Efficient Infrared-Up-Conversion Luminescence in Porous Silicon: A Quantum-Confinement-Induced Effect

Jian Wang, Hong-bing Jiang, Wen-cheng Wang, and Jia-biao Zheng
Laboratory of Laser Physics and Optics, Fudan University, Shanghai, China

Fu-long Zhang, Ping-hai Hao, Xiao-yuan Hou, and Xun Wang
Surface Physics Laboratory, Fudan University, Shanghai, China
(Received 22 May 1992)

We demonstrate for the first time that a porous silicon layer (PSL), which has a bright light-emission band in the range of 500–700 nm, exhibits a strong visible-range luminescence under the illumination of an infrared ultrashort pulsed laser. The dependence of integrated luminescence intensity on pump power shows that this is a third-order nonlinear optical effect. By comparing with UV-light-excited spectra of PSL and samples with low porosity which have inefficient luminescence, a possible explanation is proposed whereby the large nonlinear optical response is due to the quantum confinement effect.

PACS numbers: 78.55.−m, 42.65.−k, 42.70.−a, 78.65.−s

In the past years, the nonlinear optical properties of semiconductor quantum wells and microcrystallites have attracted much attention, particularly with regards to their possible application in optical signal processing [1–3]. The most prominent feature of these systems is the fact that excitons can be observed even at room temperature, because of the strong enhancement of their binding energy under quantum confinement and image forces.

Recently, efficient room-temperature visible-light photoluminescence (PL) and also electroluminescence (EL) in porous silicon (PS) have been observed [4,5]. From indirect evidence the visible-light emission from PS has been attributed to the quantum confinement effect arising from free-standing nanometer silicon quantum wires formed by the chemical etching process. A blueshift in the absorption or emission spectrum as the porosity increases has been observed [6], which is a characteristic of quantum-size materials arising from the confinement of excitons to a volume smaller than that in the bulk material. Furthermore, detailed studies [7] of PL under different temperatures and various excitation intensities also support the idea that confined excitons may be involved in the radiative process. However, there is still considerable controversy concerning the mechanism of visible-light emission from PS. A number of possibilities other than quantum confinement have been suggested, such as *a*-Si:H [8], silicon hydride complexes [9], siloxene derivatives [10], unspecified molecules [11], and surface states of crystallites [12].

It has been shown primarily [13–15] that the nonlinear optical polarizability may be greatly enhanced for an assembly of multiple-quantum-well structures and semiconductor microcrystallites, which have one- and three-dimensional confinement structures, respectively. This kind of nonlinearity enhancement has been considered [13] as exciton-localization-induced effects and exciton-exciton interaction effects in quantum confined systems. It is expected therefore that an optical nonlinearity enhancement of PS would exist if the hypothesis of quantum wires does indeed work. In this Letter, the large nonlinear optical response of a PS layer (PSL) has been observed for the first time, and a double-resonance-enhanced third-order nonlinear optical process is suggested to interpret the experimental observation.

The sample used in this work was a *p*-type Si wafer with resistivity of 10 Ω cm. It was anodized in a solution of HF:ethanol = 1:1 at constant current density ~5 mA/cm^2 for 10–20 min. After being rinsed in deionized water, the wafer was oxidized in a furnace at 350 °C for 20 min and then at 600 °C for 1 min, followed by a brief (~1 s) dip in HF. The thickness of the PSL was about 5–10 μm as determined by the anodization time. Under UV-light illumination, the sample had a bright homogeneous orange-light emission instead of a pale color in the daylight.

The experimental setup is shown schematically in Fig. 1. A passively mode-locked amplified Nd-doped yttrium

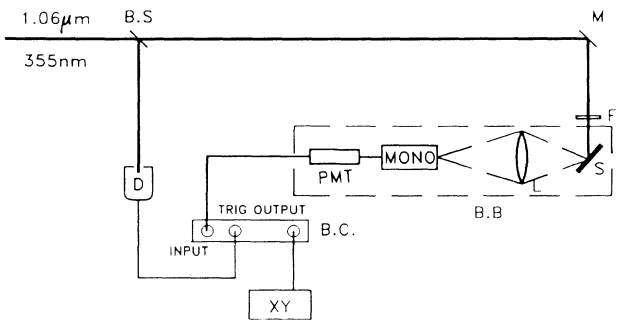

FIG. 1. Schematic illustration of experimental setup. BS: beam splitter. M: reflection mirror. F: filters. S: sample. L: lens. MONO: monochromator. PMT: photomultiplier tube. BC: boxcar averager. D: photodetector. BB: blackbox. *XY*: *X*-*Y* recorder.

