ 98

[3] Y. H. Xie, W. L. Wilson, F. M. Ross *et al.*, Luminescence and structural study of porous silicon. *J. Appl. Phys.*, 1992, **71**(5) : 2403~ 2407

[4] V. Petrova-Koch, T. Muschik, A. Kux *et al.*, Rapid-thermal-oxidized porous Si the superior photoluminescent Si. *Appl. Phys. Lett.*, 1992, **61**(8) : 943~ 945

[5] P. Deak, M. Rosenbauer, M. Stutzmann *et al.*, Siloxene: chemical quantum confinement due to oxygen in a silicon matrix. *Phys. Rev. Lett.*, 1992, **69**(17) : 2531~ 2534

[6] M. S. Brandt, H. D. Fuchs, M. Stutzmann *et al.*, The origin of visible luminescence from "porous silicon": a new interpretation. *Solid State Commun.*, 1992, **81**(4) : 307~ 312

[7] A. G. Cullis, L. T. Canham, Visible light emission due to quantum size effects in highly porous crystalline silicon. *Nature*, 1991, **353**(6342) : 335~ 338

[8] K. W. Cheah, L. C. Ho, J. B. Xia *et al.*, Luminescence centers in porous silicon. *Appl. Phys.* (*A*), 1995, **60**(6) : 601~ 606

[9] A. J. Read, R. J. Needs. K. J. Nash *et al.*, First-principles calculations of the electronic properties of silicon quantum wires. *Phys. Rev. Lett.*, 1992, **69**(8) : 1232~ 1235

[10] G. D. Sanders, Yia-Chung Chang, Theory of optical properties of quantum wires in porous silicon. *Phys. Rev.* (*B*), 1992, **45**(16) : 9202~ 9213

[11] T. Ohno, K. Shiraishi, T. Ogawa, Intrinsic origin of visible light emission from silicon quantum wires: electronic structure and geometrically restricted exciton. *Phys. Rev. Lett.*, 1992, **69**(16) : 2400

~ 2403

[12] F. Buda, J. Kohanoff, M. Parrinello, Optical properties of porous silicon: a first-principles study. *Phys. Rev. Lett.*, 1992, **69**(8): 1272~ 1275

[13] J. P. Proot, C. Delerue, G. Allen, Electronic structure and optical properties of silicon crystallites: application to porous silicon. *Appl. Phys. Lett.*, 1992, **61**(16): 1948~ 1950

[14] B. Delley, E. F. Steigmeter, Quantum confinement in Si nanocrystals. *Phys. Rev.* (*B*), 1993, **47**(3): 1397~ 1440

[15] J. B. Xia, K. W. Cheah, Temperature effect on porous silicon luminescence. *Appl. Phys.* (*A*), 1994, **59**(3): 227~ 231

平面偏振光激励的多孔硅的光致发光

吴嘉达[1] 谢国伟[2] 郑婉华[2]

(1, 复旦大学物理系, 上海 200433
2, 香港浸会大学物理系, 香港九龙)

(收稿日期: 1996 年 6 月 19 日; 收到修改稿日期: 1997 年 2 月 27 日)

摘 要 研究了以掠入射的平面偏振光激励的多孔硅的光致发光。实验结果显示, 光的入射角对多孔硅的发光行为影响不大, 然而, 以 z 方向偏振光激励的发光强度明显高于以 x 方向偏振光激励的发光强度。激励光电场相对于样品表面的不同取向引起光致发光的差异, 这反映多孔硅的光学性质是各向异性的, 也排除了纯粹的硅量子点的集合作为多孔硅结构的可能性。

关键词 光致发光, 多孔硅, 量子尺寸效应, 偏振光激励。