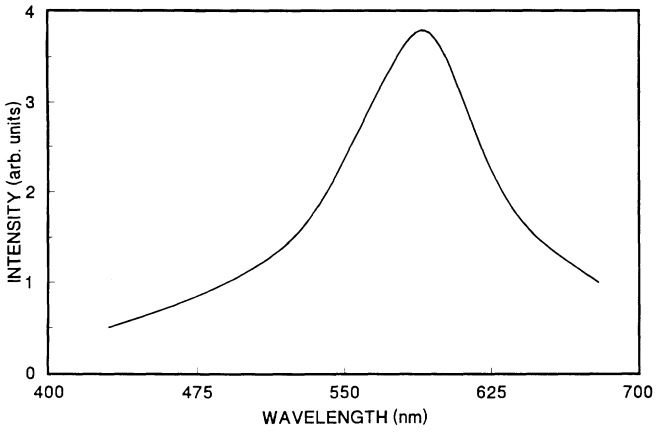

FIG. 2. Infrared-up-conversion spectrum of PS sample excited by 1.06-μm radiation.

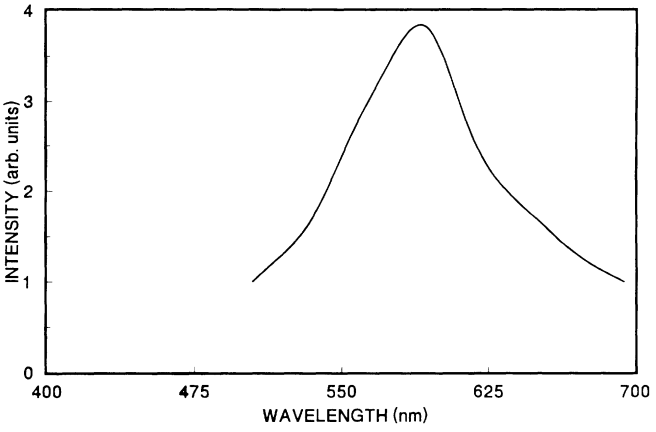

FIG. 3. PL spectrum of PS sample excited by 355-nm radiation, which was the third-harmonic generation output of a Q-switched Nd:YAG laser.

aluminum garnet (YAG) laser emitting 50-psec pulses at 1.06 μm of up to 5 mJ energy was used to study the infrared-up-conversion luminescence of PS. By using colored-glass filters it was confirmed that only 1.06-μm light can enter the blackbox. The light beam had a diameter of $\sim$1 mm with a single pulse energy of $\sim$20 μJ. Under this energy we did not observe any time-dependent signal decrease, which shows that the PSL was not damaged by laser illumination. The up-conversion efficiency was so high that the emission could be seen by the naked eye through an infrared-cut filter. The signal emitted from the PSL was collected by a relative aperture 1:1.5 lens into a $\frac{1}{2}$-m monochromator, detected by the photomultiplier and recorded by an x-y recorder after treatment by a boxcar averager.

The infrared-up-conversion spectrum of the PS sample is shown in Fig. 2. In the up-conversion region there is a broad PL band centered at 590 nm with a FWHM of $\sim$100 nm and a relatively small sharp peak at 355 nm which is not shown in Fig. 2. In order to verify that the nonlinearity enhancement is actually due to quantum confinement, another sample was prepared by only chemical anodization, without being oxidized in the furnace and dipped in HF. The difference between this comparison sample and the test sample is in their porosity. The comparison sample had lower porosity and thus inefficient light emission in the visible range, which indicated the lack of nanometer silicon quantum wires [16]. The measurement of the comparison sample showed that there was very weak light emission (the integrated intensity was 10^{-6} smaller than that of the PS sample) in the up-conversion region. In contrast with PSL samples, the measurement on a silicon single-crystal wafer (p-type, 10 Ω cm) gave only a small third-harmonic generation (THG) at 355 nm.

To compare with the nonlinear up-conversion PL spectrum, the UV-excited PL spectrum of the PS sample was also recorded by a 355-nm Q-switched laser. The spectrum is shown in Fig. 3, where the broad PL band centered at 590 nm with a FWHM $\sim$100 nm coincides fairly well with the broad luminescence band of the nonlinear up-conversion spectrum. Figures 2 and 3 were obtained by using the same detection system which was not calibrated. It is thus verified that the radiative deexcitation processes involved in the UV-excited PL and IR-excited up-conversion luminescence are actually the same, although their excitation processes are different. As a rough estimation, the luminescence efficiency of infrared up-conversion is found to be about 3 orders of magnitude smaller than that of PL excited by 355-nm light.

The dependence of up-conversion luminescence intensity on pump power I (1.06 μm) was measured by integrating the signal of up-conversion luminescence, and is shown in Fig. 4. The solid line fits fairly well with the following relation:

$$I_{\mathrm{sig}} = KI^3(1.06\,\mu\mathrm{m}), \tag{1}$$

where I_{sig} is the integrated up-conversion luminescence intensity, and K is a constant. It is quite clear that this is

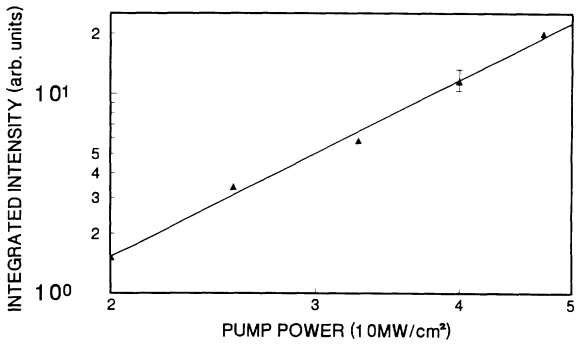

FIG. 4. Integrated up-conversion luminescence intensity vs pump intensity. The solid line shows a slope of 3, which is typical for a third-order nonlinear optical process.

a typical indication of a third-order nonlinear optical process. By comparing with the standard sample and taking into account the Fresnel factor [17], we estimated that the third-order nonlinear optical susceptibility $\chi^{(3)}$ of PS has a 2 order of magnitude enhancement relative to Si, which means

$$\chi^{(3)} \sim 10^{-8} \text{ esu}. \quad (2)$$

It has been well established [18,19] that the nature of the electronic states, the oscillator strength, and the response time of the nonlinearity of a small quantum system depend sensitively on the size of the microcrystallites relative to the Bohr radii of excitons. In the previous study [13], a very large nonlinear optical susceptibility enhancement in size-confinement structures has been attributed to two sources. One is due to the size quantization of excitons, and the other comes from the deviation of the exciton excitation from an ideal harmonic oscillator due to the strong exciton-exciton interaction in the quantum confined structure. When the size of the microcrystallites is reduced, the latter effect is prominent.

To make a qualitative explanation of the above experimental results, we suggest here that the infrared-up-conversion luminescence consists of two processes. The first one is a double-resonance-enhanced third-harmonic-generation process, which can be described by the following equation in a three-level approximation [20]:

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) \propto \frac{1}{(E_{mg}-2\hbar\omega-i\Gamma_{mg})(E_{ng}-\hbar\omega)(E_{ng}-3\hbar\omega-i\Gamma_{ng})}, \quad (3)$$

where $\Gamma/\hbar$ is the state width. In this case, the triple of the incident photon energy $\hbar\omega$ approaches the energy difference E_{ng} between the upper levels and fundamental levels as demonstrated by the strong absorption of 355-nm light in PS. In addition, there is the possibility of a two-photon resonance due to the presence of middle levels m as confirmed by the photoluminescence measurement. The middle levels arise most probably from exciton localization and exciton-exciton interaction due to the quantum confinement. As a result of the resonance, the nonlinear optical susceptibility can be greatly enhanced [21]. It is believed [22] that this two-photon resonance becomes increasingly pronounced with increasing laser intensity and is the most important source of optical nonlinearity in wide-gap materials. The second process is similar to the light-emission process of PS excited by external UV light. The signal of the enhanced THG in PS could act as an internal pump source to excite visible-light emission just as the UV light does. This explains why the infrared-up-conversion spectrum coincides almost exactly with the UV-excited PL spectrum of PS. In the three-level model, the upper levels have inverse symmetry (odd parity) relative to the fundamental levels (even parity). The middle levels which constitute the 590-nm emission band in the infrared-up-conversion process must possess the same symmetry as the fundamental levels. But like the levels near the band edge in polyacetylene [23], the middle levels may consist of states with both even parity and odd parity, and the latter are responsible for the single-photon luminescence. Further work, including lifetime measurements and the dependence of the enhancement on sample temperature, size of the microstructure, and pump wavelength, are needed to clearly understand the origin of the large nonlinear response [20].

In summary, the efficient infrared-up-conversion luminescence at room temperature is observed from a porous silicon layer. The large nonlinear response is interpreted as a result of double-resonance enhancement of the third-order nonlinear optical susceptibility, which is most possibly due to exciton localization and exciton-exciton interaction effects. Our results seem to give strong support to the quantum confinement mechanism of visible-light emission from porous silicon. This remarkable effect will possibly induce extensive studies of the nonlinear optical response of PSL, such as four-wave-mixing (FWM), phase conjugation, and bistability, which perhaps will ultimately lead to all-Si nonlinear devices.

The authors gratefully acknowledge interesting discussions with Dr. Lei Xu. This work was partially supported by the National Natural Science Foundation of China.

[1] D. S. Chemla and M. A. B. Miller, J. Opt. Soc. Am. B **2**, 1155 (1985).
[2] P. Roussignol, D. Ricard, K. C. Rustagi, and C. Flytzanis, Opt. Commun. **55**, 143 (1985).
[3] R. K. Jain and R. C. Lind, J. Opt. Soc. Am. **73**, 647 (1983).
[4] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[5] N. Koshida and H. Koyama, Appl. Phys. Lett. **60**, 347 (1992).
[6] V. Lehmann and U. Gosele, Appl. Phys. Lett. **58**, 856 (1991).
[7] S. Gardelis, J. S. Rimmer, P. Dawson, B. Hamilton, T. E. Whall, and E. H. C. Parker, Appl. Phys. Lett. **59**, 2119 (1991).
[8] R. P. Vasques, R. W. Fathauer, T. George, and A. Ksendzov, Appl. Phys. Lett. **60**, 1004 (1992).
[9] C. Tsai, K.-H. Li, D. S. Kinosky, R. Z. Qian, T.-C. Hsu, J. T. Irby, and S. K. Banerjee, Appl. Phys. Lett. **60**, 1700 (1992).
[10] M. S. Brandt, D. H. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, Solid State Commun. **81**, 307 (1992).
[11] Z. Y. Xu, M. Gal, and M. Gross, Appl. Phys. Lett. **60**, 1375 (1992).
[12] T. Ito, T. Ohta, O. Arakaki, and A. Hiraki, Mater. Res. Soc. Symp. Proc. **256**, 127 (1992).
[13] E. Hanamura, Phys. Rev. B **37**, 1273 (1988).

[14] L. Banayai and S. W. Koch, Phys. Rev. Lett. **57**, 2722 (1986).
[15] T. Takagahara and E. Hanamura, Phys. Rev. Lett. **56**, 2533 (1986).
[16] L. Canham, Phys. World **5**, No. 3, 41 (1992).
[17] W. K. Burns and N. Bloembergen, Phys. Rev. B **4**, 3437 (1971).
[18] S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, Phys. Rev. B **35**, 8117 (1987).
[19] C. Flytzanis, F. Hache, D. Ricard, and P. Roussignol, in *Digest of Technical Papers and Postdeadline Papers*, Proceedings of the Fourteenth International Conference on Quantum Electronics [J. Opt. Soc. Am. B **3** (1986)].
[20] D. S. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic, New York, 1987), Vol. 2.
[21] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[22] H. Haug and S. Schmitt-Rink, J. Opt. Soc. Am. B **2**, 1135 (1985).
[23] W.-S. Fann, S. Benson, J. M. J. Madey, S. Etemad, G. L. Baker, and F. Kajar, Phys. Rev. Lett. **62**, 1492 (1989).